

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

**REPORT OF THE  
HALONS TECHNICAL OPTIONS COMMITTEE**

**DECEMBER 2018**

**TECHNICAL NOTE #5, REVISION 2**

**DESTRUCTION TECHNOLOGIES FOR HALONS AND OTHER HALOGENATED  
GASEOUS FIRE EXTINGUISHING AGENTS**



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On Substances that Deplete the Ozone Layer**

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The text of this report is composed in Times New Roman

Co-ordination: **Halons Technical Options Committee**  
Composition of the report: **Halons Technical Options Committee**  
Reproduction: **UNEP Ozone Secretariat**  
Date: **December 2018**

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**ISBN: 978-9966-076-56-4**

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## **Acknowledgements**

The UNEP Halons Technical Options Committee (HTOC) acknowledges with thanks the outstanding contributions from all individuals and organisations that provided technical support to Committee members.

The opinions expressed are those of the Committee and do not necessarily reflect the views of any sponsoring or supporting organisations.

The following persons were instrumental in developing this report:

### **Committee Co-chairs**

Adam Chattaway  
Collins Aerospace  
United Kingdom

Dr. Sergey Kopylov  
All Russian Research Institute for Fire Protection  
Russian Federation

Dr. Daniel Verdonik  
JENSEN HUGHES, Inc.  
USA

### **Members**

Jamal Alfizaie  
Consultant - retired  
Kuwait

Johan Åqvist  
FMV (Swedish Defence Materiel Administration)  
Sweden

Youri Auroque  
European Aviation Safety Agency  
France

Seunghwan (Charles) Choi  
Hanchang Corporation  
South Korea

Dr. Michelle M. Collins  
Consultant- EECO International  
United States

Khaled Effat  
Modern Systems Engineering - MSE  
Egypt

Carlos Grandi  
Embraer  
Brazil

Laura Green  
Hilcorp  
USA

Elvira Nigido  
A-Gas Australia  
Australia

Emma Palumbo  
Safety Hi-tech srl  
Italy

Erik Pedersen  
Consultant – World Bank  
Denmark

Dr. R.P. Singh  
Centre for Fire, Explosives & Environment Safety, Defence Research & Development  
Organization  
India

Donald Thomson  
MOPIA  
Canada

Mitsuru Yagi  
Nohmi Bosai Ltd & Fire and Environment Prot. Network  
Japan

### **Consulting Experts**

Pat Burns  
Retired  
USA

Thomas Cortina  
Halon Alternatives Research Corporation  
USA

Matsuo Ishiyama  
Nohmi Bosai Ltd & Fire and Environment Prot. Network  
Japan

Nikolai Kopylov  
All Russian Research Institute for Fire Protection  
Russian Federation

Steve McCormick  
United States Army  
USA

John G. Owens  
3M Company  
USA

John J. O'Sullivan  
Bureau Veritas  
UK

Mark L. Robin  
Chemours  
USA

Dr. Joseph A. Senecal  
FireMetrics LLC  
USA

Dr. Ronald S. Sheinson  
Consultant – Retired  
USA

Robert T. Wickham  
Consultant-Wickham Associates  
USA



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## Preface

Technical Note #5, *Halon Destruction*, replaces the chapters on this subject that have been part of previous Assessment Reports of the UNEP Halon Technical Options Committee (HTOC). Reports, beginning with the 2014 Assessment Report, contain an abbreviated chapter that briefly introduces the subject of *Destruction* and refers the interested reader to this document. The HTOC elected to take this approach as much of the information that, while important to understand when developing strategies for destroying halons, has been largely reported in prior editions of Assessment Reports. The Assessment Reports contain important new updates on evolving technologies, but this usually forms only a small portion of the chapter content. As such, it was deemed by the HTOC to make the *Destruction* subject a stand-alone document that is referenced by future Assessment Reports. By this approach those having particular interest in the technical aspects of the *Destruction* subject can access a self-contained document addressing those issues.

Following the Kigali Amendment to the Montreal Protocol, the role of the HTOC has broadened to now cover alternatives to halons, HCFCs and high-GWP HFCs. As such, the title for this Technical note has been changed to *Destruction of Halons and other Halogenated Fire Extinguishing Agents*. This includes but is not limited to halons, HCFCs and HFCs used in the fire protection sector.

