

Thermal destruction of (hydro)chloro- fluorocarbons and hydrofluorocarbons

Management and destruction of existing ozone depleting substances banks

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Abbreviations

APC	Air pollution control
BMU	German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety
CFC	Chlorofluorocarbon
DE	Destruction efficiency
DRE	Destruction and removal efficiency
ESP	Electrostatic precipitator
GIZ	Deutsche Gesellschaft für Internationale Zusammenarbeit GmbH
GWP	Global Warming Potential
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
IKI	International Climate Initiative
MSWI	Municipal solid waste incineration
ODP	Ozone Depletion Potential
ODS	Ozone Depleting Substances
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans
PFDD	Polyfluorinated dibenzodioxins
PFDF	Polyfluorinated dibenzofurans
PUR	Rigid polyurethane
RAC	Refrigeration and air-conditioning (sector)
RT	Residence time
TEAP	Technology and Economic Assessment Panel
XPS	Expanded polystyrene
XPS	Extruded Polystyrene

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Summary

The use of chlorofluorocarbons (CFCs) as refrigerants and as blowing agents for heat insulating foams has been banned since the 1990s with the Montreal Protocol because of their ozone depleting potential, and the use of their successors, hydrochlorofluorocarbons (HCFCs), has been considerably limited over the last 15 years. The substances are, however, still globally present in high amounts in appliances that have become waste and amount to so-called “ozone depleting substances (ODS) banks”. Their recording, collection, and final disposal are not regulated by any international agreement and are an expensive challenge, in particular in developing countries. As a result of the Montreal Protocol, ODS have been widely replaced by hydrofluorocarbons (HFCs), which have high global warming potentials (GWP). While the ODS bank is projected to decline, the HFC bank will increase.

The present paper focuses on one aspect of ODS Banks management: The destruction of ODS through thermal processes. In industrialised countries a number of technical processes are available for the destruction of ODS, the most efficient ones often provided by big chemical companies. The number of options available in developing countries depends on the industries found locally. Since HFCs are still widely in use, there is currently little data on HFC destruction and the present paper therefore focuses on the destruction of ODS but also addresses the destruction of HFC. It is expected that HFC destruction will not differ much from ODS destruction.

The objective of this paper is to give an overview of technical measures for the destruction of ODS and a special focus is turned upon their potential application in the special situation of developing countries by looking at investment and operational costs as well as technical requirements. The report thereby first looks at the collection and pre-treatment of refrigeration equipment, where considerable ODS banks are still available for treatment (Chapter 2) before it looks at the destruction technologies of ODS (Chapter 3) and HFC (Chapter 4) themselves.

Out of the existing technical processes, selected thermal processes are discussed in detail in this document and each technology is analysed regarding its potential use in developing countries. A very promising strategy is the destruction of ODS in cement kilns which are found in almost all countries and which have a high capacity to handle pure (H)CFC as well as polyurethane (PUR) foams.

This paper has been developed as part of the project “Management and Destruction of Existing Ozone Depleting Banks” on behalf of the Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) under its International Climate Initiative (IKI) and implemented by the Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH. All guidelines of the project can be found at the GIZ Proklima Website¹ and the IKI Media Centre².

1 www.giz.de/proklima

2 <https://www.international-climate-initiative.com/en/details/project/management-and-destruction-of-ozone-depleting-substances-in-ods-banks-374>

The following complementary documents are of particular interest to the topic of ODS destruction:

- **Global banks of ozone depleting substances – country level estimate**
<https://mia.giz.de/qlink/ID=245500000>
- **Global roadmap on ODS bank management**
www.giz.de/en/downloads/giz2017-en-global-roadmap.pdf
- **Guideline to conduct an ODS bank inventory**
www.giz.de/en/downloads/giz2017-en-no1-guideline_-ods-banks-inventory.pdf
- **Guideline on policy measures for the management and destruction of ozone depleting substances**
www.giz.de/en/downloads/giz2017-en-no2-guideline-policy-measures.pdf
- **Guideline to establish a collection system for equipment containing ozone depleting substances**
www.giz.de/en/downloads/giz2017-en-no3-guideline_-policy-measures-collection-system.pdf
- **Guideline for the transboundary movement of ODS waste**
www.giz.de/en/downloads/giz2017-en-no4-guideline-transboundary-movement.pdf
- **Guideline on the manual dismantling of refrigerators and air conditioners**
www.international-climate-initiative.com/fileadmin/Dokumente/2017/171219_EN-weee.pdf

1 Options for (H)CFC disposal

1.1 Background

Chlorine and fluorine containing organic carbon compounds, such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are used as refrigerants in refrigeration and air-conditioning (RAC) units, and as blowing agents in heat insulating foams used in buildings and appliances. CFCs and HCFCs are ozone-depleting substances (ODS), mostly with a very high global warming potential. They have gradually been replaced with hydrofluorocarbons (HFCs) which are not ODS but still significantly contribute to global warming.

The excessive use of ODS led to large banks of ODS in existing equipment, chemical stockpiles and foams, that have accumulated globally resulting in annual emissions of 1.5 Gt CO₂eq. These emissions are equal to emissions of 441 coal fired power plants.

Since ODS are widely replaced by high GWP HFCs, the overall amount of refrigerants and blowing agents in the RAC and foam sector will remain at a high emission level until 2050 (Figure 2). It is estimated that the amount of ODS banks will decline, while the HFC banks will increase.

Figure 1: Annual emissions from the global ODS banks are equal to the annual emissions from 441 coal-fired power plants (GIZ, 2017a)

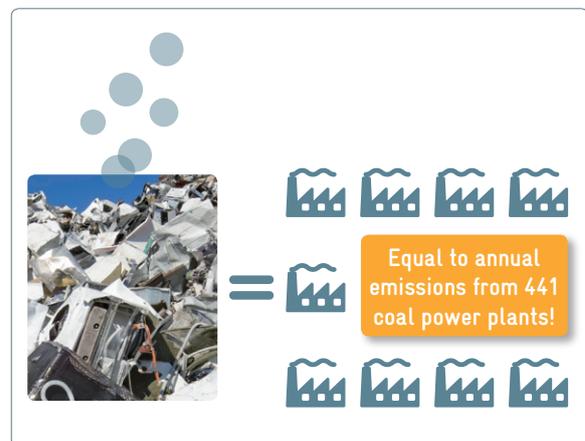
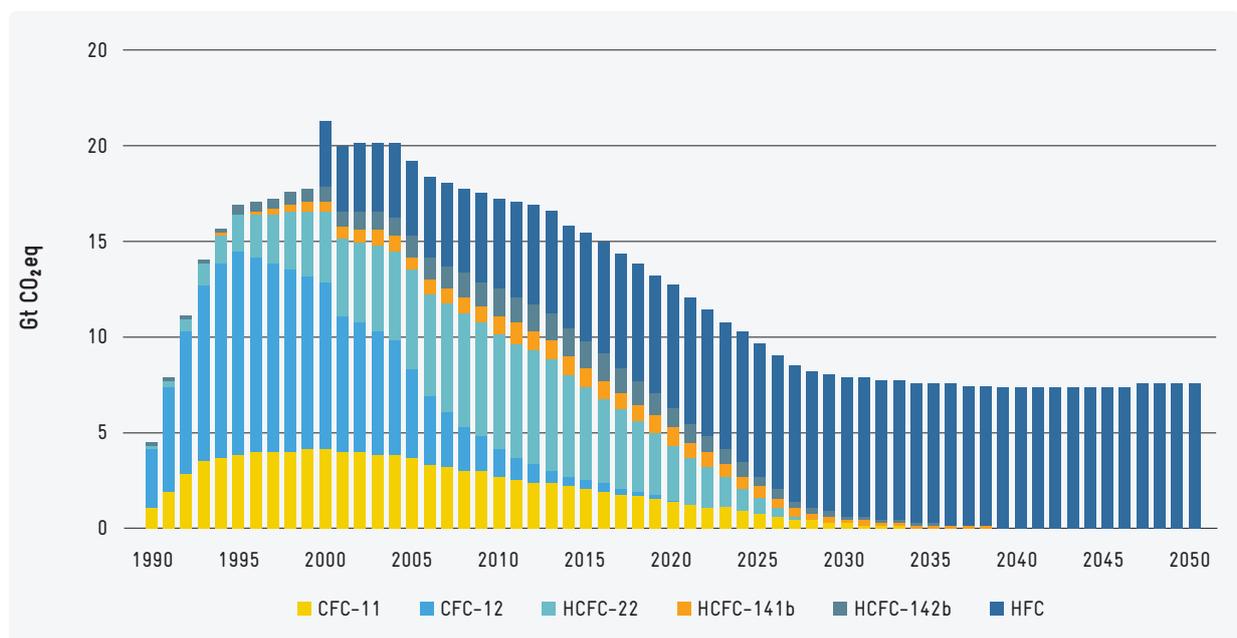


