

**MONTREAL PROTOCOL
ON SUBSTANCES THAT DEplete
THE OZONE LAYER**



UNEP

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TECHNOLOGY AND ECONOMIC ASSESSMENT PANEL**

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VOLUME 3B

**REPORT OF THE TASK FORCE ON
DESTRUCTION TECHNOLOGIES**

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**REPORT OF THE TASK FORCE ON
COLLECTION, RECOVERY AND STORAGE**

**Montreal Protocol
On Substances that Deplete the Ozone Layer**

Report of the
UNEP Technology and Economic Assessment Panel

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The TEAP thanks the Hungarian Ministry for Environment for hosting the TEAP meeting in Budapest, Hungary, where this report was reviewed, and finalised.

Foreword

The April 2002 TEAP Report

The April 2002 TEAP Report consists of three volumes:

- Volume 1:* April 2002 TEAP Progress Report
- Volume 2:* April 2002 TEAP Replenishment Task Force Report
- Volume 3:* April 2002 TEAP Task Force on Collection, Reclamation and Storage Report, together with the April 2002 TEAP Task Force on Destruction Technologies Report

Volume 1

Volume 1 contains an Executive Summary of all TEAP Report topics, as well as the Executive Summaries of Volumes 2 and 3.

Volume 1 contains

- An accounting framework for ODS production, consumption and emissions (being developed in co-ordination with the SAP);
- recommendations for essential use nominations;
- an update on laboratory and analytical uses (as requested in Decisions XI/13, X/19);
- a chapter on Campaign Production for MDIs (as requested in Decision XIII/10);
- the annual update on nPB production, use and emissions (as requested in Decision XIII/7);
- additional reports on process agent uses (as requested in Decisions X/14 and XIII/13).

Volume 1 also contains progress reports of TEAP Technical Options Committees (according to Decision VII/34). Finally, it presents an update on TEAP's changing membership and gives background and contact information for TEAP and TOC members (Decision VII/34).

Volume 2

Volume 2 is the Assessment Report of the TEAP Replenishment Task Force of the Funding Requirement for the Replenishment of the Multilateral Fund during 2003-2005, in response to Decision XIII/1.

Volume 3

Volume 3 includes reports of the Task Force on Destruction Technologies (TFDT) and the Task Force on Collection, Reclamation and Storage (TFCRS), in response to Decision XII/8.

April 2002

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REPORT OF THE TASK FORCE ON
DESTRUCTION TECHNOLOGIES

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Executive Summary

Recommended Technologies

This document presents a comprehensive assessment of technologies available for the destruction¹ of the current and anticipated global stocks of surplus ODS, including both dilute (including foams) and concentrated sources. The assessment incorporates updated information on the technologies and applies updated evaluation criteria developed by the recently reconvened UNEP Technology and Economic Assessment Panel (TEAP) Task Force on Destruction Technologies (TFDT).

The main purpose of this document is to recommend technologies for destroying surplus stocks of ODS, based on an assessment of their technical capability using available information. Although a significant amount of information specific to individual technologies is provided, it is not the intention here to rank the technologies meeting the criteria for recommendation.

The Task Force developed updated screening criteria, which were applied to 45 identified technologies. Sixteen technologies met the screening criteria. The “screened-in” technologies were then evaluated further with emphasis on actual data about ODS destruction performance. Of these, twelve technologies met the recommended criteria. Three of these twelve are in common commercial use. Only two technologies are recommended for the destruction of foams².

The recommended technologies are:

1. Concentrated sources:

- Cement Kilns
- Liquid Injection Incineration
- Gaseous/Fume Oxidation

¹ Earlier versions of this document – and some other reports referenced – have often used the terms “destruction” and “disposal” interchangeably. Based on comments from the TFDT, the former term has been used exclusively here. Technologies that do not actually destroy ODS (*i.e.*, sequestering or long-term storage approaches) are not considered within the terms of reference of this report.

² The TEAP has confirmed one technology for recommendation for both concentrated and diluted sources, namely, rotary kiln incineration. As destruction of ODS from foams has only recently emerged as significant commercial practice, the technical information on diluted sources is still emerging. However, information on both Municipal Solid Waste Incineration from Europe and Rotary Kiln Incineration from Japan were sufficient to give the TEAP the confidence to recommend these two technologies, as listed.

- Reactor Cracking
- Rotary Kiln Incineration
- Argon Plasma Arc
- Inductively-Coupled Radio-Frequency Plasma
- Nitrogen Plasma Arc
- Microwave Plasma
- Gas Phase Catalytic Dehalogenation
- Super-Heated Steam Reactor

2. Diluted Sources (foams)

- Municipal Solid Waste Incinerators
- Rotary Kiln Incinerators

This report contains summary descriptions and discussions of screened-in technologies. More detailed descriptions of all the technologies are included as an Appendix.

This work took as its starting point documents developed by the United Nations Environmental Programme (UNEP) on this subject in 1992³ and 1995,⁴ and provides the most comprehensive evaluation of destruction technologies for ODS to date. The current work builds upon previous work by incorporating material acquired from numerous sources in the course of continued work in the year 2001 on the issue of ODS destruction. Additional literature research was conducted specifically for this initiative, and several technology suppliers were contacted for detailed clarifications and updates. This document also includes detailed information that has recently become available, which was originally presented at the *International Workshop on the Destruction of Ozone-Depleting substances* in Geneva, Switzerland, July 10, 2000.

³ UNEP 1992. Report of the *Ad Hoc* Technical Advisory Committee on ODS Destruction Technologies. United Nations Environment Program. May 1992.

⁴ UNEP 1995. 1995 ODS Disposal Technology Update. United Nations Environmental Program: Report of the Technology and Economic Assessment Panel ODS Disposal Subcommittee Workshop held in Montreal, Canada, May 2-3, 1995. June 1995.

During the course of the Task Force's efforts, a number of issues have been identified which merit further consideration by the Technical and Economic Assessment Panel. The Task Force has outlined these issues in the recommendations of this report.

Comments

The TEAP and its Task Force on Destruction Technologies provides the following for consideration by the Parties:

1. The list of destruction technologies can be updated on a bi-annual basis to ensure that the latest technological developments are available to the Parties.
2. Consideration can be given to linking the work of the TFDT with other multilateral agreements (e.g. Stockholm Convention on POPs, Basel Convention) to facilitate transportation of ODS across international borders so as to increase the economic viability of ODS destruction.
3. A short practical guide for the import and export of ODS for destruction could be incorporated in future TEAP workplans.
4. Destruction of foams can be investigated further to better assess the most appropriate technologies required for destruction to maximise the ODS capture and destruction.
5. Further consideration can be given to the calculation of DRE for foams.
6. A more comprehensive review of regulations pertaining to ODS destruction in developed countries could be undertaken.
7. The overall calculation of DRE can be revisited taking into consideration ODP.
8. Technologies that convert ODS into useful compounds via chemical reactions can be investigated in the future work of the TFDT.
9. A review of existing facilities that have destroyed ODS or are commercially available for this function can be assembled. This review would be used for the development of a list of commercial destruction facilities world-wide. In this review, descriptions of the facilities would include; details about the plant, geographic location (country, city), capabilities, type of technologies, DREs, emission rates, certifications, etc. In addition, an analysis of their destruction process and their effectiveness in destroying various types of ODS can be included.

10. A more comprehensive study can be undertaken to assess ways on avoiding fugitive emissions when handling, crushing or grinding foams, prior to introduce them into the furnaces.
11. An assessment of the current total global ODS destruction capacity for CFCs, halons and foams can be considered on a country basis in an effort to put the issue of future technological developments into context.
12. An in-depth assessment of the price per kg for destruction of ODS material can be completed to better assess the cost implications for destroying anticipated stockpiles.
13. Consideration can be given to the estimation of carbon tetrachloride, which is likely to be co-produced in the production of chloromethanes and needs to be destroyed beyond 2010.
14. Possible ODS likely to be available in some of the large ODS consuming Article 5(1) Parties can be estimated and techno-economic feasibility for the destruction of those ODS can be assessed.
15. Additional information can be gathered to validate sampling and analytical methods for ODS compounds in exhaust gas streams, in order that experience in this area be shared

1 Introduction

1.1 Background

Two years after the Montreal Protocol was signed, the Technical Review Panel (the present Technology and Economic Assessment Panel (**TEAP**)) reported in its first Assessment Report in 1989 on the status of the technology for the destruction of CFCs and halons. The Panel concluded that the establishment of approval criteria required detailed technical consideration of each individual technique. At the second Meeting of the Parties, London 1990, the Parties to the Montreal Protocol decided to establish an Ad-hoc Technical Advisory Committee on Destruction Technologies; the text of the relevant Decision is given in Appendix C in this report.

In 1991, this Technical Advisory Committee (TAC) was formed. The Committee consisted of eleven full members and fourteen observers and was chaired by Mr. Abe Finkelstein from Canada. It finalised its report in the course of 1992, in which five technologies were recommended to the Parties for approval. The Parties accepted the recommendations and issued a Decision in which they approved five of the technologies recommended by TAC. In 1995 the Committee updated its report. In two Decisions, taken at the Fifth (1993) and Seventh Meeting (1995) of the Parties, the Parties approved another two technologies. This was based upon updated information provided by the technical experts.

In the year 2000, a technical workshop on ODS destruction technologies was held in Geneva, Switzerland, where also many Parties participated. In a subsequent Decision taken at the 12th Meeting of the Parties, Ouagadougou 2000, the Parties requested the TEAP to establish a Task Force on Destruction Technologies (see the relevant Decision below).

This Task Force on Destruction Technologies (TFDT) was set up by the TEAP, during its annual progress meeting, in New York, April 2001. A first meeting of the TFDT to discuss membership and procedures was held in Montreal, July 2001, back-to-back with the 19th OEWG. The Task Force consists of sixteen full members and three consulting members, selected on the basis of geographical distribution and on the basis of technical expertise. The Task Force is co-chaired by Dr. Sukumar Devotta, India, Mr. Abe Finkelstein, Canada and Dr. Lambert Kuijpers, Netherlands, who also co-chairs the TEAP.

The Task Force met three times:

- (1) in Eschborn, Frankfurt, October 2001, hosted by GTZ Germany, to discuss the set up of the report and to decide upon all necessary actions;
- (2) in Maastricht, January 2002, to review the draft of the appendix describing the technologies and the part of the body of the report that describes the screening-in of the different technologies, and to take decisions on the additional work to be performed; and
- (3) in Washington, March 2002, before the Earth Technologies Forum Meeting, hosted by the US EPA, during which meeting the report was discussed and reviewed. Decisions were taken which additional actions would be needed to complete the report and certain members were assigned with these tasks.

After a final review by the full TFDT, in April 2002, the report was submitted to the TEAP for review and will become part of the TEAP 2002 Progress Report to the Parties.

1.2 Objective of the Report

During the period 1992-2000 the necessity of the destruction of ODS has become more urgent. In 2000, Parties therefore took a decision to request the latest information from the Technology and Economic Assessment Panel on destruction technologies and on the related logistics where it concerns ODS material flows. They adopted Decision XII/8, "Disposal of controlled substances" which reads as follows:

Noting decisions II/11, III/10, IV/11, V/26 and VII/35 on destruction technologies and the previous work of the Ad Hoc Technical Advisory Committee on Destruction Technologies;

Also noting the innovations that have taken place in the field of destruction technologies since the last report of Advisory Committee;

Recognising that the management of contaminated and surplus ozone-depleting substances would benefit from further information on destruction technologies and an evaluation of disposal options;

1. *To request the Technology and Economic Assessment Panel to establish a task force on destruction technologies;*

2. *That the task force on destruction technologies shall:*
 - (a) *Report to the Parties at their Fourteenth Meeting in 2002 on the status of destruction technologies of ozone-depleting substances, including an assessment of their environmental and economic performance, as well as their commercial viability;*
 - (b) *When presenting its first report, include a recommendation on when additional reports would be appropriate;*
 - (c) *Review existing criteria for the approval of destruction facilities, as provided for in section 2.4 of the Handbook for the International Treaties for the Protection of the Ozone Layer;*

3. *To request the Technology and Economic Assessment Panel:*
 - (a) *To evaluate the technical and economic feasibility for the long-term management of contaminated and surplus ozone-depleting substances in Article 5 and non-Article 5 countries, including options such as long-term storage, transport, collection, reclamation and disposal of such ozone-depleting substances;*
 - (b) *To consider possible linkages to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal and other international treaties as appropriate regarding the issue of disposal;*
 - (c) *To report to the Parties on these issues at their Fourteenth Meeting in 2002.*

This 2002 Task Force report considers in its section “Appendix C” the decisions taken by the Parties to the Montreal Protocol in the period 1990-1997 regarding the appropriateness of destruction technologies for ODS. It summarises the findings of the Ad Hoc Technical Advisory Committee on Destruction Technologies, which published a report in 1992, via a quotation of the relevant text in Annex IV of the Fourth Meeting of the Parties to the Montreal Protocol, where the Parties considered the report by the Ad Hoc Advisory Committee. In this part the technologies that were approved by the Parties in 1992 and in subsequent years for the destruction of ODS can be found.

The 2002 Task Force report considers all innovations that have taken place in the field of destruction technologies in the period 1990-2001. The report reviews destruction technologies for concentrated, re-concentrated and diffuse sources of ODS.

This report is also based upon the fact that the management of contaminated and surplus ODS would benefit from an inventory of and recommendations for destruction technologies. It is published together with a parallel report on collection, reclamation and storage that has been developed by the TEAP Task Force on Collection, Reclamation and Storage. The reports of the two Task Forces should provide the Parties to the Montreal Protocol with sufficient information for a decision how to proceed. This decision will be taken by the 14th Meeting of the Parties in 2002, and is expected to include an updated list of approved technologies for destruction.

1.3 Status of Regulations on ODS Disposal

Many Article 2 and a few Article 5 Parties have developed regulatory programs to address the proper use and disposal of ozone-depleting substances and ODS-containing equipment. Regulations include: (1) proper recycling methods for ODS and ODS-containing equipment; (2) banning the release of ozone-depleting refrigerants; (3) placing controls on the production and consumption of ODS, including placing restrictions on the quantity of ODS imported for destruction purposes; (4) creating hazardous waste regulations that control the destruction of ODS.

1.3.1 Sector wise ODS Regulations

Countries tend to regulate ODS based upon the end-use sector in which they are used. For example, ODS used as refrigerants, solvents, fire protection systems, foam insulation, may be regulated differently and some salient features are described below.

Refrigerants Several Parties require that ODS refrigerants be removed from equipment (for example household refrigerators), recovered, and in some cases destroyed before such equipment can be disposed off. These requirements can apply to ODS in the insulating foam as well. Some countries restrict the types of ODS that may be recycled and reused until a given date (e.g. HCFCs). For ODS, which are not required to be destroyed, recovery is typically required during the servicing or before the dismantling or disposal of equipment. Many countries require that recovered ODS be sent to specific destruction facilities.

Solvents Several Parties require that all ODS solvents be recovered during servicing of equipment or prior to dismantling or disposal of equipment. These governments require that the recovery and destruction of ODS solvents be by an environmentally acceptable technology.

Fire Protection Systems: Many Parties require that halons and other ODS contained in fire protection systems be recovered during maintenance or prior to dismantling or disposing of fire protection equipment. Exceptions are generally made for halon reuse in “critical uses” categories, such as military and aviation applications.

Foams Few Parties have historically called for recovery of ODS from foams. However, this situation is changing, particularly in the European Union.

When performed, the recovered fluid is typically destroyed. Few Parties regulate destruction facilities solely on the basis of the ODS destroyed. Most destruction companies, permitted by the government to destroy other substances, also have the technology to destroy ODS. Governments that are parties to the Protocol require that the destruction of ODS is done using technologies approved by the Parties to the Montreal Protocol, namely, (1) liquid injection incineration; (2) reactor cracking; (3) gaseous/fume oxidation; (4) rotary kiln incineration; (5) cement kiln; (6) radio frequency plasma; or (7) municipal waste incinerators.

1.3.2 ODS Destruction Regulations

Regulations require a strong enforcement component in order to be effective. Although one can find many Parties regulating the ODS destruction, only a few are cited in this report to exemplify the emerging trend and should not be considered exhaustive.

The *U.S.* requires each producer of a Group I controlled substance (primarily CFCs) to report the quantity of controlled substances used in processes that resulted in their transformation or destruction, and the quantity sold for use in processes that resulted in their destruction or transformation. The Resource Conservation and Recovery Act (RCRA) of US lists 85 process wastes and approximately 400 chemicals as hazardous wastes, including CFCs and HCFCs, which are listed as hazardous wastes from non-specific sources, spent halogenated solvent, and commercial chemical products (e.g., CFC-11 and CFC-12). In 1996, EPA passed the "MACT" rule (maximum achievable control technology) to upgrade the emission standards for dioxins (PCDDs), furans (PCDFs), mercury, cadmium, lead, particulate matter, hydrochloric acid, chlorine, hydrocarbons, carbon monoxide, and several low-volatile metals produced from hazardous waste combustors. Specifically, this rule affected incinerators, cement kilns, and lightweight aggregate kilns.

The *European Union* has adopted regulations to reduce emissions of ODS. The new regulation (2037/2000) covers the use, reuse, and disposal requirements for ODS, including virgin and recycled CFCs, HCFCs, refrigerant blends, halons

(including CBM), 1,1,1-trichloroethane, and carbon tetrachloride. In addition, the regulation mandates the recovery and destruction of blowing agent from domestic and commercial refrigerators. In the EU, it is possible that some waste ODS may be classified as “special waste” and subject to more stringent disposal arrangements than most other wastes. Local Environmental Agencies are responsible for regulating these “special wastes.”

Swedish regulations require importers and distributors of refrigerants to take back the refrigerant that they supply for recycling or destruction purposes, at no charge. Industry is responsible for reclamation of recovered refrigerants. To cover these costs, the importers/distributors include a fee in the price of refrigerant sold. Recovered refrigerants that cannot be reused due to excessive contamination must be sent for destruction. Used refrigerants are classified as hazardous waste and must be destroyed according to the Swedish Waste Ordinance. A permit from the Swedish EPA is required for export of recovered/used refrigerants, and as of 1 January 1997, export permits are only issued for the purpose of destruction abroad. The recovery of foam blowing agents from domestic refrigerators has been required since the middle 1990s.

In *Switzerland*, ODS is classified as a hazardous waste and can only be incinerated in high performance incinerators. Although there is no set standard for DRE, the high emission standards guarantee that DREs for incineration are >99.99 percent.

In *Australia*, New South Wales (NSW) and Australian Capital Territory (ACT), have regulations that address destruction of ODS. In practice, all destruction of ODS in Australia occurs at the PLASCON facility at the Australian National Halon Bank in Melbourne, Victoria (see Section II for more details).

Since 1998, *New Zealand* has also collected and sent ODS to the Australian National Halon Bank for recycling and destruction. There is a 25 percent government subsidy for collection, transport, and shipping costs of Halon 1211 sent to Australia for destruction. Since 1995, the refrigeration industry has operated a levy scheme, based on national sales of HCFCs, to fund the transport and destruction of "end of life" CFCs and HCFCs. All fees collected under the levy scheme are for environmentally safe destruction. Although the government of New Zealand strongly endorses the levy scheme, there is no direct government involvement in its operation. To date, over 18,000 kilograms have been exported to Australia for destruction.

The *Japanese* government has issued manuals, to promote safe and environmentally sound management practices for more than 30 ODS destruction facilities in the country. The manual includes information on how to safely manage six different types of destruction technologies (i.e., waste incineration,

manufacturing plant, incineration in water, plasma, catalytic processes, and thermal vaporization). The manual also prescribes the targets for destruction efficiency (≥ 99.99 percent) and emission standards.

Brazilian Government regulations prohibit the destruction of chlorinated compounds in cement kilns. Other than this regulation, there are no Brazilian regulations covering the destruction of ODS. In order to be issued an operation license, destruction facilities must conduct a trial burn to demonstrate that the incinerator meets certain criteria and emission standards..

1.3.3 ODS Destruction Regulations

Brazilian Government regulations prohibit the destruction of chlorinated compounds in cement kilns. Other than this regulation, there are no Brazilian regulations covering the destruction of ODS. In order to be issued an operation license, destruction facilities must conduct a trial burn to demonstrate that the incinerator meets the following criteria and emission standards: DRE (POHPs) = 99.99%; DRE (PCBs) = 99.999%; CO \leq 100 ppm; HCl \leq 1.8 kg/hr or 99% removal for wastes containing more than 0.5% Chlorine; SO_x \leq 280 mg/std m³ (measured as SO₂); NO_x \leq 560 mg/std m³ (measured as NO₂); HF \leq 5 mg/std m³; Dioxins and Furans \leq 0.4 ng/std m³; Particulate matter \leq 70 mg/std m³; Metals: class 1 (Cd, Hg, Tl) \leq 0.28 mg/std m³ (for flow rates exceeding 1 g/hr); Metals: class 2 (As, Co, Ni, Se, Te) \leq 1.4 mg/std m³ (for flow rates exceeding 5 g/hr); Metals: class 3 (Sb, Pb, Cr, Cu, Mn, Pt, Pd, Rh, V, Sn, cyanides and fluorides) \leq 7 mg/std m³ (for flow rates exceeding 25 g/hr).

In *Australia*, New South Wales (NSW) and Australian Capital Territory (ACT), have regulations that address destruction of ODS. The NSW regulations state that destruction of halons, CFCs and HCFCs must be approved by the NSW Environmental Protection Authority.

The ACT regulations state that destruction of ODS requires authorization by the ACT Department of Urban Services. In practice, all destruction of ODS in Australia occurs at the PLASCON facility at the Australian National Halon Bank in Melbourne, Victoria (see Section II for more details). This Halon Bank is managed by DASCEM Holdings Pty Ltd. DASCEM has agreements in place with various entities such as Refrigerant Reclaim Australia (a refrigeration industry body that collects CFC refrigerants) to direct CFCs and halons to the Halon Bank. Since 1998, however, New Zealand has collected and sent all ODS to the Australian National Halon Bank for recycling and destruction. Halon Recycling Ltd, a non-profit company established by the fire protection industry, facilitates the collection and transportation of Halon 1211 for destruction and Halon 1301 for recycling. There is a 25 percent government

subsidy for collection, transport, and shipping costs of Halon 1211 sent to Australia for destruction. Since 1995, the refrigeration industry has operated a levy scheme, based on national sales of HCFCs, to fund the transport and destruction of "end of life" CFCs and HCFCs. All fees collected under the levy scheme are for environmentally safe destruction. Although the government of New Zealand strongly endorses the levy scheme, there is no direct government involvement in its operation. To date, over 18,000 kilograms have been exported to Australia for destruction.

The *Japanese* government has issued manuals, to promote safe and environmentally sound management practices in the more than 30 ODS destruction facilities that operate in the country. The latest manual includes information on the proper handling of CFCs in destruction facilities, from acceptance of CFCs, to recovery, transfer, storage, and destruction. It also includes information on how to safely manage six different types of destruction technologies (i.e., waste incineration, manufacturing plant, incineration in water, plasma, catalytic processes, and thermal vaporization). Additionally, the manual outlines the targets for destruction efficiency (e.g., equal to or greater than 99.99 percent), as well as safe operating practices, and minimum emission standards. By July 2000, more than 800 copies of this manual had been distributed throughout the country.

1.3.4 Hazardous Waste Regulations

The U.S. Congress enacted the Resource Conservation and Recovery Act (RCRA) in 1976 to regulate the management of non-hazardous waste and hazardous waste, including ODS. RCRA lists 85 process wastes and approximately 400 chemicals as hazardous wastes, including CFCs and HCFCs, which are listed as hazardous wastes from non-specific sources, spent halogenated solvent, and commercial chemical products (e.g., CFC-11 and CFC-12).

In 1996, EPA passed the "MACT" rule (maximum achievable control technology) under the joint authority of RCRA and CAAA. The purpose of the MACT was to upgrade the emission standards for dioxins (PCDDs), furans (PCDFs), mercury, cadmium, lead, particulate matter, hydrochloric acid, chlorine, hydrocarbons, carbon monoxide, and several low-volatile metals produced from hazardous waste combustors. Specifically, this rule affected incinerators, cement kilns, and lightweight aggregate kilns.

In the EU, it is possible that some waste ODS may be classified as "special waste" and subject to more stringent disposal arrangements than most other wastes. Local Environmental Agencies are responsible for regulating these "special wastes."

1.3.5 Enforcement

In the United States, EPA is charged with enforcement of the ODS treatment and disposal regulations. Enforcement actions, which are handled through EPA headquarters and at the local level primarily through EPA's ten regional offices, may include civil fines of up to \$27,500 and criminal prosecutions.

After signing the Montreal Protocol, the Brazilian government formed the Inter-ministerial Executive Committee for the Protection of Ozone Layer (PROZON) with responsibilities over all ODS-related regulations and activities. The Brazilian Environmental Crimes Law controls the handling of toxic substances that are damaging to human health and the environment, including ODS. The law also governs the handling of equipment and systems that contain CFCs and HCFCs. According to this law, anyone who violates the regulations on producing, processing, packaging, commercializing, transporting, handling, using, supplying, importing, or exporting these substances, is subject to a fine of between R\$500 and R\$2,000,000 (equivalent to approximately US\$210 to US\$837,000).

1.4 Material Flows on the Basis of Inventory Data

1.4.1 Foams

Recent legislative developments in both Europe and Japan are expected to dramatically increase the volume of foams and their blowing agents being identified for destruction. Although most global legislation is currently restricted to refrigerators, primarily because of their portability and abundance, developments in the design of building elements and the management of building waste from demolition sites could increase the material flows still further in future. However, this will take many years to significantly impact recovery rates because of the long life-cycle associated with building products. It is currently impractical to recover significant amounts of blowing agent from foams installed using traditional building methods.

Some foams will be dealt with by direct incineration, while the bulk will undergo mechanical recovery to extract the blowing agents and re-concentrate them prior to incineration. Figure 1-1 shows the expected material flows through each route.

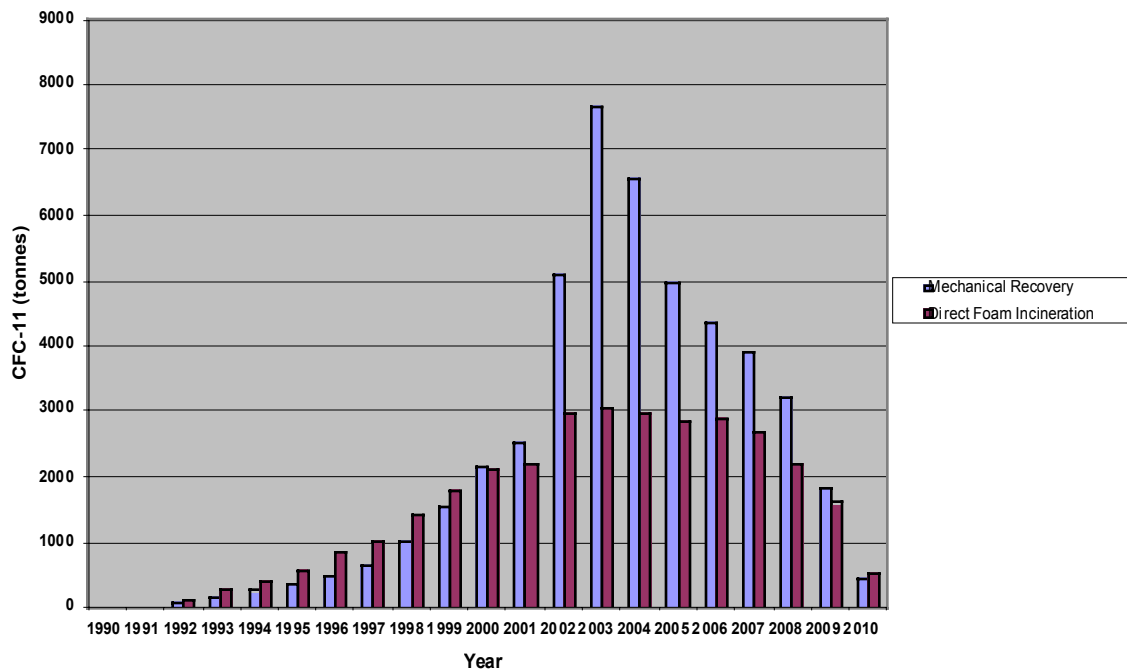


Figure 1-1: Global Recovery of CFC-11 from Foam by Method

The direct incineration of foam takes a higher profile than would be expected from a consideration of the European and Japanese experience because the information available suggests that the USA already operates more direct incineration facilities than elsewhere. It should be noted also that the weight of polyurethane foam being incinerated is typically 10 times as great as the blowing agent destroyed in the direct incineration scenario. This equates to approximately 30,000 tonnes globally on the basis of the above projections.

The mechanical recovery process is typically fed by a shredder at the front end of the unit. Accordingly, it has been possible (most notably in Japan) to modify existing shredder units at waste installations for the purpose. Shredding of refrigerators without recovery of blowing agent has been relatively widely practised globally where the recovery and recycling of metals and plastics is being encouraged or where landfill space is limited. Ironically, one of the best policies for minimising emissions over the next ten years remains to leave all refrigerator cabinets in tact! However, such an approach does not deal with the longer-term emissions that will eventually arise. With mandatory recycling targets now being introduced in Japan the opportunity is being taken to recover and destroy the blowing agents. However, in contrast with the European scene, this is not a mandatory element at present.

This complex set of parameters leads to a projected set of global CFC-11 emissions from refrigerators as shown in Figure 1-2 and Figure 1-3

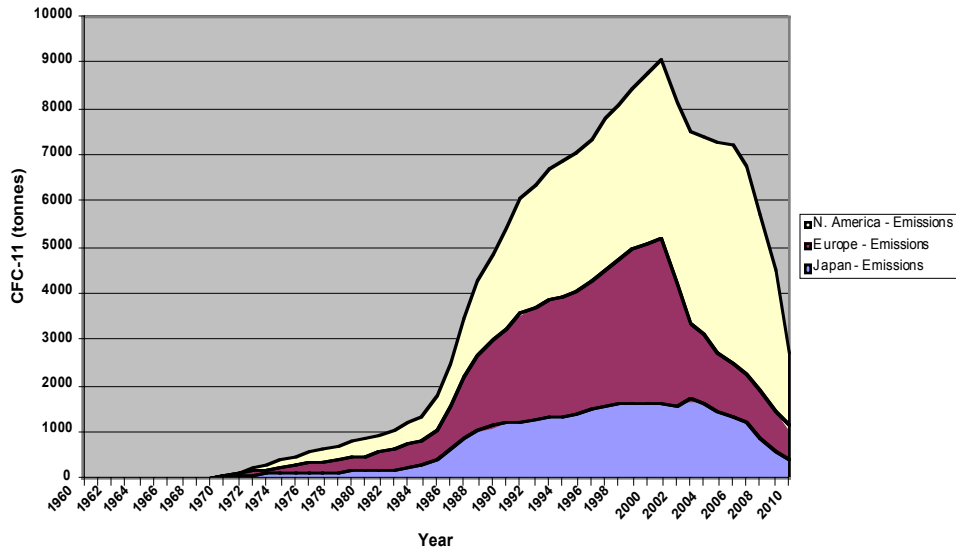


Figure 1-2: CFC11 Actual/Projected Emissions from Refrigerators

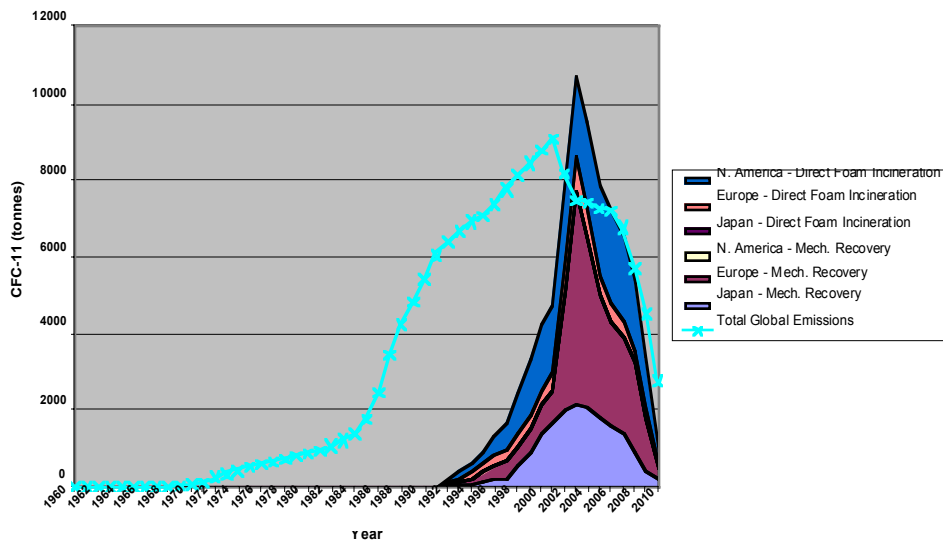


Figure 1-3: CFC-11 generated through Mechanical Recovery

It can be seen that the upward trend in emissions is arrested by the action in Europe and Japan, although the decrease in global emissions is only around 1,500 tonnes despite the fact that between 8,000 and 10,000 tonnes of CFC-11 is likely to be taken out of circulation annually over the next few years. There are two reasons for this. The first is that the act of mechanical recovery will potentially stimulate greater percentage losses in the year of destruction than

would have happened if the cabinet had been left untouched (up to 5% versus 0.5%). The second is that future emissions are mitigated. Accordingly, the emissions of CFC-11 tail off more rapidly than they otherwise would have done towards 2010.

