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Destruction Technologies for Ozone Depleting Substances

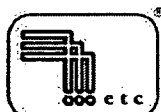
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Authors: Martin Murín, MSc.
Miroslav Kríž, PhD.
Paulína Pidaná, BSc.

Ivanka pri Dunaji
5th of May 2005

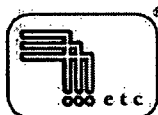


® **EKOTOXIKOLOGICKÉ CENTRUM BRATISLAVA, s.r.o.**
Nádražná 36, 900 28 Ivanka pri Dunaji, Slovenská republika
Tel./Fax: +421 2 459 437 12 / 459 452 23
e-mail: ekotox@stonline.sk, www.ekotox.sk



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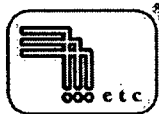
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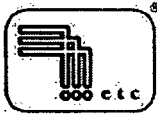
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Appendix No. 1	Advantages and Disadvantages of Relevant Destruction Technologies
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ABBREVIATIONS

AC	Alternating Current
AHMS	Australian Halon Management Strategy
BAT	Best Applicable Technologies
BCD	Base Catalysed Dechlorination
BEP	Best Environmental Practices
CFC	Chlorofluorocarbons
CIS	Container Incineration System
DE	Destruction Efficiency
DRE	Destruction and Removal Efficiency
EC	European Commission
EFDT	Environmental Friendly Disposal Technologies
EGM	Expert Group Meeting
GB	Great Britain
GWP	Global Warming Potential
HCFC	Hydrogenchlorofluorocarbons
ICRF	Inductively Coupled Radio Frequency
JP	Japan
MSW	Municipal Solid Waste
MSWI	Municipal Waste Incineration
NHB	National Halon Bank
ODP	Ozone Depletion Potential
ODS	Ozone Depleting Substances
PCB	Polychlorinated Biphenyls
PCDD	Polychlorinated Dibenzo-Dioxin
PCDF	Polychlorinated Dibenzo-Furan
PIC	Products of Incomplete Combustion
RF	Radio Frequency
TAC	Technical Assessment Committee
TEAP	Technology and Economic Assessment Panel
TFDP	Task Force on Destruction Technologies
UNEP	United Nations Environmental Programme
UNIDO	United Nations Industry Development Organization
US	United States
UV	Ultraviolet



1 INTRODUCTION

This study is concentrated on Ozone Depleting Substances (ODS) which are covered by the Montreal Protocol on Substances that Deplete the Ozone Layer. It is focused on evaluation of state of the art of available technologies for destruction of ODS with special interest in mobile or semi-mobile technologies.

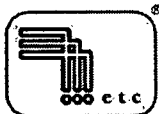
During a preparation of this study varied information were used for purpose to prepare report. A literature and internet survey in various databases was used as fundamental sources to obtain relevant data. Subsequent source of information was obtained from questioners (see Appendix No. 5) sent to the vendors of technologies which could potentially destruct ODS.

The volume of un-recycled Chlorofluorocarbons (CFCs) recovered under the scheme of refrigerant management plans in Article 5 countries of Montreal Protocol is becoming an increasing problem to many Article 5 Countries. While most of the countries are handling this problem by storing the chemicals in special cylinders, there needs to be a final solution to the problem of un-recycled CFCs. The result of this study will help to define an appropriate approach concerning identification of suitable, environmentally friendly technologies for destruction of ODS.

Destruction of hazardous chemicals by environmentally friendly technologies under economically feasible conditions is of concern not only for ODS chemicals. Extensive development is seen in the area of persistent organic pollutants and high interest is also in the area of drugs and drug precursor chemicals.

A group of chemical substances being discussed in this study concludes:

- **Chlorofluorocarbons (CFCs or freons)**
- **Hydrochlorofluorocarbons (HCFCs)**
- **Halons**
- **Other fully halogenated CFCs**
- **Carbon tetrachloride**
- **Methyl chloroform**
- **Methyl bromide**
- **Fluoroform**



Short characteristics:

Chlorofluorocarbons (CFCs or freons) are nontoxic, nonflammable and nonreactive with other chemical compounds. These chemicals contain atoms of carbon, chlorine and fluorine. They can be found in aerosol sprays, blowing agents for foams and packing materials as solvents and as refrigerants.

The chemical stability of CFCs allows them to reach the stratosphere, where intense ultraviolet radiation breaks them and release chlorine, which in turn reacts with oxygen, nitrogen and hydrogen oxides in the stratosphere. The result is a reduction in stratospheric ozone, which protects the earth from the ultraviolet rays. Some CFCs are more harmful to stratospheric ozone than others.

Freons from methane – code from 2 numbers

Freons from ethane – code from 3 numbers

Hydrochlorofluorocarbons (HCFCs) are organic compounds that are similar to CFCs but less destructive to ozone. HCFCs consist of carbon, hydrogen, chlorine and fluorine. They are used as replacements for CFCs. HCFCs are used in refrigerators, aerosols and foams and also in air conditioning.

Halons are similar to freons, they may contain also bromine. They have code consisting of 4 numbers. Halons are used in fire extinguishers.

Other fully halogenated CFC:

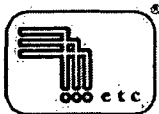
CF_3Cl , C_2FCl_5 , $\text{C}_2\text{F}_2\text{Cl}_4$, C_3FCl_7 , $\text{C}_3\text{F}_2\text{Cl}_6$, $\text{C}_3\text{F}_3\text{Cl}_5$, $\text{C}_3\text{F}_4\text{Cl}_4$, $\text{C}_3\text{F}_5\text{Cl}_3$,
 $\text{C}_3\text{F}_6\text{Cl}_2$, $\text{C}_3\text{F}_7\text{Cl}$

Carbon tetrachloride is used as a raw material and as a solvent.

Methyl chloroform is used for metal degreasing. It is also used in textile industry – textile processing and dry cleaning.

Methyl bromide is highly effective fumigant which is used to control insects, weeds, in forest and ornamental nurseries, and in wood products.

Fluoroform is generated as a by-product of the production of HCFC-22 which is a common refrigerant.



Aim of the report

The purpose of this report is to:

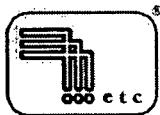
- Identify environmental friendly disposal technologies (EFDTs) for chemicals under consideration
- Identify experts to be invited and topics to be discussed at the meetings.

Expected outcomes of the report

The following results are expected from this report;

- An Assessment Study containing a list of EFDTs with associated analysis of advantages / disadvantages of each method to be presented at expert group meeting (EGM)
- List of experts and topics. Initiate contacts to experts.

The Parties to the Montreal Protocol have discussed the issue of destruction technologies and elaborated a list of recommended technologies, these technologies are expensive and not an economically viable tool for Article 5 Countries. As part of its commitment to assist Article 5 Countries to achieve their commitments towards the goals of the Montreal Protocol and its amendments, United Nations Industrial Development Organization (UNIDO) Multilateral Environmental Agreements Branch, is planning to organize an EGM in cooperation with the United Nations Office on Drug and Crime to tackle the issue of environmentally safe and economically feasible disposal/destruction technologies on industrial chemicals and drugs precursor chemicals.



2 CHEMISTRY

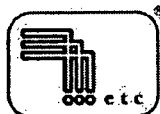
Certain properties (for example stability, non-toxicity, chemical inertness and biological, thermal, ultraviolet (UV) stability and no degradability) have made ODS ideal for use in many applications.

A bond of those CFC substances in which just C-F bond occurs in molecule is contentious and complicated in respect of decomposition of such substances. A situation is better in substances where except from C-F bond we have also a C-Cl, C-Br or C-H bond.

CHFC bonds are fissile by chemical reactions. For example: by reaction with concentrated bases or metals. But question of economy of these reactions still remains. Some specific reactions can be used for disposal of relatively vaporous dihalofluorine chemical substances also through the reactions of carbene addition. A possibility of reaction of dihalofluorocarbene on polymeric unsaturated skeleton with comparatively simple technological accomplishment exists. A reaction of difluorodibromomethane by carbene way can serve as an example. It can be used as a final reaction or difluorocyclopropane circle can be subsequently modified by opening of this circle. In these cases freons can be degraded relatively easily.

Ozone depleting substances are chemicals which, when released into the atmosphere, accumulate in the ozone layer and react with the ozone molecules to destroy them. Ozone depleting substances vary in their capacity to destroy ozone molecules, so scientists have developed a method for characterizing the relative depletion caused by different ODS. Ozone Depleting Potential (ODP) is the ratio of calculated ozone column change for each mass unit of a gas emitted into the atmosphere relative to the calculated depletion for the reference gas. This allows different chemicals to be compared using a common unit.

Another one indicator of level of ozone depletion is global warming potential (GWP). GWP (<http://www.climnet.org/resources/GWP.htm>) is index used to translate the level of emissions of various gases into a common measure in order to compare the relative radiative forcing of different gases without directly calculating the changes in atmospheric concentrations. GWPs are calculated as the ratio of the radiative forcing that would result from the emissions of one kilogram of a greenhouse gas to that from emission of one kilogram of carbon dioxide over a period of time (usually 100 years). Greenhouse gases are expressed in terms of Carbon Dioxide Equivalent.



Relevant quantities important for evaluation of harmful properties of ODS are lifetime and decomposition temperature.

Table 1: chosen representatives of ODS and their properties

	ODP	GWP	Lifetime	Decomposition Temperature
Chlorofluorocarbons				
CFC-11	1.0 ¹	5,000 ¹	50 ¹	
CFC-12	0.82 ¹	7,900 ¹	102 ¹	
CFC-113	0.9 ¹	5,000 ¹	85 ¹	
CFC-114	0.85 ¹	6,900 ¹	300 ¹	
CFC-115	0.4 ¹	6,200 ¹	1,700 ¹	
Hydrochlorofluorocarbons				
HCFC-22	0.04 ¹	4,300 ¹	13.3 ¹	480 °C ⁵
HCFC-123	0.014 ¹	300 ¹	1.4 ¹	
HCFC-124	0.03 ¹	1,500 ¹	5.9 ¹	
HCFC-141b	0.10 ¹	1,800 ¹	9.4 ¹	> 200 °C ⁵
HCFC-142b	0.05 ¹	4,200 ¹	19.5 ¹	204-260 °C ⁶
Halons				
HALON-1211	5.1 ¹	4,900 ⁴	20 ¹	500 °C ⁷
HALON-1301	12 ¹	4,900 ⁴	65 ¹	500 °C ⁸
HALON-2402	6.0 ²		20 ⁴	
Other fully halogenated CFC				
Carbon tetrachloride	1.20 ¹	2,000 ¹	42 ¹	> 100 °C ⁹
Methyl chloroform	0.12 ¹	360 ¹	5.4 ¹	> 54 °C ¹⁰
Methyl bromide	0.64 ¹	6,200 ¹	1.3 ¹	
Fluoroform	0 ¹¹	11,700 ¹²	250 ¹³	

1-http://media.wiley.com/product_data/excerpt/92/04712148/0471214892.pdf

2-<http://www.halontrader.org/halon/text/halon26.htm>

3- http://www.sepa.org.uk/pdf/data/spri/voc_explanation.pdf

4-http://www.scorecard.org/chemical-groups/one-list.tcl?short_list_name=ods

5-http://64.233.183.104/search?q=cache:g6aZfwU-QJsJ:www.unep.org/ozone/pdf/ftoc2002.pdf+%22CFC+12%22+%22decomposition+temperature%22&hl=sk&lr=lang_en

6-<http://216.239.59.104/search?q=cache:3Y6gKnTcsToJ:www.autofrost.com/autofrost-X3.pdf+%22Decomposition+temperature%22+%22hfc+142b%22&hl=sk>

7- <http://www.fire2rescue.com/webboard/msg/176.html>

8- http://www.flameskill.co.uk/pages/hazchem_halon_1301.htm

9- <http://www.catalogue.fisher.co.uk/scripts/search.dll?ViewMSDS&SheetNumber=90116>

10- <http://www.setonresourcecenter.com/msds/docs/wcd00005/wcd00581.htm>

11- <http://www.epa.gov/ozone/defns.html#hfc>

12-

http://cdm.unfccc.int/methodologies/inputam0001/Comment_AM0001_Schwank_081004.pdf

pdf

13- <http://www.fm200.biz/HFC-23.htm>



2.1 BASIC CHEMICAL CHARACTERISTICS

Chemicals of concern could be grouped into 5 categories based on their basic chemical characteristics and ability for chemical reactions:

CATEGORY I: FLUOROCARBONS (FCs)

Tetrafluoromethane	CF_4
1,1,1,2,2,2-hexafluoroethane	CF_3CF_3
1,1,1,2,2,3,3,3-octafluoropropane	$CF_3CF_2CF_3$

These chemical substances are chemically very stable and they can be hardly degraded by chemical reactions. They have a C-F bond only. Their chemical as well as biological degradation is fallible, practically impossible. Low compounds are gases, high substances are volatile liquids.

CATEGORY II: CHLOROFLUOROCARBONS (CFCs)

CFC-11	trichlorofluoromethane	CCl_3F
CFC-12,	dichlorodifluoromethane	CCl_2F_2
CFC-113	1,1,2-trichlorotrifluoroethane	CCl_2FCClF_2
CFC-114	1,2-dichlorotetrafluoroethane	$CClF_2CClF_2$
CFC-115	chloropentafluoroethane	$CClF_2CF_3$

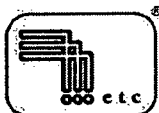
Mixture of CFCs: (refrigerator and cooling mixtures)

CFC-500 Cl_2F_2/CH_3CHF_2
dichlorodifluoromethane 73,8% + ethylidene fluoride 26,2%

CFC-502 $CHClF_2/CClF_2CF_3$
chlorodifluoromethane 48,8% + chloropentafluoroethane 51,2%

CFC-503 $CHF_3/CClF_3$
trifluoromethane 40,1% + chlorodifluoromethane 59,9%

These halogen carbons contain besides C-F bond the C-Cl bond also. Low compounds are gases in normal temperature, high substances are volatile liquids. Their chemical destruction is possible through C-Cl bond. These chemicals can react with metals, strong basis and the like.