Figure 2: Global ODS and HFC banks in Gt CO₂eq (GIZ, 2017b)



While the international community has agreed to regulate the production and consumption of ODS by the Montreal Protocol and to phase-down HFCs with its Kigali Amendment that entered into force January 2019, no agreements have been made regarding the destruction of the ODS and HFCs already produced. For developing countries in particular, the collection, recycling and destruction of waste containing ODS and HFCs present challenges.

Recovering these ODS and HFC banks for management and destruction can significantly reduce greenhouse gas emissions. The focus of this paper is on one aspect of this banks management: thermal destruction processes. A special focus is turned upon their applicability in the context of developing countries, highlighting their potential investment and operational costs as well as technical requirements.

In this report halons are not taken into consideration since their management seems to be well controlled due to their still needed properties for specific applications e.g. in fire extinguishers in air planes. HFC destruction will be addressed but not discussed in detail as the substance is still widely in use, generally recycled wherever possible and little data on their destruction is available. However, the same technical measures as for ODS would apply for their destruction and it will be crucial to further investigate and recommend technologies.

An important aspect when looking at suitable destruction technologies is the economic feasibility. Destruction technologies are expensive, not only for initial investments, but also regarding operation costs, energy use in specific. The detailed presentation will therefore be limited to combustion technologies. Plasma processes will not be included since their applicability in developing countries seems unlikely for the time being for economic reasons. The proposed and tested processes, although definitely suitable, are very costly and

there are no reliable records yet on experimental results from technical installations.

The suitability of the described combustion technologies depends highly on existing technology that can also be used for different purposes, e.g. the destruction of other hazardous waste or cement production. The establishment of a new plant for the use of ODS or HFC destruction is not realistic.

Only those technologies are considered that have been proven in test runs to be able to adhere to environmental criteria developed by the UNEP Technology and Economic Assessment Panel (TEAP).

1.2 Properties of (H)CFCs and HFCs

(H)CFCs are chemically inert, a property that made them suitable as refrigerants. At the same time, it leads to long residence times in the atmosphere and specific requirements for their destruction. Table 1 compiles data for selected compounds, which have or had a widespread application in cooling circuits and/or as blowing agents for heat insulating foams. The data have been taken from various data sheets and publications. The GWP is related to 100 years of activity, the residence time (RT) in the atmosphere is defined as the ratio of the inventory of a gas in the atmosphere and the rate of its removal from the atmosphere. Boiling points (T_b) and molecular mass (M) are also given.

The environmental effects of substance emissions in terms of ozone depletion and global warming vary depending on the specific compound. The originally used CFCs are characterised by high ODP but also high GWP. The currently still used alternative HCFCs show much lower ODP values, but their GWP is still significant. HFCs do not endanger the ozone layer but have high GWP.

The main destruction products of (H)CFC are HCl and HF, depending on the respective content of fluorine (F) and chlorine (Cl) given in Table 1. In the case of HFCs, the main destruction product is HF, but the F content can be higher compared to (H)CFCs. Both F and Cl form strong acids in contact with water and require emission control measures.

Table 1: Chemical and physical properties of selected (H)CFC and HFC (IPCC AR4, 2007; WMO, 2010)

	formula	M (g/mol)	T _b (°C)	F (wt%)	Cl (wt%)	RT (a)	ODP	GWP
CFC-11	CCl ₃ F	137.4	23.8	13.8	77.4	45	1	4,750
CFC-12	CCl ₂ F ₂	120.9	-29.8	31.4	58.6	100	0.82	10,900
CFC-113	FCl ₂ C-CClF ₂	187.4	47.7	30.4	56.8	85	0.85	14,400
CFC-115	F ₃ C-CClF ₂	154.5	-39.1	61.5	23.0	1,700	0.5	7,370
HCFC-123	F ₃ C-CHCl ₂	152.9	27.8	37.3	46.4	1.5	0.01	77
HCFC-22	CHClF ₂	86.5	-40.8	43.9	41.0	11.9	0.04	1,810
HCFC-141b	FCl ₂ C-CH ₃	116.9	32.0	16.2	60.5	9.3	0.12	725
HCFC-142b	F ₂ ClC-CH ₃	100.5	-9.8	37.8	35.3	19	0.06	2,310
HFC-134a	F ₃ C-CH ₂ F	102.0	-26.1	74.5	0	13.8	0	1,300
HFC-245fa	F ₃ C-CH ₂ -CHF ₂	134.0	15.3	70.9	0	7.2	0	950

2 Collection and pre-treatment of refrigeration equipment

The Status Quo differs considerably for industrialised countries and developing countries in terms of enabling policy frameworks and available technologies.

2.1 Situation in industrialised countries

The final destruction of ODS and HFC substances is part of the long-term goal to completely cease the use of ODS and HFCs and replace them with environmentally more beneficial solutions. This creates no major problem in most industrialised countries where the collection and disposal of waste refrigerators is regulated by national law, e.g. in the EU according to Directive 2002/96/EC on waste electrical and electronic equipment (European Parliament and Council, 2003). That means it is well organised and, in most cases, operated by the waste management authorities.

A medium-size old household refrigerator contained approximately 115–40 g CFC-12 (Dehoust & Schüler, 2007; Holst & Hesshaus, 2009; Schnepel, 2009). These can still be found in the waste stream. Today, most refrigerators contain HFC-134a or the natural refrigerant R-600a with negligible environmental impacts. The first step during dismantling is the recovery of the refrigerant from the compressor. Ideally, refrigerants are then carefully analysed and stored in cylinders for later disposal. In case of high quality HFCs or HCFCs in countries where they are still allowed, they are usually reused or sent for reclamation, a process in which the substance is processed until the purity is comparable to virgin refrigerant.

An equal or even bigger part of CFC, however, is found in the PUR foams, which were in former years blown with CFC-11. The cell structure of these foams is a good diffusion barrier and limits the CFC-11 losses during the lifetime of a refrigerator to few percent only. Data of CFC-11 inventory in

foam published by German environmental agencies state a range between 320 and 500 g per appliance (Holst & Hesshaus, 2009; Schnepel, 2009). A recent investigation on foams from old Turkish refrigerators found CFC-11 concentrations between 113 and 198 mg/g PUR. Based on an average amount of 4 kg of PUR foam per refrigerator, the CFC-11 inventory per unit is 450–780 g, which is slightly higher than the German data (Yaziki et al., 2014).