## 1.0 Introduction

Since the end of halon production for fire protection uses at the end of 1993 in non-Article 5 (non-A5) parties, many parties have used recycled halons to maintain and service existing equipment. This has allowed users to retain their initial equipment investment, allowed halons to retain a comparably higher market value to other ozone depleting substances (ODSs), and has resulted in very little halon being destroyed compared to other ODSs. With the worldwide end of halon production for fire protection uses at the end of 2009, global inventory management and responsible disposal practices become important considerations to prevent emissions during a critical period of ozone layer recovery. The options for avoiding emissions of unwanted stockpiles of halons include destruction and transformation (also referred to as conversion) to useful chemical products. Fire extinguishing agents, more than some of the other ODSs, are readily accessible for collection, storage, and disposal or reuse. Owing to the continued global demand in applications such as aviation, the HTOC has recommended that destruction as a final disposition option should be considered only if the halons are too contaminated and cannot be reclaimed to an acceptable purity.

This Technical Note provides a review of existing destruction technologies approved for halons and HCFCs and presents an update on the UNEP TEAP Destruction Task Force assessment of destruction technologies available for hydrofluorocarbons (HFCs). Much of the information with regard to halon destruction has remained unchanged since the 2010 HTOC Assessment (e.g., halon destruction technologies, halon transformation/conversion chemistry).

At their 29th Meeting, the parties requested the Technology and Economic Assessment Panel (TEAP) to report on an assessment of destruction technologies, as instructed in Decision XXIX/4. In light of the chemical similarity of HFCs, HCFCs, CFCs and halons and including at times the practice of destroying them together, the UNEP Task Force on Destruction Technologies (2018 TFDT) performed an assessment of destruction technologies with a view of confirming their applicability to HFCs and to review any other technology for possible inclusion in the list of approved destruction technologies in relation to all Montreal Protocol controlled substances.

A summary of the recommendations relevant to the assessment of approved destruction technologies for their applicability to HFCs and any other technologies for possible inclusion on the list was set out in Chapter 5 of the Supplemental Report to the April 2018 Decision XXIX/4 TEAP Task Force Report on Destruction Technologies for Controlled Substances. The recommendations range in technologies being assessed as “Recommended for Approval”, “High Potential” to “Unable to Assess”.

At their 30th Meeting, the parties in response to decision XXIX/4 approved the destruction technologies set out in Table 1.

**Table 1: Approved Destruction Technologies (Thirtieth Meeting of the Parties December 2018)**

Technology	Applicability										
	Concentrated Sources									Dilute Sources	
	Annex A		Annex B			Annex C	Annex E	Annex F			Annex F
	Group 1	Group 2	Group 1	Group 2	Group 3	Group 1	Group 1	Group 1	Group 2		Group 1
	Primary CFCs	Halons	Other CFCs	Carbon Tetrachloride	Methyl Chloroform	HCFCs	Methyl Bromide	HFCs	HFC-23	ODS	HFCs
DRE*	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%	95%	95%
Cement Kilns	Approved	Not Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Not determined		
Gaseous/Fume Oxidation	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Liquid Injection Incineration	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Municipal Solid Waste Incineration										Approved	Approved
Porous Thermal Reactor	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Not determined		
Reactor Cracking	Approved	Not Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Rotary Kiln Incineration	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved	Approved	Approved

Argon Plasma Arc	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Inductively coupled radio frequency plasma	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Not Determined	Not Determined		
Microwave Plasma	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Not Determined	Not Determined		
Nitrogen Plasma Arc	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Portable Plasma Arc	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Not Determined		
Chemical Reaction with H <sub>2</sub> and CO <sub>2</sub>	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Gas Phase Catalytic De-halogenation	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Not determined		
Superheated steam reactor	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Thermal Reaction with Methane	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Not Determined	Not Determined		
Thermal Decay of Methyl Bromide	Not Determined	Approved	Not Determined	Not Determined							

\*DRE - Destruction & Removal Efficiency

Source: Thirtieth Meeting of the Parties to Montreal Protocol on Substances that Deplete the Ozone Layer UNEP/ OzL.Pro.30/L.2 Draft Decision XXX/6 Destruction Technologies for Controlled Substances

## 2.0 Destruction and Transformation Technologies

In their 2002 report, the UNEP Task Force for Destruction Technologies (2002 TFDT) developed screening criteria for technologies for use by parties to dispose of surplus inventories of ODSs. These technologies were assessed on the basis of:

- Destruction and Removal Efficiency (DRE)
- Emissions of dioxins/furans (PCDDs/PCDFs)
- Emissions of other pollutants (acid gases, particulate matter, and carbon monoxide)
- Technical capability, where the technology has demonstrated destruction on at least a pilot scale or demonstration scale, and for which the processing capacity is no less than 1.0 kg/hr. of the substance to be destroyed, whether ODS or a suitable surrogate.

