Annex to the Report of the Technology and Economic Assessment Panel

April 2018 Volume 2

Decision XXIX/4 TEAP Task Force Report on Destruction Technologies for Controlled Substances

Submissions by parties in response to decision XXIX/4 on destruction technologies

Compilation of extracts containing substantive non-confidential information [1]

Armenia

The NOU Armenia regrettably informs that no expertize is available in Armenia on the assessment of the destruction technologies listed in the annex to decision XXIII/12 with a view to confirming their applicability to HFCs; and any other technology for possible inclusion in the list of approved technologies in relation to controlled substances.

Australia

Australia's submission was in four parts.

1. First part of the submission from Australia on the review of destruction technology. Plasma arc is already a Montreal Protocol technology. Toxfree has been using the plasma arc to destroy HFCs for many years as part of Australia's refrigerant recovery and disposal program.

   PLASCON ® process – Plasma arc technology

2. Second part of the submission from Australia for the review of destruction technology. The plasma arc is already a Montreal Protocol approved destruction technology.

Australia provided a document by Salience Solutions Pty Ltd that describes the PyroPlas™ Plasma Arc Destruction Unit, and another document that included exhaust stack test results from a Plascon process. Both documents are considered commercial in confidence.

3. Third part of the submission from Australia is a document prepared by the University of Newcastle, Australia, entitled: "Update the list of approved destruction technologies for controlled substances; adapting TEAP approved "reaction with methane" technology for treatment of fluorine-containing synthetic greenhouse gases".

The document is reproduced below:

[1] Including minor edits to improve readability.

Update the list of approved destruction technologies for controlled substances; adapting TEAP approved "reaction with methane" technology for treatment of fluorine-containing synthetic greenhouse gases

Overview

For over 25 years, we have been undertaking research in the development of processes to treat waste fluorochemical gases. Initially the team focused on treatment of ozone-depleting substances (ODS) CFCs and halons, compounds which contain carbon, fluorine and chlorine or bromine atoms. This led to the discovery that fluorochemicals react with methane to produce $C_2H_2F_2$ (vinylidine fluoride), a valuable compound used in the synthesis of high temperature and corrosion resistant fluoroelastomers. This prompted further, more fundamental research which concluded that the key step in the reaction involved the reaction of a CF_2 moiety (from decomposition of the fluorochemical) with a CH_3 radical (generated from a methane molecule) to form $C_2H_2F_2$ and a hydrogen radical. Excitingly, this pathway is now recognised to be common to all fluorocarbon feeds, and not limited to ozone-depleting compounds.

Once this key elementary reaction step was established, a detailed kinetic model, based on many elementary reaction steps, was used to establish reaction conditions which maximized the yield of $C_2H_2F_2$, including studies of multicomponent fluorocarbon feed gas mixtures (ODS and F-gases), which are typical of the composition that would constitute a waste feed should the process be developed for commercial application. Working with our Chinese collaborators, we are adopting the generic technology to treat waste HFC, with a particular focus on the treatment of CHF_3.

How it works

The treatment process is aimed at preserving carbon-fluorine bonds. This contrasts with existing, energy intensive commercial processes, which result in the destruction of these bonds.

Fluorochemicals are produced at high costs and large quantities of collected waste are available, making them potential chemical feedstocks. The team's studies on the reaction of methane with a wide range of fluorochemicals (including ODS, F-gases and mixtures there-of) disclose a novel and effective approach to the treatment of a variety of fluorochemical wastes. This process offsets, and potentially negates, the cost of treatment by producing a valuable product, and also minimises the quantity of hydrofluoric acid produced during treatment, a compound which is challenging to handle safety and has a high disposal cost.

The system works by reacting methane and fluorochemical in two distinct reactors; Reactor I: initial short residence time reactor for synthesis of VDF and other valuable product production and Reactor II, a second, longer residence time reactor that will destroy the residual waste stream, compliant with legislative requirements of 99.99% ultimate destruction. Research collaborators in China, who are world- leaders in the development of catalysts for fluorochemical reactions, are assisting in the development of catalysts which maximise the yield of VDF and other valuable compounds in Reactor I when treating HFC feeds such as CHF_3.

What destruction efficiency it achieves (and data supporting this rate)

Based on laboratory scale research results, a pilot plant was constructed to facilitate commercial development the ODS and F-gas treatment technology using a process designed for the treatment of a broad range of feed compositions. In 2012, this process received approval and is the only approved technology that maximizes the preservation of carbon-fluorine bonds present in the feed fluorochemical, while still achieving 99.99% destruction of the fluorochemical feed. The UNEP-based Task Force for Destruction Technologies (TFDT) assesses technologies on the basis of a 99.99% Destruction and Removal Efficiency (DRE) and requires extremely low emission levels of dioxins/furans and other