1.4.2 Halons

The amount of total global halon inventory depicted in Table 1-1 and Table 1-2 represents the total installed, the total recovered/reclaimed, and recovered but not yet reclaimed quantities for halon 1211 and 1301. The recovered and reclaimed quantities reside in stockpiles awaiting future disposition in other critical applications or possible future destruction. As for halon 2402, relatively little inventory data is available. In the Russian Federation, the Commonwealth of Independent States (CIS) and the Baltic countries, halon 2402 has been used for over 20 years. Halon 2402 use is still critical in some military applications, ships, aviation, gas, and oil extracting facilities and nuclear power plants. Based on the fact that production exemptions were provided for the Russian Federation, it would be reasonable to assume very little excess, if any will be available for destruction.

Considering the uncertainties surrounding possible future regulatory mandates and inventory management strategies and their impacts, it is difficult at this point in time to predict from these inventories the exact halon quantities that could become available for destruction. These uncertainties are reflected in the latest TEAP HTOC documents. The 1998 HTOC report had indicated that halon 1211 and 1301 were in balance as far as projected inventory (bank) and consumption rates. However, the latest TEAP report quoted below now indicates there may be excess halon 1211.

The April 2001 TEAP report, Section 6, Response to Decision X/7 stated:

“For the past several years the HTOC has used a computer program to estimate the size of the halon "bank" and the annual transfer of halon from less critical to more critical applications. The computer program uses historic production data and estimated recovery and emission factors for halons. It is based on a steady state flow of halon fire protection equipment reaching the end of its useful life, when the halon is then recovered, recycled and reused for more critical and essential uses. However, two events have recently taken place that has drastically changed this pattern. Firstly, the US Military established its own halon bank and has built a reserve adequate for the expected life of critical equipment. This decision has resulted in a much larger than expected flow of halon from existing installations into a single bank. Secondly, the newly adopted EC-regulation that mandates the decommissioning of all

but critical halon system within the next 3 years has resulted in a collapse of the market for recovered and recycled halons in Europe.

Based on the quantitative information provided by 3 Parties and 1 region, it appears that in these countries/regions there is a surplus of both halon 121 1 and halon 1301 in excess of the requirements for present and future critical uses. However, the information provided contained significant uncertainties regarding the quantities of stored or installed halons, the rate at which they are currently consumed, and the quantities that will be required to meet future uses. Two Parties also reported a surplus of halon 2402.

With regard to earlier assessments of the HTOC on availability of halons for critical uses, the supplied data appears to confirm the HTOC estimate of a surplus of halon 1211 in many of the countries of Parties not operating under Article 5(l). Parties therefore may wish to consider developing measures to collect and store surplus halon 1211 and proceed with the destruction of excess material.

Regarding halon 1301, the information supplied by these Parties/regions indicates a larger regional surplus of halon 1301 than HTOC estimated in its earlier assessments. However, as explained previously, the estimates provided by these Parties also contain significant uncertainties. Parties may therefore wish to consider developing measures to collect and store surplus halon 1301 while continuing to assess future needs for it. Also, to avoid a future need for any party to apply for an essential use production exemption, Parties may wish to consider not destroying the stored halons before all Parties, including Parties operating under Article 5(1), have confirmed that they have sufficient halon 1301 to meet the future needs of their critical uses.“

Based on the information in the April 2001 TEAP report there may be excess inventory of halon 1211 for destruction. With respect to halon 1301, there is considerable uncertainty regarding possible destruction of excess quantities. There are critical fire protection applications in aviation, mobile military applications and explosion prevention for which suitable alternatives to halon 1301 have yet to be identified. The following tables show the approximate distribution of potential halon inventory from 2002 to 2010.

They provide calculated results indicating that the CEIT banks of halon 1211 and halon 1301 are predicted to collapse earlier than elsewhere. This is based on the point at which they would be unable to satisfy user needs by recovered/recycled halons. This could be because there are not sufficient halons to recover/recycle or because recovery/recycling programs are not efficient

enough. In either case when these programs reach a point where they are no longer viable, the remaining halon is assumed to be emitted in the following year. Although this may not be the actual case, at this time there is no other basis to predict annual emissions. Since the last examination of recovery factors used in the model, several halon recovery/recycle programs have been undertaken in countries with economies in transition (CEIT). The possible effect that these programs will have on factors used in the model will be evaluated and if appropriate the revised factors will be applied to update the calculations. The updated calculations will be provided in the 2002 Assessment Report of the Halons Technical Options Committee.

*Table 1-1: Halon 1211 Inventory **

YEAR	2002	2003	2004	2005	2006	2007	2008	2009	2010
CURRENT INVENTORY									
North America	18770	17588	16487	15454	14482	13571	12715	11917	11179
Western Europe and Australia	21898	20520	19234	18029	16896	15832	14834	13903	13042
Japan	3324	2948	2600	2277	1978	1703	1451	1226	1029
CEIT	1604	1439	1335	0	0	0	0	0	0
Article 5(1)	79246	67959	57327	47290	35347	25444	17867	12070	7935
TOTAL INVENTORY	124843	110455	96983	83050	68704	56550	46867	39115	33185

*Table 1-2: Halon 1301 Inventory **

YEAR	2002	2003	2004	2005	2006	2007	2008	2009	2010
INVENTORY									
North America	13943	13337	12757	12199	11664	11150	10655	10181	9725
Western Europe and Australia	8718	8325	7954	7604	7272	6955	6650	6358	6078
Japan	9730	9461	9199	8945	8697	8458	8226	8001	7786
CEIT	2624	2502	2385	2273	2166	2065	1968	1877	1790
Article 5(1)	7418	7478	7537	7594	7197	6827	6479	6154	5650
TOTAL INVENTORY	42434	41103	39832	38616	36996	35454	33979	32571	31029

* Note: Columns do not always sum to the total amount due to rounding.

Table 1-1 and Table 1-2 provide calculated results indicating that the CEIT banks of halon 1211 and halon 1301 are predicted to collapse earlier than elsewhere. This is based on the point at which they would be unable to satisfy user needs by recovered/recycled halons. This could be because there is insufficient halon to recover/recycle or because recovery/recycling programs are not efficient enough. In either case when these programs reach a point where they are no longer viable, the remaining halon is assumed to be emitted the following year. Although this may not actually be the case, at this time there is no other basis to predict annual emissions in the model.

The amount of halon that may ultimately be available for destruction depends on inventory management strategies including regulatory measures. A market-based approach intended to maintain a supply and demand balance will probably not yield significant destruction quantities as halons historically have high monetary value relative to other ODS. Regulatory measures that eliminate the market for recovered and recycled halons can result in creation of waste halons that could potentially be destroyed or inappropriately vented.

Management strategies that were counting on shared availability of halons from non Article 5(1) countries to meet their critical use needs may have to look elsewhere for available quantities. The new EC regulation 2037/2000 has spread concern to other countries, including many Article 5(1) countries, that had based their halon banking strategies on a shared global supply of recovered halons to meet critical needs. It should be noted that the Multilateral Fund Executive Committee requires Article 5(1) countries that accept financial assistance to curtail imports of newly produced halons and allow only imports of recovered and reclaimed halons to meet their needs. As the only reliable source of supply for recovered and reclaimed halons has been those obtainable from non-Article 5(1) countries the possible impact of increasing reliance on newly produced halons for Article 5(1) countries should be carefully considered prior to destruction of existing global halon stocks.

1.4.3 Refrigeration

One of the most important sectors consuming ODS is the refrigeration sector. There is a major difference between the refrigeration sector and almost all other sectors where ODS are used. Refrigeration needs CFCs not only for the charging of new equipment, but also to maintain the large base of existing equipment. In most other sectors, a phase-out of the use of CFCs in production of goods leads to an immediate phase-out of the consumption. The refrigeration sector is unique due to two specific aspects:

1. In refrigeration, CFCs are needed many years after a product has been manufactured for its maintenance, or the product manufactured for use with CFCs needs to undergo a complicated conversion procedure (retrofit). There is still a considerable number of CFC chemicals contained in existing equipment in non-Article 5 Countries, and the inventory in Article 5(1) countries is still increasing; consequently, the service needs are also significant.
2. In the refrigeration sector the amount of CFC per system (or even per owner) is relatively small. This makes interactions very difficult and it could lead to the fact that possibly, large parts of the population are directly affected by any measures.

In combination with technical challenges, these two characteristics lead to the conclusion that the refrigeration sector will be very difficult to address with regards to the phase-out of CFCs.

An analysis of the potential of CFCs available for destruction has been performed. This potential defines the amount of CFCs, which can reasonably be expected for destruction if logistics and incentives are existing to enable and encourage recovery of CFCs and the collection of CFCs for destruction. Consequently, the potential will probably not be reached by the actual numbers, i.e., the numbers in practice. In determining the potential, it was also assumed that all major CFC users will employ legislation as it is at present, i.e. no additional countries will be requesting mandatory destruction of all CFCs recovered (as presently required e.g. in the European Union and in Canada), but will use the bulk of refrigerant recovered to keep the existing CFC equipment in operation.

In Europe, it is actually not allowed to service CFC refrigeration equipment at all, and recovered CFCs have to be destroyed. Due to this regulation, there is a large potential for destruction until about 2005.

The global bank of refrigerants as contained in equipment, is estimated to be about 380,000 ODP tonnes of CFCs in the year 2002, decreasing to 260,000 ODP tonnes in 2005, and to about 140,000 ODP tonnes in the year 2010. This implies that, during the period 2002-2005, an average amount of about 40,000 ODP tonnes, and, during 2005-2010, an average amount of 24,000 ODP tonnes would theoretically become available on a global scale for recovery and recycling and for destruction from equipment that is decommissioned (or retrofitted).

Where it concerns the global inventory, in the year 2002 slightly more than 10% of the total can be found in Western Europe, less than 10% in Japan, about 30% in North America and the remainder in CEIT and Article 5(1) countries (180,000 ODP tonnes). In the year 2010 this has changed in so far that, of the 140,000 ODP tonnes global inventory, 75% will be in the CEIT and Article 5(1) countries (100,000 ODP tonnes) and virtually all the rest in North America.

One can apply certain assumptions where it concerns the amounts being available from recovery and recycle (unusable refrigerant) and from CFCs available from the inventory in retired equipment. Estimates on the efficiency of R&R and regarding the percentage of recovered material are based on historic information. It should be emphasised that the percentage used for material that will potentially become available for destruction from retired equipment is rather low; it is estimated at 10-15%. This percentage could be increased in a large number of countries, but it is uncertain at this stage which regulatory framework would be needed in these countries and when, if at all, this would be in place.

Table 1-3: Total amounts that would potentially become available for destruction in the periods 2002-2004, 2005-2011 and 2012-2016, globally and split up for the regions W.-Europe, North America, Japan and CEIT/ Article 5(1)

Period	Total amounts for destruction per year (ODP tonnes)	Region	Amounts available for destruction per year (ODP tonnes)
2002-2004	6,800-9,000	W.-Europe	5,400-6,400
		North America	1,030-1,130
		Japan	600-650
		CEIT/ A5(1)	730-750
2005-2011	2,600-3,000	W.-Europe	1,200-1,300
		North America	400-470
		Japan	350-500
		CEIT/ A5(1)	640-700
2012-2016	780-1080	W.-Europe	10-50
		North America	250-360
		Japan	20-30
		CEIT/ A5(1)	600-640

As mentioned above, the relatively large quantity that becomes available for destruction in the period 2002-2004 originates largely from Western Europe, where the regulation states that refrigerant needs to be recovered and destroyed once the CFC equipment is being serviced. Should such regulations come into force in other countries the amounts that become available for destruction would increase. But it is impossible that the amount with which the global bank is decreased in the period 2002-2005 per year will be available for destruction (40,000 ODP tonnes becomes available from the annual reduction of the bank for all sub-sectors).

Where it concerns the different refrigeration sub-sectors for the period 2002-2004, about 65% of the amount that becomes available for destruction comes from large industrial equipment and from chillers, 15% from domestic refrigerators, and the remaining 20% from all other sub-sectors, including mobile air conditioning. This picture has changed by the year 2010 when more than 50% becomes available from domestic refrigerators and virtually all the rest from large industrial equipment and chillers. By the way, the latter percentages are all global figures.

A more elaborate description of the inventories in the foam, halon and refrigeration sectors, and of the amounts available for recovery and recycle, for storage and destruction can be found in the Report of the Task Force on Collection, Reclaim and Storage (TFCRS), June 2002, which is also part of the TEAP 2002 progress report. The text in the above sections has for a large part been extracted from information made available in the TFCRS report.

2 Technology Screening Process

2.1 Criteria for Technology Screening

The following screening criteria were developed by the UNEP TFDT. Technologies for use by the signatories to the Montreal Protocol to dispose of surplus inventories of ODS were assessed on the basis of:

1. Destruction and Removal Efficiency (DRE)
2. Emissions of dioxins/furans
3. Emissions of other pollutants (acid gases, particulate matter, & carbon monoxide)
4. Technical capability

The first three refer to technical performance criteria selected as measures of potential impacts of the technology on human health and the environment. The technical capability criterion indicates the extent to which the technology has been demonstrated to be able to dispose of ODS (or a comparable recalcitrant halogenated organic substance such as PCB) effectively and on a commercial scale.

For convenience, the technical performance criteria are summarized in Table 2-1. These represent the minimum destruction and removal efficiencies and maximum emission of pollutants to the atmosphere permitted by technologies that qualify for consideration by the TFDT for recommendation to the Parties of the Montreal Protocol for approval as ODS destruction technologies. The technologies must also satisfy the criteria for technical capability as defined in Section 2.1.4.

Table 2-1: Summary of Technical Performance Qualifications⁵

Performance Qualification	Units	Diluted Sources	Concentrated Sources
DRE	%	95	99.99
PCDDs/PCDFs	ng-ITEQ/Nm ³	0.5	0.2
HCl/Cl ₂	mg/Nm ³	100	100
HF	mg/Nm ³	5	5
HBr/Br ₂	mg/Nm ³	5	5
Particulates (TSP)	mg/Nm ³	50	50
CO	mg/Nm ³	100	100

2.1.1 Destruction and Removal Efficiency

Destruction Efficiency (DE)⁶ is a measure of how completely a particular technology destroys a contaminant of interest – in this case the transformation of ODS material into non-ODS by-products. There are two commonly used but different ways of measuring the extent of destruction – DE and Destruction and Removal Efficiency (DRE)⁷. For a more detailed explanation of how DRE is calculated, see section 4.2.1. The terms are sometimes interchanged or used inappropriately. DE is a more comprehensive measure of destruction than DRE, because DE considers the amount of the chemical of interest that escapes destruction by being removed from the process in the stack gases and in all other residue streams. Most references citing performance of ODS destruction processes only provide data for stack emissions and thus, generally, data is only available for DRE and not DE.

⁵ All concentrations of pollutants in stack gases and stack gas flow rates are expressed on the basis of dry gas at normal conditions of 0°C and 101.3 kPa, and with the stack gas corrected to 11% O₂.

⁶ Destruction Efficiency (DE) is determined by subtracting from the mass of a chemical fed into a destruction system during a specific period of time the mass of that chemical that is released in stack gases, fly ash, scrubber water, bottom ash, and any other system residues and expressing that difference as a percentage of the mass of the chemical fed into the system.

⁷ Destruction and Removal Efficiency (DRE) has traditionally been determined by subtracting from the mass of a chemical fed into a destruction system during a specific period of time the mass of that chemical alone that is released in stack gases, and expressing that difference as a percentage of the mass of that chemical fed into the system.

Because of the relatively volatile nature of ODS and because, with the exception of foams, they are generally introduced as relatively clean fluids, one would not expect a very significant difference between DRE and DE.

For these reasons this update of ODS destruction technologies uses DRE as the measure of destruction efficiency.

For the purposes of screening destruction technologies, the minimum acceptable DRE is:

- 95% for foams; and,
- 99.99% for concentrated sources.

It should be noted that measurements of the products of destruction of CFCs, HCFCs and halons in a plasma destruction process have indicated that interconversion of ODS can occur during the process. For example, under some conditions, the DRE of CFC-12 (CCl_2F_2) was measured as 99.9998%, but this was accompanied by a conversion of 25% of the input CFC-12 to CFC-13 (CClF_3), which has the same ozone-depleting potential. The interconversion is less severe when hydrogen is present in the process, but can nonetheless be significant.⁸ For this reason, it is important to take into account all types of ODS in the stack gas in defining the DRE.

For the reasons described in the previous paragraph, the Task Force recommends that future calculations of DRE use the approach described below⁹.

DRE of an ODS should be determined by subtracting from the number of moles of the ODS fed into a destruction system during a specific period of time, the total number of moles of all types of ODS that are released in stack gases, and expressing that difference as a percentage of the number of moles of the ODS fed into the system.

⁸ R. T. Deam, A. R. Dayal, T. McAllister, A. E. Mundy, R. J. Western, L. M. Besley, A. J. D. Farmer, E. C. Horrigan, and A. B. Murphy, Interconversion of chlorofluorocarbons in plasmas, *J. Chem. Soc.: Chem. Commun.* No. 3 (1995) 347-348; A. B. Murphy, A. J. D. Farmer, E. C. Horrigan, and T. McAllister, Plasma destruction of ozone depleting substances, *Plasma Chem. Plasma Process.* **22** (2002) 371-385.

⁹ Since different ODS have different ODP, consideration should be given to taking into account the ODP of each type of ODS present in the stack gas in calculating the DRE. An appropriate definition that takes into account the differences in ODP is: *DRE of an ODS is determined by subtracting from the number of moles of the ODS fed into a destruction system during a specific period of time, the total number of moles of all types of ODS that are released in stack gases, weighted by their ODP relative to that of the feed ODS, and expressing that difference as a percentage of the number of moles of the ODS fed into the system.*

In mathematical terms,
$$DRE = \frac{N_1^{in} - \sum_i N_i^{out}}{N_1^{in}}$$
, where N_1^{in} is the number of moles of the ODS fed into the destruction system, and N_i^{out} is the number of moles of the i th type of ODS that is released in the stack gases.

2.1.2 Emissions of Dioxins and Furans

Any high temperature process used to destroy ODS has associated with it the potential formation (as by-products) of polychlorinated dibenzo-paradioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). These substances are among the products of incomplete combustion (or PICs) of greatest concern for potential adverse effects on public health and the environment. The internationally recognized measure of the toxicity of these compounds is the toxic equivalency factor (ITEQ),¹⁰ which is a weighted measure of the toxicity for all the members of the families of these toxic compounds that are determined to be present.

The task force members note that the World Health Organization has developed a new system for calculating TEQs, however, most of the existing data on emissions is expressed in the former ITEQ system established in 1988.

¹⁰ There are 75 chlorinated dibenzo-p-dioxins and 135 chlorinated dibenzofurans that share a similar chemical structure but that have a wide range in degree of chlorination and a corresponding wide range in toxicity. Of these, one specific dioxin [2,3,7,8-Tetrachlorodibenzo-p-dioxin, or (TCDD)] is the most toxic and best characterized of this family of compounds. Since PCDDs and PCDFs are generally released to the environment as mixtures of these compounds, the scientific community has developed a system of toxic equivalency factors (TEFs) which relate the biological potency of compounds in the dioxin/furan family to the reference TCDD compound. The concentration of each specific compound is multiplied by its corresponding TEF value, and the resulting potency-weighted concentration values are summed to form an expression of the mixture's overall toxic equivalence (TEQ). The result of this exercise is a standardized expression of toxicity of a given mixture in terms of an equivalent amount of TCDD (the reference compound). The internationally accepted protocol for determining TEQ – *i.e.*, ITEQ – was established by NATO in 1988. [*Scientific Basis for the Development of International Toxicity Equivalency Factor (I-TEF), Method of Risk Assessment for Risk Assessment of Complex Mixtures of Dioxins and Related Compounds*. North Atlantic Treaty Organization/Committee on the Challenge of Modern Society. Report No. 176, Washington, D.C. 1988.]

For purposes of screening destruction technologies, the maximum concentration of dioxins and furans in the stack gas from destruction technologies is:

- 0.5 ng-ITEQ/Nm³ for foams; and,
- 0.2 ng-ITEQ/Nm³ for concentrated sources.

These criteria were determined to represent a reasonable compromise between more stringent standards already in place in some industrialized countries [for example, the Canada-Wide Standard of 0.08 ng/m³ (ITEQ)], and the situation in developing countries where standards may be less stringent or non-existent. Although a previous standard of 1.0 ng/m³ (ITEQ) had been suggested in the UNEP 1992 report, advances in technology in recent years, and the level of concern for emissions of these highly toxic substances justified a significantly more stringent level.

2.1.3 Emissions of Acid Gases, Particulate Matter and Carbon Monoxide

Acid gases are generally formed when ODS are destroyed and these must be removed from the stack gases before the gases are released to the atmosphere. The following criteria for acid gases have been set for purposes of screening destruction technologies:

- a maximum concentration in stack gases of 100 mg/Nm³ HCl/Cl₂;
- a maximum concentration in stack gases of 5 mg/Nm³ HF; and,
- a maximum concentration in stack gases of 5 mg/Nm³ HBr/Br₂.

Particulate matter is generally emitted in the stack gases of incinerators for a variety of reasons and can also be emitted in the stack gases of facilities using non-incineration technologies. For the purposes of screening technologies, the criterion for particulate matter is established as:

- a maximum concentration of total suspended particulate (TSP) of 50 mg/Nm³.

Carbon monoxide (CO) is generally released from incinerators resulting from incomplete combustion and may be released from some ODS destruction facilities because it is one form by which the carbon content of the ODS can exit the process. Carbon monoxide is a good measure of how well the destruction process is being controlled. For the purposes of screening technologies, the following criterion has been established:

- a maximum CO concentration in the stack gas of 100 mg/Nm³.

These maximum concentrations apply to both foams and concentrated sources. They were set to be achievable by a variety of available technologies while ensuring adequate protection of human health and the environment.

2.1.4 Technical Capability

As well as meeting the above performance requirements it is necessary that the destruction technologies have been demonstrated to be technically capable at an appropriate scale of operation. In practical terms, this means that the technology should be demonstrated to achieve the required DRE while satisfying the emissions criteria established above. Demonstration of destruction of ODS is preferred but not necessarily required. Destruction of halogenated compounds that are refractory, *i.e.*, resistant to destruction, is acceptable. For example, demonstrated destruction of polychlorinated biphenyls (PCBs) was often accepted as an adequate surrogate for demonstrated ODS destruction.

For this evaluation, an ODS destruction technology is considered technically capable if it meets the following minimum criteria:

- It has been demonstrated to have destroyed ODS to the technical performance standards, on at least a pilot scale or demonstration scale (designated in Table 2-2 as “Yes”).
- *It has been demonstrated to have destroyed a refractory chlorinated organic compound other than an ODS, to the technical performance standards, on at least a pilot scale or demonstration scale (designated in Table 2-2 as “P,” which indicates that the technology is considered to have a high potential for application with ODS, but has not actually been demonstrated with ODS).*
- The processing capacity of an acceptable pilot plant or demonstration plant must be no less than 1.0 kg/hr of the substance to be destroyed, whether ODS or a suitable surrogate.

These criteria of technical capability will minimize the risk associated with technical performance and ensure that destruction of ODS will be performed in a predictable manner consistent with protecting the environment.

Appendix B presents a detailed discussion of the selection of 1.0 kg/hr as the minimum capacity for a pilot plant in order to demonstrate technical capability, which represents a change from the criterion originally selected in the 1992 UNEP report.

2.2 Foams (Diluted Sources)

There is increasing attention being focused on the management of foams at end of life. With an amount in excess of 1 million t of CFC-11 still likely to be banked by 2010, the ODS material flows arising from foam sources are expected to be substantial for the foreseeable future.

Effectively, there are two ways in which these materials can arrive at an ODS destruction unit. These are:

- 1) As re-concentrated ODS blowing agents
- 2) As intact foams with blowing agents still contained inside

The handling of re-concentrated sources is, in essence, no different than that of traditional ODS supplies to an ODS destruction unit. However, in the case of foams, there are several additional factors to consider. These are discussed in the following paragraphs.

2.2.1 *Handling of Foams*

Foams can arrive at incineration facilities in a variety of forms and requiring varying treatment prior to the incineration process itself. Where the foam is consistent in composition and form (e.g. refrigerator cabinets), facilities can be tailored accordingly. Intermittent material flows and/or varying forms are more difficult to cater for and are likely to prove less economic. There is an additional risk that fugitive emissions could be greater under these circumstances (see next section).

Managers of destruction facilities need to consider the impact of such heterogeneous sources on their plants. At least one Municipal Waste Incinerator operator (based in Holland) has had to reconsider the wisdom of feeding refrigerator cabinets through the unit, following problems with the built-up of slag from the metallic parts. None of the normal material handling approaches, such as shredding or grinding, will fundamentally affect the make up of the mix unless specific separation equipment is installed. If such action was taken, the unit would effectively be the front-end of traditional mechanical recovery unit with ODS destruction being carried out on only one output stream. The change of form to smaller pieces by shredding, grinding or a combination of both, will, however, assist overall material handling.

2.2.2 Management of Fugitive Losses

Before considering the impact of fugitive emissions, there is an obvious problem associated with defining the 'mass of chemical' fed into the system in order to calculate the DRE. This arises from the fact that the blowing agent components and their quantitative presence in the foam are not consistent across even foams of the same type. Matters such as density distribution and cell structure can be significant factors. Apart from this immediate difficulty, there is an additional concern over the believed destruction efficiency of blowing agents from diffuse sources. If the DRE from diffuse environments is no better than 95%, this is only at a level equivalent to the full recovery efficiency of a mechanical recovery unit. This means that any additional fugitive emissions that may occur at the site of the destruction unit are likely to make this approach less environmentally acceptable than alternative routes. Accordingly, significant attention needs to be applied to the pre-handling of foams prior to destruction.

In practise DRE in excess of 99.95 % are reported for both Municipal Solid Waste incineration and rotary kiln incineration making the approach environmentally competitive with other disposal options in reality.

In general, fugitive emissions need to be managed by ensuring that all prior dismantling, shredding and/or grinding is carried out in an air tight, enclosed unit. The option exists to run the enclosure at negative pressure and pull any residual air through a carbon adsorption unit or to run at positive pressure and drive the air out through a similar unit. The latter is usually the more efficient approach.

2.2.3 Future Considerations

Legislative developments are expected to increase the volume of foams being identified for destruction. Although most global legislation is currently restricted to refrigerators, primarily because of their portability and abundance, developments in the management of building waste from demolition sites could increase the material flows still further in future.

Even with the current regulatory requirements, the flows are likely to be substantial. European Regulation 2037/2000 is likely to regulate the disposal of up to 15 million refrigerator cabinets per annum in Europe from 1st January 2002. With an expected average blowing agent recovery per unit of at least 250g per unit, it is reasonable to expect an additional 3750 t of ODS to become available for destruction from this regional source alone. With the total reaching over 10,000 comes globally by 2004.

The key question that remains to be answered is the proportion of cabinets that will be processed by mechanical recovery units. At present, the basic trend in

Europe is towards such mechanical recovery units, where costs are at least \$US 20/unit to process. This includes an allowance for the disposal of re-concentrated blowing agent stocks. In some cases, consideration is being given to including an on-line incinerator with such plants. Although this approach has clear logistics benefits, it means that many such mechanical processes will not be covered by typical waste management licensing procedures but by more formal pollution control legislation. This may ultimately discourage such trends.

An additional factor influencing the trend towards mechanical recovery per se is the likely requirement to achieve minimum recycling levels from appliances at end-of-life. At present, draft European legislation for waste electrical appliances is proposing a minimum recycling level of 75% by weight. This can normally be met for a domestic refrigerator through the removal and recycling of the shelving and the compressor. Should this figure subsequently increase to 80% or 85%, the carcass of the unit will need to be more actively considered. This will not be an option for those units directly destroyed, as envisaged under any discussion of diffuse sources.

Direct incineration of some foam types (including refrigerator cabinets) may still be practised on a widespread basis where the practice can be justified. In these circumstances, the sound management of foam handling and fugitive emissions are key environmental imperatives.

2.3 Screened-In Technologies

A total of forty-five technologies were evaluated against this set of criteria. Of the 45 technologies considered overall, the 16 technologies listed in Table 2-2 met the screening criteria. The ODS material for which the destruction technologies can be applied is also indicated in Table 2-2. Technologies that did not meet the screening criteria are listed by category in Table 2-3.

Table 2-2: Screened-In Technologies and Their Applicability

Technology	Applicability		
	Foams CFCs	CFCs	Halons
Cement Kilns	P	Y	P
Liquid Injection Incineration	X	Y	Y
Gaseous/Fume Oxidation	X	Y	Y
Municipal Solid Waste Incineration	Y	X	X
Reactor Cracking	X	Y	P
Rotary Kiln Incineration	Y	Y	Y
Argon Plasma Arc	X	Y	Y
AC Plasma	X	P	P
CO ₂ Plasma	X	P	P
Inductively Coupled Radio Frequency Plasma	X	Y	Y
Microwave Plasma	X	Y	P
Nitrogen Plasma Arc	X	Y	P
Gas Phase Catalytic Dehalogenation	X	Y	P
Gas Phase Chemical Reduction	X	P	P
Solvated Electron Decomposition	X	P	P
Superheated Steam Reactor	X	Y	P

Where:

- Y (Yes) = Technology demonstrated on this category of ODS
- P (High Potential) = Technology not demonstrated specifically on this category of ODS, but considered likely to be applicable based on evidence of destruction of other substances (*i.e.*, refractory halogenated organics), and on professional judgement
- X = not applicable

Table 2-3: Screened-Out Technologies (by category)

INCINERATION TECHNOLOGIES
Waste Gasification
Gas Injection Oxidation/Hydrolysis
Blast Furnaces
PLASMA TECHNOLOGIES
Plasma Conversion of CFCs into Harmless Polymer Using Ethylene or Ethane as Co-monomer
Destruction of ODS in Dilute Exhaust Stream Using Energetic Electron Induced Plasma - Adsorbent Filter Hybrid System
High Voltage Gliding Arc Plasma Discharge Reactor for CFC Destruction
Freon 113 Destruction in Air Under the Effect of Nanosecond Corona and Microwave Discharge
CHEMICAL DESTRUCTION TECHNOLOGIES
Chemical Reduction of ODS Using Metallic Sodium on a Solid Substrate
Chemical-Thermal Destruction of Halogenated Hydrocarbon with Calcium Silicate or Oxide
Mineralization of CFCs with Sodium Oxalate
Aerosol Mineralization of CFCs by Sodium Vapour Reduction
Molten Metal Technology (MMT)
Pressurized Coal Iron Gasification (P-CIG)
Dormier Incineration Process in Steel Smelter
Destruction of CFCs During Chemchar Gasification
Liquid Phase Chemical Conversion
PHOTOCHEMICAL TECHNOLOGIES
UV Photolytic Destruction
UV Laser Photolysis for the Destruction or Transformation of Halon 1301 into CF ₃ I
Photochemical Degradation of Organic Wastes with a TiO ₂ Catalyst
UV Laser Controlled Decomposition of CFCs
CATALYTIC TECHNOLOGIES
Dry Distillation Destruction System for Waste Foam and Refrigerators
Halohydrocarbon Destruction Catalyst
Catalytic Oxidation of CFCs with a Pt/ZrO ₂ -PO ₄ Based Catalyst
CFC Oxidation in a Catalyst-Sorbents Packed Bed
Transformation of CFCs to HFCs Using Dehalogenation Catalysts in a H ₂ Environment
OTHER TECHNOLOGIES
Use of Waste CFC in an Antimony Process
CFC Destruction into Biocatalytic System
Supercritical Water Oxidation (SCWO)
Electrohalogenation of CFC-113 on Pb/Pd Cathodes Combined with H ₂ Diffusion Anode

3 Technical Update of Screened-in Technologies

3.1 Introduction

The technologies that have been “screened-in” for further consideration by the Task Force are described briefly in this section. These technologies have been grouped under the categories of incineration technologies, plasma technologies and other non-incineration technologies for purposes of description. An introduction to incineration technologies and plasma technologies as well as more detailed descriptions of the screened-in technologies, including process schematics and tables summarizing their technical performance, can be found in Appendix A to this report. This Appendix also includes descriptions of emerging technologies that failed to satisfy the screening requirements of technical performance and/or capability.

