

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



**UNEP**

**REPORT OF THE  
HALONS TECHNICAL OPTIONS COMMITTEE  
DECEMBER 2014**

**TECHNICAL NOTE #5  
HALON DESTRUCTION**

HTOC Technical Note #5

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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). Future reports, including the 2014 Assessment Report, will 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.

## **1.0 Introduction**

Since the end of halon production for fire protection uses at the end of 1993 in non-Article 5 countries, 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. Halons, 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 cross-contaminated and cannot be reclaimed to an acceptable purity.

This Technical Note provides a review of current destruction technologies and the current issues related to these final options for halon disposal. Since 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), some of this information is briefly summarised below and the reader is referred to the 2010 HTOC Assessment for more details.

## **2.0 Destruction Technologies**

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

- Destruction and Removal Efficiency (DRE)<sup>1</sup>
- Emissions of dioxins/furans (PCDDs/PCBDs)
- Emissions of other pollutants (acid gases, particulate matter, and carbon monoxide)
- Technical capability

The technical performance criteria are summarized in Table 1. 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 TFDT for recommendation to the Parties of the Montreal Protocol for approval as ODS destruction technologies. The reader is referred to the 2002 TFDT report for more information on each of these criteria.

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

Performance Qualification	Units	Diluted Sources (i.e., foams)	Concentrated Sources
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

Note 4: TSP – total suspended particles

The approved destruction processes are summarized in Table 2.

Destruction of halons presents some unique considerations. A number of the technologies screened by the TFDT satisfied the criteria for the destruction of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), but had not been tested for halon destruction. The 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.

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<sup>1</sup> 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.

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 and additional information is available from the 2002 TFDT report and in Chapter 5 of the TEAP May 2011 Progress Report.

### **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 ODS are injected into the burner. These incinerators are able to handle a wide range of liquid or vapour wastes, have high turndown ratios and have no moving parts. Liquid injection incinerators are limited to treating wastes that can be pumped and atomized through the burner and are therefore susceptible to plugging if liquids with significant ash are used. However, the incineration of ODS is not likely to be limited by these constraints to a significant degree.

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

This technology provides a novel approach to the destruction of ODS and involves the thermal reaction of 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 Task Force 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 really 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 and other ODS

can be fed into the rotary kiln or directly into the afterburner. Their operating permits usually restrict the quantity of chlorine-containing waste and concern regarding HF attack on incinerator equipment usually limits the fraction of fluorine in the feed to low levels, typically in the range of 1%. The latter generally establishes the ODS incineration capacity.

Rotary kilns operating with afterburner temperatures of 1000-1200°C have demonstrated DREs in excess of 99.9999% destroying refractory compounds such as PCBs, dichlorobenzene and tetrachlorobenzene. 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 ODS 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 2500°C, where pyrolysis occurs. Steam is added together with the waste at the injection manifold; the oxygen ensures that any carbon formed during pyrolysis is converted to carbon dioxide, and the hydrogen prevents formation of  $\text{CF}_4$ , 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 HCl and other acid gases. The off-gas from the column consists mainly of Ar and  $\text{CO}_2$ .

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 onstream 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**

Process involves the thermal conversion of fluorocarbons to vinylidene chloride (as described in two US 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.