CATEGORY III:	BROMOFLUOROCARBONS (HALONS)
HALON-1211	bromochlorodifluoromethane CF_2ClBr
HALON-1301	bromotrifluoromethane CF_3Br
HALON-2402	1,2-dibromotetrafluoroethane $\text{C}_2\text{F}_4\text{Br}_2$

Haloforms are used as narcotic substances. Their chemical destruction is possible through the reaction of C-Br bond which is more stable than C-Cl bond. They can be destroyed by ways similar to the substances of Category II.

CATEGORY IV: HYDROCHLOROFLUOROCARBONS (HCFCs)

HCFC-22	chlorodifluoromethane	CHClF_2
HCFC-123	2,2-dichloro-1,1,1-trifluoroethane	CHCl_2CF_3
HCFC-124	2-chloro-1,1,1,2-tetrafluoroethane	CHClFCF_3
HCFC-141b	1,1-dichloro-1-fluoroethane	$\text{CH}_3\text{CCl}_2\text{F}$
HCFC-142b	1-chloro-1,1-difluoroethane	CH_3CClF_2

These chemical substances contain beside C-Cl and C-F bonds also a C-H bond. This factor expands destruction possibilities through the C-H bond too. Here arises a possibility of easier biodegradation.

CATEGORY V: OTHER SUBSTANCES

methylchloroform (1,1,1-trichloroethane)	CH_3CCl_3
chloroform (trichloromethane)	CHCl_3
carbon tetrachloride	CCl_4
methyl bromide	CH_3Br

Category V includes chemical substances containing Cl or Br without F. In term of chemical destruction – these compounds are the most reactive. They are used for chemical cleaning of textile, as solvents in chemical industry or as reagents in the reactions. Their chemical destruction is relatively simple with high specificity.



2.2 CHEMICAL REACTIONS TO BREAK THE MOLECULES

Chemical substances under the study were generated with properties of chemical, biological, thermal and UV stability. From this reason and also due to low boiling points, it is problematic to find an effective chemical process for final degradation. Especially for chemical substances with mentioned low boiling points an incineration methods seem to be more advantageous.

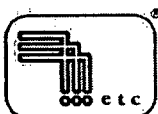
From the reason of different structural types of these compounds it is not possible to find a universal chemical method for their degradation. But various chemical methods can be applied to the group of similar compounds in reactivity.

For the destruction of CFC, HCFC, CCl_4 , CH_3Br compounds different methods could be applied.

- i. Direct chemical destruction - reactions of compounds under study with the reactive reagents to compounds which have inorganic bonded fluorine. For example melting with NaOH.
- ii. Chemical destruction via organic fluorine intermediates - reaction of compounds under consideration with reagents yielded to different organic fluorine compounds which we can transform to inactive fluorine compounds by another reaction. For example reaction of CF_2Br_2 via difluorocarbene reaction on activated double bond. By this way we can transform gas fluorine compound to solid fluorine, which we can decompose by several reactions.
- iii. Chemical destruction via dehalogenation - this method is very pure method for the decomposition by hydrogenation on different catalysts.
- iv. Chemical destruction on surface - here we can degrade mentioned compounds by reactions on solid surface state. For example reaction on zeolites.

Following examples can demonstrate some methods for the destruction of CFC, HCFC, CCl_4 , CH_3X .

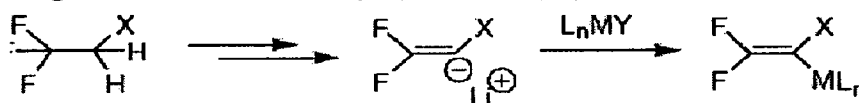
- v. In catalytic decomposition method, CFCs are decomposed by continuously circulating CFC and steam on a solid catalyst. The high performance solid catalysts include zeolite, alumina, binary oxide of TiO_2 - ZrO_2 and iron oxide supported on activated carbon.
- vi. In reagent decomposition method, CFC are reductively decomposed by a sodium naphthalene reagent dissolved in an organic solvent, which reacts with gaseous or liquid CFC and thereby gives NaCl and NaF



- through the neutralization between Na⁺ ions in the reagent and Cl and F in CFC.
- vii. The super critical water decomposition method utilizes the fact that a super critical state is formed in water beyond the critical point of water, state-facilitating hydrolysis. It is reported that CFC-11 and CFC-113 are almost completely decomposed at temperature of 400 °C and atmospheric pressure of 320 atm.
 - viii. Some chemical methods for destroying of these stable compounds are in the stage of research and development.
 - ix. Hydrogenation of CFCs adsorbed onto activated carbon represents a degree of decomposition of CFC replacements using the untreated activated carbon. (activated carbon treated with 6 N nitric acid)
 - x. Other method for destruction of CFC-11 uses a microwave torch generated atmospheric-pressure nitrogen discharge by authors Mariusz Jasinski, Jerzy Mizeraczyk, Zenon Zakrzewski, Toshikazu Ohkubo and Jen-Shih Chang. Centre for Plasma and Laser Engineering, Institute of Fluid Flow Machinery, Poland.
 - xi. Catalytic hydrolysis of chlorofluorocarbon (CFC-12) over WO₃/ZrO₂ is other method for the destruction of CFC in the presence of water vapor investigated over a series of solid acids WO₃/ZrO₂. (Weiming Hua, Feng Zhang, Zhen Ma, Yi Tang, Zi Gao Department of Chemistry, Fudan University, Shanghai 200433, PR China)
 - xii. Halocarbons undergo catalytic destruction and mineralization with silver and gold nanoparticles in solution forming metal halides and amorphous carbon. (A. Sreekumaran Nair and T. Pradeep CURRENT SCIENCE, VOL. 84, NO. 12, 25 JUNE 2003). The scheme of destruction:



- xiii. CFC replacement is a new principle for the destruction of halocarbons. They are transformed from original compounds to a friendly haloderivatives which are available for next degradation. (A.K. Brisdon, I. R. Crossley from Department of Chemistry, P.O. Box 88, Manchester, M60 1QD, UK. i.crossley-2@stud.umist.ac.uk)
Traditionally, this has involved procedures based on environmentally hazardous precursors, such as chlorofluorocarbons. More recent work has employed less damaging CFC-replacements in analogous procedures to generate trifluorovinyl (CF₂=CF⁻) systems;



X = F, Cl

M = metal/metalloid

Y = halide



Methodology which was adapted for organometallic systems;



X = F, Cl M = metal/metalloid, Y = halide

Further reduction in the indirect environmental impact of these protocols is desirable.

(J. Burdon, P. L. Coe, I. B. Haslock, R. J. Powell, *Chem. Commun.*, 1996, 49)

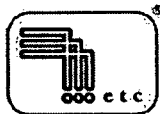
(K. K. Banger, A. K. Brisdon, A. Gupta, *Chem. Commun.* 1997, 139; A. K. Brisdon, I. R., Crossley, R. G. Pritchard, J. E. Warren, *Inorg. Chem.*, 2002, 41, 4788 – 4755)

(A. K. Brisdon, I. R. Crossley, *Chem. Commun.* 2002, 2420 – 2421)

(A. K. Brisdon, I. R. Crossley, *Angew. Chem. Int. Ed. Engl.*, 2003)

- xiv. Method for destruction by adsorption and chemical decomposition of CCl_4 by high surface-area aluminum oxide. (Khaleel A, Dellinger B. Department of Chemistry, Louisiana State University, Baton Rouge 70803, USA). High surface-area alumina holds promise as a catalytic media as well as a component of other binary catalyst systems. An alumina catalyst (that has a very high surface area of $550 \text{ m}^2/\text{g}$) using the aerogel technique was prepared. This catalyst destroys carbon tetrachloride with an efficiency $>99\%$ at $400 \text{ }^\circ\text{C}$. Its reactivity toward carbon tetrachloride is remarkably higher than that of commercial alumina, which has a surface area of $155 \text{ m}^2/\text{g}$. Carbon dioxide, is the major product.
- xv. Decomposition of halogenated methanes in oxygen-free gas mixtures by the use of a silent electric discharge. (Foglein KA, Szepvolgyi J, Dombi A. From Department of Inorganic and Analytical Chemistry, University of Szeged, H-6701 Szeged, PO Box 440, Hungary.) A silent electric discharge was applied to decompose halogenated methanes including CCl_4 , $CHCl_3$, $CFCl_3$, CF_2Cl_2 and CF_3Cl , in argon-containing gas mixtures. The decompositions of the target compounds were studied in static reactors at fixed electric field and room temperature.
- xvi. Dehalogenation on Pd-Fe⁰ bimetallic surface by trihalomethanes, water disinfection-byproducts, in potable water are of public health concern. Degradation of trihalomethanes by palladium-treated iron granules (Pd-Fe⁰). (Edwin Guasp, Robert Wei G, from Morgan Water Plant, Compliance Laboratory, Cleveland, OH 44102, USA, Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA)

Technologies for fluorocarbon destruction were described – including chemical ways of CFC degradation:

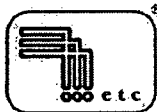


- xvii. Pyrolysis using chemical substances destroys CFCs in a reaction with silicon-compounds at a high temperature by electric heating.
- xviii. Na-naphthalenide destroys CFCs in a reaction with Na-naphthalenide in liquid phase at a low temperature of 25-150 °C.
- xix. Na-ammonia destroys CFCs in a reaction with Na dissolved in ammonia. The NaNH₂ produced is reused by the reduction to ammonia.
- xx. Molten metal destroys CFCs in molten sodium.
- xxi. Sodium oxalate destroys CFCs in a reactor containing sodium oxalate at 270 °C.

xxii.

Also catalytic types of CFC destruction are described:

- xxiii. Hydrolysis TiO₂-ZrO₂
 TiO₂-WO₃
 AlPO₄
 zealots
 H-type mordent
- xxiv. Alcohol reduction FeF₃-CuCl₂ / activated carbon
- xxv. Oxidation PO₄-ZrO₂
- xxvi. Catalytic combustion WO₃-Al₂O₃
- xxvii. Hydrogenation Pt/activated carbon



3 HISTORY

3.1 DESTRUCTION TECHNOLOGIES

In the Handbook for the International Treaties for the Protection of the Ozone Layer published by UNEP, Ozone Secretariat, and United Nations Environment Programme in 2003, a destruction process is defined as:

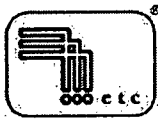
“a destruction process is one which, when applied to controlled substances, results in the permanent transformation, or decomposition of all or a significant portion of such substances”

In the Handbook for the International Treaties for the Protection of the Ozone Layer published by UNEP, Ozone Secretariat, and United Nations Environment Programme in 2003, also destruction efficiency (DE) is described: it means that less than 0.1 g of total ODS will enter the environment from flue gas emissions, liquid effluents, and solid residues, when 1,000 gram ODS are fed into the process.

The phase-out of ODS, and their substitution by less harmful substances, will lead to the recovery of the ozone layer and the use of more sustainable products. Stratospheric ozone absorbs most of the biologically damaging ultraviolet radiation. Without the filtering action of the ozone layer more UV-B radiation can penetrate the atmosphere to have profound effects on human health, animals, plants, microorganisms, marine life, materials, biogeochemical cycles, and air quality.

It is known (UNEP Report of the Technology and Economic Assessment Panel, Volume 1, April 2002) that it is technically feasible to collect and recover CFC and HCFC contained in foams, refrigeration, and air-conditioning equipment and halons contained in fire protection equipment. In the Report of the Technology and Economic Assessment Panel published in April 2002 as Volume 1, Progress Report, it is estimated that:

1. Between 350,000 and 400,000 ODP-tones of CFC are contained in refrigeration equipment in 2002;
2. 450,000 ODP-tones of halon-1301 and of 330,000 ODP-tones of halon-1211 are installed in fire fighting equipment in 2002; and
3. 1.25 million tones of CFC-11 will be contained in installed foams in 2010.



As a step in the long-term destruction of ODS process it should be mentioned that a Manual of Destruction Technologies for Chlorofluorocarbons was elaborated in Japan in 1999.

Technical Assessment Committee (TAC) was set up under the United Nations Environment Programme (UNEP) which evaluated the technologies for the destruction of ODS. As a result, TAC set the criteria for ODS destruction.

In Technology and Economic Assessment Panel (TEAP) study from 2002, updated information on the technologies and criteria was developed by the UNEP TEAP Task Force on Destruction Technologies (TFDT). The main purpose of that document was to recommend technologies for destroying surplus stocks of ODS, based on an assessment of their technical capability using available information.

The Task Force developed updated 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. Only two technologies are recommended for the destruction of foams.

The recommended technologies:

1. Concentrated sources:

Cement Kilns Incineration
Liquid Injection Incineration
Gaseous/Fume Oxidation
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

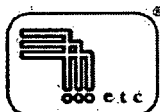
2. Diluted sources (foams):

Municipal Solid Waste Incinerators
Rotary Kiln Incinerators

Destruction technologies for ODS approved by the Parties to the Montreal Protocol divided according to the energy source of destruction:

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*]
- For foam containing ODS: rotary kiln incinerator [*approved by Decision XIV/6*]

Plasma destruction category

- Radio frequency plasma destruction technology [*approved by Decision VII/35*]
- For CFC, HCFC and halons: argon plasma arc [*approved by Decision XIV/6*]
- For CFC and HCFC: nitrogen plasma arc, microwave plasma, gas phase catalytic dehalogenation and super-heated steam reactor [*approved by Decision XIV/6*]

3.2 LEGISLATION

Global efforts to protect the stratospheric ozone layer are based on two international instruments: the Vienna Convention on the Protection of the Ozone Layer of 1985 and Montreal Protocol on Substances that Deplete the Ozone Layer of 1987. Since 1987, the Montreal Protocol has been amended and adjusted five times from several reasons: to include an increasing number of ODS, strengthen the applicable phase-out schedules and improve effective implementation of its provisions.