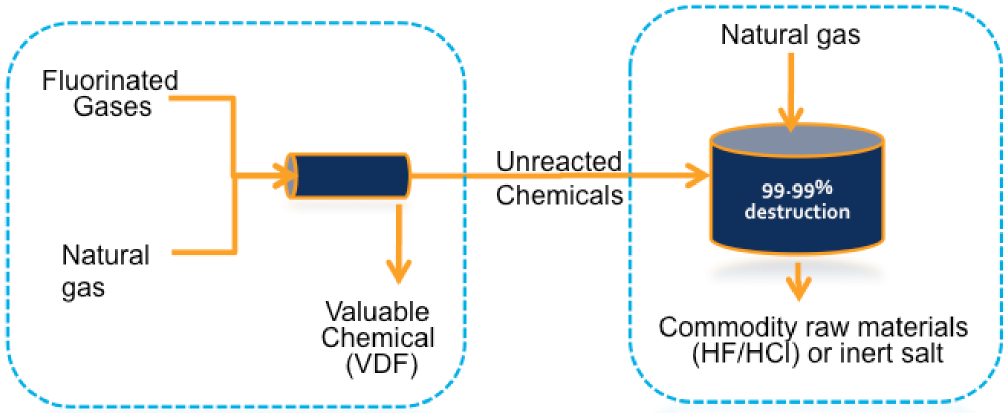


Figure 1. Overview of the treatment process, which incorporates two different reactors.

pollutants (acid gases, particulate matter, and carbon monoxide). We have not assessed the condition (especially in reactor II) required to meet TEAP emission standards for ODS, but will do so once we have developed catalysts which maximize the yield of valuable products produced in Reactor I.

What by products are produced?

We have established that $C_2H_2F_2$ can be synthesised from the reaction of virtually any fluorochemical with methane. Through the use of specialised catalysts, we have been able to increase the yield of valuable products synthesised in Reactor I. The major product for Reactor I is VDF (higher than 80%). Minor products include C_2F_4 (TFE), C_3F_6 (HFP), C_2H_3F (VF), C_2HF_3 (TrFE) and C_2H_4. They are all major fluorinated monomers for the production of fluoropolymer except for C_2H_4. These by products will be separated and purified following Reactor I.

We are now working closely with Australian industry partners to establish a treatment facility in Victoria. Ventia is an international company with an established track record in the development and operation of waste treatment facilities. Their new facility in Victoria, which is currently under construction, would be a viable location for a new waste treatment facility specially designed for fluorine-containing wastes. See http://www.sita.com.au/news/suez-and-ventia-to-open-new-soil-processing-facility-in-victoria/

Development team:

University of Newcastle: Prof Eric Kennedy
Prof Michael Stockenhuber A/Prof J Lucas

Zhejiang University of Technology and Zhejiang Research Institute of Chemical Industry:
A/Prof Wenfeng Han
Mr Shucheng Wang
Mr Wucan Liu

Suez Ventia Joint Venture: Mr Mark Bennett

4. Fourth part of the submission from Australia. Details of a new technology designed to destroy methyl bromide and other fumigants.

MEBROM Research and Development Pty. Ltd., Australia, provided a commercial-in-confidence document that described a portable system for the capture and destruction of methyl bromide.

Canada

In Canada, HFCs have been destroyed in the country and exported for destruction for a number of years. In February 2017, a levy for HFCs sold into the stationary refrigeration and air conditioning sector was implemented by Refrigerant Management Canada, which oversees the disposal of the large majority of ODS and HFCs in Canada.

The destruction facilities used by RMC (Swan Hills (Alberta, Canada) and Veolia (Texas, U.S.A.)) are both rotary kilns that meet the destruction and removal efficiency (DRE) standards for ODS approved by the Parties to the Montreal Protocol. The destruction facilities destroy both shipments of mixed of refrigerants (including HFCs) and shipments of just HFCs. The only issue that has arisen with the increase in HFCs being destroyed is the higher fluorine content in the HFCs that can cause damage to the kiln system when they are incinerated. To deal with this challenge, the destruction facilities are either using a neutralizer (e.g., caustic soda) or slowing down the feed rate into the kiln.

Below are the quantities[1] and types of CFCs, HCFCs and HFCs from Canadian sources that were destroyed by the two facilities mentioned above in 2016 and 2017:

	CFCs					
Year	**R11**	**R12**	**R113**	**R114**	**R115**	**All CFCs**
2016	357.05	6046.10	214.80	325.06	3102.02	10045.03
2017	13233.80	4110.20	1244.30	50.10	2043.60	20682.00

	HCFCs				
Year	**R22**	**R123**	**R124**	**R142b**	**All HCFCs**
2016	53734.96	3398.42	2503.74	522.54	60159.66
2017	40795.10	7801.90	2149.10	267.70	51013.80

[1] In kilograms.

	HFCs					
Year	**R32**	**R125**	**R134a**	**R143a**	**R-152a**	**All HFCs**
2016	31000.94	44856.84	36931.42	13936.68	261.92	126987.80
2017	23642.70	30075.00	30448.40	8730.10	28.90	92925.10

In addition to the technologies mentioned above, a plasma arc destruction technology is used in Canada, but to date, it appears that it has only destroyed HFCs in pilot tests. The supplier of the technology (PureSphera) indicates that the technology is able to destroy ODS and HFCs, as well as foams containing ODS and HFCs, and that there are no differences in destruction procedures related to whether the refrigerant is an ODS or an HFC. The supplier also notes that all types of HFCs can be treated with the plasma arc technology and that a DRE of 99.9999% has been obtained with the destruction of HFC-134a. Operating conditions can differ in terms of the mass flow and treatment of water resulting from the destruction (related to the reduction of the fluorine load).

China

China provides the following information regarding HFC-23 destruction as per Decision XXIX/4.