The descriptions of the technologies are presented in several parts:

1. Generic description of the technology. This section attempts to capture the essential features of the process, recognizing that individual facilities may differ somewhat in the arrangement of the process, particularly with regard to auxiliary systems such as flue gas cleaning.
2. Typical technical performance for the technology. This typical performance is an extraction from the performance tabulated in Appendix A for specific facilities. This technical performance data includes data reported by destruction facility operators and technology vendors as well as estimated quantities to fill gaps in the data. Appendix A includes comments pertaining to such estimates. All concentrations of pollutants in stack gases and stack gas flow rates are expressed on the basis of dry gas at normal conditions of 0°C and 101.3 kPa, and with the stack gas corrected to 11% O₂.
3. Technical Capability: This section presents details of the level of availability and the capacity of the technology for ODS destruction. Information about the commercial background of the technology and the geographic distribution of facilities is also included.
4. Cost and Pricing: Generally included in the Technical Capability section, these are reported to the extent that this information is available. Costs are reported in ranges of \$US/kg. This approach recognizes the difficulty of developing accurate costs on a consistent basis and also avoids the problem of disclosure of confidential information. This cost data had been reported in several currencies and the costs have been adjusted to the end of 2001 and

converted the costs into \$US as of that time. See also the explanatory note on costs below.

Note on Costs:

The indicated costs for destruction do not include transportation to the destruction facility but include receiving, storage, pretreatment if necessary and destruction of the ODS material. The costs include not only the direct costs for destruction such as raw materials and energy but also fixed costs such as operating labour, maintenance, depreciation and contractor overheads and profit. Costs quoted by existing facility operators for destruction of specific ODS materials are quoted on such an all-inclusive basis, and these costs were generally not adjusted. However, costs indicated by technology suppliers for hypothetical new facilities were generally assumed to include only direct costs and for these cases an adjustment was made to put the costs on an all-inclusive basis.

3.2 Incineration Technologies

3.2.1 Reactor Cracking

Process Description: The reactor cracking process is classified here as an incineration technology because it satisfies UNEP's definition of incineration; namely, the use of a controlled flame to destroy ODS in an engineered device. But the process is very different than conventional incineration because of the use of hydrogen and oxygen, as fuel and oxidant, avoids the generation of a large flue gas volume with consequent large emissions of pollutants and also enables the recovery of acid gases. The process uses a cylindrical, water-cooled reactor made of graphite, and an oxygen-hydrogen burner system. Waste gases and recovered refrigerants typically consisting of CFCs, HCFCs and HFCs are fed into the reaction chamber where the temperature is maintained at 2000_C. The gases are broken down to HF, H₂O, HCl, CO₂ and Cl₂. The cracked products are cooled in the absorber that is flanged directly to the reactor and the acid gases are purified and recovered as 55% HF and 33% HCl, both of technical grade quality. The resulting waste gas essentially only consists of CO₂, O₂ and water vapour and meets the requirements of the German Clean Air regulations (TA-Luft).

The process is reported to achieve a DRE exceeding 99.999%. Emissions of the pollutants of concern are tabulated below for a system destroying 200 kg/h of CFCs, for which the flue gas volume of 46.5 Nm³/h is reported.

Table 3-1: Emissions from Reactor Cracking Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	<0.01	ng/Nm ³	<0.5	ng/h
HCl/Cl ₂	<100	mg/Nm ³	<5000	mg/h
HF	<0.1	mg/Nm ³	<5	mg/h
Particulates	<10	mg/Nm ³	<500	mg/h
CO	<50	mg/Nm ³	<2500	mg/h

Technical capability: Reactor cracking is a proprietary process developed by Hoechst AG (Frankfurt, Germany). A European patent (EP 0 212 410 B1) was issued in 1986. Solvay acquired Hoechst's fluorocarbon business in 1996, and now operates the cracking destruction facility, which is located near Frankfurt. First experiences with this process date back to 1983. The process was installed to treat waste gases from the production of CFCs and, more recently, waste gases from the production of HCFCs and HFCs as well as waste CFCs. The facility consists of two reactors each with a capacity of 1,250 t/yr, (max 1,500 t/yr depending on product mix), and a third reactor is planned for 2002. Solvay has legal permission to destroy 9,700 t CFC/yr. The present capacity is about 2,500 t/yr. The process is fueled with by-product hydrogen from a manufacturing operation on the Frankfurt site. Solvay offers destruction services at its Frankfurt plant and also offers the process under license for construction by clients outside of Germany. Solvay has indicated a price in the range \$US 4-6/kg for destruction at its Frankfurt facility. Solvay is also prepared to offer its technology under license for construction of a facility outside of Germany. Solvay estimates a 2,500 t CFC/yr cracking unit would cost about \$US 4 million excluding the license fee and engineering.

Advantages: The principal advantage of this process is that it has been operating on a large commercial scale for many years. The high operating temperature achieves high levels of DRE and rapid cooling minimizes the formation of PCDD/PCDF. Its use of an oxygen-hydrogen flame limits formation of NO_x and facilitates the recovery of hydrofluoric and hydrochloric acids, which minimize the release of halide salts to the environment. Also, the use of an oxygen-hydrogen flame results in a very small volumetric release of waste gases to atmosphere, which results in extremely low mass emissions of the pollutants of concern. The indicated cost is in the low end of the range of reported costs for ODS destruction.

Disadvantages: A concern which impacts cost is the availability of an economic source of hydrogen; the process would likely be more expensive to operate without an on-site source of hydrogen. Also, the recovery of HCl and HF may

not be as practical if the destruction facility were not situated on a fluorocarbon manufacturing site. Also, the process is somewhat complex and it may not be practical or economical to apply this process on a significantly smaller scale. Furthermore, the process requires that the CFC waste be pretreated to remove oil and the process is intolerant of bromine containing ODS. Naturally, the process is limited to the disposal of CFCs, HCFCs and HFCs, and can not be used for destruction of foams or halons.

3.2.2 Gaseous/Fume Oxidation

Process Description: This process uses a refractory-lined combustion chamber for the thermal destruction of waste CFC and HCFC gases. Some of the ODS (e.g. CFC-12, CFC-114, or CFC-115) are gases at ambient temperature and can be destroyed by feeding directly from their pressurized storage into the incinerator. The fume stream is heated using an auxiliary fuel such as natural gas or fuel oil. A combustion temperature near 1100_C is required for most ODS compounds, and the specific unit described in Appendix A operates at from 1200 to 1250°C. Gaseous residence times in fume incinerators are about 1-2 seconds. Some fume incinerators are equipped with heat exchangers in the flue gas outlet to pre-heat the combustion air and/or the waste fume. These recuperative incinerators are capable of recovering up to 70% of the energy in the flue gas. Fume incinerators are designed for continuous operation and are a simple, proven technology.

The process is reported to achieve a DRE exceeding 99.999% while destroying CFCs and 99.99% destroying halons at feed rates of 165 kg/h and 15 kg/h respectively. The chamber temperature was 1200°C for CFCs and 1250°C for halons. Reported emissions to atmosphere for a fume incinerator are tabulated below. The flue gas volume was estimated at 1200 Nm³/h, except for the HBr/Br₂ emission that is at 130 Nm³/h.

Table 3-2: Emissions from Gaseous/Fume Oxidation Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.032	ng/Nm ³	40	ng/h
HCl/Cl ₂	3.2	mg/Nm ³	4000	mg/h
HF	0.5	mg/Nm ³	670	mg/h
HBr/Br ₂	1.5	mg/Nm ³	190	mg/h
Particulates	22	mg/Nm ³	2700	mg/h
CO	40	mg/Nm ³	5000	mg/h

Technical capability: Fume incinerators are almost always privately operated and are typically found in fluorochemical manufacturing plants. A typical dedicated gaseous/fume incinerator, operated by Ineos Fluor Japan Limited in Japan, has a rated capacity of from 15 to 165 kg/hr, depending on whether halons or CFCs are being destroyed. These dedicated units are not generally available for use by other parties for the destruction of ODS. However, the technology is not proprietary and could be used in a new facility to destroy ODS for others on a commercial basis. Costs for destruction of ODS waste is expected to be in the range \$US 3-5/kg CFC, and somewhat higher for halons because of reduced throughput.

Advantages: The process is well established and can be applied to both CFC and halon waste provided they are relatively free of ash, which should be the case. High DREs and low emissions are achieved because of the high temperatures and good mixing which is readily achievable in gaseous/fume incinerators. Finally, relatively low flue gas volumes are generated because these are dedicated incinerators and thus the rates of mass emissions of pollutants of concern are much lower than for incinerators destroying other waste as well as ODS. Costs are at the low end of the range for destruction technologies.

Disadvantages: The principle disadvantage of gaseous/fume incinerators used to destroy ODS is that they are generally located on a fluorocarbon manufacturing site and are not available for use by others. Although, as noted above, the technology is not proprietary to fluorocarbon manufacturers and could be applied in a new facility. The technology is not applicable to destruction of CFCs in foams.

3.2.3 Rotary Kiln Incineration

Process Description: Rotary kiln incinerators are refractory-lined rotating cylindrical steel shells mounted on a slight incline from horizontal. Capable of handling both liquid and solid wastes, the rotation of the shell enhances mixing and the inclination causes ash or molten slag to fall out. Most rotary kilns are equipped with an afterburner that ensures complete destruction of exhaust gases. Hydrocarbon fuels, such as natural gas, fuel oil or high calorific liquid waste are typically used as an energy source. Rotary kilns have been used to destroy all forms of hazardous waste (gas, liquid, solids, including sludge). Because of this flexibility, rotary kilns are most frequently incorporated into the design of commercial incinerator facilities. Liquid wastes such as CFCs, halons and other ODS can be fed into the rotary kiln or directly into the afterburner. Their operating permits usually restrict the quantity of chlorine-containing waste and concern regarding HF attack on incinerator equipment usually limits

the fraction of fluorine in the feed to low levels, typically in the range of 1%. The latter generally establishes the ODS incineration capacity.

Rotary kilns operating with afterburner temperatures of 1000-1200°C have demonstrated DREs in excess of 99.9999% destroying refractory compounds such as PCBs, dichlorobenzene and tetrachlorobenzene. A typical kiln had a total feed of 7,758 kg/h of which 956 kg/h was refractory feed and the flue gas volume was reported at 78,500 Nm³/h. It is reported that such an incinerator could process 250-500 kg/h of CFCs. Typical emissions of pollutants to atmosphere for rotary kilns are tabulated below.

Table 3-3: Emissions from Rotary Kiln Incineration

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.03-0.15	ng/Nm ³	2,300-11,800	ng/h
HCl/Cl ₂	2.8	mg/Nm ³	220,000	mg/h
HF	0.5	mg/Nm ³	39,000	mg/h
HBr/Br ₂	4.0	mg/Nm ³	314,000	mg/h
Particulates	10	mg/Nm ³	785,000	mg/h
CO	50	mg/Nm ³	3,900,000	mg/h

Technical capability: Rotary kilns are widely used in developed countries for the incineration of hazardous wastes, including chlorinated solvents (CCl₄, CHCl₃, CH₂Cl, CH₃CCl₃), and toxic waste, such as PCBs. In Europe and Japan they have been used to destroy CFCs, but as of yet there is little such experience in North America. Destruction costs for the incineration of ODS are expected to be in the \$US 3-5/kg range for CFCs and greater than \$US 7/kg for halons. European destruction costs vary from country to country, and are generally greater than in North America.

Advantages: The principal advantage of the rotary kiln is its ability to handle a wide variety of liquid and solid wastes, so they can handle both foams and concentrated sources. Furthermore, even though their capacity to handle CFCs is limited to 1% of total feed as fluorine, the resulting capacity for CFCs is still quite high.

Disadvantages: Rotary kilns are very expensive to build and maintenance costs are high, so it is unlikely that new rotary kilns will be built with the intention of destroying ODS only. The capital expense could be justified, however, where there are opportunities to destroy a variety of hazardous waste materials. Some

kilns reported PCDD/F levels exceeding 0.3 ng/Nm³, which satisfies the screening limit for foams but not for concentrated sources.

3.2.4 Liquid Injection Incineration

Process Description: Liquid injection incinerators are usually single-chamber units with one or more waste burners into which the liquid waste is injected, atomised into fine droplets, and burned in suspension. Tangential firing is frequently used to promote turbulent mixing. Problems of flame stability may result when large volumes (greater than 40%) of CFCs or other ODS are injected into the burner. These incinerators are able to handle a wide range of liquid or vapour wastes, have high turndown ratios and have no moving parts. Liquid injection incinerators are limited to treating wastes that can be pumped and atomised through the burner and are therefore susceptible to plugging if liquids with significant ash are used. However, the incineration of ODS is not likely to be limited by these constraints to a significant degree.

The DRE for a liquid injection incinerator operating at 1350°C is reported to exceed 99.99%. A total feed of between 110 and 220 kg/h of liquid waste was being fed to the unit, of which about 11 kg/h was CFC. An average flue gas volume of 3,200 Nm³/h was estimated and reported emissions of pollutants are tabulated below.

Table 3-4: Emissions from Liquid Injection Incineration

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.52	ng/Nm ³	1,900	ng/h
HCl/Cl ₂	<10	mg/Nm ³	37,000	mg/h
HF	<1	mg/Nm ³	3,700	mg/h
Particulates	no data	mg/Nm ³	no data	mg/h
CO	<10	ppm	73,000	mg/h

Technical capability: Liquid injection incinerators are generally located on manufacturing sites to dispose of wastes such as oils, solvents, including chlorinated solvents (CCl₄, CHCl₃, CH₃Cl, CH₃CCl₃), and wastewater. Liquid injection incinerators have also been used by some hazardous waste destruction service providers but these generally are not constructed with materials that have a high tolerance for fluorine-containing waste, and may have higher costs due to more frequent refractory replacement. However, the technology is offered by several vendors and a facility incorporating liquid injection incineration could be established for ODS destruction. No cost data was reported.

Advantages: Liquid injection incineration is an established destruction technology with a proven track record in ODS destruction. All of the performance criteria are met with the exception of PCDD/PCDF emission as discussed below, but this is regarded as an exception. If properly designed, all of the performance criteria would be expected to be met. Costs are expected to be in the lower end of the range for ODS destruction technologies.

Disadvantages: The particular incinerator for which performance data was reported did not meet the screening limit for PCDD/PCDF emission, although there is a strong likelihood that a unit with a properly designed gas cleaning system incorporating a rapid quench operation would satisfy this criterion. The technology is primarily designed for the destruction of liquid wastes, although it is possible that the feed system could be modified to handle liquefied gases. It cannot be applied to foams. The most serious disadvantage is the relatively high rate of emissions of pollutants given the very modest rate of ODS destruction.

3.2.5 Municipal Solid Waste Incineration

Process Description: The MSWI typically employ moving grates for destruction of solid materials including foams containing ODS. Waste is dumped into a refuse pit and then transferred mechanically to a bin that feeds the waste in a controlled manner onto the moving grate. Combustion air is drawn through the refuse pit to control odour, preheated and introduced into the combustion zone through the moving grate. Hot gases from the combustion of the waste are typically cooled in a waste heat boiler and then cleaned either by a spray drier and bag house or by a dry electrostatic precipitator. In order to obtain low dioxin and furan emissions, advanced air pollution control systems use spray-dry scrubbers with activated carbon injection, followed by bag houses. The MSWI is generally kept under negative pressure by a fan that blows the cooled and cleaned flue gas up a stack. Ash from the lower end of the moving grate is discharged to a quench pit and conveyed to discharge for destruction. The combustors may be refractory lined or, as in many newer systems, the walls may be water-cooled to recover additional heat.

The DRE for a municipal solid waste incinerator operating at 850-950°C is reported as exceeding 99.99%. The total feed was 10,000 kg/h of wet MSW while the CFC feed rate was 6.5 to 19.5 kg/h. The flue gas volume was estimated at 60,000 m³/h and the emissions of pollutants are tabulated below.

Table 3-5: Emissions from Municipal Solid Waste Incineration

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	<1.0	ng/Nm ³	60,000	ng/h
HCl/Cl ₂	300	mg/Nm ³	18,000,000	mg/h
HF	5	mg/Nm ³	300,000	mg/h
Particulates	30	mg/Nm ³	1,800,000	mg/h
CO	10	mg/Nm ³	600,000	mg/h

Technical capability: CFC-containing rigid polyurethane foam has been destroyed in Germany together with solid municipal waste in a full-scale roller grate incinerator with a capacity of 10 t/day. Municipal solid waste incinerators are common in Europe and Japan and are used less commonly in North America. No cost data was reported.

Advantages: This is the only technology currently being used for the destruction of foams containing ODS. The principal advantage of this technology is its fairly wide availability, although municipal solid waste incineration is not widely practised in developing countries. Destruction costs are also expected to be below other methods of disposing of CFCs.

Disadvantages: A major drawback to this technology is that the emission of PCDD/PCDF may exceed the screening limit of 0.5 ng/Nm³. Well maintained MSW incinerators require sophisticated air pollution control systems to achieve PCDD/F emission rates of 1.0 ng/Nm³ or lower. The technology is included for consideration only because it has been demonstrated in plant trials that PCDD/PCDF emissions can be controlled to 0.2-0.5 ng/Nm³ when the hot gases are cooled to below 300°C by injecting water after the combustion chamber. The HCl emissions also exceed the screening limit but it should be possible to scrub HCl from the flue gas to below the screening level. However, the mass emission of pollutants, especially PCDD/PCDF and HCl, is very high because of the high gas volumes generated, particularly when the very low level of CFC destruction is considered.

3.2.6 Cement Kilns

Process Description: Cement kilns are basically tilted, rotating cylinders lined with heat-resistant bricks. They vary in size depending on the particular type of cement-making process employed, and can reach 250 m in length and 8 m in diameter. The raw material is fed into the elevated or “cool” end of the kiln. As the kiln slowly rotates, the raw material tumbles down toward the hot end that

is maintained at temperatures up to 1500°C, gradually altering to form clinker. Cement kilns operate in counter-current configuration. Combustion gases enter at the hot lower end and flow upward, heating raw materials flowing in the opposite direction as they pass over, and exit the kiln at the top end. The gases then pass through pollution control devices before entering the atmosphere. These devices are typically either a fabric bag house or an electrostatic precipitator, both of which function to remove the particulate matter entrained in the gas stream before the gases are emitted into the atmosphere. This particulate matter is referred to as cement kiln dust (CKD). The process is energy intensive and it has been utilised to burn out contaminated fuels and other hazardous substances.

Existing cement kilns, when properly operated, can destroy most organic compounds including PCBs because the temperature in the burning zone is over 1500°C and residence times are up to 10 seconds. The alkaline nature of the material being processed in the kiln neutralizes the acid gases formed by the destruction of CFC. In general, most cement kilns could tolerate the controlled addition of ODS, but this would have to be evaluated on a case-by-case basis. As a broad generalization, the maximum fluorine content is about 0.25% of the raw material feed. The theoretical limit for chlorine is about 0.015% of the raw material feed but the practical tolerance is believed to be higher.

A large cement kiln operating at 1450°C has been shown to achieve a DRE exceeding 99.99% while destroying CFCs. The kiln had a capacity of 5000 t/day of clinker and destroyed CFC fed at a rate of 3.5 kg/h. The flue gas volume was estimated at 200,000 Nm³/h and emissions of pollutants to the atmosphere are tabulated below.

Table 3-6: Emissions from Cement Kilns

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.04	ng/Nm ³	18,000	ng/h
HCl/Cl ₂	0.05	mg/Nm ³	23,000	mg/h
HF	0.4	mg/Nm ³	122,000	mg/h
Particulates	10	mg/Nm ³	4,500,000	mg/h
CO	100	mg/Nm ³	45,000,000	mg/h

Technical capability: It is reported that throughout the world some 60 cement kilns have been modified so that various wastes are burned along with conventional fuels. This represents tremendous advantage for this technology because cement plants are widely distributed geographically and are available in developing countries. No costs were reported. One of the factors influencing

cost is that the cost to modify cement kilns to facilitate ODS destruction would have to be recovered from a relatively low rate of CFC destruction. Also, where there is no market for low-alkali cement, kiln operators will not be interested in this operation.

Advantages: The major advantage of this approach is that there are large existing capacities of cement kilns in the world that offer the opportunity for destruction of ODS.

Furthermore, destruction costs are expected to be at the low end of the range for ODS destruction.

Disadvantages: The disadvantage is that fluorine and chlorine input rates need to be carefully controlled and impose a destruction capacity limit on the kiln. The above referenced cement kiln with a capacity of 5000 t/day of clinker would be limited by the theoretical chlorine limit to about 50 kg/h of CFC-12, still a very respectful feed rate. Furthermore, cement kilns are not currently set up to handle or burn CFCs and halon wastes. Necessary modifications would require equipment for feeding ODS in a controlled manner and monitoring hazardous emissions. A major public concern is the magnitude of mass emissions of pollutants, especially particulates and carbon monoxide from these facilities. However, the destruction of ODS is expected to have little or no additional effect on these emissions.

3.3 Plasma Technologies¹¹

3.3.1 Argon Plasma Arc

Process Description: PLASCON is an “in flight” plasma process, which means that the waste mixes directly with the argon plasma jet. Argon was selected as the plasma gas since it is inert and does not react with the torch components. Waste is rapidly heated in the reaction chamber (a flight tube) to about 2,500°C, where pyrolysis occurs. Steam is added, together with the waste, at the injection manifold; the oxygen ensures that any carbon formed during pyrolysis

¹¹ It should be noted that a complementary process, vitrification, has been used in combination with plasma arc technologies to deal with the by-products of destroying halogenated organics. The process is offered by Pure Chem, Inc., a specialty refrigerant processor with experience in the conversion of halogenated compounds into a glass matrix. The profits of the sale of the glass frit can be used to offset the costs of destruction, and the process avoids the costs of dealing with the destruction of byproducts such as halide salts. The process has not been demonstrated on a commercial scale with ODS. Since it is not a destruction technology *per se*, vitrification has not been evaluated separately as such.

is converted to carbon dioxide, and the hydrogen prevents formation of CF₄, which is a strong greenhouse gas. The use of steam rather than oxygen gives more thorough ODS destruction for a given feed rate, since the thermodynamic mixing temperature is higher. Pyrolysis is followed by rapid alkaline quenching from about 1200°C to less than 100°C. Such rapid quenching limits the formation of dioxins and furans. The cool gas from the quench is further scrubbed with alkaline liquor in a counter-current packed column to neutralize HCl and other acid gases. The off-gas from the column consists mainly of CO₂ and Ar.

The DRE for the PLASCON process is reported to exceed 99.9998% while destroying ODS at 120 kg/h and with 150kW electrical power. The flue gas volume is about 40 Nm³/h and emissions of pollutants are reported as follows.

Table 3-7: Emissions from Argon Plasma Arc Process destroying Halon 1211 at 120

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.006	ng/Nm ³	0.2	ng/h
HCl/Cl ₂	1.7	mg/Nm ³	65	mg/h
HF	0.23	mg/Nm ³	9	mg/h
HBr/Br ₂	<4.0	mg/Nm ³	<150	mg/h
Particulates	<10	mg/Nm ³	<400	mg/h
CO	96	mg/Nm ³	3700	mg/h

Technical capability: The PLASCON process was developed in Australia by SRL Plasma Ltd. in conjunction with the Commonwealth Scientific and Industrial Research Organization (CSIRO). The process was first used in 1992 for the destruction of chlorinated organic chemicals. The PLASCON system was provided to the Department of Administrative Services Centre for Environmental Management (DASCEN) for the destruction of Australia's surplus halons and CFCs. The plant, located at Tottenham, near Melbourne, was commissioned in 1996 and since then about 1000 MT of Halon 1211 and about 200 MT of CFCs have been destroyed. Halons are destroyed at a rate of up to 150 kg/h (100 kg/h under typical operating conditions), and CFCs at a rate of up to 100 kg/h (40-60 kg/h under typical operating conditions, depending on composition). The technology is offered under license by SRL Plasma Ltd. and DASCEN is permitted to import ODS material into Australia for destruction. Halon and CFC imported from New Zealand have been destroyed. The current price for disposal of ODS is \$US 3-4/kg.

Advantages: The major advantage of this technology is that it is a non-incineration technology that has demonstrated high efficiency destruction of both CFCs and halons on a commercial scale for several years. It has also demonstrated very low emissions of PCDD/PCDFs. Mass emissions of pollutants are very low because of the relatively low volume of flue gas produced by the process. Also, the very high energy density results in a very compact process. The plant is skid-mounted, and is easily transported.

Disadvantages: One disadvantage is that the recovered ODS must be pretreated to remove oil before destruction. In the current process, the halide salts formed by the neutralization of the acid gases formed are released as a liquid effluent to the environment. Finally, the process cannot be applied to foams.

3.3.2 Inductively Coupled Radio Frequency Plasma

Process Description: Gaseous CFCs and steam are fed through the plasma torch where temperatures of 10,000°C are achieved in a 185 kW inductively coupled radio frequency torch. The gases enter directly into the destruction reactor maintained at about 2000°C for about 2 seconds. Subsequently, the gases are cooled and scrubbed with caustic solution to remove acid gases. One advantage claimed for the RF plasma over DC plasma is the elimination of electrodes that are known in DC plasmas to be subject to corrosion. It is also possible that the RF approach may lead to increased on-stream time over that observed in the PLASCON process described above. The RF plasma also has a slower gas flow rate and a larger plasma flame that results in higher residence time.

The ICRF plasma process has demonstrated a DRE exceeding 99.99% while destroying CFC at a rate of 50-80 kg/h. The flue gas volume has been estimated at 20 Nm³/h and emissions of the pollutants of concern are tabulated below.

Table 3-8: Emissions from ICRF Plasma Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.012	ng/Nm ³	0.3	ng/h
HCl/Cl ₂	4.8	mg/Nm ³	100	mg/h
HF	2.4	mg/Nm ³	50	mg/h
HBr/Br ₂	2.4	mg/Nm ³	50	mg/h
Particulates	4.8	mg/Nm ³	100	mg/h
CO	4.8	mg/Nm ³	100	mg/h

Technical capability: Based on these pilot plant results, a demonstration plant was constructed at Ichikawa City in the Chiba prefecture by a consortium of industrial concerns under the auspices of the Ministry of International Trade and Industry (MITI). . A commercial plant has operated since 1995 and over 300 MT of CFCs, HCFCs and HFCs had been destroyed by 2001. This process has demonstrated high destruction efficiencies and very low PCDD/PCDF emissions on a commercial scale. No operating costs for a commercial-scale unit are reported.

Advantages: The process has been demonstrated on a commercial scale to achieve high destruction of CFC and low emission of pollutants. As noted above, the elimination of electrodes may lead to better reliability than plasma arc processes. Also, the ICRF plasma does not require argon and may cost less to operate than the PLASCON process. Finally, the low volume of gas produced by the process results in low levels of mass emission of pollutants.

Disadvantages: One key disadvantage is the high energy consumption required for plasma generation.

3.3.3 AC Plasma

Process Description: Destruction systems incorporating their patented Plasmatron AC plasma are designed by Scientific Utilization International (SUI) for the destruction of hazardous wastes. The AC plasma is produced directly with 60 Hz high voltage power but in other respects is similar to the inductively coupled RF plasma. The system is electrically and mechanically simple and is thus claimed to be very reliable. Also, the Plasmatron process can tolerate a wide variety of working gases, including air, and can tolerate oily gases. While some information is available describing the plasma generator and its associated equipment, no information was provided describing the destruction process, but one could envisage a process very similar to the PLASCON process.

No performance data was reported for the AC plasma process but DRE and emission of pollutants are expected to be similar to the ICRF plasma process. The flue gas volume for a 50 kg/h destruction system is estimated at 20 Nm³/h and emission of pollutants is tabulated below.

Table 3-9: Emissions from the AC Plasma Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.012	ng/Nm ³	0.3	ng/h
HCl/Cl ₂	4.8	mg/Nm ³	100	mg/h
HF	2.4	mg/Nm ³	50	mg/h
HBr/Br ₂	2.4	mg/Nm ³	50	mg/h
Particulates	4.8	mg/Nm ³	100	mg/h
CO	4.8	mg/Nm ³	100	mg/h

Technical capability: These plasmas have only recently been developed to the stage where they are being applied to hazardous or toxic waste destruction. It has not yet been commercially applied to the destruction of ODS but CFC was destroyed to non-detectable levels in a 500 kW demonstration unit. No cost information was provided but destruction costs are estimated to be comparable to those of the PLASCON process, that is, in the \$US 3-5/kg range.

Advantages: As noted above, the AC plasma process is expected to exhibit the same high DRE and very low emissions as the ICRF plasma process. Furthermore, the AC torch is claimed to be an electrically simple and mechanically rugged torch, and thus very reliable. It does not require argon and in fact can operate with air or steam as plasma gases and is claimed to be tolerant of oil contamination in ODS.

Disadvantages: The AC plasma process has been demonstrated with ODS only on a pilot scale, but has been commercialised on a large scale with other waste. Another disadvantage is the high energy consumption required for the plasma generation.

3.3.4 CO₂ Plasma Arc

Process Description: A high temperature plasma is generated by sending a powerful electric discharge into an inert atmospheric gas, such as argon. Once the plasma field has been formed, it is sustained with ordinary compressed air or certain atmospheric gases depending on desired process outcomes. The temperature of the plasma is well over 5000 °C at the point of generation into which the liquid or gaseous waste is directly injected. The temperature in the upper reactor is about 3500 °C and decreases through the reaction zone to a precisely controlled temperature of about 1300 °C. The PARCON technology destroys hazardous organic compounds by a three-step process. The waste is

first decomposed in the plasma field, leaving only the constituent atoms. The atoms are then chemically reacted with oxygen in a turbulent atmosphere below the reactor, creating new molecules with predicted and known elements. The gas comprised of the newly formed molecules is then quickly cooled to 70 °C, preventing the atoms from re-organizing into dioxins and furans. The exit gas is then cleaned by conventional chemical scrubbing. A special feature of the process is the use of CO₂, which is formed from the oxidation reaction, as the gas to sustain the plasma.

The DRE for destruction of PCB and trichlorinated benzene is reported to exceed 99.9999%. The feed rate of these refractory compounds was 8 kg/h during the demonstration project and the flue gas volume is reported as 3.1 Nm³/h.

Table 3-10: Emissions from the CO₂ Plasma Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.013	ng/Nm ³	0.4	ng/h
HCl/Cl ₂	17.3	mg/Nm ³	53	mg/h
HF	4.4	mg/Nm ³	14	mg/h
Particulates	221	mg/Nm ³	680	mg/h
CO	31	mg/Nm ³	96	mg/h

Technical capability: PARCON process has been jointly developed by Kinectrics (formerly Ontario Hydro Technology) and Plasma Environmental Technologies, both of Toronto, Canada. To date the feature product has been the PARCON 125, a transportable waste treatment facility that destroys hazardous gases and liquids at a rate of up to 12.5 kg/h. The PARCON 125 is ideal for demonstrations, pilot projects and small commercial applications. Kinectrics and Plasma Environmental Technologies have developed, tested and patented advanced versions of PARCON that offer greater capacities. A demonstration project with CFC is planned for 2002. The PARCON process is applicable to ODS liquids and gases only.

Advantages: The PARCON process has demonstrated high DREs with refractory compounds at a reasonably high demonstration rate. Mass emission rates of the pollutants of interest are low, primarily because of the low volume of flue gas produced by the process.

Disadvantages: The process has not yet been demonstrated on a commercial scale although Kinectrics claims that several opportunities exist to install a commercial system in 2002. The emission of particulates violates the screening limit of 50 mg/Nm³ but a commercial system would include a properly designed gas cleaning system and there is little likelihood that the screening limit could not be satisfied. Another disadvantage is the high energy consumption required for the plasma generation.