Acts of the EU concerning ozone depleting substances:

Table No. 2: Acts of EU related to the ODS

Act	Entry into force
Regulation (EC) No. <u>2037/2000</u>	30.09.2000
Amending acts	Entry into force
Regulation (EC) No. <u>2038/2000</u>	30.09.2000
Regulation (EC) No. <u>2039/2000</u>	30.09.2000



Related acts

Notice to undertakings

Notice to importers in the European Union of controlled and new substances that deplete the ozone layer, regarding Regulation (EC) No 2037/2000 of the European Parliament and of the Council on substances that deplete the ozone layer - restricted to countries acceding to the European Union on 1 May 2004 [Official Journal C 133 of 11.05.2004].

Notice to exporters of controlled substances that deplete the ozone layer in the European Union regarding Regulation (EC) No 2037/2000 of the European Parliament and of the Council on substances that deplete the ozone layer - restricted to countries acceding to the European Union on 1 May 2004 [Official Journal C 133 of 11.05.2004].

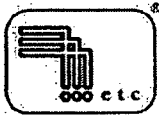
Notice to users of controlled substances in the European Union allowed for essential uses in the Community in 2004 under Regulation (EC) No 2037/2000 of the European Parliament and of the Council on substances that deplete the ozone layer - restricted to countries acceding to the European Union on 1 May 2004 [Official Journal C 133 of 11.05.2004].

Notice to importers in the European Community of controlled and new substances that deplete the ozone layer, regarding Regulation (EC) No 2037/2000 of the European Parliament and of the Council on substances that deplete the ozone layer [Official Journal C 162 of 11.07.2003].

Notice to exporters of controlled substances that deplete the ozone layer in the European Community regarding Regulation (EC) No 2037/2000 of the European Parliament and of the Council on substances that deplete the ozone layer [Official Journal C 162 of 11.07.2003].

Notice to users of controlled substances in the European Community allowed for essential uses in the Community in 2004 under Regulation (EC) No 2037/2000 of the European Parliament and of the Council on substances that deplete the ozone layer - [Official Journal C 162 of 11.07.2003].

Commission Decision 2003/256/EC of 26 February 2003 on the allocation of import quotas for controlled substances for the period 1 January to 31 December 2003 under Regulation (EC) No 2037/2000 of the European Parliament and of the Council [Official Journal L 95 of 11.04.2003].



Montreal Protocol

Decision 2002/215/EC - Official Journal L 72 of 14.03.2002
Council Decision of 4 March 2002 concerning the conclusion of the Fourth Amendment to the Montreal Protocol on substances that deplete the ozone layer. This amendment adds the following restrictions to the Protocol:

- an end to HCFC production in developed countries by 2004;
- an end to trade in HCFC with countries outside the Protocol by 2016;
- a ban on bromochloromethane;
- compulsory communication of the quantity of methyl bromide used for quarantine and pre-shipment.

Decision 2000/646/EC - Official Journal L 272 of 25.10.2000
Council Decision of 17 October 2000 concerning the conclusion of the amendment to the Montreal Protocol on substances that deplete the ozone layer.

The most significant provisions of the Montreal amendment concern trade with third countries, including:

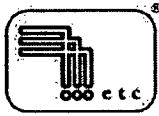
- a ban on imports or exports of methyl bromide from or to States which are not parties to the Protocol;
- a ban on exports, from States not party to the Protocol, of used, recycled and reclaimed substances regulated by the Protocol;
- compulsory licensing system for imports and exports of substances that deplete the ozone layer.

ODS destruction regulations in selected countries

ODS regulations vary noticeably from country to country, both in content and structure. They are all a result of legal and administrative structure and traditions, conveniently available general legislation, the size and type of ODS consumption, available information on alternatives at the time when the regulations were enacted and compromises between different interests, etc.

A review of legal instruments dealing with ODS in individual countries as described Montreal Protocol on Substances That Deplete the Ozone Layer published by UNEP TEAP in April of 2002 as Report on the TFDT:

The U.S. requires each producer of a Group I controlled substance (primarily CFC) 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 of US lists 85 process wastes



and approximately 400 chemicals as hazardous wastes, including CFC and HCFC, 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 (PCDD), furans (PCDF), 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.

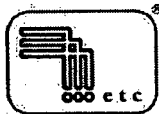
The **European Union** has adopted regulations to reduce emissions of ODS. The new regulation (2037/2000) covers the use, reuse, and disposal requirements for ODS, including virgin and recycled CFC, HCFC, refrigerant blends, halons, 1,1,1-trichloroethane, and carbon tetrachloride. In addition, the regulation 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 standard set for Destruction and Removal Efficiency (DRE), the high emission standards guarantee that DRE for incineration is >99.99%.

In **Australia**, New South Wales and Australian Capital Territory 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.

Since 1998, **New Zealand** has also collected and sent ODS to the Australian National Halon Bank for recycling and destruction. There is a 25%



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 HCFC, to fund the transport and destruction of "end of life" CFC and HCFC. 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%) 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.

3.3 PATENTS

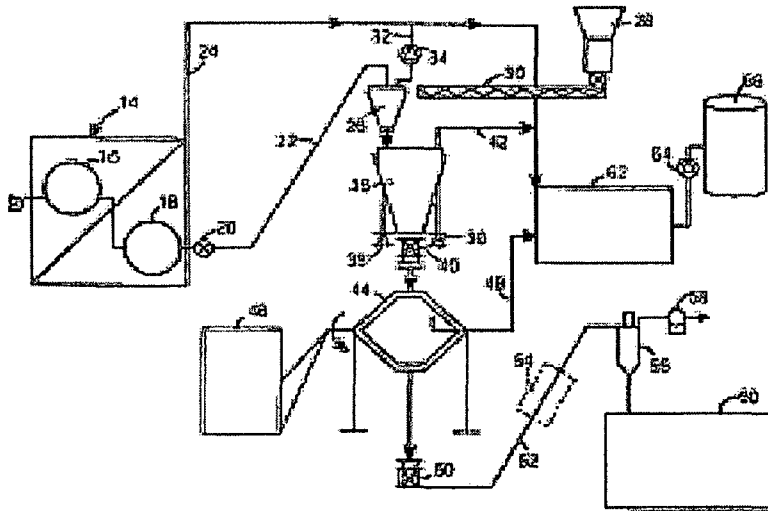
During information research a search on the different sources was realized with aim to find patents related to the destruction technologies of ODS. As a result of this survey these results were achieved:

EU patents

A method and apparatus for the processing and disposal of foam containing an ozone depleting substance was applied for a patent by Clarke Thomas and Clarke Kenneth from Great Britain in 2003. The present invention relates to the disposal of any foam containing one or more ODS, in particular a method for the environmentally friendly disposal of such foam by adding or encasing same in concrete, the foam preferably being in a fine powder like form on addition to the concrete. The invention also relates to a method of processing such foam to achieve said powder like form, in preparation for the disposal thereof, an apparatus for carrying out said method, and to concrete containing such processed foam.



Picture No. 1: Scheme of ODS destruction process by C. Thomas and C. Kenneth

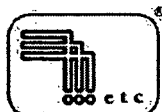


US patents:

U.S. Patents submitted by Commodore Advanced Sciences, Inc. of Albuquerque, New Mexico:

Table No. 3: Existing patents submitted by Commodore Advanced Sciences, Inc.

US Patent Number	Date Issued	Title	Application	Accompanying Foreign Patents
4,702,804	10/27/87	Methods for Electrochemical Reduction of Halogenated Organic Compounds	Dehalogenation by electrochemistry using graphitized carbon	
4,853,040	08/01/89	Processes for Decontaminating Polluted Substrates	Treatment of soils, surfaces, oils, by solvated electron solutions	Canada, Japan
4,968,393	11/06/90	Membrane Divided Aqueous-Nonaqueous System for Electrochemical Cells	Dehalogenation by electrochemistry using divided aqueous/nonaqueous cells	
5,110,364	05/05/92	Processes for Decontaminating Polluted Substrates	Treatment of soils, surfaces, oils, by solvated electron solutions	

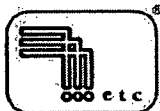


US Patent Number	Date Issued	Title	Application	Accompanying Foreign Patents
5,414,200	5/09/95	Non-Metallized and Substoichiometric Metallized Reactions with Ammonia and Other Weak Bases in the Dehalogenation of Refrigerants	CFC destruction by solvated electron and ammonia	
5,497,627	03/12/96	Methods for Purifying Refrigerant Compositions	Aqueous extraction of select refrigerants from mixes allowing recovery of the useful material	
5,559,278	09/24/96	Methods for the Destruction of Ozone Depleting Substances	CFC destruction by solvated electron and ammonia	Australia, New Zealand, Pakistan, South Africa
5,602,295	03/11/97	Methods for the Elimination of Cyanides in the Dehalogenation of Halofluorocarbons	CFC destruction	Australia
5,616,821	04/01/97	Method for Purifying and Recovering Contaminated Refrigerants with Solutions of Bases in Organic Solvents	Selective refrigerant destructive refrigerant	Australia, Israel, Pakistan, South Africa
5,698,750	12/16/97	Method for Purifying Contaminated Refrigerants with Aqueous Solutions of Bases	Selective refrigerant destruction	

Another US patents related to the destruction technologies of ODS exist too:

Destruction systems incorporating their patented Plasmatron AC plasma are designed by Scientific Utilization International for the destruction of hazardous wastes.

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)



This process has been patented worldwide by the BCD Group in the USA. Enterra Pty Ltd is a licensee of the BCD Group. Enterra Pty Ltd and the BCD Group are jointly promoting this technology as the BCD process.
(Detailed Review of Selected Non-Incineration and Incineration POPs Elimination Technologies for the CEE Region; Danish Environmental Protection Agency; 2004)

Canadian patents:

ELI Eco Logic International Inc. (Eco Logic) of Rockwood, Ontario developed and commercialized the ECO LOGIC Gas-Phase Chemical Reduction process. Eco Logic applied for a patent for this core technology in 1986.

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)

Japanese patents:

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).

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)

A list of patents dealing with ODS destruction possibilities from European Patent Office web site can be found in Appendix No. 4.

3.4 BAT / BEP

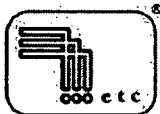
BAT (Best Available Technique) is such a method of processing or manufacturing which is environment friendly and with minimum impact to human health.

BEP (Best Environmental Practice) aims to minimize the emissions from potential pollution sources to the environment through reduction of releases.

When choosing a technology for destruction of ODS, common selection criterions for best available techniques and best environmental practices, more viewpoints for that purpose can be used.

In general, these requirements can be applied:

- low energy consumption
- low emission rates



- applicability for wide variety of ODS wastes
- mobility of destruction unit
- commerciality
- high destruction efficiency
- low cost

Detailed comparative study for a commercially available technology to destroy ODS is not available. It is to be stated, that also conditions in different countries could require different approach to deploy destruction technologies due to specific amounts and needs for long distance transport, infrastructure etc.

Comparative study on selection of appropriate technologies for destruction of ODS was done in September 1999, CANTOX ENVIRONMENTAL INC., (CEI) in partnership with the Pioneer Technology Centre (PTC) to develop a Guidance Document for the disposal of surplus CFC and halons in Canada, in consultation with appropriate experts and stakeholders.

In all, 42 ODS disposal technologies were identified and described, then evaluated on the basis of mandatory environmental criteria and commercial availability. As a result, the 42 identified technologies were categorized into two main groups:

1. Commercially available and environmentally acceptable technologies.
2. Emerging technologies.

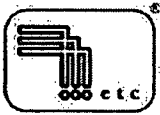
The first group of technologies was then further evaluated in two separate ways, based on two different sets of criteria:

1. environmental and technical criteria; and
2. commercial and economic criteria.

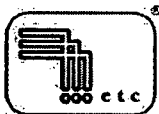
Final technical / environmental ranking (see Appendix No. 3) of ODS disposal technologies selected by CANTOX ENVIRONMENTAL INC.:

Technologies:

1. Argon Plasma Arc
2. Gas Phase Chemical Reduction
3. Catalytic Dehalogenation
4. Vitrification
5. Reactor Cracking
6. High Performance Incineration
7. ICFB Incineration



8. IC RF Plasma
9. Solvated Electron Decomposition
10. AC Plasma
11. Cement Kiln Incineration
12. Liquid Injection Incineration
13. Gas/Fume Incineration
14. Rotary Kiln Incineration
15. Liquid Phase Chemical Conversion
16. UV Photolysis



4 SCENARIOS

Need for destruction technologies on ODS appears along with deadline requirements and multilateral environmental agreements obligations for phasing-out and destruction of ODS.

Separate countries are facing the ODS destruction at different conditions in terms of the total amount, application method of the substances and technical-economic preconditions.

Reflecting the complexity of the problem it is necessary to utilize all the experience of countries that reached an adequate technical-logistic level of development in the environmental sound management of ODS.

Such experienced countries serving as examples can be Switzerland with its capacity to destroy ODS with help of high-tech incinerator or Australia providing capacities of the National Halon Bank – regional technical center for ODS destruction – not only on the national level but to the whole Asia-Pacific region.

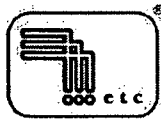
Switzerland

The RSMVA - Regional Hazardous Waste Incinerator operated by Valorec Services AG. Valorec is running a hazardous waste incineration plant in Basel (Switzerland) which is a part of the *Veolia Environnement* group with headquarters in Paris, France. The RSMVA started the commercial incineration of hazardous waste in September 1995.