There are two HFC-23 destruction technologies currently employed by HCFC-22 producers in China. One is the Nitrogen Plasma Arc technology, which is included on the list of ODS destruction technologies approved by MOP. The other technology employed by most HCFC-22 producers in China is the thermal oxidation technology, which can be related to the gaseous/fume oxidation technology and the superheated steam reactor technology included on the list, however, it is not clear which technology the thermal oxidation technology belongs to. The latter technology employed by Chinese enterprises applies hydrogen, natural gas, LPG or diesel as fuel and ejects HFC-23 into incinerator for thermal oxidation and destruction. We would very much appreciate if the TEAP can clarify whether the latter technology is already included on the list; if it is, which technology, and if it is not, we suggest adding this technology to the list.

European Union

In response to decision XXIX/4 and in view of the need to approve destruction technologies for hydrofluorocarbons (HFCs) and update the list of approved destruction technologies annexed to Decision XXIII/12, the European Commission, on behalf of the European Union, would like to present an update on destruction technologies currently used in the European Union.

There are no new technologies that Member States of the European Union wish to include to the list of the approved destruction technologies from Decision XXIII/12.

Poland, Finland and the Czech Republic indicated that rotary kiln incineration is used as a destruction method for HFCs in their countries. However, to achieve DRE 99.99% the system must have an effective wet and dry cleaning of the outlet gases.

Bulgaria prepared an analysis of destruction technologies which may be found applicable to HFCs. It is attached to this letter.

Analysis of the technologies that could be applied for the destruction of hydrofluorocarbons

I. HFC properties related to the eligibility of suitable destruction technologies for them

A. The carbon-fluorine bond

1. The carbon-fluorine bond is one of the strongest in organic chemistry (an average energy ≈ 480 kJ/mol). This is significantly stronger than the bonds of carbon with other halogens (the average bond energy of e.g. C-Cl bond is around 320 kJ/mol) and is one of the reasons why fluoroorganic compounds have high thermal and chemical stability.

2. The carbon-fluorine bond is relatively short (1.4 Å). The Van der Waals radius is 1.47 Å, which is shorter than any substituent and is close to hydrogen (1.2 Å). This is another reason why fluoroorganic compounds have high thermal stability.

3. In addition, the fluorine substituents in polyfluorinated compounds efficiently shield the carbon skeleton from possible attacking reagents. This is another reason for the high chemical stability of polyfluorinated compounds.

B. Thermal decomposition of HCFC, halons, CFC and HFC[1]

1. The decomposition temperature of HCFC, halons and CFC varies in the range of 700 – 1000ºC thus ensuring 99.99% destruction and removal efficiency (DRE). The retention time in the combustion chamber is two seconds or longer.

2. Larger fluorine atom numbers lead to higher decomposition temperatures.

3. The decomposition of HFC occurs under high temperatures: 1150ºC for trifluoromethane (HFC-23); 627-727ºC for 1,1,1,2-tetrafluoroethane (HFC-134a) and above 700ºC for pentafluoroethane (HFC-125). The decomposition temperatures of HFC-134a and HFC-125 are estimated under laboratory conditions.

4. Toxic and corrosive products can occur as a result of the thermal decomposition of HFC: hydrogen halides (HF, HCl), carbonyl halides (COF_2, $COCl_2$), hydrocarbons, dioxins and furans, carbon monoxide (CO) and carbon dioxide (CO_2).

5. Temperatures equal or above 1200ºC and at least two seconds retention time of HFC in the combustion chamber ensure the decomposition of the HFC/HCFC and minimize the formation of unwanted combustion products such as dioxins and furans, carbonyl halides (COF_2, $COCl_2$) and hydrocarbons. This is stated in the Reference document on best available techniques for Waste incineration, 2006 (http://eippcb.jrc.ec.europa.eu/reference/BREF/wi_bref_0806.pdf) as well as demonstrated by the existing technologies for trifluoromethane (HFC-23) destruction (http://cdm.unfccc.int/Projects/projsearch.html).

---

[1] The information in section B is supported by an Excel table "HCFC, CFC, Halons & HFC_properties_related_to_decomposition" given as an Annex to the current document.

II. Applicability of the approved destruction technologies to HFC

1. The destruction technologies approved with Decision XXIII/12 can be described as three types: plasma technologies, incineration technologies and other non-incineration technologies.

2. The plasma technologies (Argon plasma arc, Inductively coupled radio frequency plasma, Microwave plasma, Nitrogen plasma arc, Portable plasma arc) utilize high temperatures - 5000ºC to 15000ºC. The DRE of HFC is high > 99.99%. A waste gas treatment system (absorber and neutralisation) is required. Plasma is an established commercial technology; however the process can be very complex and expensive.

3. The incineration technologies (Cement kilns, Gaseous/ Fume oxidation, Liquid injection incineration, Reactor cracking, Rotary kiln incineration) are appropriate for the decomposition of HFC on the condition that the temperatures in the oxidation chamber are equal or above 1200ºC and the retention time of HFC is at least two seconds. A waste gas treatment system (absorber and neutralisation) is required. The Municipal solid waste destruction technology can be used for destruction of foams containing HFC if the above conditions are met. The advantages of these technologies are their relatively low costs (with the exception of Rotary kiln incineration) and their wide availability.