For the recovery of CFC-11 or HCFC-141b from the foams, the cabinets are generally shredded in an enclosed system to avoid release of the blowing agent into the atmosphere. The (H)CFC can also be liberated from the foams by heating or by compression. Cryo-condensation using liquid nitrogen is one method to recover (H)CFC, another one is adsorption on activated carbon and subsequent release at temperatures above 120 °C (LANUV, 2009). Both processes can be combined. The separated (H)CFC has to be destroyed together with the fractions drained from the cooling circuits. Technically feasible is also the co-combustion of (H)CFC blown foams in waste incineration plants. This method will be discussed in more detail below.

Only small amounts of HFCs have been used in foam production since 2002 (FTOC, 2015). These appliances are only now reaching the waste stream. They are recovered and treated the same way as (H)CFCs.

Figure 3: Waste of RAC equipment



2.2 Situation in developing countries

The situation cannot be that easily solved in developing countries and emerging economies, where often the informal sector takes care of waste collection and disposal. Its main interest is the recovery of metals from the appliances or even the reuse of the crates of old refrigerators as racks or cabinets. Only few developing and emerging countries were successful in establishing the controlled collection of compressors, their drainage, and the storage of (H)CFC and HFC in cylinders. Adequate framework conditions and collection systems are rarely well established, resulting in low amounts of ODS and HFCs being collected.

Investments in destruction technologies are only recommended when relatively high amounts of ODS and HFCs are collected annually (GIZ, 2017a). Otherwise, export for destruction in another country will probably be preferable. It is therefore key to have well-functioning framework conditions before considering investing in a destruction technology. As HFCs are still widely in use, they will only be collected for destruction if they cannot be re-used, recycled or reclaimed.

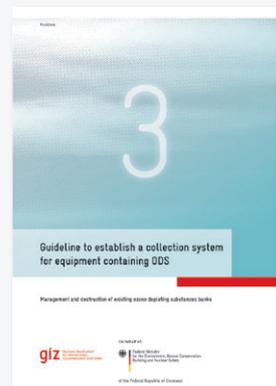
The controlled separation and storage of PUR foams is a much greater problem. In many cases, these are just burnt at the scrap yard to get easy access to the metallic crates. If the foams are (manually) dismantled, the problem arises on how to dispose of them. If a suitable combustion facility exists inside the country, the foams have to be shipped to its location which might be a logistic problem since the density of foams used in refrigerators is very low (typically $< 20 \text{ kg/m}^3$), resulting in very large piles of foam. If no such plant is available in reasonable distance to the destruction facility, the (H)CFCs and HFCs have to be extracted from the foams to reduce the volume to be transported. Liquefaction for collection in cylinders is an expensive process, requiring liquid nitrogen. Most likely the cheapest way is shredding the foam in a closed

environment and adsorption of the released (H)CFCs and HFCs on activated charcoal. This charcoal can be shipped to a destruction plant where it can be released again by heating up to 120°C . Reuse of the charcoal is cheaper than its combustion along with the adsorbed (H)CFCs and HFCs.

For more information on ODS banks framework conditions and collection systems, please refer to:



www.giz.de/en/downloads/giz2017-en-no3-guideline_-policy-measures-collection-system.pdf



www.giz.de/en/downloads/giz2017-en-global-roadmap.pdf

3 Options for (H)CFC disposal

3.1 UNEP TEAP Criteria and Recommendations for (H)CFC destruction

In the late 1980s, a great number of research programs have been launched to develop suited processes for destruction of CFC. The research covered the destruction of the gaseous respectively liquid refrigerants drained from the cooling circuit or extracted from the insulation foams, but also the direct treatment of CFC blown foams. Later, HCFCs were included.

A number of different technologies have been tested, among these biological, chemical, photochemical, catalytic, and thermal processes. The UNEP Technology and Economic Assessment Panel (TEAP) lists in Volume 3B of its April 2002 report a number of recommended technologies for (H)CFC destruction, separately for high concentration sources, which means gases respectively liquids, and low concentrated materials including foams (TEAP, 2002).

The recommendations are based on different criteria. The most important of these is the destruction efficiency (DE) which is a measure of how much of a substance is destroyed during a process compared to the original amount. However, since for many processes only emission data obtained downstream of the installed air pollution control (APC) system have been recorded and DE cannot easily be determined, the criterion for technical performance is the destruction and removal efficiency (DRE), which indicates the number of molecules removed or destroyed during a process.

Furthermore, air emission standards for products or by-products of the process, such as HCl, HF, or dioxins (PCDD/F = polychlorinated dibenzo-p-dioxins and dibenzofurans), have to be complied with. A list of selected technical performance standards is compiled in Table 2. The emission limits of the EU Waste Incineration Directive (European Parliament and Council, 2000) are included in the table (Table 2) for comparison. These standards

reflect the worldwide stringency of legislative regulations set for the operation of combustion plants burning waste or waste derived fuels.

Local emission limits, e. g. in national air pollution prevention or environmental legislation, have to be adhered to.

Table 2: Selected technical performance standards (emission concentrations: dry, 0 °C, 101.3 kPa) (European Parliament and Council, 2000)

	unit	diluted sources	concentrated sources	EU standards
DRE	%	99.99	95	
HCl/Cl ₂	mg/m ³	100	100	10
HF	mg/m ³	5	5	1
CO	mg/m ³	100	100	50
dust	mg/m ³	50	50	10
PCDD/F	ng-ITEQ/m ³	0.2	0.5	0.1

On this basis, six incineration and six plasma processes as well as four non-incineration technologies were recommended by TEAP. All accepted processes have been demonstrated in pilot plants with a minimum throughput of 1 kg/h. Costs and application of the single processes are also discussed in the report. In view of the situation in developing countries, it can be assumed that the costs of plasma processes and non-incineration technologies as well as the infrastructure requirements impede their implementation. For this reason, this report focuses on incineration technologies and processes.

Municipal solid waste incineration (MSWI) is recommended for CFC blown foam incineration only and only if state of the art technology regarding air pollution and control systems to prevent negative environmental impacts exists. The Japanese guidelines for CFC destruction, however, recommend spraying of CFC directly 'at the bottom of the incinerator', which means injected into an air

supply nozzle (Government of Japan 1999). Rotary kilns and cement kilns can accept gases and foams; the other processes are classified as suitable for gas/liquid destruction.

Based on a literature review, it has to be stated that for most processes no detailed performance data based on full scale application for CFC destruction are found. Most published DE or DRE numbers have been obtained in test trials only. For this reason, the following part gives an overview of approved destruction technologies whereby municipal solid waste incineration, rotary kiln incineration and cement kilns are discussed in more detail. These processes found application in many countries and offer, if locally available, an acceptable balance between technical effort and environmental impact. Their suitability for developing countries will be a major topic for discussion.