The RSMVA is a rotary kiln incinerator with secondary combustion chamber and heat recovery, a 6-stage wet gas scrubber and a DeNO_x selective catalytic reduction system. All wastewater undergoes physicochemical processing in an appropriate wastewater treatment plant.

Among different type of waste they also have the capability to incinerate gases or liquefied gases. Valorec is a major player in the incineration of CFC gases and halons on the Swiss market.

Over the last years they they're able to dispose an annual average amount of 100 tons of gases, consisting of CFC (mainly R11 and R12) and halons. However their treatment capacity could be increased up to 500 tons/year. Beside the incineration of liquefied gases delivered in pressurized cylinder (from 1 m³ to 20 m³) Valorec also developed an expertise in the treatment of different gases conditioned in gas bottles (up to 50 L).



Australia

Halon banking is a key component in national halon management and constitutes an important tool in helping to meet the Montreal Protocol compliance targets.

The Australian Halon Management Strategy (AHMS) outlines Australia's commitment to manage responsibly Australia's surplus halon stocks; ensuring supplies of recycled halons continue to be available for essential uses. The AHMS also maps out the important role Australia can play in providing a range of halon management services to countries in the Asia-Pacific region in order to minimize global ozone depletion.

Critical to the success of the AHMS will be the ongoing operation and development of the National Halon Bank (NHB) as a regional environmental facility for best practice in the management of ozone depleting substances. The NHB is a state of the art facility that is currently unmatched throughout the world for the completeness of its halon banking and management services.

The Australian National Halon Bank facility in Melbourne safely stores, reclaims and destroys halons and CFCs. In accordance with the Montreal Protocol, Australia's stock of halon required to meet essential use needs is stored, secured and managed at the Australian National Halon Bank.

The facility in Melbourne has the expertise to provide a range of Ozone Depleting Substances management services to international customers.

The Department of the Environment and Heritage will develop the NHB as an Asia-Pacific regional environmental facility to assist Australia and other countries to phase-out their surplus halon stocks while ensuring stocks are maintained to meet their own essential needs.

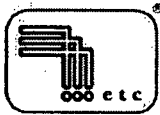
4.1 TECHNOLOGIES AND VENDORS

Descriptions of the technologies

Commercially available technologies for destruction of ODS are shortly prescribed in this chapter.

In this study overall 22 destruction technologies of ODS are described which a combination of methods is taken from 2 sources:

1. Handbook for the International Treaties for the Protection of the Ozone Layer, The Vienna Convention (1985), The Montreal Protocol (1987),



UNEP Ozone Secretariat United Nations Environment Programme;
2003

2. study realized by CANTOX ENVIRONMENTAL INC. in 2000

Information on advantages and also disadvantages are briefly described in Appendix No. 1.

Details concerning costs - if available - of all technologies can be found at Appendix No. 2,

In principle technologies are divided into 3 categories:

- incineration technologies
- plasma technologies
- non-incineration technologies

4.1.1 INCINERATION TECHNOLOGIES

4.1.1.1 Cement Kilns Incineration

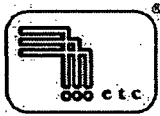
A cement kiln is a kiln that slowly rotates to expose limestone, sand and clay evenly to very high temperatures (1,400-2,000 °C) to make cement clinker. Organic waste can be injected into the kiln with the fuel or directly into the flame. The high temperature and long residence time (6-10 seconds) effectively oxidize the organic waste. Acid gases resulting from organo-chlorine chemicals are supposed to be mostly neutralized by the alkaline cement eliminating the need for a caustic scrubber.

Burning of hazardous industrial wastes in cement kilns are being used for the disposal of hazardous wastes in France and Norway and a number of other European countries.

The principal processes employed in making cement clinker can be broadly classified as either "wet" or "dry" depending on the method used to prepare the kiln feed.

In the wet process the feed material is slurred and fed directly into the kiln. In the dry process the kiln exhaust gases are used to dry the raw meal (a mixture of limestone and other raw materials) while it is being milled.

The capacity is about 500 m³ for the solid waste and 260 m³ for fluid waste.



(Detailed Review of Selected Non-Incineration and Incineration POPs Elimination Technologies for the CEE Region; Danish Environmental Protection Agency; 2004)

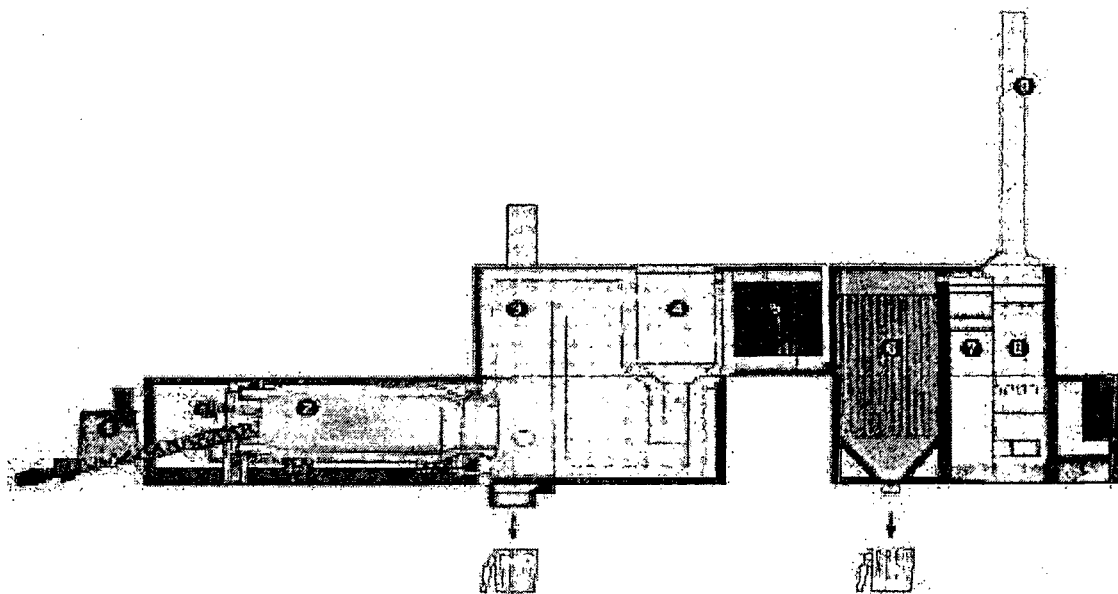
4.1.1.2 Container Based Incineration System

Chemcontrol A/S and Soil Recovery A/S have designed and constructed a mobile Container-based Incineration System (CIS), for high temperature incineration of toxic and hazardous wastes, hospital waste and other industrial wastes, designed on a modular basis to facilitate shipping and erection.

The container-based incineration system is designed for the incineration of solid, pasteous and liquid hazardous waste such as waste oil, organic solvents, paint sludge, lacquers, plastic, synthetic material, rubber halogenated waste, pesticides, PCB, hospital waste and infectious waste (optional). The CIS is a small (mobile) rotary kiln and is just now being tested in Latvia.

The capacity of the plant is 2,000-4,000 ton per year, depending on the bulk density and the heat value of the waste. The incinerator is a turnkey installation consisting of two standard 40 ft. and one 20 ft. containers thus simplifying transportation and installation on site. The unit is complete with feeding system, rotary kiln, secondary combustion chamber, flue gas cooling system, flue gas cleaning, electrical wiring, control system, etc. The CIS has a rotary kiln incineration system with a flue gas cleaning system, and works at an operating temperature of 1,100 °C to 1,200 °C.

Picture No. 2: Scheme of Container Based Incineration System



Hazardous waste incinerators have a main chamber for burning wastes and a secondary incineration chamber to achieve maximum destruction of



hazardous organic by-products. Air and natural gas are burnt to keep the combustion gases at the appropriate temperature (1,150 °C) for at least two seconds (residence time). Off gases are cooled to approx. 20 °C before entering the gas cleaning processes.

Properly managed incineration can, in principle, destroy pesticide waste with a DRE of 99.99% or higher. Some incinerators even claim DRE values of up to 99.99995%.

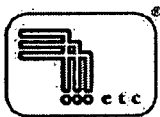
Disadvantages: effective incineration is complex and depends on many factors, such as: equipment and process design, process control and maintenance of the correct residence time, temperature and turbulence, type of products incinerated, and capacity and effectiveness of air pollution control devices. High temperature incinerators are complex pieces of equipment, which require highly skilled personnel and constant monitoring to maintain stable operating conditions.

Dioxins, which are extremely toxic and persistent in the environment, are formed as the result of a reaction during the cooling of the stack gases. The formation of dioxins has been minimised in modern incinerators either by cooling down in boilers taking out the heat of the flue gas or by quenching off gases quickly to below 250 °C and the release of dioxins, heavy metals and dust are carefully controlled by passing off gases through intensive flue gas cleaning processes.

A disadvantage though is the poor control of the residual products placed as hazardous waste on landfill, which may contain high levels of POPs and other toxic chemicals.

Advantages:

- Reduction of volume of waste from 100% to about 12-13% of slag and 6-7% of fly ash and material from flue gas cleaning;
- Detoxification of many different toxic compounds at the same time especially carcinogens, pathologic materials and all kind of toxic chemicals;
- Reduction of the impact on the environment, e.g. if the alternative is direct land filling where organic and soluble inorganic compounds easy leaks out into the environment; and
- Energy recovery, especially when big amounts of waste are available in a continuous stream from the waste producers.



Finally, the incineration processes at a single process destroys all organic compounds and change their dangerous chemistry radically to something less dangerous. These advantages, in combination with extensive use for municipal waste treatment and combined energy utilisation (distinct heating and electricity utilization) are the background for the very general use of incineration and have made the basis for the development of many different incineration systems.

DE value for organic carbon is 97-98%.

(Detailed Review of Selected Non-Incineration and Incineration POPs Elimination Technologies for the CEE Region; Danish Environmental Protection Agency; 2004)

4.1.1.3 Gaseous / Fume Oxidation

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 1,100 °C is required for most ODS compounds, and the specific unit operates at from 1,200 to 1,250 °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 1,200 °C for CFC and 1,250 °C for halons. The flue gas volume was estimated at 1,200 Nm³/h, except for the HBr/Br₂ emission that is at 130 Nm³/h.

Fume incinerators are almost always privately operated and are typically found in fluorine chemical 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 CFC 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.

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)

4.1.1.4 High Performance Incineration

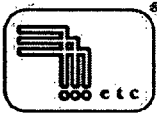
High performance incinerators designed specifically to destroy stable organic compounds, such as PCBs and ODS, operate at significantly higher temperatures, generally at 1,200 °C or higher. Such performance incinerators generally achieve 99.9999% destruction. Halogen-containing ODS have a low heat value; therefore, the required high operating temperatures can only be achieved by use of 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 produced in the case of the destruction of halons. Products of incomplete combustion (PIC) such as carbon monoxide, hydrocarbons, organic acids and partially degraded products may also be produced, but these PICs are emitted in only small amount from well-designed incineration facilities that provide high temperatures, adequate residence times (1-2 seconds), excess oxygen and good mixing.

A purpose designed system has been installed to facilitate the introduction of ODS into the incinerator in a safe and secure manner. This system employs nitrogen to pressure off the ODS from the shipping container directly into the rotary kiln. The feed rate is regulated to a nominal value of 4 to 5 kg/h although the system capacity is 10 kg/h.

The design of this system offers a number of inherent advantages:

- The ODS material does not need to be transferred to an intermediate vessel prior to incineration.
- There are no pumps involved thereby limiting the potential for leakage from seals.
- The system can be rapidly shutdown locally and through remote interlocks tied into the incinerator control system.
- The ODS container can be purged with nitrogen at completion and depressurized to atmospheric pressure.
- The system can accommodate a variety of sizes and configurations of ODS containers.
- The entire system is located inside the incinerator feed building that is



maintained under a slight negative pressure and is exhausted to atmosphere via a carbon adsorption system

(<http://www.shtc.ca/ODS%20Info.htm>)

4.1.1.5 Internally Circulating Fluidized Bed Incineration

Internally circulating fluidized bed (ICFB) incinerators can be fired with any solid, liquid or gas fuel. CFCs and air are blown through the incinerator fluidized bed, and CFCs are broken down by the presence of methane and hydrogen in the reducing atmosphere of the incinerator. Calcium carbonate is also fed into the incinerator to adsorb the corrosive HCl and HF gases formed by the breakdown of the CFCs.

In 1995, a joint effort by Japan's National Institute of Materials & Chemicals Research and the incinerator supplier Ebara Corp. of Tokyo demonstrated CFC destruction in an internally circulating fluidized bed incinerator. The incinerator was modified by attachment of a special nozzle at the bottom of the incinerator to blow CFCs and air through the fluidized bed. Tests using a 30 MT/day incinerator at Ebara's Fujisawa factory have shown that burning with wood chips can destroy more than 99.9998% of CFCs.

The main attraction of this approach is its relative simplicity.

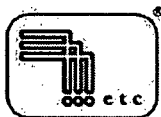
(<http://www.uneptie.org/ozonation/library/mmcfiles/multiples/3521-e-file7.pdf>)

4.1.1.6 Liquid Injection Incineration

The waste is burned directly in a burner (combustor) or injected into the flame zone or combustion zone of the incinerator chamber (furnace) through atomizing nozzles. The heating value of the waste is the primary determining factor for the location of the injection point.

Liquid injection incinerators are usually refractory-lined chambers (horizontal or vertical flow, either up or down), generally cylindrical in cross section, and equipped with a primary burner (waste and/or auxiliary fuel fired). Often secondary combustors or injection nozzles are required where low heating value materials such as dilute aqueous-organic waste are to be incinerated.

Liquid injection incinerators operate at temperature levels ranging between 1,000 °C (1,832 °F) and 1,700 °C (3,092 °F). The residence time for the combustion of products in the incinerator may vary from milliseconds to as



much as 2.5 seconds. An atomizing nozzle in the burner or the incinerator is a critical part of the system because it converts the liquid waste into fine droplets.

