Destruction of Ozone Depleting Substances using Steam Plasma

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ABSTRACT

Chlorofluorocarbons (CFCs) are potent Ozone Depleting Substances (ODS) and greenhouse gases (GHG). For example, the GHG emission factor for R-12 (dichlorodifluoromethane) is 10,900 times that of CO_2. Hydrofluorocarbon (HCFC) refrigerants are safe for the ozone layer but are potent greenhouse gases.

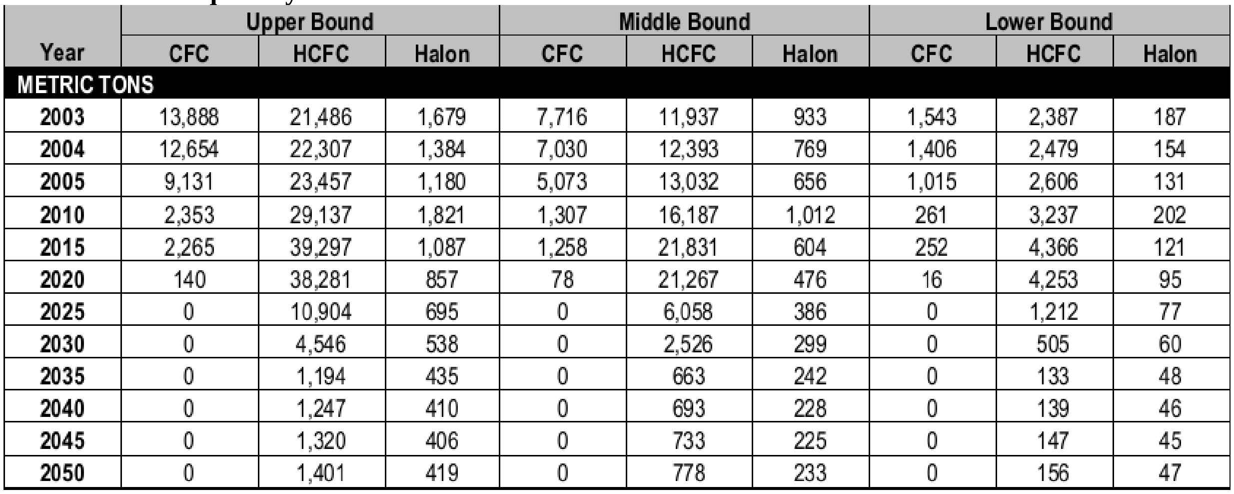
Over the past three years, PyroGenesis Canada Inc. (PCI) has developed and patented the SPARC™ (Steam Plasma Arc Refrigerant Cracking) technology which uses steam plasma to hydrolyze CFC's and HFC's into CO_2, HCl and HF. The acid gases HCl and HF are easily neutralized in a wet scrubber. Due to the high energy density of steam plasma, the volume of flue gas produced is reduced by more than 60 times compared to a conventional incinerator. The resulting compact plasma system opens the door to local treatment of used refrigerants from refrigeration systems recycling facilities, at a cost that is competitive with off-site hazardous waste incineration.

Tests on a 2 kg/h SPARC pilot plant, treating CFCs collected from used refrigeration units, have demonstrated the ability to reach destruction and removal efficiency (DRE) of 99.9999% for the R-12 type refrigerant. The emission of dioxins and furans are 10 times below the air emission standards and emissions of acid gases (HCl and HF) are 300 times below the standards. PCI recently installed a commercial scale SPARC™ system to treat up to 50 kg/hr of various streams of refrigerants at Recyclage Ecosolutions' fridge recycling facility in Laval, Quebec. This paper presents the results obtained during the pilot testing of the system.

INTRODUCTION

Chlorofluorocarbons (CFCs) are potent Ozone Depleting Substances (ODS) and greenhouse gases (GHG). ODS and GHG are slow-acting but persistent pollutants, and there have been international efforts to diminish them. Ozone depleting substances (ODS) are substances that destroy the earth's stratospheric ozone layer, a protective barrier which prevents excessive amounts of harmful ultraviolet radiation from reaching earth's surface[1]. GHG alter the global climate, which aggravates droughts and floods. HCFCs are also potent GHG which need to be destroyed and their emission into the atmosphere limited. Table 1 below provides an estimated quantity of ODS potentially recoverable from retired equipment and available for destruction.