Two commonly used but different ways of measuring the extent of destruction are Destruction Efficiency (DE) and Destruction and Removal Efficiency (DRE). DE is determined by subtracting from the mass of a chemical fed into a destruction system during a specific period of time the mass of that chemical that is released in stack gases, fly ash, scrubber water, bottom ash, and any other system residues and expressing that difference as a percentage of the mass of the chemical fed into the system. Destruction and Removal Efficiency (DRE) has traditionally been determined by subtracting from the mass of a chemical fed into a destruction system during a specific period of time, the mass of that chemical alone that is released in stack gases and expressing that difference as a percentage of the mass of that chemical fed into the system. DE is a more comprehensive measure of destruction than DRE since it considers the amount of targeted chemical that escapes destruction by being removed from the process in the stack gases and in all other residue streams. Most references citing performance of ODS destruction processes only provide data for stack emissions and thus, generally, data is only available for DRE and not DE.

The technical performance criteria are summarized in Table 2. These represent the minimum destruction and removal efficiencies and maximum emission of pollutants to the atmosphere permitted by technologies that qualified for consideration by the 2002 TFDT for recommendation to the parties for approval as ODS destruction technologies. The reader is referred to the 2002 TFDT report for more information on each of these criteria.

As well as meeting the above performance criteria, the destruction technologies had to demonstrate technical capability meaning that the technology achieved the required DRE while satisfying the emissions criteria. Demonstration of destruction of ODS is preferred but not necessarily required. Destruction of halogenated compounds that are refractory, i.e., resistant to destruction, is acceptable. For example, demonstrated destruction of polychlorinated biphenyls (PCBs) was often accepted as an adequate surrogate for demonstrated ODS destruction.

Polychlorinated Dibenzodioxins (PCDDs), commonly referred to as dioxins, and Polychlorinated Dibenzofurans (PCDFs), commonly referred to as furans, are produced from the combustion of chlorinated ODS including CFCs, HCFCs, and halons. These products of incomplete combustion are of greatest concern for potentially adverse effects on public health and the environment. The recognized measure of their toxicity is the international toxic equivalency factor (ITEQ), which

is a weighted measure of the toxicity for all members of the families of these toxic compounds that are determined to be present. The internationally accepted protocol for determining ITEQ was established by NATO in 1988.

**Table 2: Summary of Technical Performance Qualifications (1)**

<b>Performance Qualification</b>	<b>Units</b>	<b>Diluted Sources (i.e., foams)</b>	<b>Concentrated Sources</b>
DRE	%	95	99.99
PCDDs/PCDFs	ng-ITEQ (2) / Nm <sup>3</sup> (3)	0.5	0.2
HCl/Cl <sub>2</sub>	mg/Nm <sup>3</sup>	100	100
HF	mg/Nm <sup>3</sup>	5	5
HBr/Br <sub>2</sub>	mg/Nm <sup>3</sup>	5	5
Particulates (TSP (4))	mg/Nm <sup>3</sup>	50	50
CO	mg/Nm <sup>3</sup>	100	100

Note 1: All concentrations of pollutants in stack gases and stack gas flow rates are expressed on the basis of dry gas at normal conditions of 0°C and 101.3 kPa, and with the stack gas corrected to 11% O<sub>2</sub>;

Note 2: ITEQ – international toxic equivalency;

Note 3: Normal cubic metre (i.e. corrected to 0°C and 101.3 kPa);

Note 4: TSP – total suspended particles.

The TFDT developed the following minimum criteria for an ODS destruction technology to be considered technically capable:

- It has been demonstrated to have destroyed ODS to the technical performance standards, on at least a pilot scale or demonstration scale
- It has been demonstrated to have destroyed a refractory chlorinated organic compound other than an ODS, to the technical performance standards, on at least a pilot scale or demonstration scale
- The processing capacity of an acceptable pilot plant or demonstration plant must be no less than 1.0 kg/hr. of the substance to be destroyed, whether ODS or suitable surrogate.”

Destruction of halons presents some unique considerations. A number of the technologies screened by the 2002 TFDT satisfied the criteria for the destruction of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) but had not been tested for halon destruction. The 2002 TFDT, therefore, could not recommend such technologies for halon destruction, since the presence of bromine in halons can significantly alter the process parameters. In particular, molecular bromine tends to be formed and is very difficult to remove from the exhaust gases. Technologies that are recommended for CFC and HCFC destruction, but have not been tested for halon destruction, are described as potential technologies for halon destruction.