The viscosity of the waste determines whether good atomization of a liquid is possible. Two-fluid atomizers, using compressed air or steam as an atomizing fluid, are capable of atomizing liquid with viscosities up to 70 centistokes (2.7 ft²/hr).

The physical, chemical, and thermodynamic properties of the waste must be considered in the basic design of any incinerator system. Any commercial facility receiving hazardous waste requires a complete analytical laboratory on site. Most commercial operators require a sample of the waste before they will provide a treatment cost to the generator.

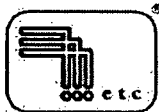
(<http://www.eurowaste.20m.com/photo6.html>)

4.1.1.7 Municipal Solid Waste Incineration

The municipal solid waste incineration (MSWI) typically employs 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 odor, 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 municipal solid waste while the CFC feed rate was 6.5 to 19.5 kg/h. The flue gas volume was estimated at 60,000 m³/h.

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.

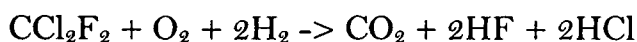
(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)

4.1.1.8 Reactor Cracking

The process is used for thermal decomposition of CFC/H-CFC/FC-mixtures in a hydrogen/oxygen flame. From the reaction gas hydrofluoric acid of about 55% concentration and hydrochloric acid of about 31% concentration are obtained downstream.

The reactor consists of a reaction chamber connected with a special cooler. The cylindrical reaction chamber is protected by a water-jacketed steel shell. A special burner for hydrogen, oxygen and CFC is flanged to the upper end of the reaction chamber. The material of the reaction chamber is graphite and it has to be protected against overheating. The cooling system used is jacket cooling. The cooler flanged directly to the reaction chamber is also made of acid proof graphite and likewise water-jacketed.

The reaction that takes place according to following chemical equation:



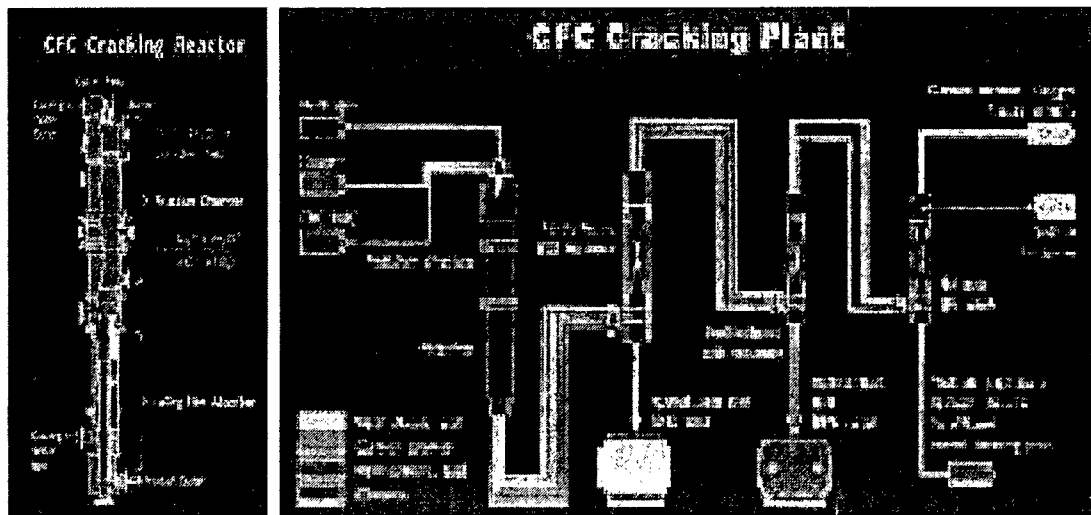
The CFCs are decomposed into hydrogen fluoride, hydrogen chloride, carbon dioxide, water and some chlorine. The decomposition products are cooled in the cooler to extend that aqueous hydrofluoric acid of about 55% concentration and the non condensable gases can be withdrawn at the cooler outlet.

In the HF-Recovery-Unit the hydrogen fluoride is separated from the non condensable gas mixture and hydrofluoric acid is formed as technical grade quality. The purified gas is then led to the HCl absorption column to recover the hydrogen chloride as hydrochloric acid. This acid is cooled down and pumped to the storage tank. The gas coming from the HCl-absorption is treated in a waste gas scrubber. Any traces of acid are absorbed by water.

The formation of polychlorinated dioxins and furans is reliably prevented by the high cracking temperatures of over 2,000 °C and the subsequent rapid cooling of the decomposition products to about 40 °C. No solid wastes are produced.



Picture No. 3: Scheme of cracking reactor and cracking plant as a whole



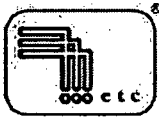
(http://www.hug-engineering.de/index.htm?DestructionTechniques_01.htm)

4.1.1.9 Rotary Kiln Incineration

The rotary kiln incineration system is commonly a two-stage operation, the first stage being the rotating kiln barrel, and a secondary combustion chamber for completion of the oxidation. The rotating kiln barrel is a refractory-lined cylinder installed at a slight slope to cause the solid material to tumble over itself and travel down the length of the barrel. Rotary kilns can be configured to accept liquid, solid, and sludge wastes. This feature is one of the reasons that rotary kilns have found such wide application in the commercial incineration field.

Combustion gases and volatilized organics from the kiln are then treated in a downstream secondary combustion chamber for complete oxidation. The kiln is typically operated at relatively high temperatures, 700 to 1,300 °C. Tumbling action in the kiln continually exposes fresh waste surface to the high temperature radiant heat from the burner and refractory walls and to the oxygen in the combustion air. Ash and noncombustibles are continuously discharged into an ash handling system. Seals are provided at both ends of the rotating kiln shell to minimize air in leakage.

Rotary kiln incinerators can be designed to operate either in a controlled air or excess air mode. In some large commercial incineration systems, 200 liter drums filled with waste can be fed into the rotary kiln. Design for injection of whole drums rotary kiln is a challenge mechanically and operationally. The operational challenge is maintaining good destruction



conditions with the instantaneous input of energy from the volatilization and subsequent combustion of the wastes. Additionally, the drums could damage the refractory as they fall into the kiln. The US Department of Energy operates rotary kiln "mixed" waste incinerators at the Oak Ridge and Savannah River sites.

(Management of low and intermediate level radioactive wastes with regard to their chemical toxicity; Waste Technology Section, International Atomic Energy Agency, 2002)

4.1.2 PLASMA TECHNOLOGIES

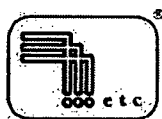
4.1.2.1 AC Plasma

Destruction systems incorporating their patented Plasmatron AC plasma are designed by Scientific Utilization International for the destruction of hazardous wastes. The alternating current (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.

DRE and emission of pollutants are expected to be similar to the inductively coupled radio frequency (ICRF) plasma process. The flue gas volume for a 50 kg/h destruction system is estimated at 20 Nm³/h.

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.

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)



4.1.2.2 Argon Plasma Arc

An argon plasma arc is generated at 10,000 °C using a special 200 kW unit which was developed by Siddons Ramset. The plasma arc atomises the halons or CFC which are then mixed with steam from an electric boiler. The gas mixture is rapidly cooled by an internal primary cooling circuit using a cooling tower mounted off the skid. The cooled gas is then quenched using caustic soda, at a controlled pH, which creates a salt solution. The salt solution is circulated with the caustic quench solution and discharged to sewer in a controlled manner via an effluent tank. The quenched gas is then scrubbed and vented to atmosphere.

(<http://www.pdf.com.au/article.asp?CategoryID=3&TopicID=15&ArticleID=30>)

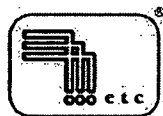
4.1.2.3 Inductively Coupled Radio Frequency Plasma

Gaseous CFC and steam are fed through the plasma torch where temperatures of 10,000 °C are achieved in a 185 kW ICRF torch. The gases enter directly into the destruction reactor maintained at about 2,000 °C for about 2 seconds. Subsequently, the gases are cooled and scrubbed with caustic solution to remove acid gases. It is also possible that the radio frequency (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.

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. This process has demonstrated high destruction efficiencies and very low PCDD/PCDF emissions on a commercial scale.

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)



4.1.2.4 Microwave Plasma

This process feeds microwave energy at 2.45 GHz into a specially designed coaxial cavity to generate 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 CFC with water vapour is fed to the plasma and is broken down at temperatures exceeding 6,000 °K into the dissociated state, after which HCl, HF, CO and CO₂ are formed. The acid gases are scrubbed in a tower with 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.

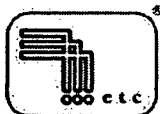
The microwave plasma process was developed in Japan by Mitsubishi Heavy Industries, Ltd. The development of the process was started in 1997 by Mitsubishi Heavy Industries, Ltd. and launched in the market in 2000. The plasma approach was selected to provide a very compact design that could be applied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

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)

4.1.2.5 Nitrogen Plasma Arc

Nitrogen plasma-arc technology for destroying solid wastes is in its infancy. In theory, a plasma-arc system consists of a nitrogen plasma-arc torch in a primary chamber, a secondary combustion chamber, exhaust-gas treatment systems, and a waste-handling system. In the primary chamber, high temperatures (2,000 °F) from "an electrical arc" produces highly ionized gases or plasma that causes instant breakdown (pyrolysis) of the waste. The organic waste is volatilized and the inorganic waste is melted into a slag maintained at 3,000 °F. In the secondary chamber, combustion air and fuel oil are added to maintain a temperature of 2,200 °F and ensure complete combustion. The exhaust gases from the secondary chamber are mixed with ambient air and cooled to 570 °F prior to exhaust gas scrubbing. The exhaust-gas system cools and cleans the exhaust gas before releasing it to the atmosphere at a temperature of about 140 °F.

(<http://www.denix.osd.mil/denix/Public/ES-Programs/Pollution/Policy/note5.html>)



4.1.3 OTHER NON-INCINERATION TECHNOLOGIES

4.1.3.1 Base Catalysed Dechlorination

Chlorinated organic compounds can be detoxified by reaction with sodium or potassium hydroxide in an oil carrier liquid at temperatures between 300 °C and 350 °C. In the presence of an organic accelerator, which is a source for free radicals in the system, the de-chlorination reaction proceeds to a very high level of completion, within a few hours, leaving a residue that is a suspension of carbon, sodium chloride and unspent sodium hydroxide in the carrier oil. This reaction product usually requires no further treatment.

This process has been patented worldwide by the BCD Group in the USA. Enterra Pty Ltd is a licensee of the BCD Group. Enterra Pty Ltd and the BCD Group are jointly promoting this technology as the BCD process.

The BCD process has the advantage of being able to treat compounds with up to 50% of chlorine (typical concentrations are usually 25-30% chlorine).

The products of the BCD reaction are carbon, sodium chloride (common salt), potassium chloride (where potassium hydroxide is used) and unspent sodium hydroxide (caustic soda) suspended in the oil carrier liquid.

The raw materials used for the Sydney Olympic project are sodium hydroxide, accelerator (a vegetable oil, fatty acid or alcohol) carrier oil and the organo-chlorine compound (i.e. waste), which can be in solid form or often in solution or a slurry in the carrier oil. The reaction process is conducted on-site in a 3 m³ carbon steel, externally electrically heated vessel equipped with appropriate condensing and vapours treatment systems. The reactor is pressurised and all oxygen is excluded by the introduction of nitrogen gas utilised as a safety blanket.

Reaction mechanism

The chemical reaction that was thought to occur is broadly represented in the following equation. It can be interpreted as a hydro-dechlorination reaction where the chlorine atoms on the aromatic nucleus are replaced by hydrogen atoms. Detailed chemical reaction mechanism can be seen in below.

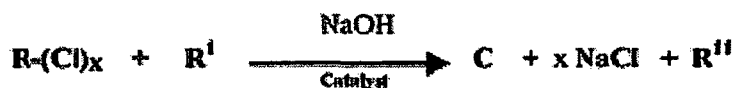


Where:



- R-(Cl)_x : organo-chlorine compound;
R^I : hydrogen donor (oil);
R - H : hydrogenated organo-chlorine compound, and
R^{II} : dehydrogenated donor.

Whilst the above reaction does occur to some extent, particularly when low concentrations of organo-chlorine compounds are treated, the main product that is observed is carbon. This cannot be explained by the simple hydro-dechlorination reaction mechanism shown above.



Intermediate products that arise from the sequential dechlorination of an aromatic nucleus are not observed to any significant degree. Thus, for hexachlorobenzene, which contains six chlorine atoms, pentachloro, tetrachloro or other lower chloro substituted benzenes are not detected - the main reaction product is carbon.

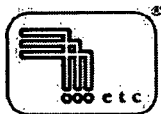
The process can be sub-divided in six unit operations:

- Waste or feed preparation;
- Caustic preparation;
- Hot oil pre-heating and transfer;
- Caustic and waste injection;
- Reaction, sampling and testing; and
- Treated product transfer.

Disadvantage: Beside the fact that this process can only treat (directly) fluids, the process also suffers from being a batch process and not a continuous process. This can be partly overcome by erecting several parallel processes, but that might influence the cost per kg treated waste. Furthermore, the process demands the heating up and successive cooling down of bearing oil for the process to run, which is demanding much energy. Finally, the process produces a rest product that needs conventional incineration, and because of the high load of chloride herein there is an intrinsic risk of dioxin production from this.

Advantage: Toxic material comprising up to 100% pure chlorinated hydrocarbons can be destroyed in 30 to 90 minutes. This is one of the big advantages of the BCD - technology compared to incineration technology that can only treat material containing from 2 to 10% chlorine. Furthermore, the gas production from the process is low and seems to be very low in dioxin emission.