Table 3: Overview of approved (H)CFC destruction technologies (based on TEAP, 2002) and their applicability in developing countries

	Approved destruction technologies	Applicability in developing countries	
Incineration technologies	Reactor cracking	<ul style="list-style-type: none"> • Complex technology • High investment and operational costs 	
	Porous reactor	<ul style="list-style-type: none"> • Effective, small, complete reaction • Limited range of application • Lower investment costs than reactor cracking but still high 	
	Gaseous/fume oxidation	<ul style="list-style-type: none"> • Intellectual property rights not easily available • Limited use, little experience 	
	Rotary kiln incineration	<ul style="list-style-type: none"> • Useful if already established (e.g. by chemical companies) • High investment and operational costs 	
	Liquid injection incineration	<ul style="list-style-type: none"> • Relatively low investment costs • Advisable to have other liquid or gaseous waste streams in the country • Difficult to implement (high co-ordination between authorities necessary) 	
	Municipal solid waste incineration (MSWI)	<ul style="list-style-type: none"> • Only existing plants are advisable for ODS • State of the art technology is a pre-requisite to prevent negative environmental impact • High investment and operational cost for new plants 	
	Cement kilns	<ul style="list-style-type: none"> • Already exist in many countries • Already established for hazardous waste treatment • Adjustments are easy and relatively cheap 	
Plasma technologies	Argon plasma arc	in operation	High costs and high requirements impede their implementation in developing countries
	Inductively coupled radio frequency plasma	in operation	
	AC plasma	not yet used for CFC	
	CO ₂ plasma arc	not commercialized	
	Microwave plasma	in operation	
	Nitrogen plasma arc	in operation	
Non-incineration technologies	Solvated electron decomposition		
	Gas phase chemical reduction		
	Gas phase catalytical dehalogenation		
	Superheated steam reactor		

3.2 Reactor cracking

The process is a form of combustion in a cylindrical reactor using a hydrogen-oxygen flame at temperatures around 2,000°C. It has been developed by a German chemical company (Hug et al. 1986) for destruction of residual gases from the production of CFCs. A two-line plant is in operation in Germany which offers services for third parties.

The process is suitable for combustion of large gas quantities in industrial complexes, e.g. for destruction of HFC by-products during chemical production and is usually operated with hydrogen as a fuel. The technology seems unsuitable for operation in most developing countries because of its industrial dimension, its complex technology as well as its high investment and operational costs.

3.3 Porous reactor

In a porous reactor, ODS are broken down into usable components such as HF and HCl. The destruction takes place in an oxidising atmosphere and under a controlled input of natural gas at very high temperatures. The destruction is not taking place in a flame but is supported by the porous and inert matrix with excellent heat transfer properties of the reaction chamber. This means that the ODS have a longer residence time in the destruction zone compared to the destruction with a flame, allowing for a more complete reaction. The products of the reaction are CO₂, HCl, HF and water vapour. The material of the porous matrix is made from graphite, which is resistant to corrosion through the acids (Brandt et al., 2006).

Because of the effective reaction, the chamber can be much smaller than in conventional systems and there is very limited formation of dangerous products. The operation is stable and independent of the load and also allows for very fast and energy efficient start up and shut down.

Even though the porous reactor is cheaper than a reactor cracking plant, it still comes with considerable initial costs. The plant further has a limited range of application, focussing on the destruction of chlorinated and/or fluorinated hydrocarbons. TEAP has approved porous reactors for the destruction of ODS and is recommending them to be approved for the destruction of HFCs as well (TEAP, 2018).

3.4 Gaseous/fume oxidation

In this special rotary kiln incineration process fueled by natural gas or oil, the combustion temperature is in the order of 1,100–1,250°C. In view of refractory corrosion risk by HF (Che et al., 2002) the CFC input has to be limited to a low percentage of the total throughput. Considering that the process is owned by one company and it is actually unclear whether their plants are still in operation, this process will not be discussed in detail.

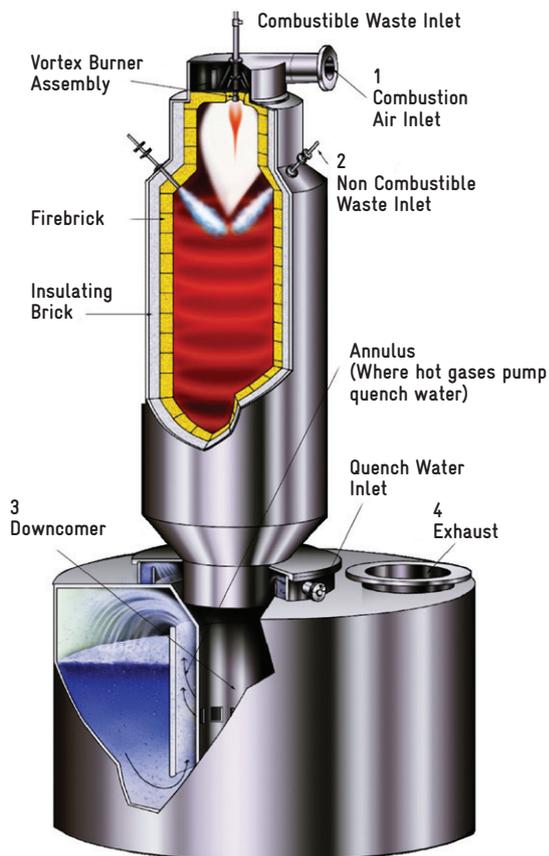
3.5 Liquid injection incineration

A liquid injection incinerator is typically a simple gas or oil fueled combustion chamber. The liquid or gas can either be mixed with the fuel or, as in most cases, separately injected. For high combustion efficiency, a cycloidal burner design is often preferred. Flame stability and corrosion risk may limit the amount of CFC to be injected. A typical liquid injection incinerator is shown in Figure 6.

A similar incinerator is operated in Chiba City, Japan, and destroyed 110 tonnes of CFC in 2004 (Asahi, 2005).

For developing countries, such a process with relatively low investment costs should only be recommended if there are other liquid or gaseous waste streams requiring high temperature treatment, which will not often be the case.

Figure 4: Scheme of a liquid injection incinerator (Linde Engineering, 2018)



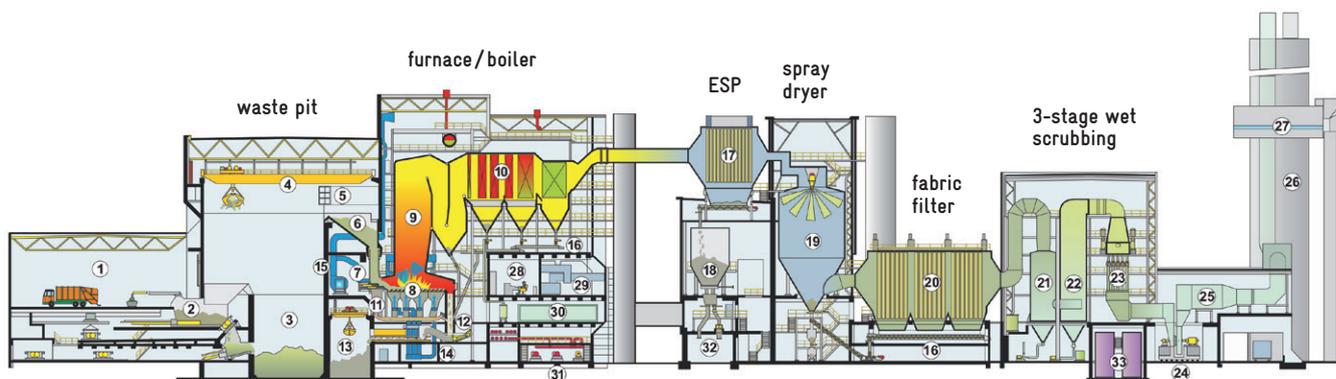
The establishment of such an incinerator requires the close co-operation of various authorities such as for example the environmental protection agency and local municipalities, which in itself is not an easy task.