4. The other non-incineration technologies (Chemical reaction with H_2 and CO_2, Gas phase catalytic dehalogenation, Porous thermal reactor, Superheated steam reactor, Thermal reaction with methane) are also appropriate for the destruction of HFC.

4.1. Chemical reaction with H_2 and CO_2 can be used in the destruction of HFC-23 – Midwest technology, USA. The chemical conversion ensures that the DRE of HFC is high > 99.99%. Organic halides (anhydrous HF) and carbon monoxide (CO) are recovered.

4.2. Gas phase catalytic dehalogenation has high efficiency in destroying of CFC and can be used for destruction of HFC. Hydrofluoroolefins (HFO) and halide salts (HF) are produced. The costs for the destruction are high. HFO have low GWP and there is a possibility for their future wide application.

4.3. Porous thermal reactor provides complete destruction of HFC due to the conditions under which the chemical reaction takes place – porous structure (reaction zone) at temperatures up to 1500ºC. A waste gas treatment system (absorber and neutralisation) is required. Instead of neutralization there is a possibility for recovery of halide salts (HF).

4.4. Superheated steam reactor – there are CDM-approved HFC-23 destruction facilities in China. This technology is widely used in Japan. It has many advantages – high destruction efficiency (> 99.99%), low emissions, simple design (safe to operate) and wide applicability. A waste gas treatment system (absorber and neutralisation) is required. Instead of neutralization there is a possibility for recovery of halide salts (HF).

4.5. Thermal reaction with methane – the major products of the reaction of HFC-23 (CHF_3) with methane (CH_4) are HFO (C_2F_4, $C_2H_2F_2$) and halide salts (HF). There is scarce information about the DRE of this technology.

III. Destruction technologies other than the sixteen approved with Decision XXIII/12

A. All incineration and co-incineration (furnaces dedicated to manufacturing like: lime calcination furnace, electric furnace, etc.) technologies that comply with the following conditions:

- the temperatures in the oxidation chamber are equal or above 1200ºC and the retention time of HFC is at least two seconds;
- the criteria of the destruction established by the Task force on destruction technologies in May 2002, are met;

should be included in the list of approved destruction technologies.

B. The following plasma technologies could be considered for inclusion in the list of approved destruction technologies:

1. AC plasma (Alternating current plasma)

"The AC plasma is produced directly with 60 Hz high-voltage power but in other respects is similar to the inductively coupled RF plasma. The system is electrically and mechanically simple and is thus claimed to be very reliable. The process does not require argon and can tolerate a wide variety of working gases, including air or steam, as plasma gases and is claimed to be tolerant of oil contamination in ODS."[2]

2. CO_2 plasma arc

"A high-temperature plasma is generated by sending a powerful electric discharge into an inert atmospheric gas, such as argon. Once the plasma field has been formed, it is sustained with ordinary compressed air or certain atmospheric gases depending on the desired process outcomes.

The temperature of the plasma is well over 5000ºC at the point of generation into which the liquid or gaseous waste is directly injected. The temperature in the upper reactor is about 3500ºC and decreases through the reaction zone to a precisely controlled temperature of about 1300ºC.

A special feature of the process is the use of CO_2, which is formed from the oxidation reaction, as the gas to sustain the plasma.

The process has demonstrated high DREs with refractory compounds at a reasonably high demonstration rate. Mass emission rates of the pollutants of interest are low, primarily because of the low volume of flue-gas produced by the process."[3]

---

[2] The description of the AC plasma technology is taken from Best Available Techniques (BAT) Reference Document on Waste Incineration, v. Draft 1, May 2017, p.2.3.5.10 (3)
[3] The description of the AC plasma technology is taken from Best Available Techniques (BAT) Reference Document on Waste Incineration, v. Draft 1, May 2017, p.2.3.5.10 (4)

Annex - HCFC, CFC, Halons & HFC – properties related to decomposition

Refrigerants			Boiling point	Decomposition temperature	
Trade names:	Components	100-Year Global Warming Potential	◦C	MSDS, ◦C	T99.99(2), ◦C
CFC					≥850
Halon 1301	Bromotrifluoromethane (CF3Br)	-			787
Halon 1211	Bromochlorodifluoromethane (CF2BrCl)	-			680
Halon 2402	1,2-dibromotetrafluoroethane (CF2BrCF2Br)	-			704
R-22/ HCFC-22	Chlorodifluoromethane	1.810	-40,8	632	705
R-123/ HCFC-123	2,2-Dichloro-1,1,1-trifluoroethane (C2HF3Cl2)	77	27,9	>250	909
HFC-41	Fluoromethane (CH3F)	92	-79	N.d.a.	
R-152a/ HFC-152a	1,1-difluoroethane (CH3CHF2)	124	-24,1	>370	
HFC-152	1,2-difluoroethane (CH2FCH2F)	53	N.d.a.	N.d.a.	
HFC-32	1,1- difluoromethane (CH2F2)	675	-51,7		
HFC-23	Trifluoromethane (CHF3)	14.800	-82,1	1150	
HFC-143	1,1,2-trifluoroethane (CH2FCHF2)	353		N.d.a.	
HFC-143a	1,1,1-trifluoroethane (CH3CF3)	4.470	-48	N.d.a.	
R-134/ HFC-134	1,1,2,2-Tetrafluoroethane (CHF2CHF2)	1.100			
R-134a/ HFC-134a	1,1,1,2-Tetrafluoroethane (CH2FCF3)	1.430	-26	360 (>370)	627-727
R-245fa/ HFC-245fa	1,1,1,3,3-Pentafluoropropane (CHF2CH2CF3)	1.030	15,3	320 (>250)	
HFC-245ca	1,1,2,2,3-Pentafluoropropane (CH2FCF2CHF2)	693	25-26	N.d.a.	
HFC-125	Pentafluoroethane (CHF2CF3)	3.500	-48,5	>250	>700
HFC-365mfc	1,1,1,3,3-pentafluorobutane (CF3CH2CF2CH3)	794	40,1	N.d.a.	
R-236fa/ HFC-236fa	1,1,1,3,3,3-hexafluoropropane (CF3CH2CF3)	9.810	-1,5	400	
HFC-236cb	1,1,1,2,2,3-hexafluoropropane (CH2FCF2CF3)	1.340			
HFC-236ea	1,1,1,2,3,3-hexafluoropropane (CHF2CHFCF3)	1.370			
HFC-227ea	1,1,1,2,3,3,3-heptafluoropropane (CF3CHFCF3)	3.220	-16,4	N.d.a.	
HFC-43-10mee	1,1,1,2,2,3,4,5,5,5-Decafluoropentane (CF3CHFCHFCF2CF3)	1.640	55 °C	>300	