3.3.5 Microwave Plasma

Process Description: This process feeds microwave energy at 2.45 GHz into a specially designed coaxial cavity to generate a thermal plasma under atmospheric pressure. The coaxial design is claimed to promote plasma stability. Argon is used to initiate the plasma but otherwise the process requires no gas to sustain the plasma. A mixture of CFCs with water vapour is fed to the plasma and is broken down at temperatures exceeding 6000 °K into the dissociated state, after which HCl, HF, CO and CO₂ are formed. The acid gases are scrubbed in a tower with a slaked lime slurry and then the process gas is combusted with air to convert the CO to CO₂.

The DRE for the microwave plasma process is reported to exceed 99.99% while destroying CFC-12 at a rate of 2 kg/h. The flue gas volume has been estimated at 32 Nm³/h based on the process description and flue gas compositions reported. Emissions of pollutants are reported below.

Table 3-11: Emissions from Microwave Plasma Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.0011	ng-ITEQ/Nm ³	0.03	ng-ITEQ/h
HCl/Cl ₂	2.45	mg/Nm ³	78	mg/h
HF	0.74	mg/Nm ³	24	mg/h
HBr/Br ₂		mg/Nm ³		mg/h
Particulates	10.6	mg/Nm ³	340	mg/h
CO	4.3	mg/Nm ³	136	mg/h

Technical capability: The microwave plasma process was developed in Japan by Mitsubishi Heavy Industries, Ltd. The development of the process was started in 1997 by Mitsubishi Heavy Industries, Ltd. and launched in the market in 2000. The plasma approach was selected to provide a very compact design that could be applied at the many sites where CFCs were recovered. The CFC feed rate of 2 kg/h was determined by market research. Capital costs were

reported at about \$US 60,000 for a 2 kg/h system, although it is not clear what such a system would include.

Advantages: Key advantages of the process are the high destruction efficiency due to the very high process temperature and the very low emissions of atmospheric pollutants. The process is reported to be capable of achieving the high operating temperatures in a very short time, thus providing operating flexibility and reduced downtime. There is no need for an inert gas to operate the process, which improved power efficiency, reduces operating cost and minimizes the volume of flue gas. Finally, the process is very compact.

Disadvantages: A disadvantage of the process is that halide salts produced by neutralization of the acid gases must be discharged to the environment. Another disadvantage is the high energy consumption required for the plasma generation.

3.3.6 Nitrogen Plasma Arc

Process Description: This process uses a thermal plasma to decompose the waste CFC, HCFC and HFC. The thermal plasma is generated by a DC non-transferred plasma torch operating with water-cooled electrodes and using the nitrogen as the working gas. The plasma torch power is 240-280V x 60A. Liquefied gases can be fed directly from their pressurized storage into the reactor, while liquids (e.g. CFC-11) are first transferred to a pressure vessel and transferred with compressed air to an evaporator before being fed to the reactor. Gases from the plasma are fed to an oxidation tube in which HCFCs and HFCs are first reacted with steam to be decomposed into carbon monoxide (CO), hydrogen fluoride (HF) and hydrogen chloride (HCl) and then air is introduced into the bottom of the tube to oxidize CO to CO₂. The destruction of CFCs is completed without additional air. The temperature at the reactor nozzle is estimated to be in the range from 1400°K to 2500°K depending on the amount of steam appropriately supplied for desirable destruction. The reaction gas mixture is immediately quenched in a scrubber after the oxidation tube, where the produced hazardous gases, HCl and HF, are absorbed by calcium hydroxide (Ca(OH)₂) suspended in water. The process is reported to achieve a DRE of 99.99% while destroying CFCs, HCFCs and HFCs at a feed rate of 10kg/h. Emissions of pollutants are reported as follows.

Table 3-12: Emissions from Nitrogen Plasma Arc Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.044	ng-ITEQ/Nm ³	95	ng-ITEQ/h
HCl/Cl ₂	2.1	mg/Nm ³	4500	mg/h
HF	0.6	mg/Nm ³	1300	mg/h
HBr/Br ₂		mg/Nm ³		mg/h
Particulates	9	mg/Nm ³	19000	mg/h
CO	26	mg/Nm ³	56000	mg/h

Technical capability: The nitrogen plasma arc destruction process was developed by Gunma University, ShinMaywa Auto Engineering and Daihen Corporation in 1995. Commercial systems based on this process are offered by ShinMaywa Auto Engineering. Five units are currently being used commercially in Japan. A total of more than 90 tons of CFCs, HCFCs, and HFCs has been destroyed by those units. Similar systems based on this process have been in operation in Australia by CSIRO since 1992 (PLASCON™) and four units are used commercially in Australia. The company has indicated a cost in the range \$US 5-6/kg for destruction of CFCs, HCFCs and HFCs.

Advantages: A key advantage of this technology is that the equipment is very compact in size. The system requires only 9 m x 4.25 m area for installation including a precipitation and dehydration unit for the by-products (CaCl₂ and CaCO₃). Therefore, the system is capable of being carried on a truck to the waste generation spot leading to an on-site treatment.

Disadvantages: A disadvantage of the process is that the destruction capacity is limited because it is difficult to scale up the plasma torch. However, by using a combination of plasma torches, it is expected to destroy 20 to 30 kg of waste per hour. Furthermore, the process generates halide salts from the neutralization of the acid gases. Another disadvantage is the high energy consumption required for the plasma generation.

3.4 Other Non-Incineration Technologies

3.4.1 Solvated Electron Decomposition

Process Description: The process is a batch process involving two simple vessels; one a heated reaction vessel and the other a refrigerated ammonia recycle vessel. The ODS compounds are decomposed in the reaction vessel with liquid ammonia and metallic sodium. The process operates at atmospheric pressure. It is expected that no dioxins and furans would be produced by this process since it does not involve oxidation and operates at relatively low temperatures. No atmospheric emissions result from the decomposition of the original ODS material. Only non-toxic waste products are formed: sodium chloride, sodium fluoride, biodegradable organic compounds, and water. Methane and ethane are also produced as by-products. Metallic sodium is consumed in the process and is the major component of operating cost. About 95-98% of the ammonia is recycled and hence does not contribute much to operating cost. The process was demonstrated on a pilot scale to destroy carbon tetrachloride, several CFCs, HFCs, refrigerant blends and halons at greater than 99.99% efficiency.

Estimated data was provided for a 50 kg/h destruction system. The flue gas volume has been estimated at 80 Nm³/h based on combustion of the methane/ethane product gas with air. Emissions of pollutants are tabulated below.

Table 3-13: Estimated Emissions from the Solvated Electron Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.001	ng/Nm ³	0.1	ng/h
HCl/Cl ₂	0.1	mg/Nm ³	9	mg/h
HF	0.1	mg/Nm ³	9	mg/h
Particulates	11	mg/Nm ³	900	mg/h
CO	11	mg/Nm ³	900	mg/h

Technical capability: Commodore Advanced Sciences, Inc. of Albuquerque, New Mexico, developed a process for the destruction of ODS in the early 1990s based on solvated electron solutions formed by dissolving metallic sodium in ammonia. A US patent for the process was issued in 1995. While developed specifically for ODS destruction, the process has never been commercially applied to ODS destruction because of lack of demand. It has been applied successfully to PCB destruction and is currently being applied to the

destruction of chemical warfare agents. Finally, operating cost is heavily dependent on the cost of metallic sodium and is reported to exceed \$US 7/kg of CFC.

Advantages: A major advantage of the process is its simplicity and its low operating temperature. It offers high destruction efficiency and very low emission of pollutants, particularly PCDD/PCDFs.

Disadvantages: A disadvantage is the lack of demonstration of ODS destruction on a commercial scale, although there appears to be little doubt that the process could be successfully applied for that purpose. Handling metallic sodium presents safety issues and will require careful attention to operating procedures. Finally, the process appears to be very expensive to operate compared to other ODS destruction technologies.

3.4.2 Gas Phase Chemical Reduction

Process Description: The GPCR technology involves the gas-phase chemical reduction of organic compounds by hydrogen at temperatures of 850 to 900°C. In contrast to conventional incineration technologies, the GPCR technology uses hydrogen to break down the bonds that hold the molecule together. The technology consists of three main components: the front end system, which heats contaminated solids, liquids or gases, rendering the contaminants into a gaseous form; the GPCR reactor, in which the gaseous contaminants are heated electrically to the reaction temperature and then broken down in less than a second by hydrogen into methane and acid; and the gas scrubbing system, which removes acid from the methane-rich gas product gas. Halogenated hydrocarbons such as CFCs are chemically reduced to methane, hydrogen chloride (HCl) and hydrogen fluoride (HF). The methane is recovered and reused as a fuel for the system components, while the acids are neutralized with caustic or lime.

Technical capability: ELI Eco Logic International Inc. (Eco Logic) of Rockwood, Ontario developed and commercialised the ECO LOGIC Gas-Phase Chemical Reduction process. Eco Logic applied for a patent for this core technology in 1986. The proprietary process is a non-incineration technology suitable for destroying organic wastes in all matrices including soil, sediment, sludge, high-strength oils, watery wastes and bulk solids such as electrical equipment. While Eco Logic has no experience with ODS, the company has destroyed PCB waste and chlorobenzene waste on a commercial scale to DREs exceeding 99.9999%. Eco Logic has also destroyed PCB, DDT and hexachlorobenzene waste on a commercial scale to DREs exceeding 99.9999%. Furthermore, the company has considerable laboratory and field data on many other hazardous wastes including chemical warfare agents. Eco Logic supplies fixed systems and provide

treatment services with transportable systems. The GPCR process is reported to destroy ODS at a cost in the range of \$US 3-5//kg.

The DRE for a GPCR process designed to destroy 25 kg/h of CFC would exceed 99.9999%. The reported volume of flue gas is 156 Nm³/h and emissions of pollutants are tabulated below.

Table 3-14: Emissions from the GPCR Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.015	ng/Nm ³	2	ng/h
HCl/Cl ₂	0.1	mg/Nm ³	12	mg/h
HF	0.1	mg/Nm ³	12	mg/h
Particulates	0.5	mg/Nm ³	70	mg/h
CO	1.1	mg/Nm ³	180	mg/h

Advantages: The major advantages of this process are that it is essentially indiscriminant with regard to the nature of the organic waste that it can destroy and that it achieves very high destruction efficiencies. It is the only non-incineration process that can handle solids, potentially including foams. Furthermore, the process achieves among the lowest emissions of pollutants due both to very low concentrations of pollutants in the flue gas and also a very low flue gas volume. The transportability of the process may also prove beneficial.

Disadvantages: The major drawback is the lack of experience on any scale in destroying ODS, although the process has been proven on refractory compounds such as PCBs. Although ELI Eco Logic claims that the process does not preclude recovery of acids, this feature has not yet been commercialised.

3.4.3 Gas Phase Catalytic Dehalogenation

Process Description: Hitachi Ltd. of Tokyo, Japan has developed a process in which CFCs are destroyed over a proprietary metal oxide catalyst at 400°C at atmospheric pressure. The HCl and HF produced are absorbed in a lime solution.

The DRE reported for disposing of CFC-12 exceeded 99.99%. A flue gas volume of 15 Nm³/h was estimated for a system destroying 10 kg/h and estimates of the emissions are tabulated below.

Table 3-15: Emissions from the Gas Phase Catalytic Dehalogenation Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	<0.01	ng/Nm ³	<0.15	ng/h
HCl/Cl ₂	1.0	mg/Nm ³	15	mg/h
HF	<0.5	mg/Nm ³	<7.5	mg/h
Particulates	2	mg/Nm ³	30	mg/h
CO	13	mg/Nm ³	195	mg/h

Technical capability: The Hitachi process has been demonstrated to successfully destroy CFCs and a similar process has been commercialised for perfluoro-carbon (PFC) decomposition as well as PCB destruction. Commercial destruction of PFCs has demonstrated a destruction efficiency exceeding 99%, and destruction of PCBs has demonstrated a destruction efficiency of 99.9998%. Hitachi estimates operating costs of about \$US 2-3/kg CFC-12 but when depreciation and other fixed costs are applied the destruction cost is more likely to be in the range \$US5-7/kg. Capital costs were estimated at about \$US 250,000 for a 1 kg/h system and \$US 1 million for a 10 kg/h system.

Advantages: It is very efficient in destroying CFCs and it is claimed that no dioxins or furans are produced in the process. The process operates at significantly lower temperatures than incineration processes, so energy input would be considerable lower. Most importantly, mass emissions are very low due to the very low flue gas volume.

Disadvantages: The destruction cost using this process appears to be higher than many other destruction technologies. Halide salts produced from the acid gases would need to be discharged as a liquid effluent for this process.

3.4.4 Superheated Steam Reactor

Process Description: In the super-heated steam reactor process, decomposition of ODS takes place in the gaseous phase at elevated temperatures. CFCs, steam, and air are first mixed and then preheated to around 500 °C, before being fed into a tubular-type reactor whose wall is electrically heated at 850-1000 °C. The decomposition of CFCs, mainly by hydration, gives HF, HCl, and CO₂. The exhaust gas is led to a scrubber cooler where the exhaust is quenched by washing with a Ca(OH)₂ solution and the acids are neutralized. As a result of the quenching of exhaust, the concentrations of PCDD/PCDF are minimized.

The process is reported to have a DRE exceeding 99.99% while destroying HCFC-22 at a rate of 10.1 kg/h. The emission of pollutants is reported in the table below.

Table 3-16: Emissions from Superheated Steam Reactor Process

Pollutant	Concentration		Mass Emission	
PCDD/PCDF	0.041	ng-ITEQ/Nm ³	1.36	ng-ITEQ/h
HCl/Cl ₂	<2.95	mg/Nm ³	<98	mg/h
HF	<0.81	mg/Nm ³	<27	mg/h
HBr/Br ₂		mg/Nm ³		mg/h
Particulates		mg/Nm ³		mg/h
CO	<11.3	mg/Nm ³	<375	mg/h

Operating Experience: The super-heated steam reactor was developed by Ohei Development Industries Co. Ltd, and the patent has been registered (Japan Patent No. 3219686 and No. 3219706). The reactor destroys mainly CFCs and HCFCs, but has been recently used to decompose HFCs. The installations of the super-heated steam reactors are installed at 11 sites in Japan as captive destruction facilities. The cost for the destruction slightly varies depending on disposal of neutralized residue, but it is claimed to be in the range of \$US 1.1-1.4/kg-CFC. As with other reported costs, it is not clear what cost elements are included, and destruction costs on an all-in basis are more likely to be in the range of \$US 2.0-3.0/kg-CFC. The capital cost for the reactor having a capacity of 10 kg/h is about \$US 300,000.

Advantages: Key advantages of the process are its high destruction efficiency and its low emissions of pollutants, which result from its high operating temperature, quench cooling of process gases and the low flue gas volume. The process is claimed to be easy to maintain because of its simple design and safe to operate because it operates under negative pressure. The compact nature of the process permits its application in mobile destruction facilities and it is applicable to all but foam ODS.

Disadvantages: The major disadvantage is the need to dispose of halide salts resulting from neutralization of acid gases, although technology to recycle the CaF₂ in the residue is being developed.

4 Recommendations

4.1 Recommended Technologies

4.1.1 Concentrated CFCs, HCFCs and Halons

This class of ODS considered by the Task Force consists of concentrated CFCs, HCFCs and halons. This class excludes ODS contained in foams, and methyl bromide, but includes pure and mixed CFCs, HCFCs and halons, and CFCs, HCFCs and halons that may be contaminated, for example by oil or moisture.

The Task Force developed a set of four criteria to determine those ODS destruction technologies that are recommended for destruction of concentrated sources. These criteria are similar to, but are more restrictive than, those used to select technologies for screening. Those screening criteria were given in Section 2.1.

Each technology was judged separately on its ability to destroy CFCs and HCFCs, and to destroy halons. A number of screened technologies satisfied the criteria for the destruction of CFCs and HCFCs, but had not been tested for halon destruction. Such technologies could not be recommended for halon destruction, since the presence of bromine in halons can significantly affect the process parameters. In particular, molecular bromine tends to be formed rather than HBr, except under reducing conditions. Molecular bromine is very difficult to remove from the exhaust gases. Technologies that are recommended for CFC and HCFC destruction, but have not been tested for halon destruction, are described as potential technologies for halon destruction.

The Task Force did, however, consider that it was reasonable for technologies that satisfied the criteria for CFC destruction to be also recommended for HCFC destruction. This was for two reasons. First, HCFCs are more easily destroyed than CFCs. Second, the presence of hydrogen in HCFCs will have only a minor influence on the process, particularly since hydrogen will already be present, either from the combustion fuel or the addition of steam, in all the recommended technologies.

The Task Force considered it reasonable that a technology that had been demonstrated to satisfy the criteria for one type of CFC could be recommended for the destruction of all CFCs and HCFCs, and that a technology that had been demonstrated to satisfy the criteria for one type of halon could be recommended for destruction of all halons. The Task Force does, however, consider it necessary that the stack gases be tested for each new ODS destroyed to ensure that the DRE and emission requirements are satisfied, since some CFCs, for example, are more easily destroyed than others.

The technologies recommended by the Task Force for consideration by the Technical and Economic Assessment Panel were selected based on those which were able to pass the screening process, and where data were available to support their technical capability to destroy ODS. The recommended technologies are listed in Table 4.1.

Table 4-1: Recommended Technologies and Their Applicability

Technology	Applicability	
	Concentrated CFCs and HCFCs	Concentrated Halons
Cement Kilns	Recommended	
Liquid Injection Incineration	Recommended	Recommended
Gaseous/Fume Oxidation	Recommended	Recommended
Reactor Cracking	Recommended	
Rotary Kiln Incineration	Recommended	Recommended
Argon Plasma Arc	Recommended	Recommended
Inductively-Coupled Radio-Frequency Plasma	Recommended	Recommended
Nitrogen Plasma Arc	Recommended	
Microwave Plasma	Recommended	
Gas Phase Catalytic Dehalogenation	Recommended	
Super-Heated Steam Reactor	Recommended	

4.1.1.1 Technical capability

As well as meeting the Criteria for Technology Screening, (see section 2.1), it was necessary that the recommended technologies demonstrated destruction of concentrated CFCs and HCFCs, or halons.

For the purposes of recommending technologies for concentrated CFCs and HCFCs destruction, a destruction technology was considered technically capable if it met the following criterion:

- It had been demonstrated to destroy a concentrated CFC or HCFC to the technical performance standards, on at least a pilot scale or demonstration scale.
- An acceptable pilot plant or demonstration plant was defined as one that had a capacity of not less than 1.0 kg/h of the concentrated CFCs or HCFCs.

For the purposes of recommending technologies for concentrated halon destruction, a destruction technology was considered technically capable if it met the following criterion:

- It had been demonstrated to destroy a concentrated halon to the technical performance standards, on at least a pilot scale or demonstration scale.
- An acceptable pilot plant or demonstration plant was defined as one that had a capacity of not less than 1.0 kg/h of the concentrated halon.

The reasons for choosing a capacity of 1.0 kg/h are discussed in detail in Appendix B.

Additionally, the Task Force notes that a preliminary survey of the industry indicates that three technologies are currently in common commercial use. These technologies are: Argon Plasma Arc, Reactor Cracking, and High Temperature Incineration. These technologies are readily available and price quotations can be obtained.

4.1.2 Foams (Diluted Sources)

Considering the various selection criteria, there is a very limited choice for the destruction of ODS in foams; only Municipal Solid Waste incinerators and rotary kiln incinerators meet the criteria. Therefore, the Task Force recommends that both of these be considered acceptable for the disposal of dilute sources of ODS such as foams. One of the major constraints in the selection of destruction technologies for foams is their ability to handle solids. This de-selects a good number of otherwise acceptable destruction technologies from the list.

4.2 Other Recommendations

The Task Force provides the following recommendations for consideration by the TEAP:

1. Technology list should be updated on an bi-annual basis to ensure the latest technological developments are available to Members of the Parties.
2. Consideration should be given to linking the work of the TFDT with other multi-lateral agreements (e.g. Stockholm Convention on POPs, Basel Convention) to facilitate transportation of ODS across international borders so as to increase the economic viability of ODS destruction.
3. A short practical guide for the import and export of ODS for destruction should be incorporated in future work of the TFDT.

4. Destruction of foams should be investigated further to better assess the most appropriate technologies required for destruction to maximize the ODS capture and destruction.
5. A more comprehensive review should be taken of ODS inventories and flows available for destruction over the next few years to assess the need for a more aggressive destruction program.
6. Further consideration should be given to the calculation of DRE for foams.
7. A more comprehensive review is suggested of regulations pertaining to ODS destruction in developed countries.
8. The overall calculation of DRE should be revisited taking into consideration ODP.
9. Technologies that convert ODS into useful compounds via chemical reactions should be investigated in future work of the TFDT.
10. A review of existing facilities that have destroyed ODS or are commercially available for this function should be assembled. This review would be used for the development of a list of commercial destruction facilities worldwide. In this review, descriptions of the facilities would include; details about the plant, geographic location (country, city), capabilities, type of technologies, DREs, emission rates, certifications, etc. In addition, an analysis of their destruction process and their effectiveness in destroying various types of ODS should be included.
11. A more comprehensive study should be undertaken to assess ways on avoiding fugitive emissions when handling, crushing or grinding foams, prior to introduce them into the furnaces.
12. An assessment of the current total global ODS destruction capacity for CFCs, halons and foams should be considered on a country basis in an effort to put the issue of future technological developments into context.
13. An in-depth assessment of the price per kg for destruction of ODS material should be completed to better assess the cost implications for destroying anticipated stockpiles.
14. Consideration should be given to the estimation of carbon tetrachloride which is likely to be co-produced in the production of chloromethanes and needs to be destroyed beyond 2010.
15. Possible ODS likely to be available in some of the large ODS consuming Art. 5(1) parties should be estimated and techno-economic feasibility for the destruction of those ODS should be assessed.
16. Additional information should be gathered to validate sampling and analytical methods for ODS compounds in exhaust gas streams, in order that experience in this area be shared.

Appendix A: Description of ODS Destruction Technologies

A-1.0 Introduction

The first section of this Appendix describes Technically Capable Technologies that passed the initial screening assessment, i.e., those that met the screening requirements of technical performance, environmental emissions, and technical capability. The second section describes Emerging Technologies that did not meet the screening criteria, typically because they failed to meet the criterion for technical capability. The ODS destruction technologies are described in terms of process type and specific features.

Descriptions of Technically Capable Technologies are organised into two parts, a generic process description and a description of one or more specific facilities including their operating experience and actual performance data. All concentrations of pollutants and flue gas volumes are expressed at the normal conditions of 0°C and 101.3 kPa on a dry gas basis and corrected to 11% O₂. The latter part also includes a discussion of the technical capability of the technology and recent cost information, to the extent that such cost information is available. Costs are reported as ranges of costs in \$US/kg ODS. Such an approach recognizes the difficulty of developing accurate costs on a consistent basis and also avoids the problem of disclosure of confidential information. The cost data on ODS destruction facilities and technologies has been accumulated over the last two years from several sources. This data had been reported in several currencies and the costs have been adjusted to the end of 2001 and converted into \$US as of that time.

Descriptions of Emerging Technologies include process descriptions but generally lack detailed performance data. Comments with respect to the stage of development towards technical capability are also included.

A-2.0 Screened-in Technologies

A-2.1 Incineration Technologies

A-2.1.1 Overview

The only technologies recommended in the 1992 UNEP report for the destruction of ODS were thermal oxidation (incineration) processes. Incineration is the use of controlled flame combustion to destroy ODS in an engineered device. Several specific processes were recommended, however not all may be appropriate for all classes of ODS. The technologies are grouped below depending on whether the process is intended for dedicated incineration of ODS, co-incineration of ODS along with other waste or whether the ODS are incinerated in a manufacturing process. The technologies are described separately below, but there are a number of characteristics common to all incineration processes.

The significance of the production products of incomplete combustion (PICs) and of greenhouse gases (GHGs) from incineration technologies is important to note. These have become major scientific and political concerns in many countries, and as a result there is significant incentive for the consideration of non-incineration technologies for the destruction of ODS. However, incineration technologies do have the general advantage of being fully developed commercially and broadly located geographically, and thus are given due consideration in terms of finding realistic and timely solutions to the destruction of ODS surplus. All of these factors have been taken into account in the evaluation of commercially-available ODS destruction technologies.

Thermal oxidation processes generally operate at temperatures of 900 °C or higher, *i.e.*, temperatures at which organic compounds are destroyed. Destruction and removal efficiencies (DRE) of 99.99% are readily achieved in well-designed units that are operated properly. High performance incinerators designed specifically to destroy stable organic compounds, such as PCBs and ODS, operate at significantly higher temperatures, generally at 1200 °C or higher. Such high performance incinerators generally achieve 99.9999% destruction. Because halogen-containing ODS has a low heat value, the required high operating temperatures can only be achieved by use of a supplementary fuel such as natural gas, fuel oil, or propane.

The primary products from the thermal destruction of ODS are carbon dioxide (CO₂), water (H₂O) and hydrochloric and hydrofluoric acids (HCl and HF). Hydrogen bromide (HBr) and/or bromine (Br₂) are also produced in the case of the destruction of halons. Products of incomplete combustion (PICs) such as carbon monoxide, hydrocarbons, organic acids and partially degraded products may also be produced, but these PICs are emitted in only small amounts from

well-designed incineration facilities that provide high temperatures, adequate residence times (1 to 2 seconds), excess oxygen and good mixing.

A more serious problem is the potential production of toxic polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in trace quantities. PCDD/PCDF formation can be minimised in well-designed incinerators. Dioxins and furans are formed^{12,13} following the gas phase formation of chemically similar precursors formed at high temperature, 800-900 °C, and by *de novo* synthesis on soot particles and metal surfaces from chemically different precursors and chlorine at lower temperatures, 250-350 °C. Both of these pathways operate simultaneously and independently, but *de novo* synthesis is several orders of magnitude faster than precursor formation in actual incinerators and is the dominant pathway to dioxin and furan formation. Since these compounds generally form in the temperature range 350 to 900 °C, their formation is unavoidable as the hot flue gases from incinerators are cooled in the associated gas cleaning system. It has also been reported that the incineration of halons increases the potential for dioxin formation. This is believed to be due to the free radical scavenging effect of bromine. However, inclusion of a quench cooling operation to rapidly cool the gas to a temperature well below the dioxin/furan formation temperature range usually limits formation of these toxic by-products to very low levels. It should be noted that the formation and control of dioxins and furans is more or less independent of the type of incinerator, although better control of the combustion process as indicated by lower concentrations of CO has been shown to produce lower concentrations of dioxins and furans. Rotary kilns that include dust removal equipment in their flue gas cleaning systems are able to inject powdered activated carbon to remove much of the dioxins/furans formed. However, the very large volumes of gases produced by incinerators result in significant emissions of dioxins and furans even if their concentration are low, and the emission of dioxins and furans from incinerators is a principal reason why their use as a means of destruction of hazardous waste continues to be criticised by environmental non-government organizations (ENGOS)¹⁴. They claim that “this method of destruction may result in the transformation of some portion of one group of POPs, e.g., PCBs

¹² Halonen, I. *et al*, ‘Formation of polychlorinated dioxins and dibenzofurans in incineration of refuse derived fuel and biosludge’, *Chemosphere*, Vol. 26, No. 10, pp. 1869-1880, 1993.

¹³ Huang, H. *et al*, ‘On the mechanisms of dioxin formation in combustion processes’, *Chemosphere*, Vol. 32, No. 9, pp. 4099-4117, 1995.

¹⁴ Costner P., Luscombe, D. and Simpson, M., ‘Technical criteria for the destruction of stockpiled persistent organic pollutants’, *Greenpeace International*, Washington, D.C., 7 October 1998.

or chlorine-containing pesticides, into another, e.g., dioxins, while shifting the environmental and public health burden from one community to another”.

Another serious technical problem is the production of the above-mentioned acid gases, which must be removed by inclusion of a gas scrubbing system. This generally involves the use of electrostatic precipitators, bag houses, Venturi scrubbers, packed bed scrubbers or plate scrubbers. The formation of molecular bromine in the case of halon incineration is particularly troublesome. In general this substance is difficult to remove; however, several approaches can be taken to minimise its formation, including the introduction of sulphur-containing compounds and the minimisation of the cooling period.

The formation of halide acids also presents some technical difficulties. An HF-resistant refractory lining and binder must be used in the combustion chambers through the quench area. Corrosion resistant fibreglass-reinforced plastic (FRP) is generally required in the scrubbing systems and the presence of fluoride requires special lining of the FRP to avoid attack of the glass fibres. Finally, the acid gases also require upgrading of the bag material in the bag house. Incineration facilities typically are not fitted with such equipment; however, modifications to existing facilities are possible. Cost factors would naturally have to be taken into consideration before performing such modifications, and operators of such incineration facilities would need to be convinced that there was a sufficiently large market for surplus ODS destruction to justify such an investment.

A-2.1.2 Dedicated ODS Incineration Processes

A-2.1.2.1 Reactor Cracking

Process Description: The reactor cracking process is classified here as an incineration technology because it satisfies UNEP’s definition of incineration; namely, the use of a controlled flame to destroy ODS in an engineered device. The process is, however, very different from conventional incineration because of the use of hydrogen and oxygen, rather than a hydrocarbon fuel and air, which avoids the generation of a large flue gas volume with consequent large emissions of pollutants. The approach also enables the recovery of acid gases as described below. The process (Figure A-1) uses a cylindrical, water-cooled reactor made of graphite, and an oxygen–hydrogen burner system. Waste gases typically consisting of CFCs, HCFCs and HFCs are fed into the reaction chamber where the temperature is maintained at 2000°C. The gases are broken down to HF, H₂O, HCl, CO₂ and Cl₂. The cracked products are cooled in the absorber that is flanged directly to the reactor and the acid gases are purified and recovered as 55% HF and 31% HCl, both of technical grade quality. The resulting waste gas

essentially consists of only CO₂, O₂ and water vapour and meets the requirements of the German Clean Air regulations (TA-Luft).

Operating Experience: Reactor cracking is a proprietary process developed by Hoechst AG (Frankfurt, Germany). A European patent (EP 0 212 410 B1) was issued in 1986. Solvay acquired Hoechst's fluorocarbon business in 1996, and now operates the cracking destruction facility, which is located near Frankfurt. Solvay works in collaboration with Westab, a company that collects and transports waste CFCs. First experiences with this process date back to 1983. The process was installed to treat waste gases from the production of CFCs and, more recently, waste gases from the production of HCFCs and HFCs as well as waste CFCs. The facility consists of two reactors each with a capacity of 1,250 t/yr (max 1500 t/yr, depending on product mix), and a third reactor is planned for 2002. Solvay has legal permission to destroy 9,700 t of CFC per year. The present capacity is about 2500 t/yr. The process is fuelled with by-product hydrogen from a manufacturing unit on the Frankfurt site. The destruction efficiency, operating requirements and air emissions are summarized in Table A-1. HF was reported as not detected and was assigned a value of 0.1 mg/Nm³ uncorrected for the O₂ concentration in the flue gas. No data was reported for particulates but this is estimated to be about 10 mg/Nm³ uncorrected for O₂, consistent with other low volume processes.

Principal advantages of the process are its use of an oxygen-hydrogen flame, which limits formation of NO_x; its very high operating temperature and rapid cooling, which achieves very high DREs and minimizes the formation of PCDD/PCDF; and the recovery of hydrofluoric and hydrochloric acids. However, the process requires that the CFC waste be pretreated to remove oil and the process is intolerant of bromine containing ODS. The process is limited to the disposal of CFCs, HCFCs and HFCs and can not be used in its present form for disposal of foams or halons. Solvay has indicated a cost in the range \$US 4-6/kg for destruction at its Frankfurt facility. Solvay is also prepared to offer its technology under license for construction of a facility outside of Germany. Solvay estimates a 2500 t/yr CFC cracking unit would cost about \$US 4 million excluding the license fee and engineering.