Table 1 Estimated quantity of ODS available for destruction[2]



Year	Upper Bound			Middle Bound			Lower Bound		
	CFC	HCFC	Halon	CFC	HCFC	Halon	CFC	HCFC	Halon
METRIC TONS									
2003	13,888	21,486	1,679	7,716	11,937	933	1,543	2,387	187
2004	12,654	22,307	1,384	7,030	12,393	769	1,406	2,479	154
2005	9,131	23,457	1,180	5,073	13,032	656	1,015	2,606	131
2010	2,353	29,137	1,821	1,307	16,187	1,012	261	3,237	202
2015	2,265	39,297	1,087	1,258	21,831	604	252	4,366	121
2020	140	38,281	857	78	21,267	476	16	4,253	95
2025	0	10,904	695	0	6,058	386	0	1,212	77
2030	0	4,546	538	0	2,526	299	0	505	60
2035	0	1,194	435	0	663	242	0	133	48
2040	0	1,247	410	0	693	228	0	139	46
2045	0	1,320	406	0	733	225	0	147	45
2050	0	1,401	419	0	778	233	0	156	47

In the US, there are only 20 identified facilities that accept ODS waste from outside sources for commercial destruction[2]. In Canada, only one facility at Swan Hills, Alberta, with a capacity of 5 kg/hr, accepts ODS waste for destruction. As of 2008, there were only 147 facilities worldwide for destroying ODS[2]. Typically, these ODS destruction facilities have limited capacity and are located far from the ODS sources, which requires transportation of ODS to the facility. Transportation of volatile ODS comes with potential risks such as leaks during transportation and handling, leading to additional GHG emissions.

There is a clear demand for local solutions which can be easily deployed at or near the source of ODS collection and processing. Towards this objective, PyroGenesis Canada Inc., (PCI) has developed the Steam Plasma Arc Refrigerant Cracking (SPARC) system which uses highly reactive steam plasma technology for the destruction of ODS substances. SPARC uses steam hydrolysis as the chief reactant for ODS destruction. Steam hydrolysis offers many advantages over the conventional incineration process, such as lower flue gas flow rate and less pollutants. Steam plasma is also an improvement over oxygen plasma because oxygen reacts with ODS to form chlorine (Cl_2) and fluorine (F_2), which are toxic and difficult to remove. Over the past three years, PCI has designed, fabricated and demonstrated a 2 kg/hr pilot SPARC system. Currently, PCI is building a 50 kg/hr SPARC system in collaboration with Recyclage Ecosolutions (RES). This paper presents the results obtained from the pilot testing of the 2 kg/hr SPARC system. The scale up efforts towards designing of the 50 kg/hr SPARC system are also presented.

PROCESS DESCRIPTION

A simplified block diagram of the SPARC process is shown in Figure 1. The process is designed to destroy ozone depleting substances (ODS) while meeting all the local effluent emissions standards. In this process, the precursor material, i.e. the ODS to be destroyed, is fed on top of the reactor in front of a steam plasma plume. Under the steam plasma plume, the stable long-chain precursor material dissociates into smaller compounds such as carbon monoxide (CO), carbon dioxide (CO_2), hydrogen fluoride (HF), hydrogen chloride (HCl) and hydrogen (H_2). This mixing and dissociation occurs in a refractory lined reactor where the necessary high temperature and residence time are maintained to complete the destruction reactions. A small amount of air is added in the second zone of the reactor to oxidize the CO to CO_2 and H_2 to H_2O. At the discharge of the reactor, the resulting gas mixture is quenched with a spray of cold water to quickly reduce the temperature of the gas stream and thus avoid the reformation of dioxins or furans. The quench water and the cold gas enter a scrubber tank located at the bottom of the quench. The water is collected and re-circulated to the top of the scrubber. The cold gas mixture passes through a caustic scrubber where the acid HCl and HF gases are neutralized and converted to harmless sodium chloride (NaCl) and sodium fluoride (NaF) salts. This neutralization is achieved using a caustic (NaOH) solution and a pH controlled loop . The off-gas leaving the scrubber, which primarily contains nitrogen (N_2) and CO_2, is discharged through a stack.