3.6 Municipal solid waste incineration (MSWI)

MSWI is an established technology for disposing of residual waste in many industrialised countries. The prerequisites, however, are high efforts to guarantee its environmental compatibility, in particular to guarantee an efficient cleaning of the offgas. Hence, the air pollution control system is a very important, complex and expensive part of a waste incineration plant. The scheme of a typical state-of-the-art European grate fired plant, the Amsterdam AEB plant, is depicted in Figure 5.

According to EU regulations, a MSWI has to be operated at combustion temperatures exceeding 850 °C and with a flue gas residence time of more than 2 s (European Parliament and Council, 2000). These conditions are promising to expect a high potential for CFC destruction. Tests on the co-combustion of CFC-11 blown PUR foams as well as on flame retarded PUR and expanded

Figure 5: Scheme of the new lines at the MSWI Amsterdam (ESP: electrostatic precipitator) (AEB 2018, modified)



polystyrene (XPS) foams have been executed in the Karlsruhe TAMARA test plant for waste incineration and in a full-scale German MSWI plant (Rittmeyer & Vehlow, 1993; Rittmeyer et al., 1994; Vehlow et al., 1996).

The results of the TAMARA tests are depicted in Figure 6, the respective destruction efficiencies are compiled in Table 4. Whereas the destruction of CFC-11 and the HCFCs is independent of the combustion temperature, CFC-12 is thermally more stable and reaches the DE values of CFC-11 only at temperatures exceeding 950 °C.

The obtained DE values for all tested compounds of >99.99 % indicate an almost complete thermal destruction and exceed by far the DRE technical performance standards set by the TEAP. Few trials were also executed with CFC gas being injected into the primary air supply of the plants. The calculated DE values were slightly below those found for foam co-combustion and did not fully reach the 99.99 % set by TEAP.

During the tests only traces of potential organic destruction products, such as chlorofluoromethane, could be detected in the low $\mu\text{g}/\text{m}^3$ range. The flue

Figure 6: Residual share of various (H)CFC in the raw gas of TAMARA during co-combustion of PUR/XPS foams as a function of the combustion temperature (Vehlow and Mark, 1996)

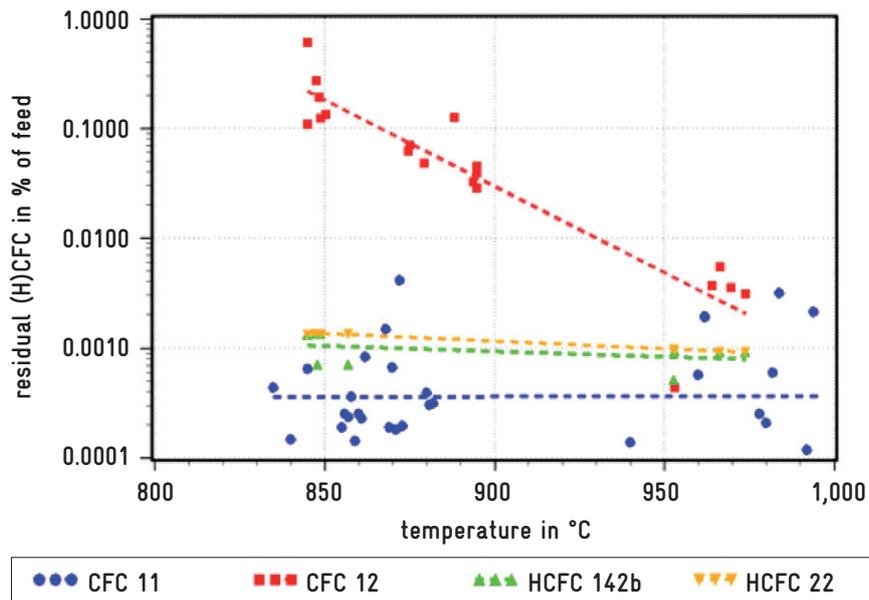


Table 4: Destruction efficiencies in % (* T >950 °C) (Vehlow and Mark, 1996)

	Foam		Gas	
	TAMARA	MSWI	TAMARA	MSWI
CFC-11	99.999 ± 0.001	99.998 ± 0.002	99.95 ± 0.02	99.95 ± 0.02
CFC-12	99.996 ± 0.003*			
CFC-113			99.95 ± 0.02	
HCFC-22	99.999 ± 0.003			
HCFC-142b	99.999 ± 0.003			
PCDD/F	99.999 ± 0.003			

gas concentration of organic micro-pollutants, such as PCDD/F, chlorobenzenes, and chlorophenols, which are always produced during waste incineration, showed no influence whether (H)CFC were added to the waste or not.

In case of incineration of F containing substances, it can be expected that approximately 40% of the element leaves the combustion chamber along with the flue gas and 60% stays as fluorides in the solid residues. The transference of chlorine as HCl into the flue gas is about 90% (Chandler et al., 1997). In well operated MSWI plants the inorganic destruction products HCl and HF in the flue gas are easily reduced well below the emission limits.

A limitation of foam input is caused by its low density. Not to risk uncovered grate sections, the TEAP recommendation to limit the share of foam to 2 wt% should be followed. Under these conditions the HF raw gas concentration is in the order of 20 mg/m³ (Rittmeyer et al., 1994) which is also recommended as upper limit for preventing corrosion attack on the refractory claddings in the furnace (Che et al., 2002). Considering a typical flue gas volume of 5,000 m³/tonne of waste, this implies a maximum input of about 100 g of F or 700 g of CFC-11 per tonne of waste.

From the above described tests, it can be concluded that MSWI could be an environmentally acceptable way for disposal of (H)CFC blown foams but only if state of the art technology regarding air pollution control systems is used to prevent negative environmental impacts. The high annual throughput of such plants – in Germany approximately 20 million tonnes per year – offers a disposal option for huge amounts of foams. However, the costs in terms of investment and operation impede the implementation of waste incineration in developing countries and with that the use of this technology for solving their CFC problem.

3.7 Rotary kiln incineration

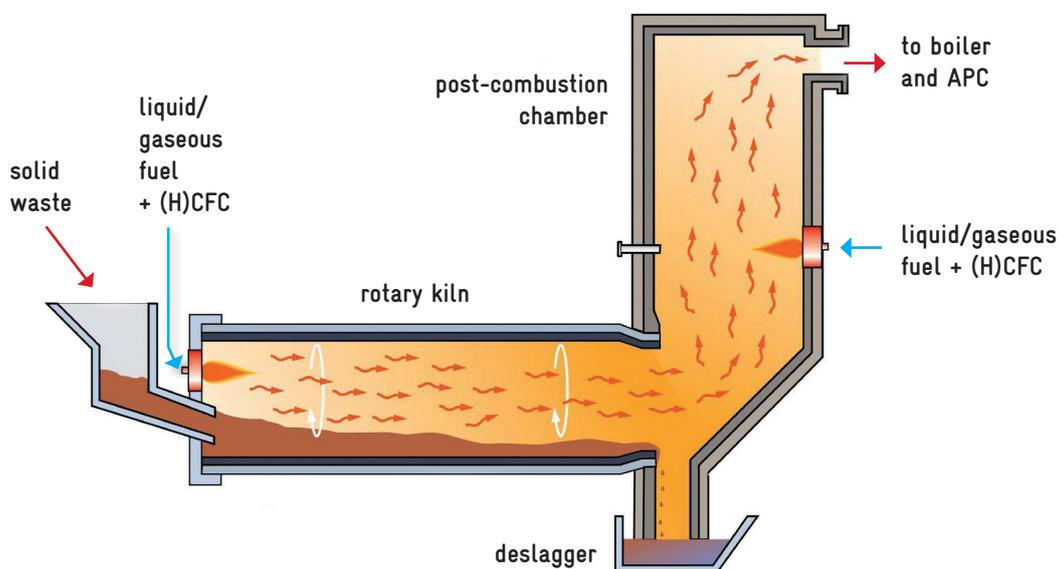
Rotary kiln furnaces are mainly used for the incineration of hazardous waste and have found wide application, especially in industrialised countries. They are operated by public waste management authorities, but to great extent also by private companies, in particular in the chemical industry. A modern hazardous waste incineration plant comprises a rotary kiln furnace followed by a high temperature post-combustion chamber, a boiler for energy recovery and an APC system for emission control. Rotary kiln incinerators are operated at 1,200 °C and a residence time of 2 s (Vandecastelle et al., 2009).