MSDS- Material Safety Data Sheet

T99.99(2) - Temperatures for 99.99% Destruction removal efficiency (DRE) in 2 sec

N.d.a.- No data avaiable

Japan

Information on both existing approved destruction technology and new one.

1. Conventional

Liquid Injection Incineration (Being used at the production facilities in Japan.)
Operating Conditions
Temperature: Maintain over 1,200 degrees
Residence time in the incinerator: more than 1 second
Destruction rate: 99.99%
Quencher: Water
Intended Substances
(HFCs) HFC-134a, HFC-410A, HFC-407C, HFC-404A, HFC-502
(HCFCs) HCFC-22, HCFC-124
(Others) SF_6
Reported destructed substances (2016)
HFC-134a, HFC-404A, HFC-407C, HFC-410A, HFC-23, HCFC-22, HFC-502

2. New technology

Electric Heater (see Attachment).

Attachments

(Conventional) Liquid Injection Incineration Flow – This is the diagram for the existing destruction technology

(New) HFC Destruction by Electric Heater – The technology has been approved under IPCC since 2006.

Luxembourg

Luxembourg does not possess destruction facilities for the controlled substances in question. Moreover, no companies performing such operations are registered. Similarly, the research sector in Luxembourg has currently no projects focusing on the topic. As such, we do not possess relevant information regarding destruction technologies.

Mexico

The Government has consulted with the two installed facilities in México that have destroyed CFC and HCFC; and also HFC; these facilities are one Argon Plasma Arc and a Cement Kiln.

The main results they have reported are:

1. Both Argon Plasma Arc and Cement Kiln are available and with similar performance to destroy HFC as for the destruction of HCFC and CFC.

2. The costs are not available since they may be variable due to the conditions of the gas, but they are similar as for the destruction of CFC and HCFC.

3. The operation and lab tests are very similar to the CFC and HCFC, for that reason the HFC can be destroyed trough any of both technologies.

The communications from both companies are attached.

1st Submission document: Letter from Quimobásicos, Mexico

(Translation from Spanish)

Information on the technology used by Quimobásicos, S.A. de C.V. to destroy HFCs:

Section 1: Description of the technology used

Section 2: Types and quantities of HFCs destroyed

Section 3: Destruction and removal efficiency

Section 4: Emissions data

Section 1: Description of the technology used

According to the "Report of the Task Force on Destruction Technologies" (Appendix A: Description of ODS Destruction Technologies, A-2.2 Plasma Technologies), the HFC-destruction technology endorsed by the Technology and Economic Assessment Panel (TEAP) is plasma technology.

Plasma is formed when an electric current is applied (between an anode and a cathode) to a medium containing an inert gas (argon), generating a temperature of 12,500°C (see image 1), which facilitates the process of pyrolysis[1] that destroys refrigerant gases.

Any organic molecule that is injected into the plasma is broken down into its atoms and ions owing to the high temperature and the short residence time (of up to 23 milliseconds).