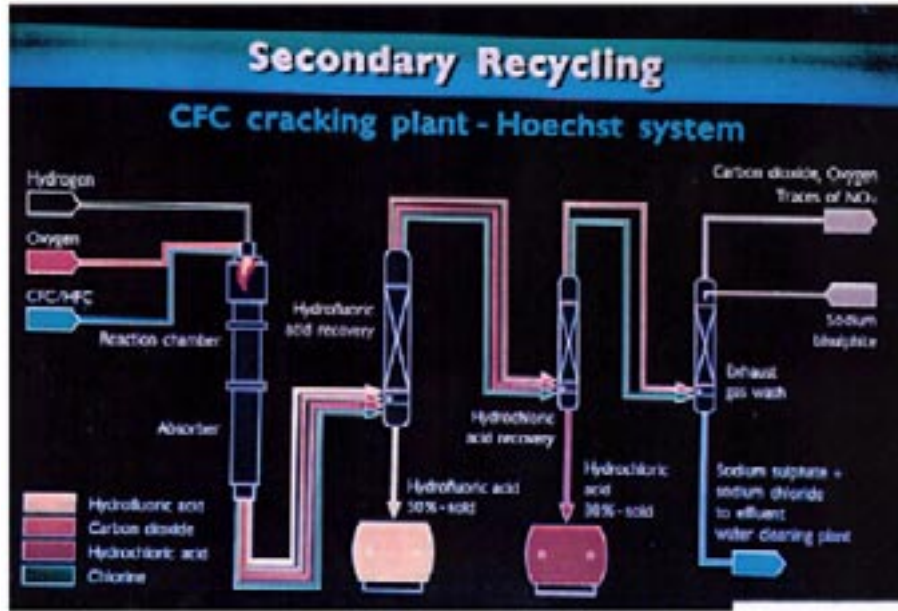


Figure A-1: Process Schematic for Reactor Cracking System, Solvay Fluor und Derivate GmbH

Table A-1: Performance Data for Reactor Cracking Process

Operating Parameters and Destruction Efficiency			Air Emissions		
CFC feed	kg/h (R-12)	200	PCDD/F	ng/Nm ³	< 0.01
Raw Materials	O ₂ Nm ³ /h	57	HF	mg/Nm ³	< 0.1
	H ₂ Nm ³ /h	95	HCl/Cl ₂	mg/Nm ³	< 100
Cool. Water	m ³ /h	50	Particulates	mg/Nm ³	< 10
Elec. Power	kW	50	CO	mg/Nm ³	< 50
Chemical Recovery	55% HF kg/h	120			
	31% HCl kg/h	390	Flue Gas	Nm ³ /h	46.5

A-2.1.2.2 Gaseous/Fume Oxidation

Process Description: This process uses a refractory-lined combustion chamber for the thermal destruction of waste CFC and HCFC gases. Some of the ODS (e.g. CFC-12, CFC-114, or CFC-115) are gases at ambient temperature and can be destroyed by feeding directly from their pressurized storage into the incinerator. The fume stream is heated using an auxiliary fuel such as natural gas

or fuel oil. A combustion temperature near 1100_C is required for most ODS compounds. Gaseous residence times in fume incinerators are about 1-2 seconds. Some fume incinerators are equipped with heat exchangers in the flue gas outlet to pre-heat the combustion air and/or the waste fume. These recuperative incinerators are capable of recovering up to 70% of the energy in the flue gas, but are unlikely to be used for the combustion of chlorine-containing waste because energy recovery precludes rapid quenching which is an effective feature to minimize dioxin/furan formation. Fume incinerators are designed for continuous operation and are a simple, proven technology.

Operating Experience: Fume incinerators are almost always privately operated and are typically found in fluorochemical manufacturing plants. An example of a dedicated gaseous/fume incinerator is the one operated by ICI-Teijin Fluorochemicals Co. Ltd. (ITF) in Mihara City, Hiroshima Prefecture, Japan (Figure A-2). Along with the waste gas, LPG fuel and a large quantity of steam is injected into the incinerator that operates at a temperature of 1200 to 1250°C. The rated capacity of the unit is from 15 to 165 kg/h, depending whether CFCs or halon are being destroyed as illustrated in Table A-2. The flue gas volume was estimated from the data provided. Costs for destruction of ODS waste is expected to be in the range \$US 3-5/kg CFC, and somewhat higher for halons because of reduced throughput.

Table A-2: Operating Parameters and Performance of Fume Incinerator

ODS Feed		CFC-12, HCFC-22	Halon 1301
Feed rate	kg/h	165	15
Temperature of chamber	°C	1200	1250
Residence time	seconds	1 to 2	2.4
DRE	%	> 99.999	> 99.99
PCDD/F	ng-ITEQ/Nm ³	< 0.032	<0.001
HCl	mg/Nm ³	< 3.2	< 2.3
HF	mg/Nm ³	< 0.5	< 0.3
Br ₂	mg/Nm ³		< 1.5
Particulates	mg/Nm ³	< 32	< 22
CO	mg/Nm ³	< 37	< 40
Gas Volume	Nm ³ /h	1240	125

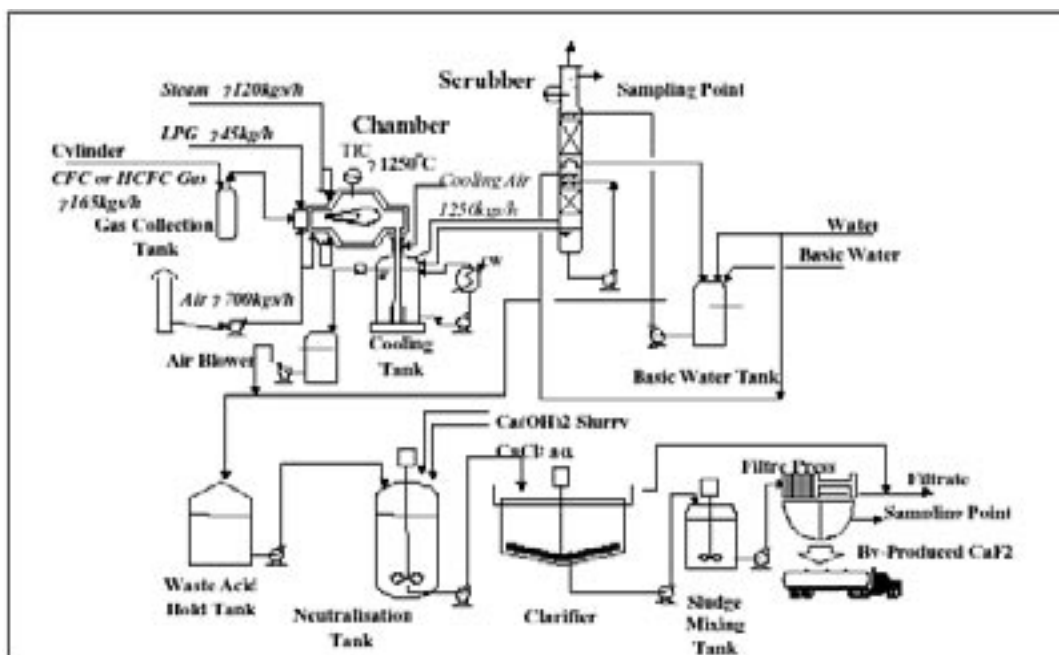


Figure A-2: Process Schematic for Gaseous/Fume Oxidation ICI-Teijin Fluorochemicals Co., Ltd

A-2.1.3 Co-incineration With Other Waste

A-2.1.3.1 Rotary Kiln Incineration

Process Description: Rotary kiln incinerators are refractory-lined rotating cylindrical steel shells mounted on a slight incline from horizontal. Capable of handling both liquid and solid wastes, the rotation of the shell enhances mixing and the inclination causes ash or molten slag to fall out. Most rotary kilns are equipped with an afterburner that ensures complete destruction of exhaust gases. Hydrocarbon fuels, such as natural gas or fuel oil, or high calorific liquid waste, are typically used as an energy source.

Rotary kilns have been used to destroy all forms of hazardous waste (gas, liquid, solids, including sludge). Because of this flexibility, rotary kilns are most frequently incorporated into the design of commercial incinerator facilities. The principal advantage of the rotary kiln is its ability to handle a wide variety of liquid and solid wastes. However, these kilns are very expensive to build and maintenance costs are high. Also, because of the production of acid by-products noted above, their operating permits generally restrict the rate of chlorine-containing wastes that can be fed to the kiln. Furthermore, concerns regarding HF attack on incinerator equipment usually limit the fraction of fluorine in the feed to low levels, typically in the range of 1%. The latter generally establishes

the ODS incineration capacity. Liquid wastes such as CFCs, halons and other ODS can be fed into the rotary kiln or directly into the afterburner.

Rotary kilns are widely used in developed countries for the incineration of hazardous wastes, including chlorinated solvents (CCl_4 , CHCl_3 , CH_3Cl , CH_3CCl_3), and toxic waste, such as PCBs. In Europe and Japan they have been used to destroy CFCs, but as of yet there is little such experience in North America.

Costs for destruction of ODS with rotary kilns vary considerably depending upon the type of ODS, quantities to be destroyed, and market conditions. Low pressure ODS such as CFC-11 and CFC-113, which are usually mixed with other solvents, are less expensive to incinerate than high pressure ODS such as CFC-12 and CFC-22, while halons are in the high pressure category and also pose additional problems because of their bromine content. Destruction costs for the incineration of ODS are expected to be in the \$US 3-5/kg range for CFCs and greater than \$US 7/kg for halons. European destruction costs vary from country to country, and are generally greater than in North America.

Operating Experience: Rotary kiln incinerators vary considerably in their design, particularly in how the secondary combustion chamber, or afterburner, is arranged and in the selection of equipment and their arrangement in the flue gas cleaning system. The specific facilities described below illustrate this diversity of approach and demonstrate the range of technical performance that can be achieved with these systems.

Swan Hills Treatment Centre:

This facility located in Swan Hills, Alberta, Canada is a fully integrated state-of-the-art high performance incineration facility that has been operating since 1987 destroying a wide range of hazardous and toxic wastes including PCBs. The smaller of the two incineration units has been shut down leaving the larger unit as the only currently operating unit. The facility has had very little experience destroying CFCs because there has been virtually no demand for such destruction in Canada. Sensor Environmental Services Ltd. currently manages the operation of the Swan Hills Treatment Centre while the Alberta Government, the owner of the site, explores the feasibility of selling the facility to interested parties to ensure its continued operation.

The incineration facility consists of a 4.4 m diameter by 12 m long Ford Baker Davis rotary kiln that includes a secondary combustion chamber. The kiln is maintained at a temperature of 900°C and the secondary combustion chamber at 1200 °C using natural gas as fuel. Waste CFCs would be introduced into the rotary kiln and, at a residence time of greater than 2 seconds, almost complete

destruction of the CFCs would occur due to excess oxygen and good mixing. The secondary combustion chamber is followed by a spray drier, an activated carbon addition system, a bag house to remove particulate matter, and a scrubbing system that removes other pollutants from the flue gases. Activated carbon is injected into the flue gas to control the reformation of dioxins and furans in a proprietary technique developed at Swan Hills.

The Swan Hills Treatment Centre submits its unit to a three-day compliance test every 6-16 months and these compliance tests have consistently demonstrated higher than 99.9999% DRE. Data from the most recent compliance test performed in 2000 are included in Table A-3 below. The site is also subject to comprehensive environmental monitoring under its operating permit.

The SHTC is approved for the destruction of CFCs under its operating permit from the Government of Alberta, specifically Alberta Environment Operating Approval 1744-01-02.

The SHTC is currently limited to destroying only 35 to 50 t/yr of waste CFCs because the fluorine loading that has been set to minimize potential hydrofluoric acid attack of the fabric filter bags in the bag-house as well as FRP components in the scrubbing system. The capacity could be increased to about 800 t/yr if the facility invested in HF resistant bags and a lime injection system to neutralize HF, but the facility has indicated that it would require a guaranteed supply of surplus refrigerants to justify such an investment. The facility is capable of incinerating halons but at a lower rate. Levels of oil and grease contaminants typically found in recovered CFCs are not a problem for incineration.

Safety-Kleen Services Inc.:

Safety-Kleen operates a fully integrated waste destruction facility in Deer Park, Texas that has been in operation since 1971 and is the largest RCRA Part B permitted and TSCA (PCB) authorized commercial waste incineration facility in the USA. As a point of interest, Safety-Kleen also operates two incinerators in Canada, one at Mercier in Quebec and the other at Sarnia in Ontario, but neither is capable of handling CFCs. Their Certificates of Approval (C of A) severely limit the allowed chlorine containing organic feed to 0.5% and 2.0% of total feed respectively. Furthermore, their materials of construction preclude the feed of fluorine containing organic material. However, the Deer Park facility is capable of disposing of CFCs.

It should be noted that the Safety-Kleen parent company is under Chapter 11 protection in the USA. The Canadian operation is claimed to be profitable and Safety-Kleen expects the parent company to emerge from Chapter 11 within a

year. Laidlaw, which holds a 40% interest in Safety-Kleen, is also under bankruptcy protection in Canada.

Two incinerator trains are situated on the Deer Park site. Train I includes a 3.6 m diameter slagging rotary kiln, a Loddby liquids burner and a horizontal afterburner. Train I is the smaller of the two trains and is TSCA authorized for PCBs. Train II has a 4.4 m diameter rotary kiln, the Rotary Reactor, a vertical afterburner and four McGill liquid burners. The combustion product gases are maintained at 1150-1200 °C for a minimum of 2 seconds. The off-gases flow to a refractory lined quench tower where they are cooled to approximately 80 °C. The gases then pass into twin packed-bed condensers where they are scrubbed by a countercurrent water spray. The gases then pass into an impact scrubber, a set of demisters and finally through an induced draft fan and out a stack in common with Train II scrubbed off-gases.

The capacity of the Deer Park site to incinerate CFCs is about 1,800 t/yr based on limiting the fluorine content of the total feed to about 1.7%, a value based on experience on a New Jersey incinerator which has since been shut down. Performance data from the most recent compliance test are included in Table A-3 below. No data was provided for HF emissions but performance comparable to gaseous/fume incineration uncorrected for O₂ was assumed.

Table A-3: Performance of Rotary Kilns in CFC Incineration

		Safety-Kleen Deer Park, TX		SHTC Swan Hills, AB
		Train I	Train II	
Total Feed	kg/h	5942	7758	
Chlorine Feed	kg/h	1854	2121	
Temperatures				
Kiln	°C	881	886	900
Rotary Reactor	°C		490	
Afterburner	°C	997	979	1200
POHC		Dichlorobenzene		PCB (liq+sol)
	kg/h	392	482	924
	DRE	99.99996%	99.99998%	99.999997%
		Tetrachlorobenzene		
	kg/h	426	474	
	DRE	99.99997%	99.99998%	
ITEQ PCDD/F	ng/Nm ³	0.0056	0.0056	0.066
HCl/Cl ₂	mg/Nm ³	5.0	4.3	1.1
HF	mg/Nm ³	0.4	0.4	0.5
Particulates	mg/Nm ³	28	23	1.7
CO	mg/Nm ³	83	83	8.5
Flue Gas	Nm ³ /h	92900	78500	47,600

Dowa Clean Technological Service:

Dowa Clean Technological Service owns and operates a rotary kiln incinerator that is located in Akita Prefecture, Japan. Data for incineration of halons at both high and low feed rates are presented in Table A-4. As expected, higher DREs and lower emissions of pollutants are generally associated with the lower feed rates.

Table A-4: Performance of a Rotary Kiln in Halon Incineration

		High Feed Rate		Low Feed Rate	
Total Feed	kg/h	1392	1392	1392	1392
Halon		H-1211	H-2402	H-1211	H-2402
Halon Feed	kg/h	38	40	20	20
DRE		99.753%	99.88%	99.99%	99.55%
ITEQ PCDD/F	ng/Nm ³	2.7	1.5	0.38	0.31
HCl	mg/Nm ³	29	149	1.8	1.8
HF	mg/Nm ³	0.5	0.5	0.5	0.5
HBr	mg/Nm ³	9.5	155	4	4
Particulates	mg/Nm ³	1	1	1	1
CO	mg/Nm ³	18	20	42	15
Stack Gas	Nm ³ /h	5540	7820	25300	23200

A-2.1.3.2 Liquid Injection Incineration

Process Description: Liquid injection incinerators are usually single-chamber units with one or more waste burners into which the liquid waste is injected, atomized into fine droplets, and burned in suspension. Tangential firing is frequently used to promote turbulent mixing. Problems of flame stability may result when large volumes (greater than 40%) of CFCs or other ODS are injected into the burner. These incinerators are able to handle a wide range of liquid or vapour wastes, have high turndown ratios and have no moving parts. Liquid injection incinerators are limited to treating wastes that can be pumped and atomized through the burner and are therefore susceptible to plugging if liquids with significant ash are used. However, the incineration of ODS is not likely to be limited by these constraints to a significant degree.

Operating Experience: Asahi Glass Company operates a liquid injection incinerator at its Chiba Plant in Japan. The plant incinerates waste CFCs and HFCs along with waste oil and wastewater. The process is schematically illustrated in Figure A-3 and performance data is summarized in Table A-5. No data was provided for flue gas volume or O₂ concentration but these were estimated from the data provided.

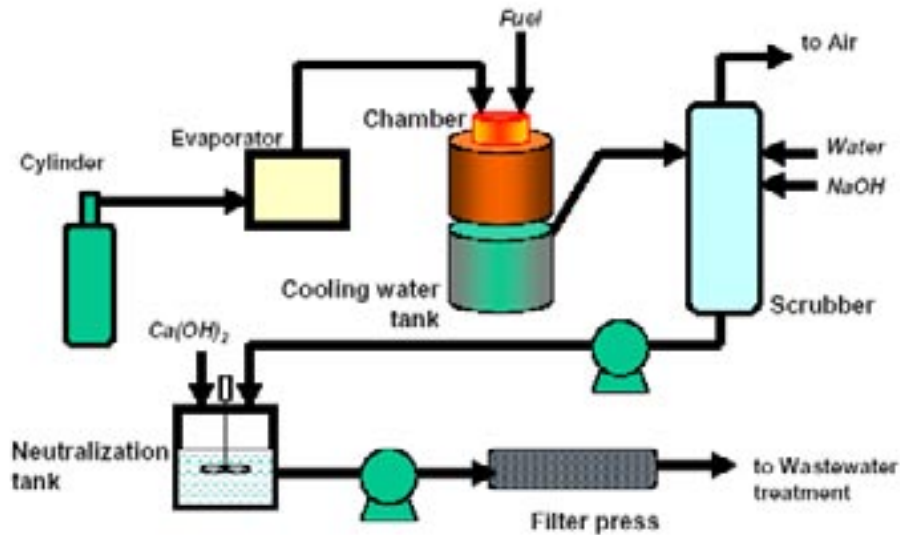


Figure A-3: Liquid Injection Incinerator Asahi Glass, Chiba Plant

Table A-5: Performance Data for Liquid Injection Incinerator

Operating Conditions and Destruction Efficiency			Atmospheric Emissions		
Total Feed	kg/h	110 to 220	PCDD/F	ng-ITEQ/Nm ³	< 0.52
CFC Feed	kg/h	11	HCl	mg/Nm ³	< 10
Temperature	°C	1350	HF	mg/Nm ³	< 1
Residence Time	s	1.3	Particulates	mg/Nm ³	< 23
DRE		>99.99%	CO	ppm	no data
			Gas Volume	Nm ³ /h	3180

A-2.1.3.3 Municipal Solid Waste Incineration

Process Description: Three major types of municipal solid waste incinerators (MSWI) are used: mass burn, modular and refuse-derived fuel (RDF) fired. The MSWI typically employ moving grates for destruction of solid materials, including foams containing ODS.

Mass burn incinerators burn municipal solid waste that has not been pre-processed, except to remove items too large to pass through the feed system. Waste is dumped into a refuse pit and then transferred mechanically a bin that feeds the waste in a controlled manner onto the moving grate. Combustion air is

drawn through the refuse pit to control odour, preheated and introduced into the combustion zone through the moving grate. Hot gases from the combustion of the waste are typically cooled in a waste heat boiler and then cleaned either by a spray drier and bag house or by a dry electrostatic precipitator. The MSWI is generally kept under negative pressure by a fan that blows the cooled and cleaned flue gas up a stack. Ash from the lower end of the moving grate is discharged to a quench pit and conveyed to discharge for destruction. The combustors may be refractory lined or, as in many newer systems, the walls may be water-cooled to recover additional heat.

Modular combustors also burn waste without pre-processing but they are smaller in size. These are most commonly of the two-chamber, controlled-air type. Waste is fed in batches into the primary chamber, which is operated with air at sub-stoichiometric levels (usually 40% of theoretical). As hot, fuel-rich gases pass into the secondary combustion chamber, they are mixed with excess air to complete the burning process. Both primary and secondary chambers are usually equipped with auxiliary burners for start-up and for maintaining design temperatures.

Operating Experience: CFC-containing rigid polyurethane foam has been destroyed in Germany together with solid municipal waste in a full-scale roller grate incinerator with a capacity of 10 t/day. The operating conditions and DRE are listed in Table A-6 below. Emissions of dioxins/furans and other pollutants as well as the flue gas volume have been estimated based on information in the technical literature^{15,16,17} and have also been tabulated below. PCDD/F emissions for MSWIs have been reported to range from 1 to 100 ng-ITEQ/Nm³ and in a MSWI where the flue gas was quickly quenched to below 200°C to range from 0.2 to 0.5 ng-ITEQ/Nm³. A nominal value of 1.0 ng-ITEQ/Nm³ was taken to represent typical emissions since most MSWIs recover waste heat and do not quench the hot flue gas. HCl emissions are reported to range from 300 to 600 mg/Nm³. CO emissions for a well-operated MSWI are reported at 10 mg/Nm³. Values for particulates and HF are estimated; HF emissions are assumed to be an order more than for a rotary kilns and particulate emissions are assumed to be equal to rotary kiln emissions. The flue gas volume from MSWIs

¹⁵ M. J. Kanters *et al.*, Chlorine input and chlorophenol emission in the lab-scale combustion of municipal solid waste, *Environ. Sci. Technol.* **30** (1996) 2121-2126.

¹⁶ R. Takeshita, Relationship between the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans and the control of combustion, hydrogen chloride level in flue gas and gas temperature in a municipal waste incinerator. *Chemosphere* **23**, No. 5 (1992) 589-598.

¹⁷ H. Muto *et al.*, Concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans from chemical manufacturers and waste destruction facilities, *Environmental Research* **54** (1991) 170-182.

is calculated on the basis of 5 Nm³/kg wet MSW, as reported in the technical literature.

Table A-6: Performance Data for Municipal Solid Waste Incinerators

Operating Conditions and Destruction Efficiency			Atmospheric Emissions		
Total Feed	kg MSW/h	10000	PCDD/F	ng-ITEQ/nm ³	1.0
CFC Feed	kg/h	6.5 to 19.5	HCl	mg/Nm ³	300
Temperature	°C	850 to 950	HF	mg/Nm ³	5
DRE	%	>99.99	Particulates	mg/Nm ³	30
			CO	mg/Nm ³	10
			Gas Volume	Nm ³ /h	60,000

A-2.1.4 Incineration in Manufacturing

A-2.1.4.1 Cement Kilns

Process Description: Portland cement is produced by heating calcium (usually limestone), silica and alumina (typically clay or shale) and iron (steel mill scale or iron ore) in cement kilns to temperatures of up to 1500°C. Under this intense heat, the raw materials blend to form a pebble-like substance called “clinker” which is later cooled and ground with a small amount of gypsum to produce cement.

Cement kilns are basically tilted, rotating cylinders lined with heat-resistant bricks. They vary in size depending on the particular type of cement-making process employed, and can reach 250 m in length and 8 m in diameter. The raw material is fed into the elevated or “cool” end of the kiln. As the kiln slowly rotates, the raw material tumbles down toward the hot lower, or “flame” end, gradually altering to form clinker. Cement kilns operate in counter-current configuration. Combustion gases enter at the hot lower end and flow upward, heating raw materials flowing in the opposite direction as they pass over, and leave the kiln at the top end. The gases then pass through pollution control devices before entering the atmosphere. These devices are typically either fabric bag houses or electrostatic precipitators, both of which function to remove the particulate matter entrained in the gas stream before the gases are emitted into the atmosphere. This particulate matter is referred to as cement kiln dust (CKD).

It should be clear from the above process description that the manufacture of cement requires a large quantity of energy. This has led to the use of hazardous

waste fuel to supplement the use of conventional fuel. This applies especially to the older wet process in which the raw material is blended with water to homogenize the material; this process is the most energy intensive because the water must be evaporated out of the slurry mixture. This has led to the use of hazardous waste fuel to supplement the use of conventional fuel.

Existing cement kilns, when properly operated, can destroy most organic compounds including PCBs because the temperature in the burning zone reaches 1500°C and residence times of combustion gases at these temperatures are up to 10 seconds. Tests have demonstrated CFC destruction efficiencies of greater than 99.99%. In general, most cement kilns could tolerate the controlled addition of ODS, but this would have to be evaluated on a case-by-case basis. Fluorine can be beneficial to the cement making process because it allows the cement clinker formation to occur at lower temperatures, thus offering the opportunity for reduced fuel consumption. However, higher levels of fluorine have negative effects on cement quality. As a broad generalization, the maximum fluorine content is about 0.25% of the raw material feed. Chlorine is regarded as an unwanted constituent because it creates operating problems and the newer pre-heater/pre-calciner dry process kilns are expected to have the lowest tolerance for chlorine. The theoretical limit for chlorine is about 0.015% of the raw material feed but the practical tolerance is believed to be much higher.

The major advantage of this approach is that there are large existing capacities of cement kilns in the world that offer the opportunity for destruction of ODS. It has been reported that there are some 60 cement kilns throughout the world that have been modified so that various wastes can be burned along with conventional fuels.¹⁸ The disadvantage is that fluorine and chlorine input rates need to be carefully controlled. Furthermore, the great majority of cement kilns are not currently set up to handle or burn CFCs and halon wastes. Necessary modifications would require equipment for feeding ODS in a controlled manner and monitoring hazardous emissions.

The use of cement kilns for the destruction of hazardous waste is not without critics. It is reported¹⁹ that about 60% of the 4.5 million tonne of hazardous waste burned annually in the United States is burned in boilers and industrial furnaces (BIFs) which use waste as an auxiliary fuel. Virtually all of these are

18 R. Stowe, The use of hazardous waste as an alternative fuel in cement kilns – a working document, Copenhagen, Denmark: Danish Environmental Protection Agency, February 1997.

19 M. Richardson, Recycling or destruction? Hazardous waste combustion in cement kilns: A briefing paper of the American Lung Association Hazardous Waste Incineration Project, Washington, D.C: American Lung association, April 1995.

cement kilns or lightweight aggregate kilns, which operate by a similar process. The regulations under which BIFs operate are less stringent than those regulating the operation of fully permitted RCRA hazardous waste burning incinerators: specifically, BIFs are not required to upgrade controls for particulates; they are not subject to stringent opacity regulations; and they are not required to immediately report RCRA violations. Furthermore, cement kilns burning hazardous wastes are reported to emit dioxins in their stack gases at rates 80 times higher than those of cement kilns burning conventional fuels. Similarly, dioxins found in CKD are about 100 times more concentrated than those from kilns burning only conventional fuels. Finally, cement kilns burning hazardous wastes produce from 75 to 104% more CDD than do kilns burning only conventional fuels.

Operating Experience: Destruction experiments using a cement kiln were carried out Chichibu Plant No.2 in Saitama Prefecture in Japan. The plant is owned by the Taiheiyo Cement Corporation and is now in commercial operation for CFC destruction. The kiln was a dry rotary type equipped with a new suspension preheater with a diameter of 5.5 m and a length of 83 m. The plant produces clinker for Portland cement with a manufacturing capacity of 5000 t/day. The cement kiln is schematically illustrated in Figure A-4 and its performance data for CFC destruction is summarized in Table A-7. The concentration of particulate matter and CO in the flue gas were assumed to be similar to other rotary kilns burning only conventional fuels. The conditions of the flue gas were estimated based on the description of the process.

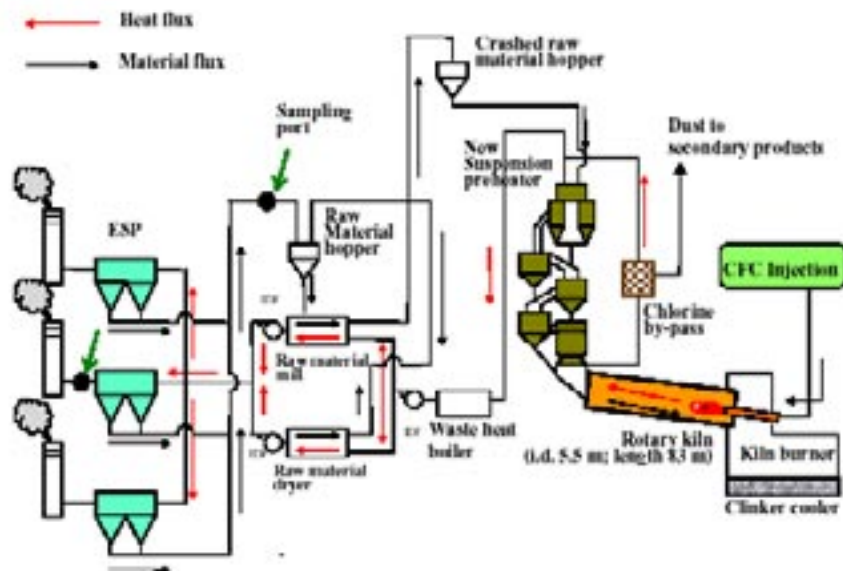


Figure A-4: Schematic Diagram of Cement Kiln Taiheiyo Cement Corporation

Table A-7: Data for Incineration of CFCs in a Cement Kiln

Process Conditions and Destruction Efficiency			Atmospheric Emissions		
Clinker Prod	t/day	5000	PCDD/F	ng-ITEQ/Nm ³	0.04
Kiln Temp	°C	1450	HCl	mg/Nm ³	0.5
Residence Time	s	6 to 7	HF	mg/Nm ³	0.3
CFC-12 Feed	kg/h	3.5	Particulates	mg/Nm ³	30
DRE		99.99%	CO	mg/Nm ³	100
			Gas Volume	Nm ³ /h	200,000

A-2.2 Plasma Technologies

A-2.2.1 Overview

Plasma, which is often described as the fourth state of matter, is a mixture of electrons, ions and neutral particles (atoms and molecules). This high temperature, ionized, conductive gas can be created by the interaction of a gas with an electric or magnetic field. Plasmas are a source of reactive species, and the high temperatures promote rapid chemical reactions.

There are many types of plasma. Cold plasmas, such as those used in etching of semiconductors and in fluorescent lights, operate at very low pressures. The ions and neutral particles are at close to ambient temperatures, while the

electrons are generally at temperatures around 10,000 K. The large temperature difference is maintained because the collision rate between the electrons and other species is low, due to the low pressure.

All the plasma technologies considered in this section use plasmas at or near atmospheric pressure. At such pressures, collision rates between the species are high. Plasmas at atmospheric pressure can be divided into non-equilibrium and thermal plasmas. The individual discharges in non-equilibrium plasmas have very short lifetimes, of the order of 10 ns. In dielectric-barrier discharges, this is due to the presence of a dielectric interposed between the electrodes. There is sufficient time for reactive species to be formed, but not for significant heating of the ions and neutral particles. Such dielectric-barrier discharges can be used for removal from a gas of hazardous species present in low concentrations, and are being investigated for the removal of low concentrations of CH_3Br from air.

In thermal plasmas, the electrons, ions and neutral particles are at close to the same temperature, typically between 5000°C and 30,000°C. The high temperatures lead to very rapid chemical reactions. Such plasmas are often used for the destruction of concentrated streams of hazardous chemicals, including CFCs and halons.

The ionization of a gas to form a plasma is not a combustion process. Electrical energy is converted directly to thermal energy. Applying reaction heat with plasma technology renders it possible to control heat and the chemical environment independently. For example, it is possible to heat a reducing gas to a high temperature without the use of oxygen, or to obtain an oxidizing environment without the introduction of any fuel. Thermal plasmas can be generated by passing a DC or AC electric current through a gas between electrodes, by the application of a radio frequency (RF) magnetic field without electrodes, or by application of microwaves.

The choice of using a direct current (DC) plasma torch is based on its technical capability at a power range up to 2 megawatts (MW) and at reasonably high energy conversion efficiencies. The efficiency of the transformer and rectifier together is generally 95% to 98%, while the transfer of electrical energy to thermal energy is normally in the range 65% to 85%. Since losses are generally associated with the need to cool the torch with water, the higher efficiencies are achieved at higher gas flow rates and at higher power levels. With a DC plasma torch, the plasma gases that can be used depend on the torch design and in particular on the electrode material. For example, oxygen and air cannot be used with a tungsten electrode. Depending on the design, plasma gases such as argon, nitrogen, air, and argon-hydrogen mixtures are used. The plasma volume that is formed is relatively small with high energy density.