The high temperature has to be maintained by several burners fuelled by natural gas, propane, oil or high calorific gaseous production residues. The main burner is installed at the front-end of the kiln, one or more burners are installed in the post-combustion chamber. The high temperature level makes rotary kiln combustion an appropriate tool for CFC destruction as has been recommended by TEAP and also by the Japanese Guideline. Gases are easily injected into the feeding line of the main burner and foams can be introduced along with the solid waste via the feeding chute. To avoid HF corrosion of the refractory cladding of kiln and combustion chamber the fluorine input by (H)CFC has to be limited (see 3.5).

A scheme of a rotary kiln furnace and post-combustion chamber with indication of potential feeding ports is depicted in Figure 7.

Although being well suited, only few developing countries with big chemical companies in residence can make use of this disposal route, since implementing such systems requires high investment and operational costs which can rarely be raised by the public sector.

Figure 7: Scheme of a rotary kiln with post combustion chamber with indication of potential (H)CFC feeding (Eisenmann, modified)



3.8 Cement Kiln

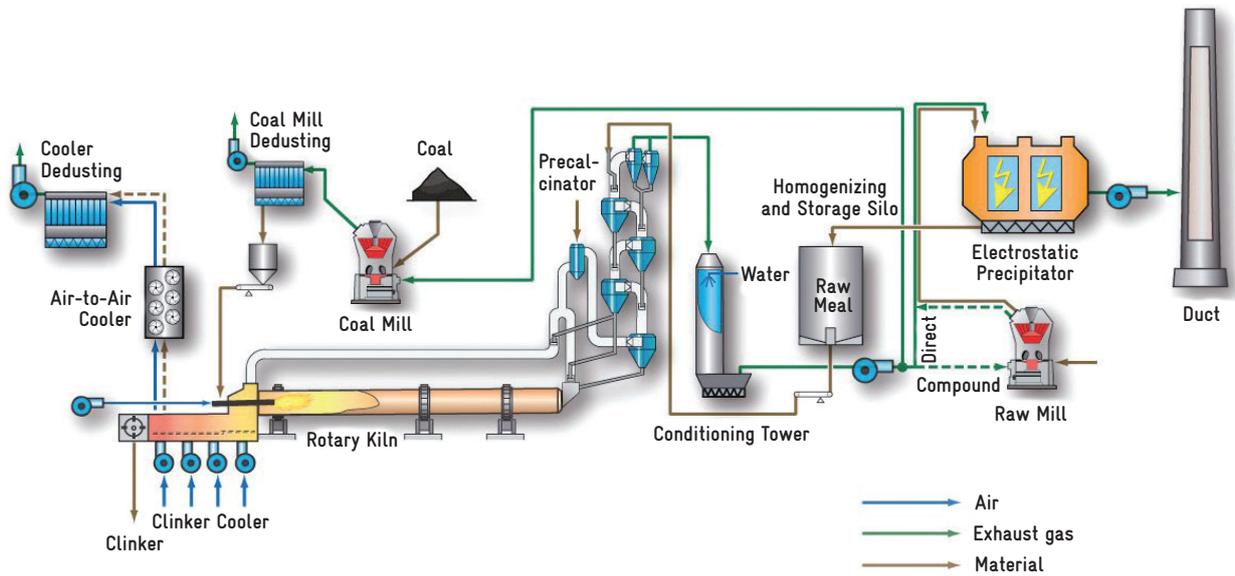
The most suited and most available thermal destruction technology in developing countries listed in the TEAP protocol as well as in the Japanese Guideline is the cement kiln. Whereas MSWI plants and rotary kiln incinerators are not common in emerging and developing countries, cement kilns are found almost everywhere. More than 2,500 cement plants are in operation all over the world, China not included (CemNet, 2017). Adjustments of cement kilns are easy and relatively cheap. A closed area for the reception and storage of refrigerant cylinders is necessary, where cylinders can be stored at ambient temperature. Further, a dosage area has to be established from where the gases can be injected into the kiln. These can include a water bath to facilitate the extraction of the gas, a system of manifolds and gauges to attach the cylinders to the kiln (via a pressure regulator and automatic control panel), a vacuum pump to fully recover the gas from the cylinder and other items such as filter systems, insulating materials and scales for cylinders.

The process

The cement kiln is the core of a plant producing clinker from oxides of calcium, silicon, aluminium, and iron in a high temperature process. The raw material is preheated in a stack of cyclones and then fed into the huge rotary kiln, typically 60–90 m in length and up to 6 m in diameter. The scheme of a cement kiln with raw material pre-heating and clinker cooling is shown in Figure 8.

The clinker production process requires temperatures in the order of 1,400–1,600 °C. The main heat source is a burner situated at the back end of the kiln. The burner is fired with pulverized coal, oil, or even gaseous fuels. The flame temperature reaches 2,000 °C. The temperature profile in a cement kiln is depicted in Figure 9. It documents a temperature regime of 1,000–2,000 °C for a residence time of approximately 10 s which guarantees the almost total destruction of any organic compound, including (H)CFC. These can easily be injected into the primary fuel to pass the hot flame of the burner.

Figure 8: Scheme of a cement kiln with infrastructure (Pacra 2018, modified)