The plant is a mobile structure and re-location costs only count for 10% of the initial capital costs. The pricing for re-location is assessed to be higher



and follows in line with e.g. GPCR and Semi mobile incineration units (up to 40-50% of investment capital costs).

(Detailed Review of Selected Non-Incineration and Incineration POPs Elimination Technologies for the CEE Region; Danish Environmental Protection Agency; 2004)

4.1.3.2 Gas Phase Catalytic Dehalogenation

Hitachi Ltd. of Tokyo, Japan has developed a process in which CFC 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.

The Hitachi process has been demonstrated to successfully destroy CFC and a similar process has been commercialized for perfluorocarbon decomposition as well as PCB destruction. Commercial destruction of PFC has demonstrated a destruction efficiency exceeding 99%. 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 \$US 5-7/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.

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)

4.1.3.3 Gas Phase Chemical Reduction

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 CFC are chemically reduced to methane, hydrogen chloride (HCl) and hydrogen fluoride. The methane is recovered and reused as



a fuel for the system components, while the acids are neutralized with caustic or lime.

ELI Eco Logic International Inc. (Eco Logic) of Rockwood, Ontario developed and commercialized 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. The company has destroyed PCB waste and chlorobenzene waste on a commercial scale to DRE exceeding 99.9999%. Eco Logic has also destroyed PCB, DDT and hexachlorobenzene waste on a commercial scale to DRE 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.

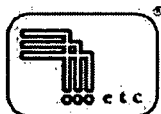
(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)

4.1.3.4 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 lab-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 and 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 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. Costs are estimated to be less expensive than incineration for ODS, based on extrapolation from experience with PCB waste disposal.

(Guidance Document on Disposal Technologies for Ozone – Depleting Substances (ODS) in Canada; Cantox Environmental Inc.; 2000)



4.1.3.5 Solvated Electron Decomposition

The process is a batch process involving two simple vessels; one a heated reaction vessel and the other 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 CFC, HFC, refrigerant blends and halons at greater than 99.99% efficiency.

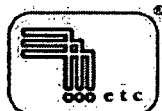
Estimated data was provided for a 50 kg/h destruction system. The flue gas volume has been estimated at 80 Nm³/h based on combustion of the methane/ethane product gas with air.

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. It has been applied successfully to Polychlorinated Biphenyls (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.

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)

4.1.3.6 Super Heated Steam Reactor

In the super-heated steam reactor process, decomposition of ODS takes place in the gaseous phase at elevated temperatures. CFC, 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 850-1,000 °C. The decomposition of CFC, 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 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 CFC and HCFC, but has been recently used to decompose HFC. 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. Destruction costs on 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.

(UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002)

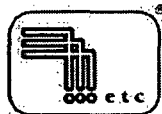
4.1.3.7 UV Photolysis

UV-photolysis is the process by which chemical bonds of the contaminants are broken by the energy associated with UV light. When light is incident on an object, the photons may be reflected, transmitted, or absorbed. When UV photons enter a medium (water, for example), they are both transmitted and absorbed by the medium and its constituents (dissolved species including organic and inorganic substances). Photons that are absorbed may initiate a photolysis reaction. In other words, the treatment of a contaminant starts with energy (in the form of photons from a UV light source) being absorbed by a contaminant molecule. A contaminant molecule will undergo the photolysis reaction if:

- The contaminant molecules in water are capable of absorbing UV photons
- The energy holding the chemical bonds in the molecule together is less than the energy of the UV photons absorbed.

In other words, the treatment of a contaminant starts with energy (in the form of photons from a UV light source) being absorbed by a contaminant molecule.

(<http://www.trojanuv.com/en/business/ECTadditionalinfo.aspx>)



4.1.3.8 Vitrification

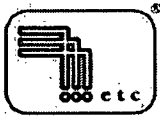
A high-temperature vitrification process can convert hazardous waste into a nonhazardous glass/ceramic matrix, which can be used as a commercial product. Organic components in the waste stream are gasified by the system and utilized as an auxiliary energy source. Inorganic components of the waste stream are incorporated into the glass/ceramic matrix. The glass/ceramic matrix is extremely stable and passes typical regulatory leachate tests.

The vitrification system consists of four sections: (1) feed preparation, (2) preheater, (3) vitrifier/converter, and (4) air pollution control/off gas treatment system. The feed preparation system consists of a counter-current rotary drum dryer, batch surge bin to maintain uniform waste feed and allow for the addition of glass formers, and auger feeders to convey the waste to the preheater. The preheater is an indirect gas-fired auger preheater that heats the waste to over 1,100 °F. This temperature effectively gasifies the organic contaminants contained in the waste stream to allow them to be used as fuel. The vitrifier/converter heats the inorganic waste to 2,700 °F in a well-mixed chamber. Oxygen enriched natural gas is the primary energy source for the vitrifier/converter. The molten glass/ceramic exits the vitrifier through a discharge system that allows the molten material to be shaped into useful products. Flue gas from the vitrifier flows through a high temperature heat exchanger. The cooled flue gases pass through a dry baghouse for particulate capture, a wet acid/gas packed tower venturi scrubber, an ammonia scrubber to remove NO_x, and an activated carbon filter to remove any trace organics. Dust from the baghouse is recycled back into the vitrification process.

Benefits:

- The system is compact and transportable.
- Can treat a variety of metal contaminated wastes while achieving regulatory leachate and land disposal limit requirements.
- Can process mixed organic/inorganic waste streams in solid and/or sludge forms on a batch or continuous basis.
- Uses the energy content of the organic waste contaminants to minimize operating costs.
- Converts hazardous wastes into nonhazardous forms which can be used to manufacture commercial products and provides a permanent treatment solution.

Capital costs, including installation, range from \$2,000,000 for a solid/dust system to \$2,500,000 for a sludge system. Both systems process 500-1,000 kilograms per hour of waste material. Operating costs of the vitrification process range from \$100 to \$420 per ton.



(http://p2library.nfesc.navy.mil/P2_Opportunity_Handbook/11_5.html)

Biodegradation Technology

History of microbial decomposition of ODS was described by Oremland. Lovley and Woodward first demonstrated bacterial removal of near-atmospheric concentrations (i.e., mixing ratios) of CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) during incubation of anoxic soils, sediments, and bacterial cultures. Krone and Thauer observed degradation of high concentrations of CFC-11 by *Methanosarcina barkeri*, and reductive dehalogenation was implicated. Removal of CFC-11 and CFC-113 (CH_3CF_3) in denitrifying groundwaters and dechlorination of CFC-11 in aquifer material undergoing sulfate reduction has been reported. Vertical profiles of CFC-11 and CFC-12 in the anoxic waters of the Black Sea and Saanich Inlet suggest that biodegradation is occurring. All together prove that anoxic ecosystems remove CFC from the atmosphere. However, elsewhere, CFC display conservative distribution patterns hence, their biodegradation is confined to anoxic environments. Such restricted locales have a minor impact on the atmospheric residence times for CFC.

In contrast, HCFC are more reactive and should be more susceptible to bacterial attack. Metabolism of some HCFC by methanotroph has been reported, and complete oxidation was implicated by the stoichiometric recovery of fluoride. However, no work has been done with soils or sediments to determine if the observations made with cultures can be extrapolated to natural systems. In addition, the experiments with methanotroph cultures were conducted at very high concentrations (1,000 ppm), whereas troposphere mixing ratios of HCFC-21 are about 0.1 ppb. It is not known whether soil microbes can degrade HCFC present at low concentrations (e.g., parts-per-billion levels), let alone at troposphere mixing ratios (e.g., sub-parts-per-billion levels). This study examined the ability of soils and sediments to metabolize HCFC-21 (CHCl_2F) and HCFC-123 (CHCl_2CF_3) and observed ongoing microbial degradation at concentrations as low as a few parts per billion.

The literature survey demonstrates that in many cases, chlorinated compounds are completely mineralized to benign end products and biodegradation can occur rapidly. Most compound categories include chlorinated structures that are used to support microbial growth. Combinations of redox conditions are favourable for the biodegradation of highly chlorinated structures that are recalcitrant to degradation under aerobic conditions. However, under anaerobic conditions, highly chlorinated structures are partially dehalogenated to lower chlorinated counterparts. The lower chlorinated compounds are subsequently more readily mineralized under aerobic conditions.



Principles of biodegradation

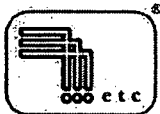
Basic principles of ODS biodegradation was described by Field and Alvarez in 2004. The microbial degradation of a contaminant typically occurs because a micro-organism can benefit from the use of the contaminant as an electron donor and carbon source to support growth. The redox reactions result in the flow of electrons from the substrate to a terminal electron acceptor (e.g. an oxidant such as O_2) and the release of energy that is used to support cell synthesis. Growth of the microbial population results in an increase in the biocatalyst and, thus, the rates of biodegradation can increase. Aside from O_2 , a large number of alternative terminal electron acceptors can be utilized in the absence of O_2 to support anoxic respiration. Ecological significant electron acceptors include: the use of NO_3^- , known as denitrification; the use of Fe^{3+} bearing minerals such as ferrihydrite ($Fe(OH)_3$), known as dissimilatory iron reduction; the use of SO_4^{2-} , known as sulfate reduction; and the use of CO_2 , known as methanogenesis.

On the other hand, the chlorinated compound can serve as the electron acceptor in a process known as halorespiration. During this type of metabolism anoxic decomposition of simple organic substrates (e.g. lactic acid) is linked to the use of chlorinated compounds as electron acceptors resulting in their reductive dehalogenation. Halorespiration is also linked to growth contributing to increases in biocatalyst concentration as degradation proceeds. Halorespiration is an energetically favourable microbiological process.

Microorganisms can also fortuitously transform chlorinated compounds while they are degrading non-halogenated primary substrates. In this case, enzymes expressed to degrade the primary substrate accidentally display activity with the chlorinated compound. This type of metabolism is referred to as co-metabolism. A special type of co-metabolism involves the oxidation of chlorinated solvents by oxygenases, which is known as co oxidation. The classic example is the oxidation of chlorinated solvents by the methane monooxygenase expressed by methylotrophic organisms to oxidize methane. Under anaerobic conditions, a common form of co-metabolism is the reaction of reduced enzyme cofactors with chlorinated solvents, resulting in their reductive dehalogenation. The degradation of chlorinated solvents during co-metabolism is not linked to growth. Thus the concentration of the biocatalyst will depend on the addition of the primary electron donating substrates and electron acceptors to the system.

Biodegradation of ODS

This method is a perspective method for destruction of minor amount of CFC compounds. Degradation by microorganisms is kinetically exacting process. The reaction itself is realized at low concentrations of these



compounds. That is the reason why optimal conditions for realization of such a processes are wanted.

Criteria can be set:

- Reactor volume
- Process temperature
- Microorganisms used
- Process duration
- Aeration of reaction mixture by oxygen or by air
- Nutrient for microorganisms
- Physical-chemical properties of chemical substances for degradation
- Methods of process controlling
- Regenerativity of microorganisms
- Way of disposal of degraded products

As we can see, biological systems have a lot of variables which are needed to be defined for successful bioprocess. Some of them are technically simple; vice versa some of them can be more difficult for direct application in commercial scale.

4.2 APPLICATIONS

Special preconditions are required for technologies which are appointed to destruct halons and foams containing ODS.

Destruction technologies for foams

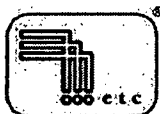
- municipal solid waste incinerators
- rotary kiln incinerator

Destruction technologies for halons and HCFC

- CFC, HCFC and halons: argon plasma arc
- CFC and HCFC: - nitrogen plasma arc, microwave plasma, gas phase catalytic dehalogenation and super-heated steam reactor

4.3 PROPOSAL FOR FURTHER STEPS

In general, it can be said that there is a variety of technologies which can fulfill criteria defined by Montreal Protocol for destruction of ODS.



Environmental criteria are related mainly to destruction efficiency, energy consumption and environmental emissions.

To define economically appropriate technologies for ODS destruction there specific conditions in different countries and different amount of chemicals to be destroyed have to taken into account. Both, investment costs as well operational costs should be considered as well.

Based on available data, destruction costs are lowest in plasma technologies, but these are technologies of high power consumption. Emission levels are relatively low.

Non-incineration technologies have low emission rates but economical feasibility depends on specific type of ODS and technology to be applied due to fact that these technologies are chemical reactions specific.

Low power consumption is required for incineration technologies, but these have a high emission levels. Investment costs are high that pose difficulties for many countries.

Among emerging technologies a biological degradation of ODS can be mentioned. It is proven in some research and science reports that microorganisms are able to decompose ODS. These methods are not commercially used for ODS directly but for decontamination of environmental media. Microorganisms are used just for bioremediation of soils or polluted waters. However, this method could be a new contribution on the field of destruction technologies. Further steps should be done in this area of research and progress to find practical applications.

Two types of reactors could be of further interest:

1. "Fermentationer"

It is working on principle that microorganisms are in water phase and substances for biodegradation are anchored in porous material (SiO_2 , zeolites, limewashes, activated carbon and the like) – they are adsorbed. Process will take place on the boundary of phases and the metabolites will be in a dilution. For better contact of phases an emulsifiers can be added.

2. "Mediator"

This process is opposite one to the previous. Microorganisms will anchor – react with solid phase and degraded substance will be released on the medium or it will be saturated in water.

In this case process is at work on contact of phases. After adequate quantity of layers of microorganisms, these will get in water phase. A combined process will be running.



Temperature for biodegradation ranges from 20 to 40 °C by type of microorganisms and pH ranges from 5.2 to 7.5.

Nutrient for microorganisms consists of donors of nitrogen, carbon and phosphorus – elements essential for life of microorganisms. For example: sucrose in the form of peeled molasses, methanol, nitrates, and phosphates. Basically it can be said that this process is non-problematic. Problem of regulation of optimal concentration of microorganisms can be solved by nitrate supply or acutely by addition of H_2O_2 .