**Table 2: Approved Destruction Processes (2011)**

Technology	Applicability							
	Concentrated Sources							Dilute Sources
	Annex A		Annex B			Annex C	Annex E	
	Group 1	Group 2	Group 1	Group 2	Group 3	Group 1	Group 1	
Primary CFCs	Halons	Other CFCs	Carbon Tetrachloride	Methyl Chloroform	HCFCs	Methyl Bromide		
<b>Destruction &amp; Removal Efficiency (DRE)</b>	<b>99.99%</b>	<b>99.99%</b>	<b>99.99%</b>	<b>99.99%</b>	<b>99.99%</b>	<b>99.99%</b>	<b>99.99%</b>	<b>95%</b>
Argon Plasma Arc	Approved	Approved	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
Cement Kilns	Approved	<i>Not Approved</i>	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
<b>Chemical Reaction with H<sub>2</sub> and CO<sub>2</sub></b>	Approved	Approved	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
Gas Phase Catalytic De-halogenation	Approved	<i>Not Determined</i>	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
Gaseous/Fume Oxidation	Approved	<i>Not Determined</i>	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
Inductively coupled radio frequency plasma	Approved	Approved	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
Liquid Injection Incineration	Approved	Approved	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
Microwave Plasma	Approved	<i>Not Determined</i>	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
Municipal Solid Waste Incineration								Approved
Nitrogen Plasma Arc	Approved	<i>Not Determined</i>	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
<b>Porous Thermal Reactor</b>	Approved	<i>Not Determined</i>	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
<b>Portable Plasma Arc</b>	Approved	<i>Not Determined</i>	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
Reactor Cracking	Approved	<i>Not Approved</i>	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
Rotary Kiln Incineration	Approved	Approved	Approved	Approved	Approved	Approved	<i>Not Determined</i>	Approved
Superheated steam reactor	Approved	<i>Not Determined</i>	Approved	Approved	Approved	Approved	<i>Not Determined</i>	
<b>Thermal Reaction with Methane</b>	Approved	Approved	Approved	Approved	Approved	Approved	<i>Not Determined</i>	

Source: Annex to Decision XXIII/12 of the Twenty-Third Meeting of the Parties (see UNEP/OzL.Conv.9/7-UNEP/OzL.Pro.23/11, pg. 42)

### 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 2014 HTOC Assessment report showing a significant global inventory of both halon 1301 and halon 1211. As discussed earlier in this report, this situation is attributable to the fact that the demand for halons has largely been met through the availability of substitutes and alternative technologies and to a limited extent halon recycling. Table 3 below lists the amounts of halons destroyed and reported under Article 7.

**Table 3: Article 7 Reporting for Halon Destruction**

HALON	1996	1997	1998	1999	2000	2001	2002	2003	2004
1211 (MT)	1.0		6.5		3.9	1.1	14.2	265.3	183.8
1301 (MT)		6.0	3.7	29.0	50.0	22.0	18.5	242.2	296.2
2402 (MT)									
<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>3,513.5</b>

HALON	2005	2006	2007	2008	2009	2010	2011	2012
1211 (MT)	84.4	331.9	306.9	111.5	13.7	11.8	49.3	51.3
1301 (MT)	29.8	32.9	16.8	47.7	36.4	12.2	10.8	8.5
2402 (MT)			0.1	1.3		0.9	1.6	2.5
<b>Total (ODP tonnes)</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>253.3</b>

Source: UNEP Ozone Secretariat, 2014

### 4.0 Transformation of Halons

The term “transformation” refers to the conversion of halon into useful, commercially viable products. Ideally this transformation would produce environmentally friendly products that could be sold for profit. More information on the reaction chemistry for transformation of halons 1211 and 1301 can be found in Chapter 9 of the 2006 HTOC Assessment report.

The Chemicals Technical Options Committee (CTOC) has determined 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 MT per annum, but was predicted to increase. Except for a dip in 2009, between 2006 and 2012 total global feedstock production has increased annually as shown in Table 4 below:

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

HALON	2006	2007	2008	2009	2010	2011	2012
Halon 1301 MT	741	855	1,202	758	900	1,270	1,471
Total (ODP Tons)	7,410	8,550	12,020	7,580	9,000	12,700	14,710

Source: UNEP Ozone Secretariat, 2014

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 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.

## 5.0 Conclusions

Halons, 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 cross-contaminated and cannot be reclaimed to an acceptable purity. Approved ODS destruction technologies and facilities can be found in many countries, and some already have experience destroying some types of ODS including, to a very limited extent, halons.

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