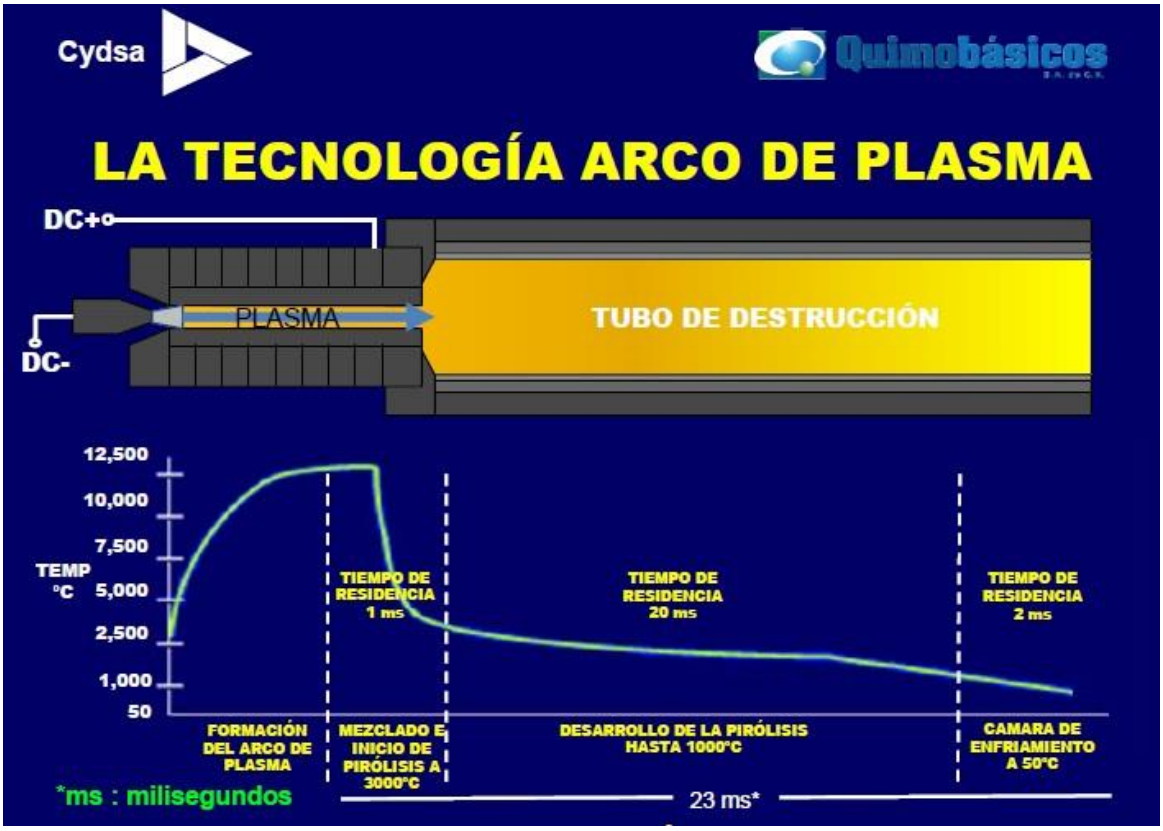
Pursuant to letter No. DGGIMAR.710/003985, licence No. 19-VI-19-16 issued by the Undersecretariat for Environmental Protection Management authorizes Quimobásicos to destroy the following substances:

Trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), chlorotrifluoromethane (CFC-13), chlorodifluoromethane (HCFC-22), trifluoromethane (HFC-23), difluoromethane (HFC-32), 1,1,2-trichlorotrifluoroethane (CFC-113), 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114), 1-chloro-1,1,2,2,2-pentafluoroethane (CFC-115), hexafluoroethane (HFC-116), 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123), 2,3,3,3-tetrafluoro-1-propene (HFC-123yf), pentafluoroethane (HFC-125), 2-chloro-1,1,2-tetrafluoroethane (HCFC-124), 1,1,1,2-tetrafluoroethane (HCFC-134a), dichlorofluoroethane (HCFC-141b), chlorodifluoroethane (HCFC-142b), 1,1,1-trifluoroethane (HCFC-143a), 1,1-difluoroethane (HCFC-152a), octafluoropropane (HC-218), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236a), 1,1,1,3,3-pentafluoropropane

[1] Pyrolysis: the thermal decomposition of organic compounds at elevated temperatures in an oxygen-limited environment with associated cooling and very short residence times, all of which prevents the formation of dioxins and furans. Plasma arc destruction differs from conventional incineration in that the latter requires an excess oxygen level (of around 10 per cent) and longer residence times (of between two and five seconds), which facilitate the formation of dioxins and furans when their chemical precursors are present.

(HFC-245fa), propane (HC-290), 1,1,1,3,3-pentafluorobutane (HFC-365mfc), n-butane (HC-600), isobutane (HC-600a), isopentane (HC-601), propylene (HC-1270).

Image 1



La tecnología arco de plasma = plasma arc technology
Tubo de destrucción = decomposition chamber
Tiempo de residencia = residence time
Milisegundos = milliseconds
Formación del arco de plasma = plasma arc formation
Mezclado e inicio de pirólisis a 3000°C = mixing and commencement of pyrolysis at 3000°C
Desarrollo de la pirólisis hasta 1000°C = continuation of pyrolysis down to 1000°C
Cámara de enfriamiento a 50°C = cooling chamber at 50°C

Section 2: Types and quantities of HFCs destroyed

From September to December 2015, Quimobásicos destroyed 26,702 kg of HFC-134a (1,1,1,2-tetrafluoroethane).[2]

[2] The destruction was carried out in cooperation with the **United Nations Industrial Development.** Organization as part of the following project:
Name of project: Destruction of unwanted ODS collected in Mexico.
Project No.: RFX 700001057.
Contract No.: 3000028375.

Section 3: Destruction and removal efficiency

A destruction efficiency in excess of 99.99 per cent has been achieved with HFC-134a feeding.

Section 4: Emissions data

The gases emitted when using plasma technology are cooled quickly at a temperature of around 50°C with an atomized alkaline solution. Rapid cooling prevents the formation of undesirable organic molecules such as dioxins and furans.

Typical emissions resulting from the destruction of HFCs by means of plasma technology:

✓ Acid gases (HCl and HF).