Based on a further evaluation of destruction technologies by the TEAP in response to Decision XXII/10, the following technologies were approved by the Parties (Decision XXIII/12 and Annex, UNEP/OzL.Pro.4/15) for the destruction of halons:

- Liquid injection incineration
- Chemical reaction with Hydrogen and Carbon Dioxide
- Rotary kiln incineration
- Argon plasma arc
- Inductively coupled radio frequency plasma
- Thermal reaction with methane

These approved halon destruction technologies are described below, these technologies continue to remain approved. It should be noted that these technologies are also approved for HCFCs. Only the first four are approved for HFCs at this time; the remaining two have not been determined for HFCs.

At the 30<sup>th</sup> Meeting of the parties and in contrast to previous positions, the destruction and removal efficiency was the criterion considered in approving destruction technologies for the groups of controlled substances in Table 1. At the same meeting the Parties requested the TEAP to assess those destruction technologies listed as not approved or not determined in Table 1, as well as any other technologies, and to report to the Open-Ended Working Group prior to the Thirty-Third Meeting of the Parties, with the understanding that if further information is provided by parties in due time the TEAP should report to an earlier meeting of the Open-Ended Working Group.

## **2.1 Liquid Injection Incineration**

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

## **2.2 Chemical Reaction with Hydrogen and Carbon Dioxide**

This technology provides a novel approach to the destruction of ODSs and involves the thermal reaction of the ODS with hydrogen and carbon dioxide. The process results in an irreversible transformation and the performance criteria currently in place for ODS destruction are met, although there was initially some concern within the 2002 TFDT concerning the process flow adopted and the level of analytical verification. However, this has subsequently been resolved. Since the process is targeted to create hydrogen halides and/or halide salts as saleable bi-products of the destruction process, the normal screening criterion related to maximum HCl or HF levels in the stack gases do not apply.

### 2.3 Rotary Kiln Incineration

Rotary kiln incinerators are refractory-lined rotating cylindrical steel shells mounted on a slight incline from horizontal. Capable of handling both liquid and solid wastes, the rotation of the shell enhances mixing and the inclination causes ash or molten slag to fall out. Most rotary kilns are equipped with an afterburner that ensures complete destruction of exhaust gases. Hydrocarbon fuels, such as natural gas, fuel oil or high calorific liquid waste are typically used as an energy source. Rotary kilns have been used to destroy all forms of hazardous waste (gas, liquid, solids, including sludge). Because of this flexibility, rotary kilns are most frequently incorporated into the design of commercial incinerator facilities. Liquid wastes such as CFCs, halons, HCFCs, and HFCs can be fed into the rotary kiln or directly into the afterburner. Their operating permits usually restrict the quantity of chlorine-containing waste and the concern regarding HF attack on incinerator equipment usually limits the fraction of fluorine in the feed to low levels, typically in the range of 1%. The latter generally establishes the ODS incineration capacity. Concerns for HBr would also exist for halons.

Rotary kilns operating with afterburner temperatures of 1000-1200°C have demonstrated DREs in excess of 99.9999% destroying thermally stable compounds such as PCBs, dichlorobenzene and tetrachlorobenzene. Rotary kilns are widely used in developed countries for the incineration of hazardous wastes, including chlorinated solvents ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ), and toxic waste, such as PCBs. The principal advantage of the rotary kiln is its ability to handle a wide variety of liquid and solid wastes, so they can handle both foams and concentrated sources. However, rotary kilns are very expensive to build, and maintenance costs are high, so it is unlikely that new rotary kilns will be built with the intention of destroying ODSs only. The capital expense could be justified, however, where there are opportunities to destroy a variety of hazardous waste materials.

### 2.4 Argon Plasma Arc

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

There are many types of plasma. Cold plasmas, such as those used in etching of semiconductors and in fluorescent lights, operate at very low pressures. The ions and neutral particles are at close to ambient temperatures, while the electrons are generally at temperatures around 10,000 K. The large temperature difference is maintained because the collision rate between the electrons and other species is low, due to the low pressure.

Argon plasma arc technology is an “in flight” plasma process, which means that the waste mixes directly with the argon plasma jet. Argon was selected as the plasma gas since it is inert and does not react with the torch components. Waste is rapidly heated in the reaction chamber (a flight tube) to about 3000°C, where pyrolysis occurs. Steam is added together with the waste at the injection manifold; the oxygen ensures that any carbon formed during pyrolysis is converted to carbon dioxide, and the hydrogen prevents formation of  $\text{CF}_4$ , which is a strong greenhouse gas. The use of steam rather than oxygen gives more thorough ODS destruction for a given feed rate,

since the thermodynamic mixing temperature is higher. Pyrolysis is followed by rapid alkaline quenching from 1200 °C to less than 100 °C. Such rapid quenching limits the formation of dioxins and furans. The cool gas from the quench is further scrubbed with alkaline liquor in a counter-current packed column to neutralize acid gases. The off-gas from the column consists mainly of Ar and CO<sub>2</sub>.