Volume for mobile unit could be approximately 500 l, for stationary one 1,500 l.

Duration of the process is different for individual type of microorganism and for type of chemical substance under the process. However, it should not exceed few weeks. Here we have to consider an amount of chemical compound and also the concentration.

It is possible to use special microorganisms (based on to the literature data) or activated sludge. Combination of both is also possible.

Degraded products – probably HF- are needed to be removed from the reaction environment. They can be simply neutralized by buffering in reaction medium. Another way is neutralization with alkali medium or by addition of fine-grained calcite. This would be removed from medium after filtration and process could continue in a new cycle.

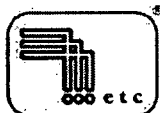
Analytical monitoring should be focused on the conditions in bioreactor: temperature, pH, nutrients, oxygen, volume of products, and volume of decomposed and undecomposed substances.

There is possible biodegradation in some types of substances, in some there is not. These types of chemicals are identified in the literature. But during the research and development of new – also genetically modified – microorganisms it is possible to expand this group of chemicals in the future.

For successful decomposition process it is necessary to choose a proper chemical compound for degradation and at the process conditions certain compromise should be accepted to optimize it for separate substance and microorganism.

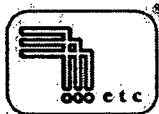
Conclusions:

- Comparative study for commercially available technologies should be done taking into account state of the art;



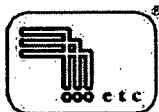
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- Guidance document for disposal of ODS should be developed with aim to advice countries based on the specific needs and conditions;
- Specific concern of chemical treatment based on national vs. regional needs should be defined ;
- Biological methods for mobile units to address relatively small amounts of ODS on local level should be investigated.



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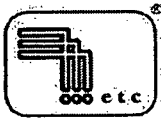
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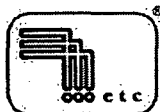
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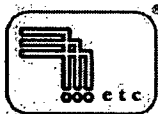
APPENDIXES



Appendix No. 1

Advantages and Disadvantages of Relevant Destruction Technologies

Technology	Advantages	Disadvantages
Incineration Technologies		
<i>Cement Kilns Incineration</i>	<ul style="list-style-type: none"> * large existing capacities in the world * relatively low cost 	<ul style="list-style-type: none"> * need to controll an input rates of fluorine and chlorine * not applicable for destruction of CFC and halon wastes
<i>Container Based Incineration System</i>	<ul style="list-style-type: none"> * mobile * high DRE 	<ul style="list-style-type: none"> * depending on many factors * high skilled personnel needed * poor control of residual prodcpts
<i>Gaseous/Fume Oxidation</i>	<ul style="list-style-type: none"> * applicable for CFC and halon waste * high DRE * low emissions * relatively low cost 	<ul style="list-style-type: none"> * generally located on fluorocarbon manufacturing site/not available for use of others * not applicable for destruction of CFC in foams
<i>High Performance Incineration</i>	<ul style="list-style-type: none"> * high DRE 	
<i>ICFB</i>	<ul style="list-style-type: none"> * high DRE * simplicity 	
<i>Liquid Injection Incineration</i>	<ul style="list-style-type: none"> * established and proven technology * relatively low cost 	<ul style="list-style-type: none"> * screening limit for PCDD/PCDF emission not met/relatively high rate of emissions * not applicable for destruction of foams
<i>Municipal Solid Waste Incineration</i>	<ul style="list-style-type: none"> * technology being used for the destruction of foams containing ODS * faire wide availability * relatively low cost 	<ul style="list-style-type: none"> * potentiall possibility of exceeding of screening limit for PCDD/PCDF
<i>Reactor Cracking</i>	<ul style="list-style-type: none"> * large commercial scale/many years * low formation of PCDD/PCDF * relatively low cost 	<ul style="list-style-type: none"> * concern about the availability of an economic source of hydrogen * intolerrant process for bromine containing ODS/can not be used for destruction of foams and halons
<i>Rotary Kiln Incineration</i>	<ul style="list-style-type: none"> * wide variety of liquid and solid wastes/foams and concentrated sources 	<ul style="list-style-type: none"> * very expensive



Technology	Advantages	Disadvantages
Plasma Technologies		
<i>AC Plasma</i>	<ul style="list-style-type: none"> * high DRE/CFC and halons * low emissions * torch electrically simple/mechanically rugged * possible to operate with air/steam/plasma gases * tolerant of oil contamination in ODS 	<ul style="list-style-type: none"> * high energy consumption
<i>Argon Plasma Arc</i>	<ul style="list-style-type: none"> * non-incineration technology * high DRE/CFC and halons * low emissions of PCDD/PCDF * easily transported 	<ul style="list-style-type: none"> * need to remove oil before destruction * not applicable for destructio of foams
<i>Inductively Coupled Radio Frequency Plasma</i>	<ul style="list-style-type: none"> * commercial available * high destruction of CFC * low emissions 	<ul style="list-style-type: none"> * high energy consumption
<i>Microwave Plasma</i>	<ul style="list-style-type: none"> * high destruction efficiency * low emissions 	<ul style="list-style-type: none"> * production of halide salts * high energy consumption
<i>Nitrogen Plasma Arc</i>	<ul style="list-style-type: none"> * very compact in size/9 m x 4.25 m * mobile by truck/on-site treatment 	<ul style="list-style-type: none"> * limited destruction capacity * production of halide salts * high energy consumption
Other Non-Incineration Technologies		
<i>Base Catalysed Dechlorination</i>	<ul style="list-style-type: none"> * process being able to treat compounds with up to 50% of chlorine * on-site treatment * low dioxin emissions 	<ul style="list-style-type: none"> * direct peocessing of fluids only * batch process * high energy consumption
<i>Gas Phase Catalytic Dehalogenation</i>	<ul style="list-style-type: none"> * high efficiency in destroying of CFC * no PCDD/PCDF emissions * low operating temperature * low mass emissions 	<ul style="list-style-type: none"> * higher destruction cost * production of halide salts
<i>Gas Phase Chemical Reduction</i>	<ul style="list-style-type: none"> * very high destruction efficiency * low emissions * applicable for solids/potentially including foams * transportability 	<ul style="list-style-type: none"> * lack of experience in destroying of ODS
<i>Liquid Phase Chemical Conversion</i>	<ul style="list-style-type: none"> * low capital investment * almost emissions free * mobile 	<ul style="list-style-type: none"> * for ODS just tested, not commercially used



Technology	Advantages	Disadvantages
<i>Solvated Electron Decomposition</i>	<ul style="list-style-type: none"> * simplicity * low operating temperature * high destruction efficiency * low emissions 	<ul style="list-style-type: none"> * lack of demonstration of a destruction on a commercial scale * careful attention to operating procedures needed * very expensive
<i>Super Heated Steam Reactor</i>	<ul style="list-style-type: none"> * high destruction efficiency * low emissions * simple design/safe to operate * applicable for mobile destruction/to all but foams * applicable to all but foams 	<ul style="list-style-type: none"> * production of halide salts
<i>UV</i>	<ul style="list-style-type: none"> * relatively simple 	
<i>Vitrification</i>	<ul style="list-style-type: none"> * compact and transportable technology * minimizing of operating costs 	



Appendix No. 2

Cost Information on Relevant Destruction Technologies

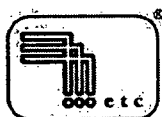
Technology		Capital cost/USD	Destruction costs/USD/kg	Source
1	AC Plasma		3-5	1
2	Argon Plasma Arc			
3	Base Catalysed Dechlorination	0.8 - 1.3 mill.	3.3-6.6	3
4	Cement Kilns Incineration	92* mill.		3
5	Container Based Incineration System	2.6 - 3 mill.	0.3	3
6	Gaseous/Fume Oxidation		3-5	1
7	Gas Phase Catalytic Dehalogenation	1 mill.	2-3	1
8	Gas Phase Chemical Reduction		3-5	1
9	High Performance Incineration			
10	ICFB Incineration			
11	IC RF Plasma			
12	Liquid Injection Incineration			
13	Liquid Phase Chemical Conversion			
14	Microwave Plasma			
15	Municipal Solid Waste Incineration			
16	Nitrogen Plasma Arc			
17	Reactor Cracking	4 mill.		4
18	Rotary Kiln Incineration			
19	Solvated Electron Decomposition		7	1
20	Super Heated Steam Reactor	0.3 mill.	2-3	1
21	UV Photolysis			
22	Vitrification	2-2,5 mill.	0.3	5

* Comprises 24 million USD investments in the cement kiln and 68 million USD for the hazardous waste treatment plant. Both investments are necessary for the correct treatment

Legend:

-  destruction technologies of ODS recommended by Parties to the Montreal Protocol
-  destruction technologies of ODS recommended by Cantox Environmental Inc.

- 1 UNEP Report of the Technology and Economic Assessment Panel, Volume 3B, Report on the Task Force on Destruction Technologies, 2002
- 2 <http://www.pdf.com.au/article.asp?CategoryID=3&TopicID=15&ArticleID=30>
- 3 Detailed Review of Selected Non-Incineration and Incineration POPs Elimination Technologies for the CEE Region; Danish Environmental Protection Agency; 2004
- 4 http://www.hug-engineering.de/index.htm?DestructionTechniques_01.htm
- 5 <http://www.uneptie.org/ozonaction/library/mmcfiles/multiples/3521-e-file7.pdf>

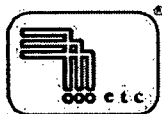


Appendix No. 3

Ranking of Destruction Technologies of ODS Realized by CANTOX ENVIRONMENTAL, INC.

Overall Ranking

1. Argon Plasma
2. Cement Kiln Incineration
3. Catalytic Dehalogenation
4. Reactor Cracking
5. Vitrification
6. Rotary Kiln Incineration
7. AC Plasma
8. Liquid Injection Incineration
9. Gas/Fume Incineration
10. Liquid Phase Chemical Conversion
11. IC RF Plasma
12. High Performance Incineration
13. Gas Phase Chemical Reduction
14. ICFB Incineration
15. Solvated Electron
16. UV Photolysis

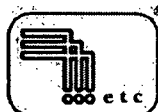


Incineration Technologies

Technology	Liquid Injection Rotary Kiln Gas/Fume ICFB	Cement Kiln	High Performance	Reactor Cracking
Vendor	Generic	Generic	Bovar	Solvay
Operating Temp (°C)	900 to 1100	1500	1200	2000 to 2600
Residence Time (sec)	1-2	10	2	
DE	99.99% to 99.999%	99.99%	99.9999%	99.999%
PCDD/PCDF	0.1	0.1	0.1	0.1
Effluents	GHG Halide salts	GHG	GHG Halide salts	
Features	Co-incineration	Limited coincineration	Co-incineration	Dedicated HF, HCl recovery
Cost (\$/kg CFC)	3.50	3.25	4.00	3.75

Plasma Technologies

Technology	Inductively Coupled RF	DC Argon	AC
Vendor	MITI	SRL Plasma	SUI
Operating Temp (°C)	2000	3000	
Residence Time (sec)	2	0.020	
Efficiency	Elec	95%	95% to 98%
	Thermal	50%	65% to 85%
DE	99.99%	99.9999%	99.99%
PCDD/PCDF	0.025	0.025	
Effluents	Halide salts	Halide salts	Halide salts
Features	No electrodes enables wide range of gases	Requires inert gas	No need for high frequency AC Tolerates oily gases
Cost (\$/kg CFC)	2.50	2.75	2.50



Other Non-Incineration Technologies (1)

Technology	Solvated Electron	UV Photolytic	Gas Phase Chemical Reduction
Vendor	Commodore Advanced Sciences	Process technologies, Inc.	Eli Eco Logic International Inc.
Process Description	Reaction with liquid ammonia and metallic sodium	UV irradiation of FC in air	Reaction at 850 C under reducing conditions
DE	99.99%	99.7%	99.9999%
PCDD/PCDF	0.01	0.01	0.06
Effluents	Halide salts	Non hazardous spent liners	Halide salts
Features	Methane & ethane byproducts Ammonia recycled	Liner is PTI proprietary mixture	Hydrogen, methane recovered and used as fuel
Cost (\$/kg CFC)	11.00	11.00	6.00

Other Non-Incineration Technologies (2)

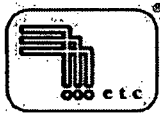
Technology	Gas Phase Catalytic Dehalogenation	Liquid Phase Chemical Conversion	Vitrification
Vendor	Hitachi Corp.	Ontario Hydro Technologies	Pure Chem, Inc.
Process Description	Reaction over metal oxide catalyst at 400 °C at atmospheric pressure	Reaction with KOH and polyethylene glycol at 100 °C	Plasma ODS destruction and fixation into glass frit
DE	99.999%	99.7%	99.9999%
PCDD/PCDF	0.01	0.01	0.1
Effluents	Halide salts	Halide salts	Glass frit capable of being returned to commerce
Features	Proprietary catalyst	Mobile systems	Proprietary chemicals used to form glass
Cost (\$/kg CFC)	3.60	4.00	3.80



Appendix No. 4

Questionnaire Table with list of Vendors

Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
Bond Retail Services Ltd	United Kingdom	Garry Hodge Account Manager Bond House, New Road, Sheerness, Kent. ME12 1BB Tel: 01795-668515 Fax: 01795-660206 E-mail: garryh@bond-group.co.uk Brian Hurkett Supervisor Bond House Tel: 07885-055353 Fax: 01795-430673 E-mail: info@bond-group.co.uk Website: www.bond-group.co.uk		
DASCEM Holdings Pty Ltd	Australia	P.O. Box 285, World Trade Centre Melbourne Victoria 3005 Australia +61 3 9649 7405 +61 3 9649 7410 susanne.clarke@dascem.com.au http://www.dascem.com.au /	CFCs Halons HCFCs Other (the process is suitable for destruction of all liquid and gaseous ODS).	
Eco Solutions Ltd	United Kingdom	Yianni Stamataris Managing Director 91, Ware Rd, Hoddesdon, EN119AD Tel: 01992 461229 or 07960 835757 Fax: E-mail: ecosolutions@fsmail.net Website: www.ecosolutionsrecycling.com		