✓ Particulate matter.

✓ Carbon monoxide.

✓ Metals and traces of other pollutants.

The destruction of 26,702 kg of HFC-134a referred to in **section 2** of this document produced 1.9276 kg of emissions (destruction efficiency in excess of 99.99 per cent).

2nd Submission document:

Mexico sent a second document in Spanish, and subsequently the link to a different report in English, noting that the information submitted in the original document in Spanish could be found in Annexes III and IV of the report. These Annexes are reproduced below.

United Nations Industrial Development Organization and the Government of France, Demonstration Project for Disposal of Unwanted ODS in Mexico, 2017, Annexes III and IV.

Annex III. ODS destruction pilot test results in Argon plasma arc

ODS destruction pilot test at Quimobásicos Argon plasma arc took place from August 27th to 30th, 2013. As per the test protocol approved by SEMARNAT, 480 kg of ODS were supplied in four test cycles as seen in Table 1.

Table 1 ODS composition of samples used during pilot test in Argon Plasma Arc

Test cycle	ODS tested	Composition	Quantity (kg)
1	HFC-134a	100%	120
2	HFC-134a	100%	120
3	HFC-134a /HCFC-22	85%/15%	120
4	HFC-134a /HCFC-22	85%/15%	120
Total			**480**

Source: Quimobásicos.

The results of the destruction tests showed that average destruction efficiency was 99.9994%. Five samples were tested, as one of the cycles (August 28th) was interrupted due to issues in one of the equipment components. ODS destruction efficiency was analyzed by a certified laboratory from the US.

Table 2 ODS destruction efficiency results during pilot test in Argon Plasma Arc

Date	Operation time (h)	ODS tested	Destruction Efficiency
August 27th	4.09	100% HFC-134a	99.9994%
August 28th	4.45	100% HFC-134a	99.9994%
August 29th	4.05	85% HFC-134a / 15% HCFC-22	99.9998%
August 29th	4.02	85% HFC-134a / 15% HCFC-22	99.9983%
August 30th	4.03	100% HFC-134a	99.9999%
Mean value			**99.9994%**

Source: Quimobásicos.

Annex IV. ODS destruction pilot test results in cement kiln

ODS destruction pilot test at Holcim Mexico facilities took place on May 19 and 20th, 2015 in the cement kiln 1 of Tecomán plant. 2,050 kg of recovered unwanted ODS contained in three cylinders of varying compositions of HFC-134a, CFC-12 and HCFC-22 were supplied through SEMARNAT (Table 3). A dedicated feeding pipe with instrumentation was installed in order to supply the ODS into the main burner´s primary air inlet. ODS handling was performed by Geocycle (formerly Ecoltec), while Holcim staff supervised the flow of gases supplied into the cement kiln.

Table 3 ODS composition of samples used during pilot test in cement kiln

	Cylinder 1	Cylinder 2	Cylinder 3
HFC-134a (%)	35.6	23.8	30.5
CFC-12 (%)	52.6	53.2	10.2
HCFC-22 (%)	10.8	23.0	59.4
Gross weight (kg)	1320	1290	550
ODS net weight (kg)	**840**	**810**	**150**

Source: Holcim Mexico/Geocycle.

In each test, samples of fuels supplied in the cement kiln were analyzed (Table 5). Results are shown in Table 4. It is relevant to mention that between 12 and 21% of alternative fuels were supplied in the kiln, including tire and sludge residues.

Table 4 Results of analysis performed to fuels supplied during the pilot test in cement kiln

Parameter	Units	Solids	Tires	Liquids	Sludge
Moisture	%	17.30	2.36	93.6	89.90
Chlorine	%	0.31	$\leq$ 0.03	0.15	0.18
Caloric value	MJ/kg	25.8	30	0	6.0
Sulfur	%	0.42	1.6	1.2	0.48
Na_2O	%	0.30	0.02	1.88	0.18
K_2O	%	0.18	0.05	0.02	0.05
pH	%	7.90	8.1	4.05	4.67
Ashes	%	17.90	NA	1.09	6.97

Source: Holcim Mexico/Geocycle.

Table 5 Amount and type of fuels supplied into the cement kiln during the pilot test

Test date	Tire chips (tonnes)	Solids (tonnes)	Liquids (tonnes)	Sludge (tonnes)	% Alternative fuels
May 20th	21.7	16.3	6.5	13.8	12.2
May 21st	38.6	26	0	24.8	20.7

Source: Holcim Mexico/Geocycle.

Combustion gases were analyzed through the CEMS installed in the stack of line number one, which consists of a dust analyzer and a gas analyzer, according to NOM-040-SEMARNAT-2002 requirements. CEMS allow the measurement of NO_x, SO2, HCl, CO, Particles and Hydrocarbons. Other parameters, including Dioxins and Furans, heavy metals and ODS, were point measured by third party laboratories.

Operating conditions of the pilot tests are summarized in the Table 6.

Table 6 Cement kiln pilot test operating conditions in 2015

Test date	Average gas flow (kg/h)	Maximum gas flow (kg/h)	Gas feed period (h)	Gas fed (kg)
May 20	43	52	23	980
May 21	153	277	7	1070

Source: Holcim Mexico/Geocycle.