In RF applications, inductively coupled plasma torches are used, and energy coupling to the plasma is accomplished through the electromagnetic field of the induction coil. The absence of electrodes allows operation with a large range of gases, including inert, reducing or oxidizing atmospheres. In fact, the ability to use steam alone as the gas offers a cost saving compared to the DC plasma torch, particularly those that require an inert gas such as argon. This kind of discharge produces a relatively large plasma volume. These plasmas are common at power levels up to 100 kilowatts (kW) and scale-up has been demonstrated up to the 1 MW range. The transfer from line AC to high frequency AC is quite efficient at about 95%. About 40% of the input power is lost in the oscillator and tank circuit. Efficiencies of coupling AC current in the coil to the plasma fireball of 65-75% have been reported with tube-type oscillation power supplies and up to 90% with solid-state power supplies. Overall efficiencies are in the range 20-50%.²⁰

AC plasmas can be produced from 480 V 3-phase power at 50 or 60 Hz stepped up through a high voltage transformer. Significantly, there is no need for high frequency AC as in the RF plasma. The equipment required to produce these plasmas is much smaller and less costly than that required for RF plasmas. Electrical efficiencies are higher than for DC plasmas because there is no need for rectification and the electrical to thermal conversion is 85% to 90% efficient. The AC plasma volume produced is also large, comparable to that produced by RF. A particular AC technology was developed in Russia and has been further refined by Scientific Utilization International, of Huntsville, Alabama over the last seven years. There has been very little published about this technology in refereed journals.

Most microwave plasmas operate at low pressures. However, atmospheric pressure microwave discharge are becoming more common. They are typically formed by the coupling of 2.45 GHz microwaves, generated by a magnetron, to a gas flowing through a dielectric tube (the plasma applicator). Power levels of up to about 50 kW are possible. Typically, electron temperatures are around 10,000 °C and the ions, atoms and molecules are at about 2000 °C, but temperatures up to 5 times higher than these have been reported.²¹

During the past decade, thermal plasma technology has evolved as one of the more promising innovative technologies for the thermal destruction of hazardous wastes. The current interest in applying plasmas to the destruction of

²⁰ J. R. Roth, *Industrial Plasma Engineering*. Vol. 1. Principles, IOP Publishing, Bristol, UK, 1995, pp. 406-410.

²¹ J. R. Roth, *loc. cit.*, pp. 508-511.

hazardous wastes is related to the availability of both DC and RF plasma torches in the power range up to 1.0 MW. The most notable use of this technology for ODS destruction is in Australia's halon and CFC destruction program, discussed below.

A-2.2.2 Description of Plasma Technologies

A-2.2.2.1 Argon Plasma Arc

Process Description: PLASCON is an "in flight" plasma process, which means that the waste mixes directly with the argon plasma jet. Argon was selected as the plasma gas since it is inert and does not react with the torch components. Waste is rapidly heated in the reaction chamber (a flight tube) to about 2500°C, where pyrolysis occurs. Steam is added together with the waste at the injection manifold; the oxygen ensures that any carbon formed during pyrolysis is converted to carbon dioxide, and the hydrogen prevents formation of CF₄, which is a strong greenhouse gas. The use of steam rather than oxygen gives more thorough ODS destruction for a given feed rate, since the thermodynamic mixing temperature is higher. Pyrolysis is followed by rapid alkaline quenching from 1200 °C to less than 100 °C. Such rapid quenching limits the formation of dioxins and furans. The cool gas from the quench is further scrubbed with alkaline liquor in a counter-current packed column to neutralize HCl and other acid gases. The off-gas from the column consists mainly of Ar and CO₂.

Key advantages of this process are the very high destruction efficiencies and negligible dioxins/furans emissions demonstrated on a commercially operating system. A destruction efficiency of 99.9998% has been achieved at destruction rates of 120 kg/hr and an electrical power of 150 kW. Also, the very high energy density results in a very compact process.

Operating Experience: PLASCON, an argon plasma arc process, was developed in Australia by SRL Plasma Ltd. in conjunction with the Commonwealth Scientific and Industrial Research Organisation (CSIRO). The process was developed over an eight-year period and commercialised in 1992. Following extensive pilot studies on various CFCs and halon compounds in 1993, the PLASCON system was provided to the Department of Administrative Services Centre for Environmental Management (DASCEM) for the destruction of Australia's surplus halons and CFCs. The plant, located at Tottenham, near Melbourne, was commissioned in 1996, and since then about 1000 t of Halon 1211 and about 200 t of CFCs have been destroyed, including some from New Zealand. Halons are destroyed at a rate of up to 150 kg/h (100 kg/h under typical operating conditions), and CFCs at a rate of up to 100 kg/h (40-60 kg/h under typical operating conditions, depending on composition). On-stream time is currently about 93%. The halide salt solution from the scrubbing system is

stored and discharged on weekends to Melbourne's municipal wastewater treatment system during periods of reduced industrial activity. Waste CFCs and halons must be pre-treated for removal of oil and other contaminants prior to processing in the PLASCON unit. Destruction costs are \$US 3-4/kg. There are now four PLASCON plants in operation in Australia, destroying PCBs and other chlorinated organics, as well as ODS.

The process is illustrated in Figure A-5 and performance data under typical operating conditions is summarized in Table A-8.

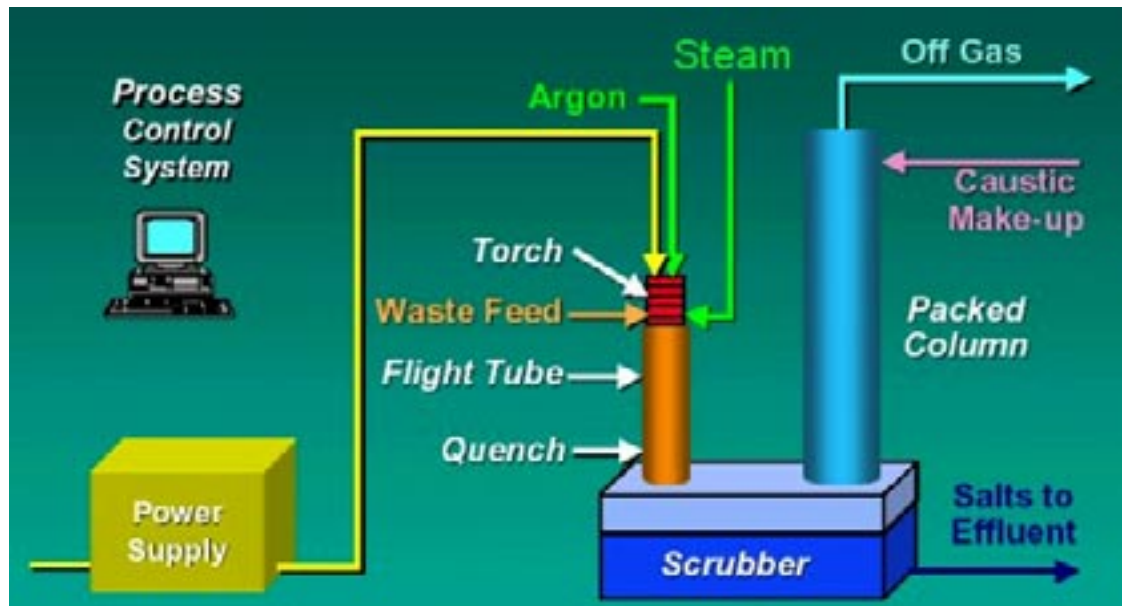


Figure A-5: Process Schematic of PLASCON Process SRL Plasma Ltd.

Table A-8: Performance Data for PLASCON Argon Plasma Arc Process

Operating Conditions and Destruction Efficiency			Atmospheric Emissions		
Halon 1211 Feed Rate	kg/h	118	PCDD/F	ng-ITEQ/Nm ³	0.006
			HCl	mg/Nm ³	1.7
			HF	mg/Nm ³	0.23
DRE	%	99.9998	HBr	mg/Nm ³	<4.0
			Particulates	mg/Nm ³	<10
			CO	mg/Nm ³	96
			Gas Volume	Nm ³ /h	38.5
CFC-12 Feed Rate	kg/h	80	PCDD/F	ng-ITEQ/Nm ³	–
			HCl	mg/Nm ³	1.4
			HF	mg/Nm ³	0.4
DRE	%	99.9999	HBr	mg/Nm ³	–
			Particulates	mg/Nm ³	<10
			CO	mg/Nm ³	79
			Gas Volume	Nm ³ /h	40.3

A-2.2.2.2 Inductively Coupled Radio Frequency Plasma

Process Description: In 1994, several Japanese researchers from government, academia and industry collaborated in experiments that demonstrated the destruction of CFC-12 and Halon 1301 in a pilot-scale Inductively Coupled Radio Frequency Plasma (ICRFP) reactor. Gaseous CFCs and steam are fed through the plasma torch, where they are heated and enter directly into the destruction reactor, in which they are maintained at about 2000°C for about 2 seconds. Subsequently, the gases are cooled and scrubbed with caustic solution to remove acid gases. One advantage claimed for the RF plasma over DC plasma is the elimination of electrodes, which are known in DC plasmas to be subject to corrosion. It is also possible that the RF approach may lead to increased on-stream time over that observed in the PLASCON process described above. The RF plasma also has a slower gas flow rate and a larger plasma flame that results in a higher residence time.

Operating Experience: Based on the pilot plant results, a demonstration plant was constructed at Ichikawa City in the Chiba prefecture by a consortium of industrial concerns under the auspices of the Ministry of International Trade and Industry (MITI). Plasma temperatures of 10,000 °C were achieved in a 185 kW inductively coupled radio frequency torch. The equipment for the demonstration plant was essentially the same as that used in the pilot plant

except for the electric power supply, which was 132 kW (2.4 MHz, 8.8 kV, 15.0 A). A commercial plant has operated since 1995, and over 300 t of CFCs, HCFCs and HFCs had been destroyed by 2001. This process has demonstrated high destruction efficiencies and very low PCDD/PCDF emissions on a commercial scale. No operating costs for a commercial-scale unit are reported. The process is illustrated in Figure A-6 and performance data is summarized in Table A-9 below.

Table A-9: Performance Data for RF Plasma Process

Demonstration Conditions and Destruction Efficiency			Air Emissions		
CFC and Halon Feed Rate	kg/h	> 50	PCDD/F	ng-ITEQ/Nm ³	0.012
			HCl	mg/Nm ³	4.8
Nominal output power	kW	100	HF	mg/Nm ³	2.4
Plasma energy Consumption	kWh/kg CFC-12	1.28	HBr	mg/Nm ³	2.4
			Particulates	mg/Nm ³	4.8
			CO	mg/Nm ³	4.8
DRE	%	>99.99	Gas Volume	Nm ³ /h	21

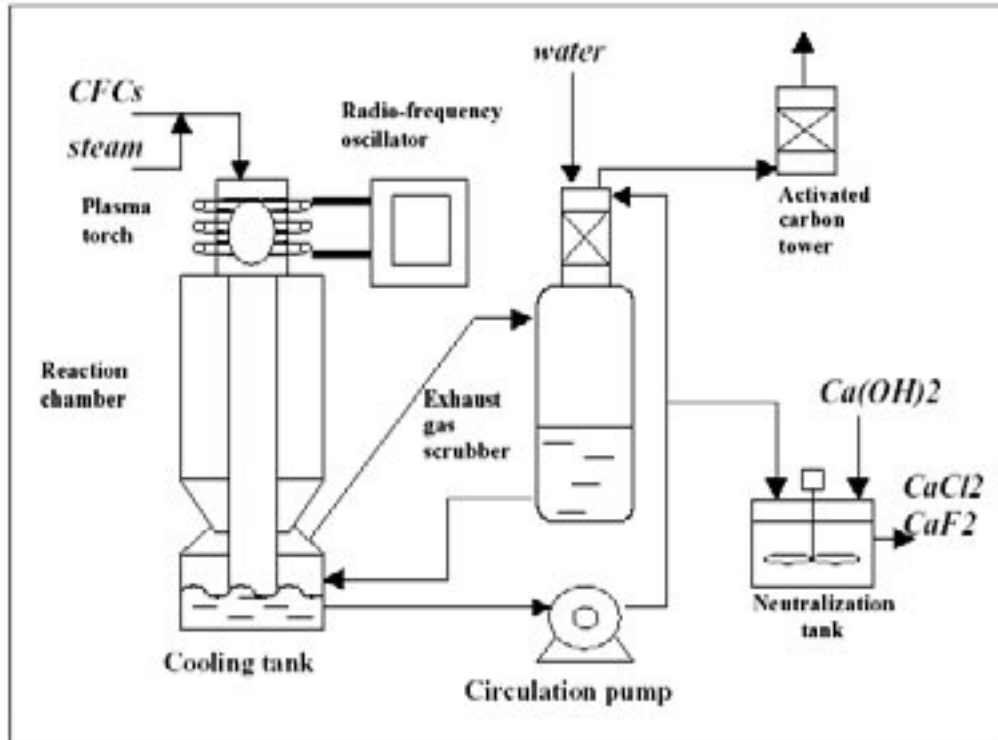


Figure A-6: Process schematic of RF Plasma Process Ichikawa Kankyo Engineering

A-2.2.2.3 AC Plasma

Process Description: Systems incorporating their patented Plasmatron AC plasma are designed by Scientific Utilization International (SUI) for the destruction of hazardous wastes. As discussed above, the AC plasma is produced directly with 60 Hz high voltage power but in other respects is similar to the inductively coupled RF plasma. The system is electrically and mechanically simple and is thus claimed to be very reliable. Also, the Plasmatron process can tolerate a wide variety of working gases, including air, and can tolerate oily gases. While some information is available describing the plasma generator and its associated equipment, no information was provided describing the destruction process, but one could imagine a process very similar to the PLASCON process.

Operating Experience: These plasmas have only recently been developed to the stage where they are being applied to hazardous or toxic waste destruction. It has not yet been commercially applied to the destruction of ODS but CFC was destroyed to non-detectable levels in a 500 kW demonstration unit. A 1 MW AC plasma system was shipped in late February 2000 to the U.S. Customs Service in California for destruction of narcotics. The technology satisfies US

EPA and State of California environmental requirements. SUI is prepared to offer Plasmatron systems designed for the destruction of ODS. No cost information was provided but destruction costs are expected to be comparable to those of the PLASCON process, that is in the \$US 3-5/kg range.

Performance data for the AC plasma process are tabulated below. No specific performance data has been provided but destruction efficiency and emission of pollutants are expected to be comparable to the ICRF plasma process. Gas volume and feed rate have also been taken as equivalent to the ICRF plasma process.

Table A-10: *Estimated Performance Data for AC Plasma Process*

Operating Conditions and Destruction Efficiency			Air Emissions		
ODS Feed	kg/h	50	PCDD/F	ng-ITEQ/Nm ³	0.012
			HCl	mg/Nm ³	4.8
DRE	%	>99.99	HF	mg/Nm ³	2.4
			HBr	mg/Nm ³	2.4
			Particulates	mg/Nm ³	4.8
			CO	mg/Nm ³	4.8
			Gas Volume	Nm ³ /h	21

A-2.2.2.4 CO₂ Plasma Arc

Process Description: A high temperature plasma is generated by sending a powerful electric discharge into an inert atmospheric gas, such as argon. Once the plasma field has been formed, it is sustained with ordinary compressed air or certain atmospheric gases depending on desired process outcomes. The temperature of the plasma is well over 5000 °C at the point of generation into which the liquid or gaseous waste is directly injected. The temperature in the upper reactor is about 3500 °C and decreases through the reaction zone to a precisely controlled temperature of about 1300 °C. The PARCON technology destroys hazardous organic compounds by a three-step process. The waste is first decomposed in the plasma field, leaving only the constituent atoms. The atoms are then chemically reacted with oxygen in a turbulent atmosphere below the reactor, creating new molecules with predicted and known elements. The gas comprised of the newly formed molecules is then quickly cooled to 70 °C, preventing the atoms from reorganizing into dioxins and furans. The exit gas is then cleaned by conventional chemical scrubbing. A special feature of the process is the use of CO₂, which is formed from the oxidation reaction, as the

gas to sustain the plasma. The process can be arranged to compress and recover surplus CO₂ for sale.

Operating Experience: The PARCON process has been jointly developed by Kinectrics (formerly Ontario Hydro Technology) and Plasma Environmental Technologies, both of Toronto, Canada. To date the feature product has been the PARCON 125, a transportable waste treatment facility that destroys hazardous gases and liquids at a rate of up to 12.5 kg/h. The PARCON 125 is claimed to be ideal for demonstrations, pilot projects and small commercial applications. Kinectrics and Plasma Environmental Technologies have developed, tested and patented advanced versions of PARCON that offer greater capacities.

Performance data for a pilot project using the PARCON 125 is tabulated below.

Table A-11: Performance Data for CO₂ Plasma Arc Process

Operating Conditions and Destruction Efficiency			Air Emissions		
ODS Feed	kg/h	8	PCDD/F	ng-ITEQ/Nm ³	0.013
POHC		PCB, TriCB	HCl	mg/Nm ³	17.3
DRE	%	>99.99	HF	mg/Nm ³	4.4
			Particulates	mg/Nm ³	220
			CO	mg/Nm ³	31
			Gas Volume	Nm ³ /h	3.1

A-2.2.2.5 Microwave Plasma

Process Description: This process features a microwave-discharge thermal plasma at atmospheric pressure that consists only of CFCs and steam, resulting in low gas emission and high electrical efficiency because no other gas such as Ar, He, LNG, or LPG is needed in the process. In the process, microwave at 2.45 GHz is used to generate the plasma. The microwaves, by a magnetron, are fed into a coaxial cavity of unique structure. The introduced microwaves resonate in the TM₀₁₀ mode, creating a high electric field in the gap between the probe antenna and the end plate inside the coaxial cavity. The plasma is generated inside a discharge tube, composed of an inner tube and an outer tube, which is situated coaxially within the cavity. The gas flows between the two tubes. The use of two tubes helps to create a stagnation point at the end of the inner tube, which aids the formation of a steady plasma flame. The process can be broadly divided into four parts: gas supply section, plasma generation section, decomposition reaction section, and exhaust gas treatment section.

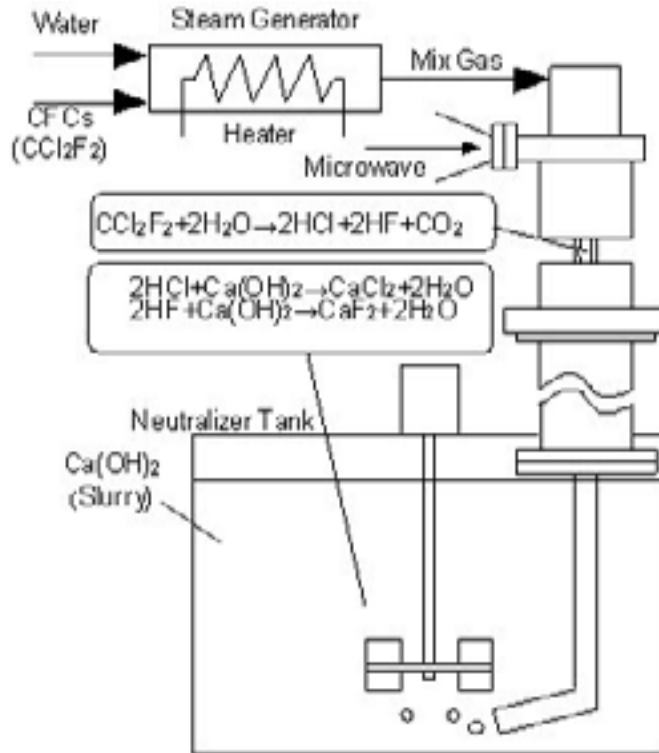


Figure A-7 Schematic of Microwave Plasma for CFC Destruction

Argon is used only at the time of plasma ignition, and is not used as a process gas during operation. The mixture of CFCs and steam supplied to the plasma generation section is ionised and dissociated by the microwave fields. The dissociated substances react with one another in the reaction tube connected to the downstream side to form hydrogen chloride, hydrogen fluoride, and carbon dioxide. In order to neutralize the two acid gases, hydrogen chloride and hydrogen fluoride, the bubbling tower method using slaked lime slurry was selected. Finally, the CO-bearing process gas is combusted in air to convert the CO to CO₂.

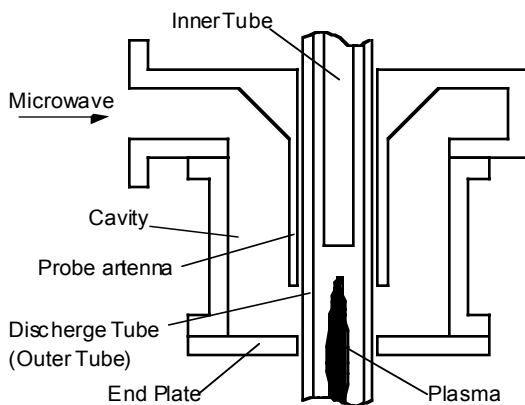


Figure A-8 Structure of Cavity and Decomposition Section

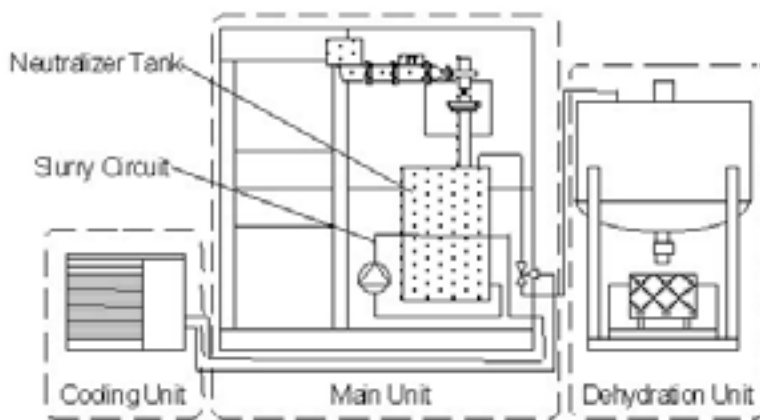


Figure A-9 Unit Total System of Microwave Plasma Reactor

Operating conditions and performance data for a system destroying 2 kg/h of CFC-12 are tabulated below. The flue gas volume was estimated based on the process description and flue gas composition data reported.

Table A-12: Performance Data for Microwave Plasma Process

Operating Conditions and Destruction Efficiency			Atmospheric Emissions		
CFC Feed Concentration	kg/h %	2 23-33	PCDD/F	ng-ITEQ/Nm ³	0.0011
			HCl	mg/Nm ³	0.32
			HF	mg/Nm ³	0.74
MW Freq	GHz	2.45	HBr	mg/Nm ³	
Temperature	K	6000 or over	Particulates	mg/Nm ³	10.6
Residence Time	s	0.5-1.0	CO	mg/Nm ³	4.3
Power Cons.	kW	5.5	Gas Volume	Nm ³ /h	32
DRE	%	>99.99			

Key advantages of the process are the high destruction efficiency due to the very high process temperature and the very low emissions of atmospheric pollutants. The process is reported to be capable of achieving the high operating temperatures in a very short time, thus providing operating flexibility and reduced downtime. There is no need for an inert gas to operate the process, which improved power efficiency, reduces operating cost and minimizes the volume of flue gas. Finally, the process is very compact; a 2 kg/h system occupies a space 1.8 m wide, 1.1 m deep and 1.9 m high. A disadvantage of the process is that halide salts produced by neutralization of the acid gases are discharged to the environment. The process cannot be applied to foams and has not been applied to halons.

Operating Experience: The microwave plasma process was developed in Japan by Mitsubishi Heavy Industries, Ltd. The development of the process commenced in 1997, and it was launched commercially in 2000. The plasma approach was selected to provide a very compact design that could be applied at the many sites where CFCs were recovered. The CFC feed rate of 2 kg/h was determined by market research. Capital costs were reported at about \$US 60,000 for a 2kg/h system, although it is not clear what such a system would include.

A-2.2.2.6 Nitrogen Plasma Arc

Process Description: This process uses a thermal plasma to decompose waste CFC, HCFC and HFC. Liquefied gases can be fed directly from their

pressurized storage into the reactor, while liquids (e.g. CFC-11) are first transferred to a pressure vessel and transferred with compressed air to an evaporator before being fed to the reactor. The thermal plasma is generated by a dc non-transferred plasma torch operating with a water-cooled hafnium cathode and a water-cooled copper cylindrical anode. The plasma gas is nitrogen that has been concentrated from air. The plasma torch power is 240-280V × 60A.

A reactor nozzle of a special alloy is aligned below the anode, and connected to an oxidation tube. Two inlet-pipes are connected to the nozzle: one is located at the upper part for steam, and the other is located at the bottom of the nozzle for air. HCFCs and HFCs are first reacted with steam, being decomposed into carbon monoxide (CO), hydrogen fluoride (HF) and hydrogen chloride (HCl). The CO is subsequently oxidized to carbon dioxide (CO₂) with air in the oxidation tube. The destruction of CFCs is completed without additional air. Immediately after the oxidation tube, the reaction gas mixture is quenched in a scrubber, where the acid gases HCl and HF are absorbed by calcium hydroxide (Ca(OH)₂) suspended in water.

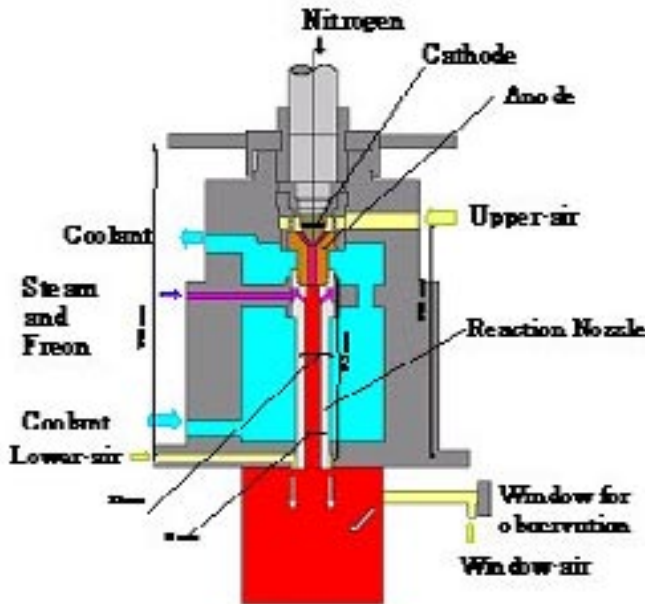


Figure A-10 Plasma Generation Section and Reaction Nozzle of Nitrogen Plasma Arc

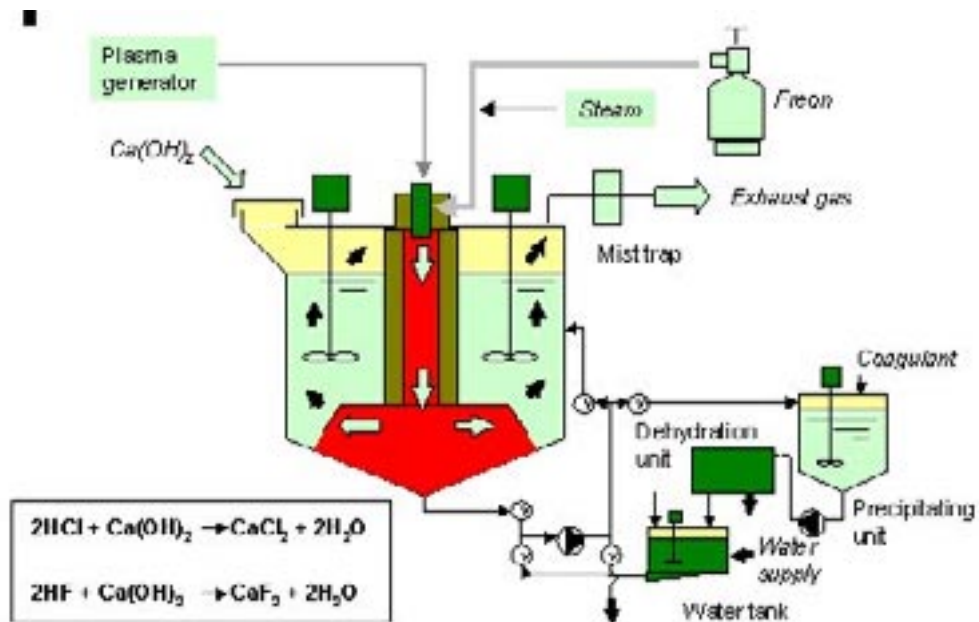


Figure A-11 Schematic Diagram of CFC (Freon) Decomposition System

The process is reported to achieve a DRE of 99.99% while destroying CFCs, HCFCs and HFCs at a feed rate of 10 kg/h. The temperature at the reactor nozzle is estimated in the range from 1100 °C to 2200 °C depending on the amount of steam supplied is appropriate for destruction. The results of destruction tests indicated DREs of better than 99.99% and CO concentrations below 100 ppm in the exhaust for the treatment of CFC-12, HCFC-22, HFC-134a, CFC-11, and R-502 (azeotropic mixture of HCFC-22 and CFC-115).

Typical operating conditions and emissions of pollutants to the atmosphere for a nitrogen plasma arc reactor are tabulated below.

Table A-13: Performance Data for Nitrogen Plasma Arc Process

Operating Conditions and Destruction Efficiency			Atmospheric Emissions		
CFC Feed Rate	kg/h	10	PCDD/F	ng-ITEQ/Nm ³	0.044
			HCl	mg/Nm ³	2.1
			HF	mg/Nm ³	0.6
DRE	%	99.9999	Particulates	mg/Nm ³	9.0
			CO	mg/Nm ³	26
			Gas Volume	Nm ³ /h	2150

A key advantage of this technology is that the equipment is very compact in size. The system requires an area of only 9 m × 4.25 m area for installation, including a precipitation and dehydration unit for the by-products (CaCl₂ and CaCO₃). Therefore, the system is capable of being carried on a truck for on-site waste treatment. A disadvantage of the process is that the destruction capacity is limited because it is difficult to scale up the plasma torch. However, by using a combination of plasma torches, it is expected that 20 to 30 kg/h of waste could be destroyed.

Operating Experience: The nitrogen plasma arc destruction process was developed by Gunma University, ShinMaywa Auto Engineering and Daihen Corporation in 1995. Commercial systems based on this process are offered by ShinMaywa Auto Engineering. Five units are currently being used commercially in Japan. These units have destroyed a total of more than 90 t of CFCs, HCFCs, and HFCs. The company has indicated a cost in the range \$US5-6/kg for destruction of CFCs, HCFCs and HFCs. Similar systems that use argon as the plasma gas (PLASCON™) have been in operation in Australia since 1992; four such units are used commercially in Australia for destruction of hazardous waste including ODS.

A-2.3 Other Non-Incineration Technologies

A-2.3.1 Solvated Electron Decomposition

Process Description: The process is a batch process involving two simple vessels; one a heated reaction vessel and the other a refrigerated ammonia recycle vessel. The ODS compounds are decomposed in the reaction vessel with liquid ammonia and metallic sodium. The process operates at atmospheric pressure. It is expected that this process would produce no dioxins and furans, since it does not involve oxidation and operates at relatively low temperatures. No atmospheric emissions result from the decomposition of the original ODS material. Only non-toxic waste products are formed: sodium chloride, sodium fluoride, biodegradable organic compounds, and water. Methane and ethane are also produced as by-products. Metallic sodium is consumed in the process and is the major component of operating cost. About 95-98% of the ammonia is recycled, and hence does not contribute much to the operating cost. The process was demonstrated on a pilot scale to destroy carbon tetrachloride, several CFCs, HFCs, refrigerant blends and halons at greater than 99.99% efficiency.

Operating Experience: Commodore Advanced Sciences, Inc. of Albuquerque, New Mexico, developed a process for the destruction of ODS in the early 1990s

based on solvated electron solutions formed by dissolving metallic sodium in ammonia. A US patent for the process was issued in 1995. While developed specifically for ODS destruction, the process has never been commercially applied to ODS destruction because of lack of demand. It has been applied successfully to PCB destruction and is currently being applied to the destruction of chemical warfare agents. A major advantage of the process is its simplicity. A disadvantage is the lack of demonstration of ODS destruction on a commercial scale, although there appears to be little doubt that the process could be successfully applied for that purpose. Handling metallic sodium presents safety issues and will require careful attention to operating procedures. Finally, operating cost is heavily dependent on the cost of metallic sodium and is reported to exceed \$US 7/kg of CFC.

Performance data for the solvated electron process are tabulated below. No specific performance data has been provided except for destruction efficiency, but emission of pollutants can be estimated based on the understanding of the process. Emissions of PCDD/F are expected to be very low because of the low operating temperature, and are estimated at 0.001 ng-ITEQ/Nm³. Similarly acid halides are not formed in the gas phase and thus relatively low values are expected. Levels of particulates and CO comparable to plasma processes are expected. The gas volume has been estimated based on destruction of 50 kg/h of CFC-12 and incineration of the methane/ethane product gas with air.