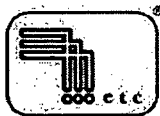
EKOTOXIKOLOGICKÉ CENTRUM BRATISLAVA, s.r.o.
 Nádražná 36, 900 28 Ivanka pri Dunaji, Slovak Republic

Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
Environcom	United Kingdom	Neil Pattison Environmental Manager Houghton Road Industrial Estate, Houghton Road, Grantham, Lincolnshire Tel: 01476564942 Fax: 01476564948 <u>E-mail:</u> neilnsue@pattison26.freese.rve.co.uk Ian Gray Factory Manager Houghton Road Industrial Estate, Houghton Road, Grantham, Lincolnshire Tel: 01476564942 Fax: 01476564948		
Environcom	United Kingdom	Gary Thomson Sales Elvingstone Science Centre East Lothian EH33 1EH Tel: 07966502288 Fax: 0131 663 2712 <u>E-mail:</u> Gthomson25@aol.com Website:		
Earth Tech Canada Inc.	Canada	Mail Bag 1500 City Swan Hills Alberta ToG 2Co Canada +1 780-333-4197 +1 780-333-4196 http://www.shtc.ca/	CFCs Halons HCFCs Methyl bromide Foam that contains ODS	
Ekokem Oy Ab	Finland	PL 181, Kuulojankatu 1 Riihimäki 11101 Finland +358 10 7551 000 +358 10 7551 300 http://www.ekokem.fi/	CFCs HCFCs Halons Foam that contains ozone depleting substances Methyl bromide	



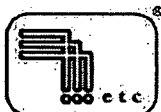
EKOTOXIKOLOGICKÉ CENTRUM BRATISLAVA, s.r.o.
 Nádražná 36, 900 28 Ivanka pri Dunaji, Slovak Republic

Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
Evans Logistics	United Kingdom	Howard Evans General Inquiries Park Avenue, Aberystwyth, Ceredigion Tel: 01970 626277 Fax: 01970 639042 E-mail: howard		
Global Environmental Recycling Company Ltd	United Kingdom	Bob Shepherd Director Unit D, Maritime Business Park, Campbeltown Road, Birkenhead, Merseyside CH41 9B Tel: 0151 647 2211 Fax: 0151 647 0022 E-mail: robert@shepherdg90.fsnet.co.uk		
Goodearth Recycling Ltd	United Kingdom	George Watts Managing Director 12 Bedehouse Bank, Bourne, Lincs PE10 9JX Tel: 01778 421052 Fax: 01476 576263 E-mail: gw.goodearth@freeuk.com		
HW Martin Waste Ltd	United Kingdom	Steve Pollard General Inquiries Fordbridge Lane, Alfreton, Derbyshire DE55 5JY Tel: 01773 860600 Fax: 01773 813305 E-mail: hwmartinwaste@aol.com		
INDAVER N.V.	Belgium	Poldervliet 5, Haven 550 Antwerp 2030 Belgium +32-3-568.49.11 +32-3-568.49.99 http://www.indaver.com/	CFCs Halons HCFCs Foam that contains ODS	



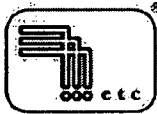
EKOTOXIKOLOGICKÉ CENTRUM BRATISLAVA, s.r.o.
 Nádražná 36, 900 28 Ivanka pri Dunaji, Slovak Republic

Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
International Waste Management Group	United Kingdom	John Burnett Director Unit 27, Mayfield Industrial Estate, Dalkeith, Midlothian Tel: 01316631131 Fax: 01316638138 E-mail: iwmg@btconnect.com Website: www.iwmg.co.uk		
JCM Group	United Kingdom	Paul Cynamon General Inquiries Tel: 01642 566003 Fax: 01642 566515 E-mail: fridges@jcm-uk.co.uk		
John Hornby & Sons Ltd	United Kingdom	Stephen Hillas Birkshall Lane, Bradford, BD4 8TB Tel: 01274 390856/01484 652777 Fax: 01484 461460 E-mail: stephen.hillas@refrigerationrecycling.co.uk Website: www.refrigerationrecycling.co.uk		
M Baker Recycling Ltd	United Kingdom	Julie-Ann Adams Client & Marketing Manager Baring House, 6 Baring Crescent, Exeter, Devon, EX1 1TL Tel: 01392-433912 Fax: 01392-411951 E-mail: ja@mbakergroup.co.uk Website: www.weedirective.co.uk		
New Hartley Recycling	United Kingdom	Geoff Copp 24 Bristol Street, New Hartley, Tyne and Wear NE25 0RJ Tel: 0191 2374661 Fax: 0191 2371262		

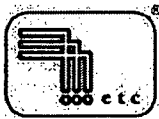


EKOTOXIKOLOGICKÉ CENTRUM BRATISLAVA, s.r.o.
 Nádražná 36, 900 28 Ivanka pri Dunaji, Slovak Republic

Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
NSD Global Ltd	United Kingdom	Harriet Mountford Projects Manager Greetwell Place, Limekiln Way, Greetwell Road, Lincoln, LN2 4US Tel: 0845 090 0027 Fax: 0845 090 0028 <u>E-mail:</u> sales@nsdglobal.com Steven Dipper MD Greetwell Place, Limekiln Way, Greetwell Road, Lincoln, LN2 4US Tel: 0845 090 0027 Fax: 0845 090 0028 <u>E-mail:</u> steve.dipper@nsdglobal.com		
NWP Recycling	United Kingdom	Shane Woods Marketing Manager 55 Cargaclougher Rd, Keady, Co Armagh, BT60 3RA Tel: 028 3753 1591 Fax: 028 3753 9426 <u>E-mail:</u> shane@nwp-recycle.com <u>Website:</u> www.nwp-recycle.com		
Onyx Magyarország Ltd.	Hungary	Bécsi út 131 Dorog Komárom-Esztergom H-2510 Hungary +36 (33) 512-700 +36 (33) 512-857 <u>titkarsag@onyyxmagyarorszag.hu</u> <u>http://www.onyyxmagyarorszag.hu/</u>	Halons	



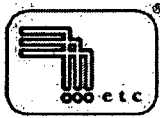
Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
Overton Recycling Ltd	United Kingdom	Dean Overton Director Alma St, Smethwick, Birmingham B66 2RX Tel: 01869 277998 Fax: 01869 278613 <u>E-mail:</u> fridges@overtonrecycling.com <u>Website:</u> www.overtonrecycling.com		
RAL Quality Assurance Association for the Demanufacturing of Refrigeration Equipment Containing CFCs	United Kingdom	Jeff Weeks UK Director 3 Carlton House, Stamford, Lincs PE9 1XP Tel: 01780 751 017 Fax: 01780 751 018 <u>E-mail:</u> infoUK@RAL-online.org Danik Humbles Co-ordinator 3 Carlton House, Stamford, Lincs PE9 1XP Tel: 01780 751 017 Fax: 01780 751 018 <u>E-mail:</u> infoUK@RAL-online.org <u>Website:</u> www.ral-online.org		
Redibag Recycling Plc	United Kingdom	Enquiries 43 Portland Place, London Tel: 01483 211002 Fax: 01483 479912 <u>E-mail:</u> enquiries@redibagplc.plus.com		



Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
Refrigerator Recycling UK Ltd	United Kingdom	Robert Sant Director Oak Works, Hopton Heath, Craven Arms, Shropshire, SY7 0QD Tel: 01547 530 317 Fax: 01547 530 228 <u>E-mail:</u> robert.sant@refrigeratorrecycling.co.uk Kim Tomkins Enquiries Oak Works, Hopton Heath, Craven Arms, Shropshire, SY7 0QD Tel: 01547 530 317 Fax: 01547 530 228 <u>E-mail:</u> enquiries@refrigeratorrecycling.co.uk <u>Website:</u> www.refrigeratorrecycling.co.uk		
RemTec International Corporate Headquarters	USA	6150 Merger Drive Holland, OH 43528 419/867-8990 419/867-3279 FAX Toll Free: 888/8REMTEC www.remtec.net	CFCs Halons HCFCs HFCs	
Shanks Waste Services Ltd	United Kingdom	Ms Jo Fitzpatrick Dunedin House, Auckland Park, Mount Farm, Milton Keynes, MK1 1BU Tel: 01908 202120 or freephone 0800 0282877 Fax: 01908 202131 <u>E-mail:</u> jo.fitzpatrick@shanks.co.uk John Brewster/Bob Seeley Scotland/Wales Tel: 0141 552 4347/01269 846203 <u>Website:</u> www.shanks.co.uk		



Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
Shore Recycling Ltd	United Kingdom	Shore Recycling Ltd Friarton Bridge Park Friarton Road PERTH PH2 8DD Tel. 01738 492950 Fax. 01738 563800 enquiries@shore-recycling.co.uk	CFCs	no destruction
Sims Group UK Limited	United Kingdom	Myles Pilkington Communications Coordinator Long Marston, Stratford-upon-Avon, Warwickshire, CV32 6DL Tel: 01789 720 431 Fax: 01789 720 940 E-mail: mpilkington@uk.sims-group.com Website: www.sims-group.com		no destruction
SimsMetal UK	United Kingdom	Pam Williams South Dock.Newport.Gwent.NP9 2WE Tel: 01633 250 650 Fax: 01633 250 850 E-mail: pwilliams@simsmetal.co.uk Website: www.simsmetal.co.uk		
SOLVAY FLUOR GmbH	Germany	Brüningstr. 50 Frankfurt 65926 Germany 495 118 572 721 495 118 572 178 http://www.solvay-fluor.com/	CFCs HCFCs HFCs	



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Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
Sulo MGB Ltd.	United Kingdom	Mrs Terry Brown Project Manager Unit 6 Lincoln Business Park, Lincoln Road, High Wycombe HP12 3RD Tel: 01494 511055 Fax: 01494 511044 E-mail: t.brown@sulo.co.uk		
TdB Incineração Ltda	Brazil	Avenida Ibirama, 518 Taboão da Serra SP 06785-000 Brazil (11) 41388317 (11) 41388311 fsouza@essencis.com.br http://www.essencis.com.br/	CFCs Halons HCFCs Methyl bromide	
Technowaste Limited	United Kingdom	Mark Hadley Director of Technical Services PO Box 27, Dorking, Surrey RH5 5AN Tel: 01306 631911 Fax: 01306 631901 E-mail: mark@technowaste.com Website: www.technowaste.com		
The WS Group	United Kingdom	David.W.Bavaird Operations And Logistics Director Bede House, St Cuthberts Way, Aycliffe Industrial Park, Newton Aycliffe, DL5 6DX Tel: 01325-379020 Fax: 01325-379036 E-mail: dbavaird@wastesolution.co.uk Website: www.wastesolution.co.uk		



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Company Name	Country	Contact	Substances that can be destroyed at this facility	Response
Valorec Services AG	Switzerland	Neuhausstrasse 90, Porte 91, Postfach 118 Basel 4019 Switzerland +41 61 468 86 55 + 41 61 468 86 60 werner.wagner@valorec.com http://www.valorec.ch/	CFCs Halons HCFCs Foam that contains ozone depleting substances Methyl bromide Other (methyl iodide)	Incineration of CFCs
Viromet Ltd	United Kingdom	John Taylor Manager North Lodge, Standon Lane, Ockley, Surrey RH5 5QR Tel: 01306 628068 Fax: 01306 628064 E-mail: sales@viromet.co.uk		
West Herts Recycling	United Kingdom	Nigel/Geoff Partners 1 The Guildhouse Croxley Green Rickmansworth Hertfordshire WD3 3HD Tel: 07870 534335 Fax: 01923 448228 E-mail: nigelc456@hotmail.com		



Numbers of questionnaires sent: 37

Number of answers received: 3



Table (appendix) of questionnaires

TECHNOLOGY/UNIT DATA

 	Destruction capacity	Unit		Cost	
		S	M	Investment	Operational
Chlorofluorocarbons	500 t				
	50 t				
Halons	500 t				
	50 t				
Other Fully Halogenated CFCs	500 t				
	50 t				
Carbon Tetrachloride	500 t				
	50 t				
Methyl Chloroform	500 t				
	50 t				
Hydro-chlorofluorocarbons	500 t				
	50 t				
Methyl Bromide	500 t				
	50 t				
HFC23	500 t				
	50 t				
Legend to the table:	Unit	S - stationary			
		M - mobile			



Appendix No. 5

List of Patents on Destruction Technologies of ODS

1. A Method and Apparatus for the Processing and Disposal of Foam Containing an Ozone Depleting Substances
- by Clarke Thomas (GB), Clarke Kenneth (GB); 2003
2. Destruction of Ozone Depleting Substances with Bases
- by Mouk Robert W, Abel Albert E, COMMODORE LAB. INC.; 1996
3. Methods for Destroying Ozone Depleting Substances
- by Mouk Robert W, Abel Albert E; COMMODORE LAB. INC.; 1996
4. Methods and Apparatus for the Decomposition and Re-Use-as-Resource Treatment of Ozone-Layer-Depleting Substances by Application of UV
- by Othaku Kuninobu (JP), Ohyama Takeshi (JP); TOKYO ELECTRIC POWER CO. (JP);1998
5. Methods for Destroying Ozone Depleting Substances
- by Mouk Robert W, Abel Albert E; SANDPIPER A.L. CORP. (US); 1995
6. Method for treating Ozone Layer Depleting Substances
- by Uchiyama Hiroshi (JP); EC CHEM IND. CO. (JP), ITOCHU FINE CHEMICAL CORP. (JP)