The results of the emission parameters measured through the CEMS are shown in Table 7. It must be noticed that CO emissions are expected be high as alternative fuels, such as tires and sludge, were supplied to the kilns. Nevertheless, these emissions are kept well below NOM-040-SEMARNAT-2002 specifications as seen below.

Table 7 Continuous monitoring results of emission parameters regulated by NOM-040-SEMARNAT-2002

Parameter	Emission limits [a]	Units	Test date	
			May 20th	May 21st
CO	4,000	mg/m^3	340.71	585.93
SO_2	1,200	mg/m^3	0.88	0.08
NO_x	1,200	mg/m^3	480.81	454.67
THC	70	mg/m^3	24.08	28.47
HCl	70	mg/m^3	10.34	5.92

[a] Emission limits set as per NOM-040-SEMARNAT-2002

Source: Holcim Mexico/Geocycle.

Moreover, the results of point measurements to regulated emission parameters is depicted in Table 8.

Table 8 Point measurement results of emission parameters regulated by NOM-040-SEMARNAT-2002 and TEAP

Parameter	Emission limits [a]	Test date	
		May 20th	May 21st
Sb, As, Se, Ni, Mn	0.70 mg/m^3	< 0,0770	< 0,073 2
Cd	0.07 mg/m^3	0,0015	~ 0,000 6
Hg	0.07 mg/m^3	< 0,0023	~ 0,003 5
Pb, Cr, Zn	0.70 mg/m^3	~ 0,0463	~ 0,039 8
Dioxins and Furans	0.2 (ng ITEQ/m^3)	0,0010	0,001 4
Particles (TSP)	26.7 kg/h	0,1910	0,242

[a] Emission limits set as per NOM-040-SEMARNAT-2002, except for Dioxins and Furans, which are set according to UNEP/TEAP (2002).

Source: Holcim Mexico/Geocycle.

Finally, the results of analysis performed to combustion gases on ODS composition is summarized in Table 9.

Table 9 ODS concentration in combustion gases during pilot tests

ODS	May 20th			May 21st		
	Sampling time	Gas flow (kg/h)	Concentration (mg/m^3)	Sampling time	Gas flow (kg/h)	Concentration (mg/m^3)
CFC-12	13:35-14:06	50	< 0.0243	10:05-10:54	200	< 0.0240
	14:07-14:21	50	< 0.0265	11:00-11:30	240	< 0.0253
	14:22-14:46	50	< 0.0249	11:48-12:40	277	< 0.0251
HCFC-22	13:35-14:06	50	~ 0.0577	10:05-10:54	200	< 0.0142
	14:07-14:21	50	< 0.0157	11:00-11:30	240	< 0.0150
	14:22-14:46	50	< 0.0148	11:48-12:40	277	< 0.0149
HFC-134a	13:35-14:06	50	< 0.0193	10:05-10:54	200	< 0.0191
	14:07-14:21	50	< 0.0148	11:00-11:30	240	< 0.0200
	14:22-14:46	50	< 0.0198	11:48-12:40	277	< 0.0199

~ Results are between detection limit (DL) and quantification limit (QL).
< Results are below the detection limit (DL).

Source: Holcim Mexico/Geocycle.

According to pilot test performance results it was concluded that ODS destruction is feasible without increasing toxic and regulated emissions, and without impacting the quality of the clinker produced.

A maximum gas feed flow of 277 kg/h was achieved in 7 hours of test during the second day. This feed flow was attained by supplying the gases through the primary airline of the main burner. The destruction efficiency reached was 99.99865%.

All the measured parameters complied with the regulations established in NOM-040-SEMARNAT-2002 and the UNEP/TEAP (2002). It was further noticed that during the tests a reduction of 16% of NO_x was accomplished in comparison to 2014 average value.

The applied operation and safety measures allowed to ensure that unwanted ODS destruction:

1. Safety of workers and community is not put at risk

2. Emissions limits set by NOM-040-SEMARNAT-2002 and TEAP are not exceeded.

3. No disturbances are introduced into the process or quality of cement produced.

4. Destruction of unwanted ODS is compatible with clinker manufacturing.

United States of America

The party submitted the attached report in response to Decision XXIX/4 on destruction technologies for controlled substances, noting that, while this report provides information specific to the scope of Decision XXIX/4 to support the work of the TEAP, the report was also developed to fulfil other purposes and as such provides additional information.

Attachment: ODS Destruction in the United States and Abroad, Prepared for the U.S. Environmental Protection Agency by ICF, February 2018:

ODS Destruction in the United States and Abroad

Venezuela (Bolivarian Republic of)

(*Translation from Spanish*)

The verification of the protocol for the destruction of ozone-depleting substances was carried out in Venezuela in accordance with the guidelines established in the Basel Convention for the disposal of hazardous waste. A total of 240 kg of CFC-12 was disposed of during the tests, at a rate of 10 kg/h. The process was carried out in the furnace of a State-owned cement company, which has a successful track record in the co-processing of persistent organic materials and other wastes. Although the results were positive, the Ministry of Popular Power for Eco-socialism and Water has not yet authorized the destruction services because it has not been decided whether tests should be carried out on other ozone-depleting substances and hydrofluorocarbons. In addition, it is necessary to acquire and install a dispenser for directly discharging the gases into the furnace burner and to establish the mechanism for collecting and transferring refrigerants for destruction. Destruction services cannot be offered until such obstacles are overcome.