Table A-14: Performance Data for Solvated Electron Process

Operating Conditions and Destruction Efficiency			Air Emissions (estimated)		
CFC Feed	kg/h	50	PCDD/F	ng-ITEQ/Nm ³	0.001
			HCl	mg/Nm ³	0.1
DRE	%	>99.99	HF	mg/Nm ³	0.1
			Particulates	mg/Nm ³	11
			CO	mg/Nm ³	11
			Gas Volume	Nm ³ /h	80

A-2.3.2 Gas Phase Chemical Reduction

Process Description: The GPCR technology involves the gas-phase chemical reduction of organic compounds by hydrogen at temperatures of 850 to 900 °C. In contrast to conventional incineration technologies, the GPCR technology uses hydrogen to break down the bonds that hold the molecule together. The technology consists of three main components: the front end system, which heats contaminated solids, liquids or gases, rendering the contaminants into a gaseous

form; the GPCR reactor, in which the gaseous contaminants are heated electrically to the reaction temperature and then broken down in less than a second by hydrogen into methane and acid; and the gas scrubbing system, which removes acid from the methane-rich product gas. Halogenated hydrocarbons such as CFCs are chemically reduced to methane, hydrogen chloride (HCl) and hydrogen fluoride (HF). The methane is recovered and reused as a fuel for the system components, while the acids are neutralized with caustic or lime. The process does not preclude recovery of the acids for sale to industry but this feature has not yet been applied.

Operating Experience: ELI Eco Logic International Inc. (Eco Logic) of Rockwood, Ontario developed and commercialised the ECO LOGIC Gas-Phase Chemical Reduction process. Eco Logic applied for a patent for this core technology in 1986. The proprietary process is a non-incineration technology suitable for destroying organic wastes in all matrices including soil, sediment, sludge, high-strength oils, watery wastes and bulk solids such as electrical equipment. While Eco Logic has no experience with ODS, the company has destroyed PCB waste and chlorobenzene waste on a commercial scale, and the performance data from that project is summarized in Table A-13. Eco Logic has also destroyed PCB, DDT and hexachlorobenzene waste on a commercial scale to DREs exceeding 99.9999%. The company has considerable laboratory and field data on many other hazardous wastes including chemical warfare agents. Eco Logic supplies fixed systems and provide treatment services with transportable systems.

The major advantages of this process are that it is essentially indiscriminate with regard to the nature of the organic waste that it can destroy, and that it achieves very high destruction efficiencies. The transportability of the process may also prove beneficial. The major drawback is the lack of experience on any scale in destroying ODS, although the process has been proven on equally stable compounds such as PCBs. The GPCR process is reported to destroy hazardous waste at a cost in the range of \$US 3-5/kg.

Performance data for the GPCR process is tabulated in the Table A-13. No data has been reported for HF emissions but they are expected to be very low and comparable to the level of HCl emitted, which has been reported as 0.0025 mg/Nm³. Emissions of both acid gases have been taken as 0.1 mg/Nm³.

Table A-15: Performance Data for GPCR Process

Destruction Efficiency Data			Air Emissions		
POHC	Oil	48-54% PCBs	PCDD/F	ng/Nm ³	0.015
DRE	%	99.99999	HCl	mg/Nm ³	0.1
			HF	mg/Nm ³	0.1
POHC	Oil	25-33% CBs	Particulates	mg/Nm ³	0.5
DRE	%	99.9999	CO	mg/Nm ³	1.1
			Gas Volume	Nm ³ /h	156

A-2.3.3 Gas Phase Catalytic Dehalogenation

Process Description: Hitachi Ltd of Tokyo, Japan has developed a process in which CFCs are destroyed over a proprietary metal oxide catalyst at 400°C at atmospheric pressure. The HCl and HF produced are absorbed in a lime solution. Destruction efficiencies greater than 99.99% were achieved for CFC-12.

Operating Experience: The Hitachi process has been demonstrated to destroy CFCs. A process similar to the Hitachi process has been commercialised for perfluorocarbon (PFC) decomposition as well as PCB destruction. Commercial destruction of PFCs has demonstrated a destruction efficiency exceeding 99%, and destruction of PCBs has demonstrated a destruction efficiency of 99.9998%. It is claimed that no dioxins or furans are produced in the process, although the process operates at a temperature that would generally result in the formation of PCDD/PCDFs. The Hitachi process is also very efficient in destroying CFCs. Hitachi estimates operating costs of about \$US 2-3/kg CFC-12 but when depreciation and other fixed costs are applied the destruction cost is more likely to be in the range \$US5-7/kg or higher. Capital costs were estimated at about \$US 250,000 for a 1 kg/h system and \$US 1 million for a 10 kg/h system.

Performance data are tabulated below for a 1kg/h system. PCDD/F emissions may be expected to be comparable to those from rotary kilns. HCl, HF, particulate and CO emissions are expected to be comparable to plasma processes. Flue gas volume was estimated based on the process description.

Table A-16: Performance Data for Gas Phase Catalytic Dehalogenation Process

Operating Conditions and Destruction Efficiency			Air Emissions		
ODS Feed	kg/h	1	PCDD/F	ng-ITEQ/Nm ³	<0.01
			HCl	mg/Nm ³	1.0
DRE	%	>99.99	HF	mg/Nm ³	<0.5
			Particulates	mg/Nm ³	2
			CO	mg/Nm ³	13
			Gas Volume	Nm ³ /h	15

A-2.3.4 Super-Heated Steam Reactor

Process Description: In the super-heated steam reactor process, decomposition of ODS takes place in the gaseous phase at elevated temperatures. CFCs, steam, and air are first mixed and then preheated to around 500 °C, before being fed into a tubular-type reactor whose wall is electrically heated at 850-1000 °C. The decomposition of CFCs, mainly by hydration, gives HF, HCl, and CO₂. The exhaust gas is led to a scrubber cooler, where the exhaust is quenched by washing with a Ca(OH)₂ solution, and the acids are neutralized. As a result of the quenching of exhaust, the concentrations of PCDD/PCDF are minimized. The process is schematically illustrated below.

The operating conditions and emission of pollutants to atmosphere for a system destroying waste HCFC-22 are tabulated below.

Table A-17: Performance Data For Super-Heated Steam Reactor Process

Operating Conditions and Destruction Efficiency			Atmospheric Emissions		
HCFC Feed Rate	kg/h	10.1	PCDD/F	ng-ITEQ/Nm ³	0.041
			HCl/Cl ₂	mg/Nm ³	<2.95
			HF	mg/Nm ³	<0.81
Temperature	°C	850	HBr	mg/Nm ³	
Residence Time	s	0.8	Particulates	mg/Nm ³	10
			CO	mg/Nm ³	<11.3
DRE	%	>99.99	Gas Volume	Nm ³ /h	33.2

Key advantages of the process are its high destruction efficiency and its low emissions of pollutants, which result from its high operating temperature, quench cooling of process gases and the low flue gas volume. The process is claimed to be easy to maintain because of its simple design and safe to operate because it operates under negative pressure. The compact nature of the process permits its application in mobile destruction facilities and it is applicable to all but foam ODS. A disadvantage is the need to dispose of halide salts resulting from neutralization of acid gases, although technology to recycle the CaF_2 in the residue is being developed.

Operating Experience: The super-heated steam reactor was developed by Ohei Development Industries Co. Ltd, and patents have been registered (Japan Patent No. 3219686 and No. 3219706). The reactor destroys mainly CFCs and HCFCs, but has been used recently to decompose HFCs. Super-heated steam reactors are installed at 11 sites in Japan as captive destruction facilities. The cost for the destruction varies slightly depending on the means of disposal of the neutralized residue, but it is claimed to be in the range of \$US 1.1-1.4/kg-CFC. As with other reported costs, it is not clear what cost elements are included, and destruction costs on an all-in basis are more likely to be in the range of \$US 2-3/kg-CFC. The capital cost for a reactor having a capacity of 10 kg/h is about \$US 300,000.

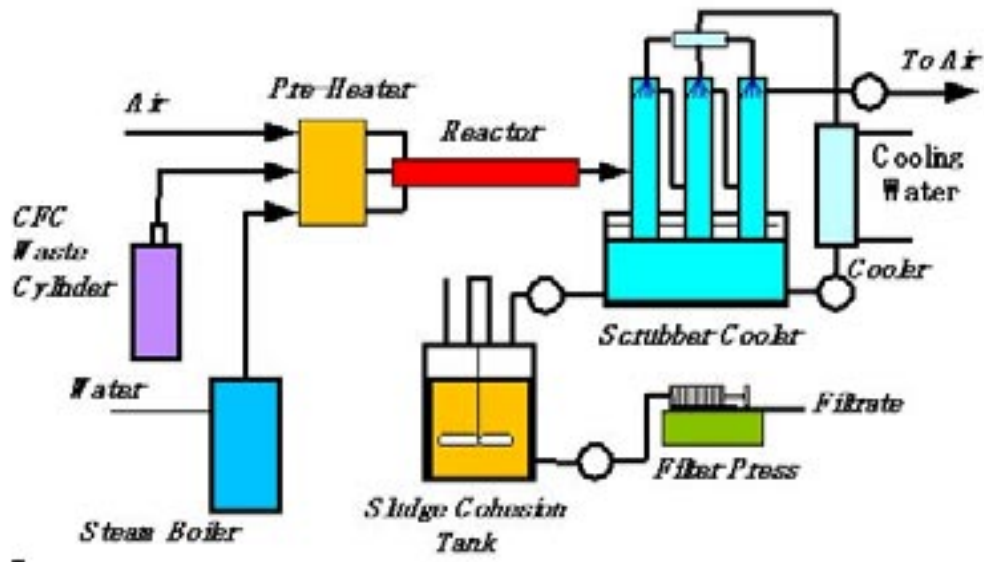


Figure A-12 Schematic drawing of Super-Heated Steam Reactor

A-3.0 Description of Screened-Out Technologies

The following ODS destruction technologies were reviewed and evaluated, and judged not to represent realistic solutions within the time frame required for stakeholders in possession of surplus ODS. In most cases the main reason for this determination was the lack of evidence of technical capability. Where other reasons applied, they were included in the brief descriptions below.

The decision not to include a particular technology in the previous discussion of technically capable technologies does not necessarily mean that the technology could not become a viable contender for the destruction of ODS surplus stocks should circumstances change or unforeseen developments ensue. Many of the technologies described certainly have merit from a theoretical point of view, particularly those that involve chemical transformation and the potential recovery of a valuable chemical product. Should a particular technology be promoted actively, and sufficient resources made available, it is conceivable that it could become technically capable in a relatively short time frame, and could then compete favourably with the technically capable technologies discussed previously. In practice, however, the time required to develop a new technology and make it available on a commercial scale should be kept in mind. The current review presents a picture of the technology situation at this point in time and given the available data; allowance should be made for future reconsideration of the technologies described in this section should circumstances change.

A-3.1 Incineration Technologies

A-3.1.1 Waste Gasification

Waste is gasified at 1600 °C, forming a molten ash bath. The hot gases generated are further treated in a hot coke bed where any unconverted halogenated hydrocarbons are decomposed. The molten ash is dripped into water, where it forms a glass-like agglomerate for destruction. Dioxin and furan formation is unlikely. The system consumes coke, which may introduce additional ash and sulphur. A Dutch facility using this process has an annual capacity of 5000 t of waste.

Originally classified as a recommended technology in the 1992 UNEP document, this process is not considered to be a likely candidate as a solution for surplus ODS. Only limited tests were performed with CFCs and halons were not tested at all and, more importantly, confirmation of destruction efficiency with ODS is lacking.

A-3.1.2 Gas Injection Oxidation/Hydrolysis

Also known as “burn box” technology, this was commercialised as a packaged fume incinerator. It was not specifically tested on ODS, but rather on similar compounds. The 1992 UNEP document reported that two US vendors were beginning a testing project to evaluate destruction efficiency for CFCs. No additional information was found to determine current status. Essentially, this is simply a smaller version of commercially available incinerators, and it was felt unlikely that someone would buy such an incinerator specifically to destroy CFCs.

A-3.1.3 Blast Furnaces

A blast furnace produces molten iron from iron ore and other iron bearing feed materials. A moving bed of iron ore, coke and limestone descends through the blast furnace tower. In the combustion zone, located between the moving bed and the hearth at the bottom of the furnace, temperatures exceeding 1650 °C are reached as part of the coke combines with the oxygen in the air to produce carbon monoxide, the principal iron ore reducing agent. Another part of the coke reacts with the iron oxide in the ore to release free iron that melts, drips to the bottom of the furnace and collects in the hearth. Limestone is the principal fluxing material used to remove impurities from the raw materials. It is calcinated by the heat of the hot blast air, and the resulting CaO reacts with the impurities to form a molten slag, which descends to the hearth and floats above the molten iron. The molten iron and slag are periodically removed from the furnace. The energy for the iron smelting process is supplied by the combustion of the coke supplemented by some other fuel. Thermal economy demands that the combustion air be preheated to 1050 to 1100 °C before it is blown into the furnace. Preheating is achieved by passing the combustion air through a vertical regenerator chamber known as a stove, which is heated by firing some of the gases generated by the blast furnace reducing reactions. Each furnace uses three or four stoves, one of which is heating the blast air while the others are being heated by burning the blast furnace gas. Because this gas is laden with dust, it is passed through a high efficiency dust removal system before being combusted in the stoves. Only about a quarter of the blast furnace gas is required to heat the blast air; the balance is used to produce steam for air compression and other process steam requirements.

As noted above a fuel is generally used to supplement the use of coke. The economy of iron ore production is strongly dependent upon the amount of coke required to produce a tonne of iron product, and auxiliary fuel injection is an effective method of reducing the requirement for coke. Several fuels have been used including natural gas, oil, pulverized coal and waste organic solvents. The

auxiliary fuel is generally injected with lances into the blowpipes, which convey the blast air to the nozzles, or tuyeres, in the lower section of the furnace. In spite of the economic advantage of using organic waste as supplementary fuel there is nevertheless some reluctance to do so because of the risk of product contamination, the cost of which would greatly offset any cost benefit from burning waste. But there have been limited use of waste use as discussed below.

A test was conducted at a major steel mill in the United States to evaluate typical waste disposal performance when burning liquid organic waste.²² The waste contained about 5% toluene, 0.5% o-xylene, 0.3% tetrachloroethene, and numerous other chlorinated and non-chlorinated solvents totalling about 7% organics and less than 0.1% chlorine. The waste fuel was fed into the furnace continuously at about 0.25 m³/h. The blast furnace produced about 3600 t/day of metal. DREs for the various organic constituents generally exceeded 99.99% and dioxins and furans in the flue gas were reported at less than the 0.015 ng/Nm³ detection limit.

Since 1994 mixed plastic packaging waste has been used to reduce the requirement for heavy oil as supplementary fuel in a German steel mill. A recent test has demonstrated that treated shredder residue derived from motor vehicles can also be used.²³ The material consists of shredder granulate and agglomerated shredder fluff derived from the separation of shredder residues by mechanical treatment to reduce the amount of inert matter and increase the organic content. To avoid the blockage of the lances the pretreated shredder residue is blown into the furnace at high pressure. During a test in which the pig iron and slag were monitored by chemical analysis, no variation in the quality of these products was observed. However, the HCl content of the blast furnace waste gas increased slightly to about 2 mg/Nm³ (30 mg/Nm³ permitted) due to the higher PVC input. No DRE data or dioxin/furan data were reported.

Blast furnaces would appear to offer some opportunity for destruction of both concentrated and dilute ODS but no references could be found to document destruction of ODS, or even refractory compounds such as PCBs, at the required DRE. However, the DRE for 1,1-trichloroethane, fed at about 12 kg/h, was reported at 99.98%, so it is likely that ODS could be destroyed at the required DRE. Furthermore, dioxin/furan emissions appear to meet the specified limit. However there is no data for HF and no reference to destruction of any

²² R. C. Adams *et al.*, Evaluation of hazardous waste destruction in a blast furnace, Radian Corporation, Research Triangle Park, NC, USA, 1985.

²³ http://www.plastics-in-elv.org/structure/htm/home_03_13.htm

fluorine containing compounds, possibly due to concerns regarding the attack on furnace and stove refractory material due to HF. Most importantly, there does not appear to be any current destruction of refractory compounds in blast furnaces, which may be due to the risk of product contamination by the waste. This raises a serious question about the technical capability of this destruction process. Correspondingly, this process has been judged as an emerging technology.

A-3.2 Plasma Technologies

A-3.2.1 Plasma Conversion of CFCs into Harmless Polymer Using Ethylene or Ethane as Co-monomer

This technology was developed by Samco International Inc. in Kyoto and uses a radio-frequency plasma to co-polymerise CFCs with ethylene or ethane. The resultant copolymer is highly cross-linked. A lab-scale apparatus treated 10 g/h of CFC-113 with an efficiency of 80% in 1994. Samco has already done all of the basic development work for this CFC stabilization process, and has patents in the US and Japan. Commercialised equipment is expected to have a treatment capacity of 1 kg/h, and maximum recovery efficiency would be achieved with multi-stage units. Samco International Inc. has no immediate plans to develop equipment for higher volumes of CFC. The technology could be licensed, and it could represent an interesting alternative technology if applications for the copolymer were found. Despite the above, the technology was classified as an emerging technology because of the lack of a commercial-scale operation and because the vendor is apparently not developing and promoting the technology for such larger scale operations.

A-3.2.2 Destruction of ODS in Dilute Exhaust Stream Using Energetic Electron Induced Plasma - Adsorbent Filter Hybrid System

This is a low temperature (non-equilibrium) plasma technology developed at McMaster University in Hamilton, Ontario, Canada. Reaction by-products are adsorbed into an activated carbon bed. A destruction efficiency of greater than 90% was achieved with trichloroethylene. The development of the technology is at the bench-scale; neither ODS destruction nor DREs of 99% or better have been demonstrated.

A-3.2.3 High Voltage Gliding Arc Plasma Discharge Reactor for CFC Destruction

This non-equilibrium plasma technology was developed by GREMI (Université d'Orléan, France). CFCs are fed into the plasma along with water vapour.

There is potential formation of synthesis gas (CO and H₂) that could be recovered. HCl and HF could be scrubbed or recovered. Destruction efficiency of CFCs greater than 90% was demonstrated. The development of this technology is limited to bench-scale tests.

A-3.2.4 CFC-113 Destruction in Air Under the Effect of Nanosecond Corona and Microwave Discharge

This non-equilibrium plasma technology is described in a study to develop better understanding of CFC destruction mechanisms in plasma, and is at the R&D developmental stage only.

A-3.3 Chemical Destruction Technologies

A-3.3.1 Chemical Reduction of ODS Using Metallic Sodium on a Solid Substrate

The ODS gas stream is fed to a column filled with a solid substrate coated with sodium metal. The process operates under an inert atmosphere. In bench-scale tests, destruction efficiency for CFCs was shown to be greater than 99%, and greater than 98% for halons. No toxic gaseous or liquid effluents are generated. This is a relatively simple destruction process, however, the preparation of the solid substrate with coated sodium metal may be more complicated. The process was developed by a German company, and E.A. Technology Ltd. has also developed such a process. The technology was expected to be available within 5 years in 1992, however there is no indication that the technology is commercially available at present.

A-3.3.2 Chemical-Thermal Destruction of Halogenated Hydrocarbon with Calcium Silicate or Oxide

Waste is fed to a reactor along with calcium silicate or oxide at 700°C and 98 kPa. The halogen reacts with the solid reagent. A destruction efficiency of greater than 99.99% was obtained with halogenated hydrocarbons, and no dioxins were detected. The process has not been tested for ODS destruction. The solid reagent can be recovered by superheated steam, which produces HCl. The process has been demonstrated at the pilot scale. In 1992, a commercial facility was expected to be in operation within 2-3 years; however there is no indication that the technology is commercially available at present.

A-3.3.3 Mineralisation of CFCs with Sodium Oxalate

This process was developed at the Department of Chemistry of Yale University, New Haven. Gaseous CFCs are fed into a packed bed filled with sodium oxalate powder at 290°C, which generates solid NaF, NaCl and C and gaseous CO₂. Residual sodium oxalate can be pyrolysed to carbonate at 350°C if desired. The inventors claim complete destruction of CFCs and CCl₄. This is a relatively simple process that could likely be scaled up with little difficulty. Economical success would depend on cost and availability of sodium oxalate. There is no indication that this technology is commercially available at this time, or will be in the near future.

A-3.3.4 Aerosol Mineralisation of CFCs by Sodium Vapour Reduction

The process was developed by the National Institute of Standards and Technology, Maryland, USA. Gaseous CFCs are fed along with argon (Ar) and sodium (Na) vapour into a reactor maintained at 1400°C, which generates NaF, NaCl and C. The fine solids are separated from the argon by filtration. Residual sodium vapour can be condensed and the argon recompressed for recovery and recycle. The carbon can be separated by washing out the salt. A destruction efficiency for CF₄ greater than 99% was obtained. The technology development was at the bench scale in 1997; no additional development has been done since, and there are apparently no intentions to continue development.

A-3.3.5 Molten Metal Technology (MMT)

The molten metal bath is at the core of the Catalytic Extraction Process developed by Molten Metal Technology Inc., which converts hazardous waste into products of commercial value. This technology involves the injection of the wastes along with oxygen in a reactor containing metallic solvent at 1650°C, which dissociates the wastes into their atomic constituents. The resultant acid gases are then scrubbed. A ceramic product stream can be recovered by the addition of select co-reactants. The technology was being tested for CFCs destruction at the bench scale in 1992. If successful, a prototype was anticipated. No information was available confirming the further development of this technology. After a rapid rise in the period 1989-1995, the company declined in the period 1996-1997 and filed for bankruptcy protection in 1998.

A-3.3.6 Pressurized Coal Iron Gasification (P-CIG)

P-CIG is a process for the gasification of coal that is injected into a slag-covered iron bath along with oxygen at 1450°C. The technology was tested at the lab scale for halon destruction, and pilot-scale development of this technology was

being planned in 1992. No information was available confirming the further development of this technology.

A-3.3.7 Dormier Incineration Process in Steel Smelter

The volume of wastes is first reduced by pyrolysing the organic material at 700°C in a rotary kiln. Wastes are then fed into a molten-steel bath at 1600°C to reduce waste to their chemical constituents. The resultant acid gases are then scrubbed. The first pilot plant was expected to be in operation in a West German steel plant in 1992. No information was available confirming the further development of this technology.

A-3.3.8 Destruction of CFCs During Chemchar Gasification

In a process developed at the University of Missouri (Columbia, Mo.), CFCs are oxidized in a heated column filed with char and 5% KOH. The chlorine from the CFCs is recovered as KCl and the fluorine recovered as non-leachable carbon fluoride. A destruction efficiency of greater than 99.996% was obtained with CFC 113 and CFC 13 in bench-scale tests in 1998. The formation of carbon fluoride was considered to be problematical.

A-3.3.9 Liquid Phase Chemical Conversion

This technology uses a liquid-phase chemical conversion process operating at between 80-120°C, where ODS is reacted with a blend of potassium hydroxide and polyethylene glycol. Based on laboratory-scale demonstrations, the destruction efficiency is greater than 99.7% for CFCs and halons. It has been tested on ODS in pilot-scale tests and is used commercially for PCB wastes. The process is claimed to require a low capital investment and to be almost emission free. No dioxins/furans are generated in this relatively low-temperature process.

This mobile system technology was developed by Ontario Hydro Technologies (now Kinectrics) to destroy a variety of wastes. Two mobile units are currently in operation for PCB destruction. Although commercial destruction of ODS is not currently available using this process, Ontario Hydro has indicated that modifications to existing equipment, demonstration testing, and regulatory approval could be obtained in a relatively short time (3-4 months claimed), should a demand for this service materialize. Costs are estimated to be less expensive than incineration for ODS, based on extrapolation from experience with PCB waste destruction. However, the technology can only be applied to

gases and liquids with low concentrations of halogenated organics.²⁴ Since it currently has no practical application to either high concentration sources of ODS that are gases or liquids, or to low concentrations sources in solid media (*i.e.*, foams), LPCC has been categorized as an emerging technology for ODS destruction.

A-3.4 Photochemical Technologies

A-3.4.1 UV Photolytic Destruction

Process description: The process involves mixing the ODS material in the gaseous state with air and directing the mixture into a reactor fitted with low pressure mercury ultraviolet (UV) lamps emitting light with wavelengths in the range 185-254 nm. Photons emitted from these lamps are capable of breaking apart the chemical bonds of the ODS molecule, forming free radicals. PTI affixes a dry, porous reagent liner to the inner surface of the reaction chamber that chemically reacts with the free radicals produced by the photochemical destruction of the ODS molecules. The chemical reaction forms stable, inorganic, solid reaction products within the liner material. The only other by-products from the photochemical destruction of ODS are CO₂, water vapour and air. Laboratory bench and pilot-scale tests with a feed rate of 11.4 kg of Halon 1211 per day demonstrated destruction efficiencies of 99.66%. Test results on other ODS demonstrated destruction efficiencies greater than 99.9%. It was believed optimised commercial equipment would achieve greater than 99.99% destruction efficiency. No formation of dioxins and furans is expected due to the low temperature of the entire process. The liner is a PTI proprietary mixture of calcium oxide, calcium hydroxide, magnesium hydroxide and other ingredients. Spent liners are not a hazardous waste as defined by the U.S. Resource Conservation and Reclamation Act (RCRA) and can be disposed of as an ordinary solid waste, or even recycled as a cement ingredient.

Operating History: Process Technologies, Inc. (PTI) of Boise, ID developed and patented a proprietary process for the destruction of chlorinated compounds including ODS based on UV photo-dissociation. The process has never been commercialised for ODS destruction due to lack of demand. Advantages of the PTI process are that it is a non-thermal process achieving high destruction efficiencies without dioxin/furan formation, that the liner prevents the formation of HF and HCl in the exhaust, and that the process is

²⁴ Kinectrics 2002. Luciano Gonzalez, personal communication, February 18, 2002.

simple and modular in design. Costs are reported to be about \$US 7.5/kg of ODS. It was not possible to obtain further information from PTI; the technology may no longer be actively promoted.

A-3.4.2 UV Laser Photolysis for the Destruction or Transformation of Halon 1301 into CF₃I

This technology was developed in Israel by Spectronix Ltd.. It uses an ArF excimer laser to irradiate Halon 1301 in the presence of I₂ to generate CF₃I. The inventors claim that CF₃I is a potential halon replacement. The technology is fully described in the U.S Patent 5,211,821. Technology development is at the bench scale. The development of a working prototype was not continued due to lack of resources and timing considerations.

A-3.4.3 Photochemical Degradation of Organic Wastes with a TiO₂ Catalyst

This technology involves irradiation of the organic waste with an UV lamp over a TiO₂ catalyst. The technology was tested for the destruction of chlorinated organics, but has not been tested for ODS. In 1992, commercialisation was expected to occur in the “near future,” however, no information was available confirming the further development of this technology.

A-3.4.4 UV Laser Controlled Decomposition of CFCs

This technology was presented in a patent held by the U.S. as represented by the Secretary of the Navy. CFCs are decomposed by UV light, and decomposition products are reacted with Group IV chemical element-based mediating species (Si, SiO₂, etc), prior to being scrubbed into water. The acid scrubbing solution requires neutralization. Tetrachloroethylene is a product of the CFC decomposition. This process was used in the electronics industry and was not considered to be applicable to large-scale CFC destruction.

A-3.5 Catalytic Technologies

One of the challenges of the catalytic destruction of ODS is to prevent catalyst deactivation due to the presence of halogens. The development of all catalytic technologies presented below is at the bench scale. The duration of the catalyst would need to be quantified to determine replacement costs.

A-3.5.1 Dry Distillation Destruction System for Waste Foam and Refrigerators

This technology was developed by Toshiba Co., Japan. This is a two-step technology for treating foam containing CFCs. The foams are first dry distilled at 200°C to release the CFCs. The gaseous CFCs are then decomposed in a catalytic reactor using a Cr₂O₃-based catalyst. The oil from the resin may be reclaimed. Waste CFCs can also be treated directly with the catalytic reactor. A continuous bench-scale system was being developed in 1996, but no information confirming further development could be located.

A-3.5.2 Halohydrocarbon Destruction Catalyst

This process use a proprietary catalyst to decompose ODS along with water vapour or hydrocarbon to provide the hydrogen source. In 1992, a full-scale system was scheduled for start-up in Taiwan. No information was available confirming the further development of this technology.

A-3.5.3 Catalytic Oxidation of CFCs with a Pt/ZrO₂-PO₄ Based Catalyst

The catalyst was developed by Sumitomo Metal Mining Company, Japan. CFCs are oxidized in an air-water vapour environment at 500°C. The generated acid gases are required to be scrubbed. In bench-scale tests in 1994, the destruction efficiency for CFCs was greater than 93%. Catalyst activity was maintained for a 300-hr trial. Longer-term activity would require to be validated.

A-3.5.4 CFC Oxidation in a Catalyst-Sorbents Packed Bed

The process was developed by the Department of Chemical Engineering of Lehigh University, USA. Diluted CFCs streams (30-350 ppm) are oxidized with air into a catalyst bed. The Cu/Mn catalyst is supported on Na₂CO₃. The generated acid gases are absorbed by the Na₂CO₃ catalyst support, which help minimizing catalyst deactivation. A destruction efficiency for CFC-11 of greater than 80% was achieved in bench-scale tests. The inventors claim their catalyst is better than noble metal and metal oxide.

A-3.5.5 Transformation of CFCs to HFCs Using Dehalogenation Catalysts in a H₂ Environment

The Department of Chemistry of Simon Fraser University, Canada has done work to develop this technology. Bench-scale tests of various catalysts showed that a Pt/charcoal catalyst was the most efficient. The process generates HFCs that are presumed to degrade in the troposphere. Further development was

realized by the Department of Chemical Process Technology of Delft University of Technology, The Netherlands. Bench-scale tests were performed for the conversion of CFC 12 into HFC 32 over a Pd/charcoal catalyst in an H₂ Environment. No catalyst deactivation was observed after an 800-h trial. The inventors claim to be able to achieve 100% destruction efficiency of CFC using multi-fixed bed reactor, but this has not been demonstrated.

A-3.6 Other Technologies

A-3.6.1 Use of Waste CFC in an Antimony Process

This technology was presented in an abstract, and few details were given. The process exists at a commercial scale in Lanstar, Manchester UK. Waste CFCs and HCFCs come from ICI in Runcorn, UK. About 200 TM/y of CFCs were destroyed in 1994. This was considered to be a specialized technology application that is unlikely to be available for significant quantities of surplus ODS in other countries.

A-3.6.2 CFC Destruction into Biocatalytic System

An INRS-Santé paper concluded that biocatalytic destruction of CFCs was feasible, but only with limited potential capacity. Experimental scale tests with CFCs achieved up to 99.9% destruction efficiency in an anaerobic liquid stream. No test data on gaseous CFC streams were presented.

A-3.6.3 Supercritical Water Oxidation (SCWO)

This technology is available from Weatherly Inc and is used commercially to destroy organic waste. Diluted organic wastes into water are mixed with pure oxygen, heated and pumped to 600°C and 25.4 Mpa in a tubular reactor. Under these extreme conditions, the presence of halogen salts lead to severe corrosion of the equipment. It would not be feasible to treat ODS in a commercial operation due to these corrosion issues.

A-3.6.4 Electrohalogenation of CFC-113 on Pb/Pd Cathodes Combined with H₂ Diffusion Anode

This technology was developed at the University of Barcelona, Spain. It treats CFCs in a 70-80% MeOH solution. The development of the technology is at the early R&D stage.

Appendix B: Rationale for minimum pilot plant capacity

It has been agreed that data derived from pilot plants and demonstration plants are to be considered in assessing ODS destruction technologies. In order to meet the criterion of technical capability, it is essential to set a minimum capacity for pilot plants or demonstration plants, so as to differentiate them from bench scale tests. Bench scale tests are normally done on a very small scale and their primary purpose is generally to demonstrate proof of principle. The larger scale test facilities are designed to demonstrate performance for a proposed process or new application for an existing process (*i.e.*, a demonstration plant) or to obtain detail design data for a commercial plant (*i.e.*, a pilot plant). Given these distinctions, the pilot plant is typically the smallest unit used to prove a technology is commercially workable; we will therefore discuss the minimum sizing of pilot plants for proving ODS destruction technologies.