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

## **2.5 Inductively coupled radio frequency plasma**

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

## **2.6 Thermal reaction with methane**

This process involves the thermal conversion of fluorocarbons to fluorinated vinyl monomers (as described in two U.S. patents). This technology is a transformation process producing a useful product (in this case vinylidene fluoride). The critical aspect of any transformation process is whether the transformation is irreversible or not. In this instance, a conversion factor of 99.99% has been reported for both CFCs and halons.

### 3.0 Reported Destruction of Halons

Under Article 7 of the Montreal Protocol, parties are required to report annual destruction of halons. Historically, very little halon has been reported as destroyed, supporting the findings in the 2014 HTOC Assessment report showing a significant global inventory of both halon 1301 and halon 1211. Table 3 below lists the amounts of halons destroyed and reported under Article 7 through 2017.

**Table 3: Article 7 Reporting for Halon Destruction (in metric tonnes where not specified)**

<b>HALON</b>	<b>1996</b>	<b>1997</b>	<b>1998</b>	<b>1999</b>	<b>2000</b>	<b>2001</b>	<b>2002</b>	<b>2003</b>
1211	1.0		6.5		3.9	1.1	14.2	265.3
1301		6.0	3.7	29.0	50.0	22.0	18.5	242.2
2402								
<b>Total (ODP tonnes)</b>	<b>3.0</b>	<b>60.0</b>	<b>56.9</b>	<b>290.0</b>	<b>511.8</b>	<b>223.4</b>	<b>227.1</b>	<b>3,218.3</b>

<b>HALON</b>	<b>2004</b>	<b>2005</b>	<b>2006</b>	<b>2007</b>	<b>2008</b>	<b>2009</b>	<b>2010</b>	<b>2011</b>
1211	183.8	84.4	331.9	306.9	111.5	13.7	11.8	49.3
1301	296.2	29.8	32.9	16.8	47.7	36.4	12.2	10.8
2402				0.1	1.3		0.9	1.6
<b>Total (ODP tonnes)</b>	<b>3,513.5</b>	<b>550.6</b>	<b>1,324.6</b>	<b>1,089.3</b>	<b>819.4</b>	<b>405.1</b>	<b>162.8</b>	<b>265.8</b>

<b>HALON</b>	<b>2012</b>	<b>2013</b>	<b>2014</b>	<b>2015</b>	<b>2016</b>	<b>2017</b>
1211	51.3	11.3	10.7	10.3	2.7	0.3
1301	8.5	3.3	12.2	28.3	30.4	14.3
2402	2.5				0.6	
<b>Total (ODP tonnes)</b>	<b>253.3</b>	<b>67.5</b>	<b>154.2</b>	<b>317.0</b>	<b>312.1</b>	<b>143.9</b>

Source: UNEP Ozone Secretariat, January 2019

## 4.0 Transformation

The term “transformation” refers to the conversion of an ODS or HFC into useful, commercially viable products. Ideally this transformation would produce environmentally friendly products that could be sold for profit. As there is nothing different about the HCFCs and HFCs used for fire protection, opportunities for the transformation of those fire extinguishants would be on par with those used as refrigerants, foam blowing agents etc. Therefore, this chapter focuses on halons because they are chemically unique from most other ODS since they contain bromine.

The following information was originally contained in the HTOC 2006 Assessment. It has not been updated and is copied here verbatim.

### 4.1.1 Halon 1301

The term “transformation” refers to the conversion of halon 1301 into useful, commercially viable products. Ideally this transformation would produce environmentally friendly products that could be sold for profit.

Halon 1301 (CF<sub>3</sub>Br, bromotrifluoromethane) is in general a very thermally and chemically stable compound. Halon 1301 fails to undergo S<sub>N</sub>2 type reactions with nucleophiles. This alteration in chemical reactivity is due to the extreme electron-withdrawing nature of the fluorine atom. As a result of the strong electron-attracting properties of the fluorine atom, the polarization in the halon 1301 molecule is such that the bromine atom in halon 1301 can be regarded as having a slightly positive nature. Nucleophilic attack on the carbon in halon 1301 and in other polyfluorohaloalkanes is highly disfavoured, but attack on *halogen* by one or two electron transfer processes is possible, and often involves difluorocarbene-mediated processes.