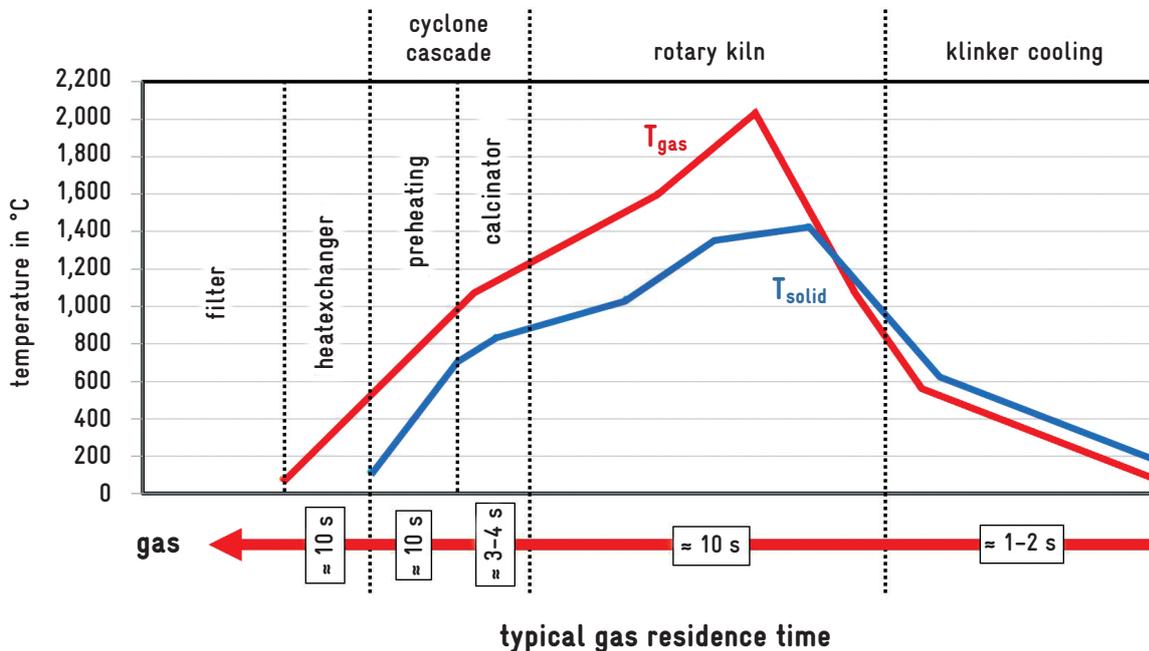


The destruction products HCl and HF are neutralized by the high alkaline environment in a cement kiln. Approximately 90–95% of Cl and F entering a cement kiln are incorporated into the clinker, the remaining fraction are almost totally bound in the fly ash (26). Gaseous HCl or HF virtually do not exist in the strongly alkaline atmosphere of a

cement kiln, hence there is no real emission problem concerning these destruction products.

Feeding of CFCs into a cement kiln is limited by the Cl and F standards set for the clinker product. At Cl concentrations exceeding 0.6 wt % volatile alkali chlorides are formed, which cause problems

Figure 9: Temperature profile of a cement kiln and associated devices (VDI 2003, modified)



in clogging gas ducts (Ahling, 1979). Because of corrosion risk in steel enforced concrete structures, however, for portland cement the Cl concentration should be limited to < 300 mg/kg. The industrial Cl standards are lower in most countries; the F content in clinker is not standardised. Small F-concentrations of 0.2–0.3 wt % improve its mechanical quality (Tran, 2011), though higher concentrations should be avoided (European Commission, 2010).

Test runs

First tests on destruction of chlorinated organic compounds have already been executed in the 1970s in a Swedish cement kiln (Ahling, 1979). The kiln had a length of 140 m, the peak temperature reached 1,450 °C. Additionally to tests feeding aliphatic and aromatic chlorinated compounds, also CFC-113 was injected. The analysed destruction efficiency was > 99.999 %.

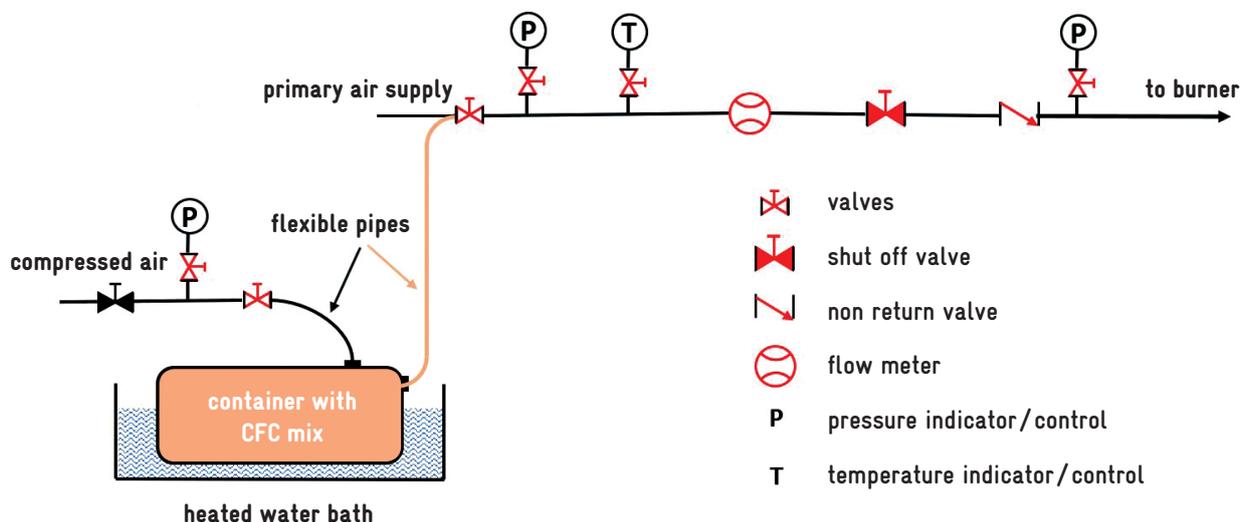
An extended test program on CFC destruction in a 5,000 tonnes/d cement kiln was executed in Japan directly after the ban of CFC production (Ueno et al. 1997). The kiln was fired with coal, but at times also with spent tires or other waste fuel. The temperature was 1,450 °C, the residence time 6–7 s and the flue gas flow rate $\approx 350,000 \text{ m}^3/\text{h}$. The feeding mix comprised CFC-11, CFC-12, and CFC-113; the feeding rate was determined by the tolerable Cl inventory in the clinker. The Japanese Industrial Standard of Cl concentration is 200 mg/kg of clinker; the typical concentration in clinker is 60–70 mg/kg. During the tests the Cl concentration increased by 10 mg/kg only.

The obtained DE values after 10 replica tests were 99.99 % for CFC-11 and CFC-12, for CFC-113 no DE could be calculated since the CFC-113 concentration in the flue gas of the blank test was higher than that measured during the feeding test. This fact indicates that the analysed DE have to be looked upon as minimum values only. The analytical results were at all times close to detection limit.

During the tests, potential organic destruction products have also been analysed in the flue gas. The concentration of for example dichlorobenzenes, showed a 10 % increase on a basis of < $1 \mu\text{g}/\text{m}^3$ during the blank tests which indicates that such substances will also cause no emission risks and characterise, in addition to the high DE values, the excellent performance of cement kilns for CFC destruction.

Respective tests have recently been executed in a state-of-the-art Indian cement kiln (Karstensen et al., 2014). The daily clinker production was 4,626 tonnes, respectively 192.75 tonnes/h, the gas residence time at a temperature exceeding 1,300 °C was approximately 6.5 s. The main pulverised coal fired burner had a primary air consumption of almost 9,600 m^3/h , which is slightly more than 12 tonnes/h. The CFC was mixed with the primary air. The design of the simple CFC feeding system is depicted in Figure 10.

Figure 10: CFC feeding system (tonner: CFC container) (Adjusted after Karstensen, 2014)



The CFC was stored in containers which were, in case of feeding liquid species, heated in a water bath. The test campaign started with basic tests followed by feeding of 30 kg/h of CFC-11 and 40 kg/h of CFC-12 and CFC-113 under the same operation conditions. The CFC input was calculated to keep the Cl concentration in the clinker at ≈ 120 mg/tonne. Each test lasted one day, the flue gas was sampled three times per test condition.

The tests revealed extremely good destruction performance with DRE $> 99.9999\%$ for all CFC. PCDD/F were also analysed and stayed below 0.003 ng-ITEQ/m³ during all test runs.

Based on the above considerations it can be concluded that, without endangering the emission or the product quality, 0.5 kg/h of CFC-11 or 0.2 kg/h of CFC-12 can be destroyed in a cement kiln.