The 1992 UNEP report recommended a minimum pilot plant capacity of 10 kg/h and a maximum scale-up factor of 200 from pilot capacity to commercial capacity. Typically, for pilot plants to be meaningful they would preferably be 1/10 - 1/20 of the actual size. There are, however, other considerations: the minimum acceptable size depends on the nature of the process and its complexity, for example with regard to fluid mechanics and heat transfer effects. In some cases, scale-up factors of over 1000 can be acceptable (e.g., for two-phase nitration reactions, where reaction rate is the only significant uncertainty factor). This appears to apply to ODS destruction technologies to some extent, as the pilot plant is trying to establish destruction rates and the rates of formation of Products of Incomplete Combustion (PICs). Given these considerations, the 200-fold scale-up factor for pilot plants for ODS destruction technologies appears reasonable.

The minimum pilot plant capacity suggested in the 1992 UNEP report is 10 kg/h. In our opinion this limit is set too high, in that it would exclude technological options that could provide practical solutions to the problem of destroying ODS stocks.

At 200 kg/h, the German facility using the Solvay process is the highest capacity dedicated CFC destruction plant in the world. If this process were being piloted to qualify under the 1992 UNEP rules, the minimum 10 kg/h pilot capacity would be scaled down from the commercial facility by a factor of 20. It would be difficult to imagine a destruction facility 10 times larger than the Solvay facility, therefore, if the minimum capacity is 10 kg/h, the scale-up factor of 200 is unnecessary.

There are persuasive arguments for lowering the minimum pilot plant capacity limit. There may be practical applications for facilities much smaller than the Solvay plant – possibly portable or mobile units – for the destruction of ODS in various situations around the world. Furthermore, it is likely that new, dedicated commercial facilities using new technologies that may be proposed would have lower capacities than the Solvay units. A higher-than-necessary minimum pilot plant capacity would increase the cost of process development and could discourage such new process development. The minimum pilot capacity should be considerably lower than 10 kg/h, in order for the assessment of appropriate destruction technologies to avoid being too restrictive.

It is proposed that the appropriate limit should be 1 kg/h. Using the suggested maximum scale-up factor of 200, a minimum pilot capacity of 1 kg/h would facilitate a commercial plant the size of the Solvay facility, with a capacity of 200 kg/h (1600 MT/y). The lowered limit therefore would retain its usefulness for providing information about larger-scale plants. It would allow a much greater range, however, for the testing of various technologies, including those designed to operate commercially on a smaller scale.

A case could be made for an even lower pilot capacity, if an argument could be made that a small-scale mobile unit could have practical application in some instances. It is difficult to imagine, however, a situation where a workable pilot unit capable of processing a maximum of 1 kg/h of ODS would be prohibitively expensive in comparison with one whose maximum capacity were, say, 0.1 kg/h. Furthermore, the smallest pilot units for ODS destruction we are aware of are capable of processing significantly more than 1 kg/h (e.g., ELI Eco-Logic's mobile unit previously used for destroying small quantities of chemical weapons, which has a capacity of at least 5 kg/h).

Another consideration is that some facilities disposing of CFCs in incineration units used for production purposes, e.g., cement kilns, feed CFCs at rates in the range of 5 kg/h. These clearly should be considered as technically capable alternatives for the destruction of ODS, however they would not qualify as such using a 10 kg/h criterion.

The 1 kg/h limit appears to be a reasonable compromise: it is high enough so that it ensures that test results will be indicative of the performance of larger scale commercial plants, and it is low enough not to exclude technologies that could provide a practical solution to ODS destruction requirements in some situations. The recommendation is therefore that the minimum pilot plant or demonstration plant capacity to establish technologies as “technically capable,” should be 1 kg/h.

APPENDIX C: DECISIONS OF PARTIES (RELEVANT TO ODS DESTRUCTION)

The Parties of the Protocol have taken a number of decisions that need to be mentioned here. Decision I/12F gave a clarification of the definition of a destruction process. Decision IV/11 approved a number of destruction technologies, which were listed in an Annex (Annex VII to the Meeting Report of the 4th Meeting of the Parties). Decision V/26 and VII/35 added “municipal solid waste incinerators” and “radio frequency plasma destruction” to the list of approved technologies. Decision XII/8, taken in 2000, contains the request of the Parties to establish a Task Force on Destruction Technologies and to report on all new developments in the field of destruction technologies for ODS.

The text of the Decisions and the Annex to the Meeting Report of the Fourth Meeting in 1992 are given below.

Decision I/12F: Clarification of terms and definitions: Destruction

The *First Meeting of the Parties* decided in *Dec.I/12F* with regard to destruction:

- (a) to agree to the following clarification of the definition of Article 1, paragraph 5 of the Protocol: “a destruction process is one which, when applied to controlled substances, results in the permanent transformation, or decomposition of all or a significant portion of such substances”;
- (b) to request the Panel for Technical Assessment to address this subject for the Parties to return to it at its second and subsequent meetings with a view to determining whether it would be necessary to have a Standing Technical Committee to review and recommend for approval by the Parties methods for transformation or decomposition and to determine the amount of controlled substances that are transformed or decomposed by each method.
- (c)

Decision II/11: Destruction technologies

The *Second Meeting of the Parties* decided in *Dec.II/11* with regard to destruction technologies to establish an *Ad Hoc* Technical Advisory Committee on Destruction Technologies and to appoint its Chairman, who shall appoint in consultation with the Secretariat up to nine other members on the basis of nomination by Parties. The members shall be experts on destruction technologies and selected with due reference to equitable geographical distribution. The Committee shall analyse destruction technologies and assess their efficiency and environmental acceptability and develop approval criteria and measurements. The Committee shall report regularly to meetings of the Parties.

Decision III/10: Destruction technologies

The *Third Meeting of the Parties* decided in *Dec.III/10* to note the constitution of the *Ad Hoc* Technical Advisory Committee on Destruction Technologies, established by the Second Meeting of the Parties, and to request the Committee to submit a report to the Secretariat for presentation to the Fourth Meeting of the Parties, in 1992 at least four months before the date set for that meeting;

Decision IV/11: Destruction technologies

The *Fourth Meeting of the Parties* decided in *Dec.IV/11*:

1. to note the report of the Ad Hoc Technical Advisory Committee on Destruction Technologies and, in particular, the recommendations contained therein;
2. to approve, for the purposes of paragraph 5 of Article 1 of the Protocol, those destruction technologies that are listed in Annex VI to the report on the work of the Fourth Meeting of the Parties which are operated in accordance with the suggested minimum standards identified in Annex VII to the report of the Fourth Meeting of the Parties unless similar standards currently exist domestically;
3. to call on each Party that operates, or plans to operate, facilities for the destruction of ozone-depleting substances:
 - (a) to ensure that its destruction facilities are operated in accordance with the Code of Good Housekeeping Procedures set out in section 5.5 of the report of the *Ad Hoc* Technical Advisory Committee on Destruction Technologies, unless similar procedures currently exist domestically; and
 - (b) for the purposes of paragraph 5 of Article 1 of the Protocol, to provide each year, in its report under Article 7 of the Protocol, statistical data on the actual quantities of ozone-depleting substances it has destroyed, calculated on the basis of the destruction efficiency of the facility employed;
4. to clarify that the definition of destruction efficiency relates to the input and output of the destruction process itself, not to the destruction facility as a whole;
5. to request the Technology and Economic Assessment Panel, drawing on expertise as necessary:
 - (a) to reassess ozone-depleting substances destruction capacities;
 - (b) to evaluate emerging technology submissions;
 - (c) to prepare recommendations for consideration by the Parties to the Montreal Protocol at their annual Meeting;
 - (d) to examine means to increase the number of such destruction facilities and making available the utilization to developing countries which do not own or are unable to operate such facilities;

6. to list in Annex VI to the report on the work of the Fourth Meeting of the Parties approved destruction technologies; [*see Section Destruction Procedures*]
7. to facilitate access and transfer of approved destruction technologies in accordance with Article 10 of the Protocol, together with provision for financial support under Article 10 of the Protocol for Parties operating under paragraph 1 of Article 5.

Decision V/26: Destruction Technologies

The *Fifth Meeting of the Parties* decided in *Dec. V/26*, further to decision IV/11 on destruction technologies:

- (a) That there shall be added to the list of approved destruction technologies, which was set out in Annex VI to the report of the work of the Fourth Meeting of the Parties [*see Section 2.4 in this Handbook*], the following technology:

Municipal solid waste incinerators (for foams containing ozone-depleting substances);
- (b) To specify that pilot-scale as well as demonstration-scale destruction technologies should be operated in accordance with the suggested minimum standards identified in Annex VII to the report of the Fourth Meeting of the Parties [*see Section 2.4 in this Handbook*] unless similar standards currently exist domestically.

Decision VII/35: Destruction technology

The *Seventh Meeting of the Parties* decided in *Dec. VII/35*:

1. To note that the Technology and Economic Assessment Panel examined the results of testing and verified that the “radio frequency plasma destruction” technology of Japan meets the suggested minimum emission standards that were approved by the Parties at their Fourth Meeting for destruction technologies;
2. To approve, for the purposes of paragraph 5 of Article 1 of the Protocol, the radio frequency plasma destruction technology and to add it to the list of destruction technologies already approved by the Parties.

Annex: DESTRUCTION PROCEDURES

[*Source: Annex VI of the report of the Fourth Meeting of the Parties, as subsequently amended*]

Approved destruction processes

Thermal oxidation category

- Liquid injection incineration [*approved by Decision IV/11*]
- Reactor cracking [*approved by Decision IV/11*]

- Gaseous/fume oxidation [approved by Decision IV/11]
- Rotary kiln incinerators [approved by Decision IV/11]
- Cement kilns [approved by Decision IV/11]
- Municipal solid waste incinerators (for foams containing ozone-depleting substances) [approved by Decision V/26]

Note: These technologies are described in the report of the Ad Hoc Advisory Committee on Destruction Technologies.

Plasma destruction category

- Radio frequency plasma destruction technology [approved by Decision VII/35]

Suggested regulatory standards for destruction facilities

[Source: Annex VII of the report of Fourth Meeting of the Parties]

Pollutant	Stack Concentration ^a	Comments
PCDD/PDCF HCl HF HBr/Br ₂ Particulates	<1.0 ng/m ³ <100 mg/m ³ 5 mg/m ³ <5 mg/m ³ <50 mg/m ³	Frequency, method of sampling, and limit for the ODS that is being destroyed as recommended by national regulatory agencies
CO	<100 mg/m ³	Continuous emission monitoring with 1 hour rolling average
ODS		Atmospheric releases of ODS shall be monitored at all facilities with air emission discharges (where applicable) to ensure compliance with the recommendations of the report of the ad hoc Technical Advisory Committee on Destruction Technologies.

^a Toxic equivalence using international method. Emissions limits are expressed as mass per dry cubic metre of flue gas at 0°C and 101.3 kPa corrected to 11% O₂

APPENDIX D: DEFINITIONS AND ABBREVIATIONS

Definitions

Approved Technology - Any destruction technology approved by the Parties to the Montreal Protocol for destruction of ODS.

Blowing Agent - A gas, a volatile liquid, or a chemical that during the foaming process generates gas. The gas creates bubbles or cells in the plastic structure of a foam.

By-product - A chemical substance produced without specific commercial intent during the manufacturing or processing of another chemical substance or mixture.

Chlorofluorocarbon (CFC) – A family of organic chemicals composed of chlorine, fluorine and carbon atoms, usually characterized by high stability contributing to a high ODP. These fully halogenated substances are commonly used in refrigeration, foam blowing, aerosols, sterilants, solvent cleaning and a variety of other applications. CFCs have the potential to destroy ozone in the stratosphere.

Commercially Available – A technology that is viable, available on an industrial scale, and not significantly limited in capacity by any factor or combination of factors.

Destruction Process - Any combination of unit operations and unit processes, including piping and instrumentation, that is used to destroy ODS. Included in the process are any add-on or supplementary pollution control equipment required to minimize product and environmental releases.

Destruction Facility - The total plant including the process and supplementary operational requirements connected with the receiving of ODS material together with their sampling, storage, handling, preparation, and their destruction via the process(es) itself. The term generally refers to the location on which these activities are sited.

Destruction Technologies - Processes that transform ODS to a non-ODS.

Disposable Container – A container designed to be used only once for transportation or storage of CFCs or HCFCs; designed in accordance with regulations and requirements of the country for which the container is to be used.

Disposal – The method used to eliminate a substance that will no longer be used for the original purpose for which it was made. The method may include transformation, destruction, or disposal as a hazardous waste if mixed with other substances.

Emerging Technology - Any technology demonstrated in the laboratory, bench, or pilot scale, or any commercial technology developed to destroy other compounds, but not yet proven to be effective at destroying ODS.

Environmental Release - Any release into the environment (multi-media; via air, water, and land). These release streams are commonly referred to as air emissions, wastewater discharges and solid residues.

Existing Technology - Any technology commercially demonstrated to destroy ODS.

Feedstock - ODS used in a chemical process. Any ODS not transformed in the chemical process must go to an approved destruction process in order to be exempt from production. (Feedstock can come directly from an ODS production unit, from a unit in which the ODS is a by-product, or from ODS that is first used in other ways and recovered).

Fugitive Losses - Releases to the environment from miscellaneous sources such as flanges, valve packing, seals, safety devices, etc. Quantities are to be estimated through the use of good engineering practices.

Global Warming Potential (GWP)- The relative contribution of certain substances (greenhouse gases), e.g. carbon dioxide, methane, CFCs, HCFCs and halons, to the global warming effect when the substances are released to the atmosphere by combustion of oil, gas and coal (CO₂), direct emission, leakage from refrigerating plants etc. The standard measure of GWP is relative to carbon dioxide (GWP=1.0), which is consistent with the Intergovernmental Panel on Climate Change (IPCC) indexing approach. The GWP can be given with 20, 100, or 500 years integration time horizon. There is not a complete agreement within the scientific community on what is the proper time horizon, but 100 years is most commonly used.

Greenhouse Gas (GHG) - A gas, such as water vapour, carbon dioxide, methane, CFCs and HCFCs, that absorbs and re-emits infrared radiation, warming the earth's surface and contributing to climate change.

Halocarbon– A compound derived from hydrocarbon, where one or more hydrogen atoms are replaced with chlorine (Cl), fluorine (F), and/or bromine (Br). When all hydrogen atoms are replaced the compound is called fully

halogenated. When only part of the hydrogen atoms are replaced, the compound is called partly halogenated. Fully halogenated hydrocarbons are more stable and have higher atmospheric lifetimes than partly halogenated hydrocarbons. Examples of fully halogenated hydrocarbons are halons, listed in Annex A, Group II of the MP and CFC listed in Annex A, Group I and Annex B, Group I. HCFs, HCFCs and HBFCs are partly halogenated hydrocarbons.

Halon – A family of hydrocarbons. Under the MP the term covers fully halogenated hydrocarbons derived from methane and ethane, in which hydrogen atoms are replaced by fluorine and bromine or by fluorine, bromine, and chlorine atoms (Annex A, group II). Halons are commonly used as fire extinguishing or fire suppression agents. They have the highest ODP-values from all ODS regulated under the MP.

Hydrobromofluorocarbon (HBFC)– A family of partly halogenated hydrocarbons, with bromine and fluorine replacing hydrogens. Under the MP these substances are listed in Annex A, Group II. As HBFCs have lower ODP values than halons they were expected to be used as fire fighting chemicals.

Hydrocarbon (HC) - A chemical compound consisting of one or more carbon atoms surrounded by hydrogen atoms only. Examples of hydrocarbons commonly used as replacements of ODP are propane (C₃H₈, HC-290), propylene (C₃H₆, HC-1270) and butane (C₄H₁₀, HC-600). HCs are used as a substitute for CFCs in aerosol propellants and refrigerant blends. The hydrocarbons have an ODP of zero. Hydrocarbons are volatile organic compounds and their use may be restricted or prohibited in some areas. Although they are used as refrigerants, their highly flammable properties normally restrict their use as low concentration components in refrigerant blends.

Hydrochlorofluorocarbon (HCFC) – A family of partly halogenated hydrocarbons, containing one or more fluorine or chlorine atoms. HCFCs have much lower ODP than the CFCs. Examples of HCFC refrigerants are HCFC-22 (CHClF₂) and HCFC-123 (CHCl₂CF₃).

Hydrofluorocarbon (HFC) – A family of partly halogenated hydrocarbons, containing one or more fluorine atom. Since no chlorine or bromine is present, HFCs do not deplete the ozone layer. HFCs are widely used as refrigerants. Examples of HFC refrigerants are HFC-134a (CF₃CH₂F) and HFC-152a (CHF₂CH₃).

Incineration–See Thermal Oxidation, below.

Incinerator - An engineered device using controlled flame combustion to thermally destroy ODS. Examples of incinerators include rotary kilns, liquid injection incinerators, and high temperature furnaces.

Methyl Bromide (MeBr) – A colourless, odourless, highly toxic gas composed of carbon, hydrogen and bromine, used as a broad spectrum fumigant in commodity, structural and soil fumigation. Methyl bromide has an ODP of approximately 0.6.

Montreal Protocol – An international agreement limiting the production and consumption of chemicals that deplete the stratospheric ozone layer, including CFCs, Halons, HCFCs, HBFCs, methyl bromide and others. Signed in 1987, the Protocol commits Parties to take measure to protect the ozone layer by freezing, reducing or ending production and consumption of controlled substances. This agreement is the protocol to the Vienna Convention. It was developed under the auspices of the United Nations Environment Programme (UNEP) to provide a coordinated response to the global problem of ozone depletion. More than 160 countries have signed the Protocol.

Non-incineration Technologies – Those technologies that destroy ODS without using thermal oxidation (e.g., chemical reaction, UV photolysis) or use processes that break down the chemical bonds of the ODS in an oxygen-free atmosphere.

Ozone-depleting Substance (ODS) – Any substance with an ODP greater than 0 that can deplete the stratospheric ozone layer. Most of ODS are controlled under the Montreal Protocol and its amendments and they include CFCs, HCFCs, halons and methyl bromide.

ODS Production - The amount of controlled substances produced, minus the amount destroyed by technologies to be approved by the Parties and minus the amount entirely used as feedstock in the manufacture of other chemicals. The amount recycled and reused is not to be considered as “production”.

ODS Consumption - Production plus imports minus exports of ODS.

Ozone Depletion Potential (ODP) – A relative index indicating the extent to which a chemical product may cause ozone depletion. The reference level of 1 is the potential of CFC-11 and CFC-12 to cause ozone depletion. If a product has an ozone depletion potential of 0.5, a given weight of the product in the atmosphere would, in time, deplete half the ozone that the same weight of CFC-11 would deplete. The ozone depletion potentials are calculated from mathematical models which take into account factors such as

the stability of the product, the rate of diffusion, the quantity of depleting atoms per molecule and the effect of ultraviolet light and other radiation on the molecules. The substances implicated generally contain chlorine and bromine.

Particulates - Includes solids and condensable organics (aerosols). Measurable sub-micron particles are included.

Perfluorocarbon (PFC) – A non-ozone depleting chlorinated solvent commonly used in a variety of metal, electronic and precision cleaning applications. There are potential health problems associated with its use, which makes it important to enact strict health and safety measures to prohibit excessive exposure to the chemical.

Plasma Technologies—Those technologies in which the thermal energy to break the chemical bonds of the ODS is provided by a plasma. The plasmas used in the recommended ODS destruction technologies are thermal plasmas, and are at temperatures between 5000 and 30000 Kelvin. The plasma is a mixture of electrons, ions and neutral particles, created by the ionization and heating of a gas through its interaction with a DC or AC electric field, or a radio-frequency or microwave-frequency electromagnetic field. The energy source in plasma technologies is thus electricity rather than combustion as in Thermal Oxidation technologies.

Product Release - Any ODS in the products leaving a destruction facility (e.g. carbon tetrachloride in hydrochloric acid produced by a destruction facility).

QA/QC - Program of quality assurance and quality control to ensure compliance with national regulations on environmental and product releases.

Reclamation – Processing and upgrading of a recovered controlled substance through such mechanisms as filtering, drying, distillation and chemical treatment in order to restore the substance to a specified standard of performance. Chemical analysis is required to determine that appropriate product specifications are met. It often involves processing off-site at a central facility.

Recommended Technology - Any destruction technology recommended by the TFDF for approval by the Parties to the Montreal Protocol for the purpose of destroying ODS.

Recovery – The collection and storage of controlled substances from machinery, equipment, containment vessels, etc., during servicing or prior to disposal without necessarily testing or processing it in any way.

Recycling – Reuse of a recovered controlled substance following a basic cleaning process such as filtering and drying. For refrigerants, recycling normally involves recharge back into equipment and it often occurs “on-site”.

Refillable Container – A container, used to ship and store refrigerant. Refillable containers are designed to be used over and over again, but should be re-tested at least every five years. The container must meet the requirements of regulations and specifications outlined by authorities in the country for which the container is to be used.

Thermal Oxidation–Thermal oxidation (incineration) is a process that ideally converts organic compounds, whether hydrocarbon or oxygenated, to CO₂ and H₂O. Incineration is widely used for the destruction of a wide variety of compounds. There are two main types of incinerators: thermal and catalytic. In thermal incineration, the organic compounds are heated to very high temperatures to oxidize the organic compounds in the gas phase. In catalytic incineration, a catalyst promotes the oxidation reaction on its surface (i.e., solid-gas interface) at lower temperatures by providing alternative reaction pathways that have faster rates than the corresponding gas-phase reactions. A thermal incinerator burns the compounds at very high temperatures, usually in the 750° to 1,000°C range; catalytic incinerators typically operate between 350° and 500°C.

Abbreviations

A/C	Air conditioning
CFC	Chlorofluorocarbon
CFC-11	Trichlorofluoromethane
CFC-12	Dichlorodifluoromethane
CFC-115	Chloropentafluoroethane
GHG	Greenhouse gas
GWP	Global Warming Potential
Halon 1211	Bromochlorodifluoromethane
Halon 1301	Bromotrifluoromethane
HBFC	Hydrobromofluorocarbon
HCFC	Hydrochlorofluorocarbon
HCFC-22	Chlorodifluoromethane
HFC	Hydrofluorocarbon
HRAI	Heating, Refrigerating and Air Conditioning Institute
ICFB	Internally Circulated Fluidized Bed
ICRF	Inductively Coupled Radio Frequency
MeBr	Methyl bromide (bromomethane)
MSWI	Municipal solid waste incinerator
NO_x	Nitrogen oxides
ODP	Ozone Depletion Potential
ODS	Ozone-depleting Substance
PCDD	Polychlorinated dibenzo- <i>paradioxins</i>
PCDF	Polychlorinated dibenzofurans
PIC	Products of incomplete combustion
PFC	Perfluorocarbon
R/R	Recovery and Recycling
R/R/R	Recovery, Recycling, and Reclamation
R-134a	1,1,1,2-tetrafluoroethane
R-502	An azeotropic refrigerant blend of HCFC-22 and CFC-115
ITEQ	International Toxic Equivalence Factor
TDGR	Transportation of Dangerous Goods Regulations
TEAP	The Technology and Economic Assessment Panel of the UNEP
TFDT	The Task Force on Destruction Technologies of the UNEP Technology and Economic Assessment Panel
UNEP	United Nations Environment Programme

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Appendix F: Sampling and Analytical Methods

Introduction

In the course of discussion during the first meeting of the Task Force on Destruction Technologies (TFDT), it was noted that some jurisdictions may benefit from provision of an overview of the available test methods for the contaminants of interest. This Appendix is intended to provide a summary of the more readily available information on sampling and analysis for the compounds used as screening criteria in the work of this Task Force with information on where to obtain copies of them. It is not intended to serve as an exhaustive listing of applicable methods, nor to provide the detailed methods here.

The pollutants used for screening purpose include: total particulate matter; hydrogen chloride and chlorine, hydrogen fluoride, hydrogen bromide and bromine (treated together in the following text); carbon monoxide; polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [commonly referred to as dioxins and furans]; and the ozone depleting substances (ODS) of concern, used to determine the Destruction and Removal Efficiency (DRE) achieved by a technology. The ODS of concern include the chlorofluorocarbons or CFCs (CFC-11, 12, 13, 111, 112, 113, 114, 115, 211, 212, 213, 214, 215, 216, 217), Halon 1211, Halon 1301, Halon 2402, carbon tetrachloride, 1,1,1-trichloroethane, methyl bromide, and the hydrobromofluorocarbons (HBFCs) and hydrochlorofluorocarbons (HCFCs).

Note that in determining DREs, it is necessary to test both the input to a destruction technology and the exhaust gas stream. Sampling methods for the feed material to a destruction technology must be selected taking into account the specific physical and chemical characteristics of the waste. This appendix focuses on methods applicable to the exhaust gas stream, although analytical methods applicable for this stream may also be useful for other media (e.g., feed streams).

One of the more comprehensive treatments on the issue of measuring the performance of destruction technologies is the United States Environmental Protection Agency's (US EPA's) document SW-846, entitled "Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods." An on-line version of this document can be found at URL <http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm>. The document provides advice on selecting methods as well as detailing methods recommended (but not required) to determine compliance of incinerators subject to that country's Resource Conservation and Recovery Act. Determination of DRE is one necessary component of that legislation.

In the following pages, applicable test methods are noted for each of the pollutants listed as screening criteria by the TFDT. While many of these are US EPA methods, other reference methods are noted where information was available to TFDT members.

Applicable Test Methods for Pollutants Used as Screening Criteria

Particulate Matter

Many jurisdictions have source testing methods for particulate matter; for sources emitting particulate matter in the range of the screening criterion (i.e., 50 mg/Nm³) methods similar to US EPA Method 5 are generally appropriate. This method incorporates several other methods (Methods 1 through 4), several of which have alternate methods to permit use of different measurement technology or accounting for unique source characteristics. The full list of these methods is available on the US EPA web site at URL <http://www.epa.gov/ttn/emc/promgate.html>, where they are also available for download.

Note that US EPA has a specific method for use after baghouse particulate collectors (Method 5D) and for sources with very low emission levels (Method 5I, applicable where the expected total particulate catch from a test is predicted to be less than 50 mg). These methods are available at the URL noted above also.

A similar method is published in Canada and is available as Environment Canada (EC) report EPS 1/RM/8. This document can be requested through EC's inquiry centre, accessible on the World Wide Web at URL <http://www.ec.gc.ca/prod/inqry-e.html>.

Hydrogen Chloride, Chlorine, Hydrogen Fluoride, Hydrogen Bromide and Bromine

The US EPA Methods 26 and 26A were developed to perform determinations of all of these compounds in one sampling train. The sampling train for Method 26A is based on that used for Method 5 (total particulate, noted above) and can be used with specific precautions noted in the method to determine particulate matter as well as the halogens of interest. These methods can be obtained at URL <http://www.epa.gov/ttn/emc/promgate.html>, where they are available for download.

Carbon Monoxide

Methods 10 and 10B from US EPA have been developed to perform source sampling determinations for carbon monoxide emissions using differing analytical techniques. A third method, Method 10A, has been developed for the application of certifying continuous emission monitors at stationary sources. All three methods can be obtained at URL <http://www.epa.gov/ttn/emc/promgate.html>, where they are available for download.

Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans

Several jurisdictions have developed sampling and analytical methods to determine these compounds at sufficient resolution to permit assessment of emissions using the North American Treaty Organization's Committee on Challenges to Modern Society (NATO/CCMS) toxicity equivalence scheme. These methods are generally considered to be amenable to determination of the coplanar polychlorinated biphenyls (PCBs) included in the World Health Organization's toxicity equivalence system, but the methods may not in all cases have been formally validated for the PCBs as yet.

US EPA has Method 23 promulgated under the US Code of Federal Regulations, and available for download at URL <http://www.epa.gov/ttn/emc/promgate.html>. In addition, in SW-846 an updated method designated Method 0023A is described as a revision to Method 23. This revised method makes specific note of the possibility of further modifications to address emissions of PCBs and polynuclear aromatic hydrocarbons (PAHs), but cautions that detailed modification of the methodology is required. It can be viewed or downloaded from URL <http://www.epa.gov/epaoswer/hazwaste/test/under.htm>. Also available from this source is method 8290 which is employed for the determination of PCDDs and PCDFs by high resolution gas chromatography/high resolution mass spectrometry; this technique is required in order to yield the congeners used in calculating toxicity equivalents using the NATO/CCMS system.

Environment Canada employs several methods used together to determine emissions of PCDDs, PCDFs and PCBs. Report EPS 1/RM/2, entitled "Reference Method for Source Testing: Measurement of Releases of Selected Semi-Volatile Organic Compounds from Stationary Sources," details a sampling methodology for semivolatile organic compounds (SVOCs) including PCDDs, PCDFs and PCBs. Report EPS 1/RM/3, entitled "A Method for the Analysis of Polychlorinated Dibenzo-para-Dioxins (PCDDs), Polychlorinated

Dibenzofurans (PCDFs), and Polychlorinated Biphenyls (PCBs) in Samples from the Incineration of PCB Waste,” provides analytical methods for determining the subject pollutants, however this method may require modification for determination of the congeners required to determine toxicity equivalence.

Of particular use to jurisdictions where determination of these compounds has not been previously conducted may be report EPS 1/RM/23, entitled “Internal Quality Assurance Requirements for the Analysis of Dioxins in Environmental Samples,” which details the requirements for ensuring reliable results when attempting analysis of these pollutants. Both the low levels typically sought and the possibility of interferences from other contaminants raise issues which must be addressed in laboratory work through rigorous quality assurance planning and quality control checks.

The European Union has also established European Standard EN 1948 entitled “Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs.” This standard describes seven alternative sampling methodologies (three basic configurations as well as variations on each), sample extraction and clean-up methodologies, and identification and quantification procedures. It is published in three parts by the European Committee for Standardization, Rue de Stassart, 36, B-1050 Brussels, Belgium.

Determination of ODS Compounds in Stack Gases

There are two dominant sampling techniques for ozone depleting substances in exhaust gases; collection of a representative stack gas sample in Tedlar bag (US EPA Method 18, SW-846 method 0040) and collection of a representative sample to adsorb contaminants onto suitable media for subsequent desorption and analysis (SW-846 method 0030, also termed “Volatile Organic Sampling Train” or VOST). The Tedlar bag based methods are subject to loss of sample when gases with very small molecules are of interest, and can have higher detection limits than methods which concentrate the analyte during sampling. However, the VOST technique is limited in application to analytes which have boiling points in the range of $-15 - 121^{\circ}\text{C}$.

A number of analytical techniques can be employed to determine the quantity of ODS compounds of interest present; of these, the gas chromatography/mass spectrometry (GC/MS) technique (SW-846 method 8260) is most likely to be generally applicable for exhaust stack samples from destruction facilities as it is inherently capable of identifying analytes. However, gas chromatography used

with a photoionization or electrolytic conductivity detector may also produce acceptable results (SW-846 method 8021).

Table F-1 following provides a list of compounds for which some determination has been made by US EPA in the documentation for these methods. Note that it does not cover the majority of ODS compounds of interest, and that there are compounds for which one or the other sampling technique appears to have limitations. However, from this listing it appears that in many cases one of the two sampling techniques may be appropriate. It is likely that researchers outside of US EPA have used these basic techniques with one of the listed analytical methods or an alternative method, and the data has not yet been made available to TFDT members. Additional information gathering appears to be warranted concerning experience measuring the remaining 15 CFCs and halons, as well as the HBFCs and HCFCs. In the interim, the most promising sampling and analytical method combination from among the US EPA methods available appears to be SW-846 method 0030, desorption according to method 5041, and analysis using method 8260 (i.e., VOST analyzed by GC/MS).

Table F-1: Validated Sampling and Analytical Methods for Ozone Depleting Substances

Compound	Chemical Formula and IUPAC Name	Sampling Method	Analytical Method(s)
CFC-11	CCl ₃ F trichlorofluoromethane	SW-846 0030 ¹ , 0040	8021, 8260 ³
CFC-12	CCl ₂ F ₂ dichlorodifluoromethane	*	8021, 8260
CFC-113	C ₂ Cl ₃ F ₃ trichlorotrifluoroethane	SW-846 0040 (candidate) ²	8260 ³
Carbon tetrachloride	CCl ₄ tetrachloromethane	SW-846 0030, 0040	8021, 8260 ³
1,1,1-trichloroethane	C ₂ H ₃ Cl ₃ 1,1,1-trichloroethane	SW-846 0030, 0040	8021, 8260 ³
Methyl bromide	CH ₃ Br bromomethane	SW-846 0030	8021, 8260

- ¹ SW-846 method 0030 also requires use of method 5041 to desorb collected analytes for quantitative determination.
- ² US EPA has identified compound as candidate analyte from the literature, but validation has not been performed.
- ³ SW-846 0040 cites method 8260 as preferred for analysis of stack gas because of its ability to provide positive identification of compounds in complex mixtures.
- * CFC-12 failed validation for SW-846 method 0040 using US EPA's Method 301 validation protocol; however, this analyte is not specifically noted as one for method 0030 has been shown applicable.