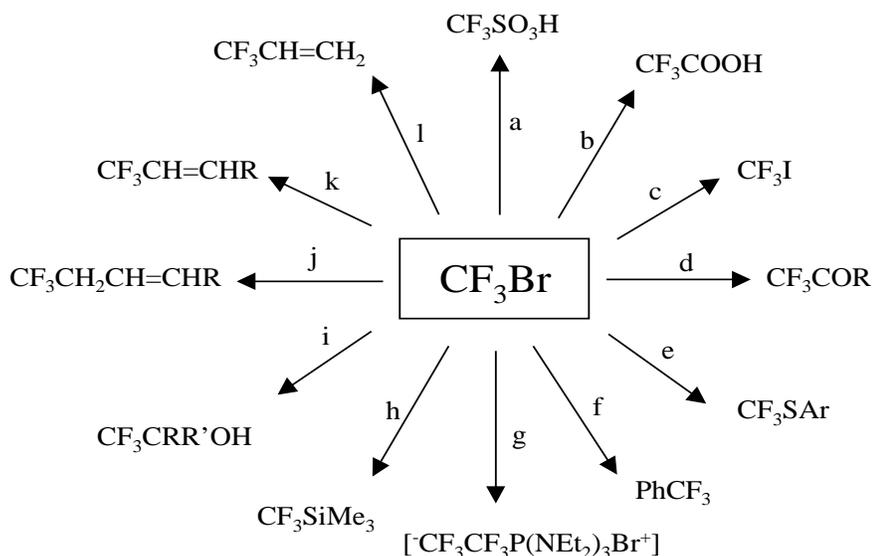
Despite its lessened reactivity, halon 1301 undergoes numerous chemical reactions. The chemical reactions of halon 1301 can be divided into three basic types, which involve three separate mechanisms:

- 1) Reactions in Zn/aprotic solvent systems
- 2) Reactions in SO<sub>2</sub> media
- 3) Reactions with powerful nucleophiles

Reactions involving metals (Zn, Cd) in aprotic solvents such as pyridine or dimethylformamide have been explained by radical or carbanionic intermediates. Reactions in SO<sub>2</sub> media proceed via a radical process. Reaction of halon 1301 with disulphides in the presence of SO<sub>2</sub> has been employed in the production of trifluoromethyl thioether precursors to insecticides such as Fipronil. Finally, reaction with strong nucleophiles such as thiophenoxides is believed to proceed via an S<sub>N</sub>1 mechanism.

Owing to the decreased reactivity of halon 1301, several of the reactions depicted in Figure 1 proceed with low yields, due to the vigorous reaction conditions required, and as result these processes are not commercially attractive. A successful halon 1301 transformation process must not only produce a commercially useful product but must also be characterized by high enough yields and conversions to render the process economical compared to simple destruction of halon 1301.

Numerous fluorine-containing products of potential use as monomers, pharmaceutical intermediates and agricultural intermediates can be envisioned as candidates for synthesis from halon 1301. Given recent advances in synthetic techniques, catalysis and other areas, it is believed that the development of a halon 1301 transformation process capable of producing a commercially viable product is an attainable goal.



**Reagents:** (a) Zn/DMF, SO<sub>2</sub>; (b) Zn/DMF, CO<sub>2</sub>; (c) Zn/DMF, I<sub>2</sub>; (d) Zn/pyridine, RCOOR'; (e) ArSK/pyridine; (f) benzene, Zn, SO<sub>2</sub>, DMF; (g) P(NEt<sub>2</sub>)<sub>3</sub>; (h) P(NEt<sub>2</sub>)<sub>3</sub>, SiMe<sub>3</sub>Cl; (i) Zn/pyridine, RCOR'; (j) RCH=CHCH<sub>2</sub>R, Zn; (k) RCCH, Zn, CuI, THF; (l) CH<sub>2</sub>=CH<sub>2</sub>, Δ

**Figure 1: Portion of Known Chemistry of Halon 1301**

#### 4.1.2 Halon 1211

Halon 1211 is somewhat more reactive than halon 1301, and a number of reactions of halon 1211 have been reported in the open literature. The reaction chemistry of halon 1211 includes:

- 1) Non-oxidative gas phase reactions
- 2) Oxidative gas phase reactions
- 3) Additions to olefins
- 4) Reactions with nucleophiles

Non-oxidative reactions include reaction with hydrogen to produce the hydro-dechlorination products CF<sub>2</sub>HCl and CH<sub>2</sub>F<sub>2</sub> and the reaction with methane to produce CF<sub>2</sub>HCl, CH<sub>3</sub>Br, and CH<sub>2</sub>F<sub>2</sub> as the major products. Oxidative gas phase reactions result in the ultimate production of carbonyl fluoride (COF<sub>2</sub>), bromine and chlorine. Catalytic pyrolysis of halon 1211 over alumina and aluminium trifluoride has been employed to produce CF<sub>3</sub>Br and CF<sub>3</sub>Cl.