As Table 5 points out, the measured destruction and removal efficiency was in all test trials DRE $> 99.9999\%$.

This underlines the high potential of cement kilns for thermal destruction of various types of hazardous waste (Dempsey & Oppelt, 1993). The measured emission of HCl and HF during the tests was always very low. These acid gases are nearly neutralized by the high alkaline environment in a cement kiln. The retention of HF is in the order of 95 to 98 % and the emission, analysed as fluoride ions, is mainly caused by fine particulate fluorides in the clean gas. Hence, the compliance with the respective air emission limits is assured in a cement kiln.

Table 5: Test conditions and results (Karstensen et al., 2014)

		unit	base test	CFC-11	CFC-12	CFC-113
input	coal	tonne/h	11.7	11.8	11.6	11.8
	CFC	kg/h	0	30	40	40
	Cl	kg/h	0	23	23	23
	F	kg/h	0	4	13	12
	V	m ³ /h	446,500	456,500	446,900	436,400
output	CFC	ng/m ³	nd/nd/nd	24/23/30	5/nd/nd	nd/nd/nd
	η	%	>99.9999	>99.9999	>99.9999	>99.9999
	HCl	mg/m ³	<1.5	<1.5	<1.5	<1.5
	HF	mg/m ³	<0.5	<0.5	<0.5	<0.5
	PCDD/F	ng-ITEQ/m ³	<0.003	<0.003	<0.003	<0.003

Potential for foam

Many cement kilns have an additional burner close to the entrance of the kiln as marked in Figure 10. The temperature at this location is around 1,000–1,200 °C with a gas residence time exceeding 2 s which is high enough to guarantee satisfying (H)CFC destruction. This burner accepts solid fuel of small particle size and is used in many plants for feeding waste-derived fuels in order to save fuel costs (Achternbusch Bräutigam, 2000). Theoretically the burner could be used to mix PUR foams from old refrigerators into the fuel. However, respective tests are not known.

Recommendation

Theoretical considerations and experimental results like those obtained in Sweden, Japan, and India show that cement kilns are one of the best suited destruction technologies for developing countries. They combine good technical characteristics with a high local availability and relatively low costs³ for adapting the kilns for (H)CFC destruction. Stable high temperatures in a highly alkaline environment lead to very high destruction efficiencies without the formation of residual acids and without impacting the cement production.

³ Cement kiln conversion costs of as little as 120,000 US\$ have been given. Higher costs have to be planned for if pilot and quality testing are financed (Source: MLF Project proposals for ODS destruction, own evaluation).

4 Options for HFC Disposal

TEAP has recently published a task force report on destruction technologies for controlled substances (TEAP, 2018), for the first time looking in more detail into the destruction of HFCs with regard to the Kigali phase-down schedule. Technologies considered are only approved ODS destruction technologies. The criteria for approval are the same as for ODS destruction and because of the similarities between CFCs, HCFCs and HFCs, a general compatibility is considered.

As there is currently very little data on HFC destruction, only two established ODS destruction technologies were recommended for approval – Gaseous/Fume Oxidation and Porous Thermal Reactor (not for HFC-23). All other incineration technologies were stated to have high potential. It is assumed that they will be recommended for approval as soon as more test results are available.

As the fluorine content in HFCs is higher than in most CFCs and HCFCs, a higher HF formation resulting from combustion process needs to be observed during the operation of destruction technologies. Counter measures are to co-combust HFCs with other non-fluorinated substances or to reduce the HFC intake in order to keep the overall fluorine content at an acceptable limit. This leads to a lower HFC destruction capacity per hour and has to be taken into account when deciding on destruction technologies.

A second potential topic of concern is the formation of organic fluorine containing destruction products, in particular the formation of fluorine containing dioxins. Dioxins are persistent environmental pollutants and highly toxic and their formation has to be avoided. However, theoretical investigations (Weber & Hagenmaier, 1997) have shown that these substances cannot be synthesised in these combustion processes. This is caused by the high electronegativity of fluorine, which exceeds that of oxygen and prevents fluorides to be oxidised to form elementary fluorine. This step is a funda-

mental reaction step in the synthesis of halogenated dioxins during waste incineration from other molecules (Weber & Hagenmaier, 1997). In light of this, there is no reason to exclude combustion for the destruction of HFC.

The situation is different for pyrolysis processes where organic fluorine compounds such as hexafluorobenzene are present. Under these conditions, polyfluorinated dibenzodioxins (PFDD) and polyfluorinated dibenzofurans (PFDF) can easily be formed (Weber et al., 1995). For HFC destruction the presence of such organic fluorine compounds needs to be accounted for.

5 Conclusions

For a long time (H)CFCs have been used as refrigerants and blowing agents for heat insulating foams. Due to their high ODP, their use has been banned since the 1990s. However, they are still globally in use in old appliances which show up in the waste streams. Their recording, collection, and final disposal is a challenge, in particular in developing countries.

In developing countries, waste management is to a great extent carried out by the informal sector which is driven by recovery of valuable and marketable waste fractions, in case of old refrigerators of the metal crates. In order to make investment in destruction technology profitable, adequate framework conditions and collection systems have to be established in order to ensure a minimum amount of ODS to be collected. It is important to get hold of the whole devices in order to extract the CFC from the still intact cooling circuit. Many countries have set up programs in this regard. The controlled separation and adequate management of PUR foams is more difficult to establish under these constraints, but it is meanwhile performed in a number of places.

The technical challenge is always the final disposal of CFCs to avoid further emissions. TEAP set process conditions for acceptable technology for destruction and published a list of recommended processes, which are suited for this purpose. Out of this list, only incineration processes have been discussed in this paper and out of these, just municipal and hazardous waste incineration, destruction in rotary kilns and cement kilns in more detail. The other thermal processes are special applications and in part not everywhere available. Furthermore, the selected processes are the only ones for which detailed full-scale tests have been published.

Municipal and hazardous waste incineration are typical processes applied in industrialised countries, in many cases already for the purpose in question. Their performance is high but so are their costs. If they are not already established or in the planning

stage in a country, their installation is not very likely. Before existing plants are used for the incineration of ODS, it is advised to monitor flue gas emissions for contaminants. State of the art technology regarding air pollution control systems are a pre-requisite to prevent negative environmental impacts.

The best strategy is the destruction of (H)CFC as such, but also of (H)CFC blown foams, in cement kilns. Such plants are found in most countries around the globe, their adjustment for the task is easy and not expensive. Hence, the process is on the TEAP list and is also recommended by Japan's authorities. The only obstacle may be to get the operators of such plants interested. Most industrial companies try to avoid dealing with waste materials, mainly because of the bureaucratic burden associated with it.

This situation will only be changed after intensive and most likely delicate negotiations between authorities and operators to balance the differing interests. One critical topic may be the limited amount of (H)CFC for destruction considering the high destruction potential of cement kilns in the order of 0.5 kg per tonne produced clinker. This argument can be counteracted by the option to use the kiln in question for other residues such as spent oils from transformers, capacitors, or switches. The disposal of such substances might be a profitable action and pay for the burner modification, which will anyway not impede the regular burner operation if it is not in use.

The destruction technologies described in this report have not been scientifically tested yet for the destruction of HFCs. However, because of the general similarity between CFCs, HCFCs and HFCs, it is expected that they will be approved by TEAP in the near future. The higher fluorine content in some HFCs has to be taken into consideration when HFCs are thermally destroyed, by reducing their concentration in the overall amount in the substance mix to be destroyed.

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