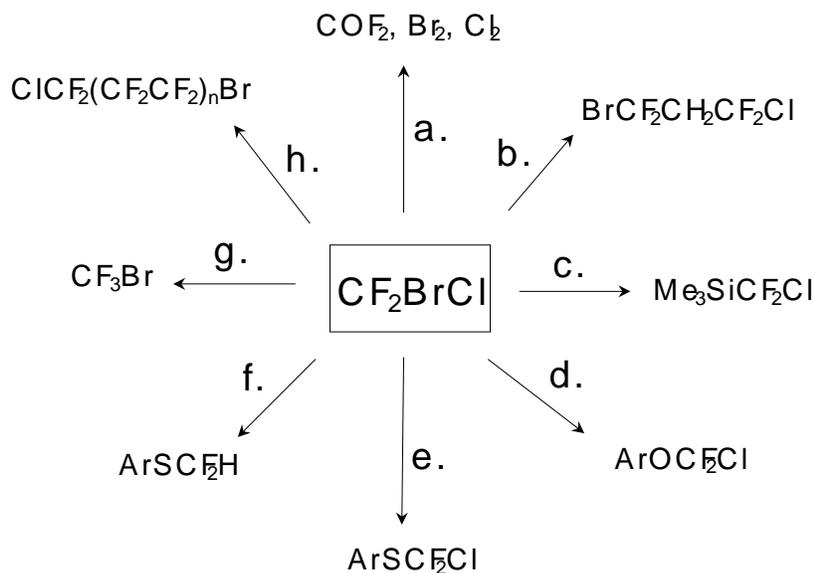
Additions to olefins include additions to partially fluorinated olefins, e.g., addition to  $\text{CF}_2=\text{CH}_2$  to produce  $\text{BrCF}_2\text{CH}_2\text{CF}_2\text{Cl}$ , which can be further fluorinated and dehydrofluorinated to produce  $\text{CF}_3\text{CH}=\text{CFCl}$ . Telomerization with tetrafluoroethylene,  $\text{CF}_2=\text{CF}_2$ , produces the telomers  $\text{ClCF}_2(\text{CF}_2\text{CF}_2)_n\text{Br}$ .

Similar to the reaction chemistry of halon 1301, halon 1211 undergoes reaction with nucleophiles. Reactions with nucleophiles proceed via both carbene and radical processes. For example, treatment of  $\text{PhSNa}$  with halon 1211 in DMF produces  $\text{PhSCF}_2\text{Br}$  and  $\text{PhSCF}_2\text{H}$ , via the difluorocarbene intermediate. Reaction under radical conditions affords  $\text{PhSCF}_2\text{Br}$  and  $(\text{PhS})_2\text{CF}_2$ .

Reaction of alkali phenoxides with halon 1211 provides a route to bromodifluoro-methoxy compounds  $\text{ArOCF}_2\text{Br}$ , useful as insecticides and agricultural intermediates.

Reaction of halon 1211 with chlorotrimethylsilane affords chlorodifluoromethyl-trimethylsilane, a useful chlorodifluoromethylation agent.

Like halon 1301, halon 1211 undergoes reactions in  $\text{Zn}$ /aprotic solvent systems and in  $\text{SO}_2$  media, but products are often mixtures due to reactions involving both the  $\text{C-Br}$  and  $\text{C-Cl}$  bonds. Figure 2 summarizes the reaction chemistry of halon 1211.



**Reagents** (a)  $\text{O}_2$  or  $\text{hv}/\text{O}_2$ ; (b)  $\text{CF}_2=\text{CH}_2$ ; (c)  $\text{Me}_3\text{SiCl}$ ,  $\text{Al}$ ,  $\text{NMP}$ ; (d)  $\text{ArOK}$ ; (e)  $\text{ArSK}$ ; (f)  $\text{ArSK}$ ,  $\text{DMF}$ ; (g)  $\text{CF}_3\text{I}$ ,  $\text{Cr}$ ; (h)  $\text{CF}_2=\text{CF}_2$

**Figure 2: Summary of the Reaction Chemistry of Halon 1211**

Numerous fluorine-containing products of potential use as monomers, pharmaceutical intermediates and agricultural intermediates can be envisioned as candidates for synthesis from halon 1211. Given recent advances in synthetic techniques, catalysis and other areas, it is believed that the development of a halon 1211 transformation process capable of producing a commercially viable product is an attainable goal.

#### 4.1.3 Known Transformations of Halons

The former Chemicals Technical Options Committee, now the Medical and Chemicals Technical Options Committee (MCTOC), confirmed that halon 1301 is a very useful feedstock for the preparation of bioactive compounds. In the 2006 HTOC Assessment report, the HTOC reported that halon 1301 had been produced as a feedstock since the mid-1990s in order to support the production of Fipronil, a broad-spectrum insecticide. At that time global halon feedstock production averaged approximately 400 metric tonnes per annum but was predicted to increase. Total global feedstock production generally increased annually up to 2013, followed by a decrease until 2017, as shown in Table 4 below:

**Table 4: Global Halon 1301 Feedstock Production and Transformation**

<b>Year</b>	<b>2006</b>	<b>2007</b>	<b>2008</b>	<b>2009</b>	<b>2010</b>	<b>2011</b>
Halon 1301 (tonnes)	741	855	1,202	758	900	1,270
Total (ODP Tonnes)	7,410	8,550	12,020	7,580	9,000	12,700

<b>Year</b>	<b>2012</b>	<b>2013</b>	<b>2014</b>	<b>2015</b>	<b>2016</b>	<b>2017</b>
Halon 1301 (tonnes)	1,471	2,106	1,342	871	753	1,338
Total (ODP Tonnes)	14,710	21,060	13,420	8,710	7,530	13,380

Source: UNEP Ozone Secretariat, January 2019

What is of concern, is that in 2011 the World Bank, on behalf of the government of China, in response to ExCom decision 59/8(b)(iii), reported to ExCom that there are eight enterprises in China that use halon 1301 as a feedstock for the production of Fipronil, and that despite measures being taken to reduce tail gas emissions of halon 1301 from the process, the annual tail gas emissions of halon 1301 were 32.4 ODP tons in 2009 and 67.4 ODP tons in 2010 (source: UNEP/OzL.Pro/ExCom/63/15 ). Additional measures were recommended and have been implemented, but it is unknown to HTOC to date whether or not they have been effective in reducing tail gas emissions or if the latter have continued to increase in line with feedstock production.

Anecdotally, the HTOC has learned that the global use of Fipronil will be on the increase. Some parties may be tempted to divert decommissioned stocks of halon 1301 from fire protection systems for use in Fipronil production to meet the growing demand. The use of halon from decommissioned fire protection systems for Fipronil production should be strongly discouraged and the halon be made available for meeting global fire protection needs which are projected continue well into the latter half of this century for at least civil aviation, but likely military and oil and gas production as well.

## **5.0 Conclusions**

Halons, more than some of the other ODS, are readily accessible for collection, storage, and disposal. Options for disposal of surplus halons include destruction and transformation. The actual amounts of the global halon inventory potentially available for destruction or transformation is highly uncertain due to business planning and economic considerations by users, local and regional imbalances of supply and demand, the availability of destruction or transformation technologies and facilities, inventory management approaches, and applicable disposal regulations. Owing to the continued global demand for halons in applications such as aviation, oil and gas, militaries, etc., the HTOC strongly recommends that destruction as a final disposition option should be considered only if the halons are too contaminated and cannot be reclaimed to an acceptable purity. The HTOC also discourages transformation of halons, particularly halon 1301, because of these on-going uses.

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## **7.0 List of Acronyms and Abbreviations**

CFC	Chlorofluorocarbon
CO	Carbon monoxide
DE	Destruction Efficiency
DRE	Destruction Removal Efficiency
GWP	Global Warming Potential
HBr	Hydrogen bromide
HCFC	Hydrochlorofluorocarbon
HCl	Hydrogen chloride
HF	Hydrogen fluoride
HFC	Hydrofluorocarbon
HTOC	Halons Technical Options Committee
ICRFP	Inductively Coupled Radio Frequency Plasma
ITC	International Toxic Equivalency
MSDS	Material Safety Data Sheet
ODS	Ozone Depleting Substance
PCDD	Polychlorinated Dibenzodioxin
PCDF	Polychlorinated Dibenzofuran
TEAP	Technology and Economic Assessment Panel
TFDT	Task Force on Destruction Technologies
TSP	Total Suspended Particles
UK	United Kingdom
UNEP	United Nations Environment Programme
U.S.	United States