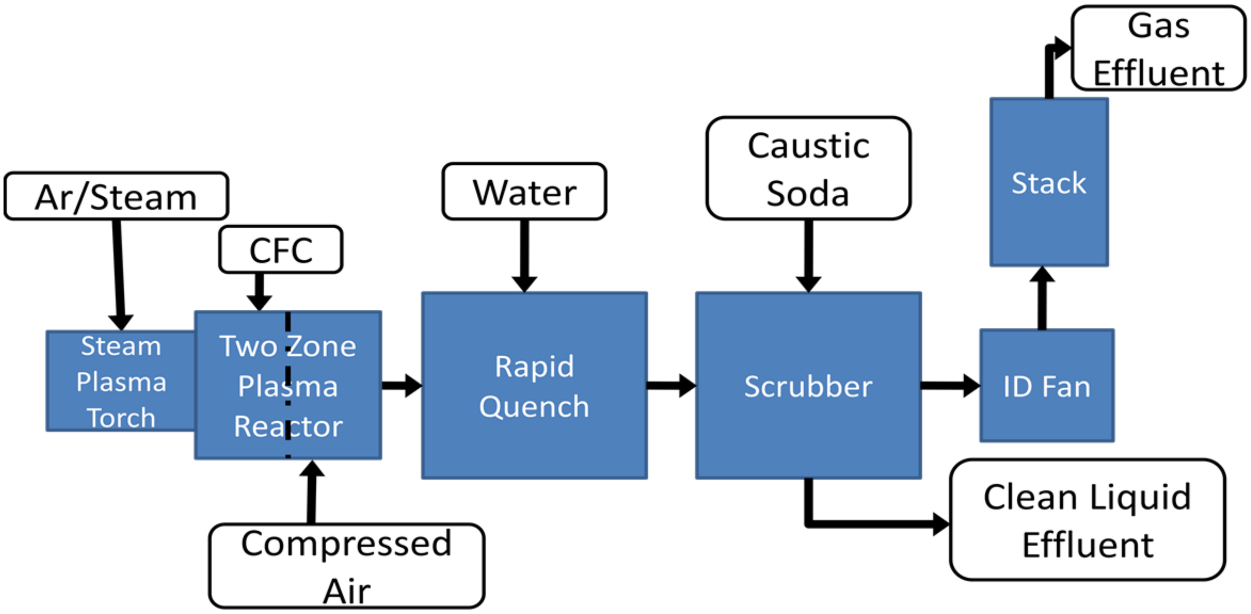


Figure 1: Block Diagram of the SPARC process

EXPERIMENTAL APPARATUS AND TEST PROTOCOLS

Apparatus

Figure 2 shows a picture of the pilot plant. The pilot plant was designed to destroy R-12 at up to 2 kg/h. It consisted of:

1) a process skid, equipped with a steam plasma torch, refractory lined reactor and gas cleaning system,
2) a steam skid, for supplying superheated and saturated steam to the process.
3) a water cooling skid for cooling the plasma torch.
4) a programmable logic controller (PLC) and a human/machine interface (HMI) to control the system.

Figure 2: Picture of the 2 kg/hr SPARC pilot plant

Testing

The objectives of the pilot tests were:

1) To demonstrate that steam plasma hydrolysis can be successfully used to destroy R-11 and R-12 refrigerants to the desired DRE of 99.9999%.
2) To measure the off gas composition of the SPARC system.
3) To gather necessary scale up data for designing a larger scale 50 kg/hr demonstration ODS destruction plant.

These objectives were achieved by developing a pilot-scale steam plasma torch, assembling a pilot-scale system, and performing a series of experiments. PCI conducted a first series of in-house tests. During these tests, the system was heated to different operating temperatures and the precursor material was fed to the system under steady state conditions. The stack gases were sampled and analyzed for their composition. In addition, PCI conducted a second series of external sampling and analysis tests during which the stack gases were sampled and analyzed by a third party.

The external sampling and analysis tests occurred over 4 working days. The analytical equipment used in the third-party stack sampling corresponded to the recommendations of the government of Quebec (*Guide d'échantillonnage à des fins d'analyses environnementales*).

- The DRE was measured as follows: The off-gas was collected in a canister over 1 hour according to US Environmental Protection Agency (EPA) method TO-15, and a cryogenic gas chromatograph/mass spectrometer (GC/MS) was used to quantify the trace amounts of residual ODS. The feed gases were also sampled and analyzed., The DRE was calculated from the difference between the input and output from the system.
- Dioxins and furans were collected over 3 hours according to Environment Canada (EC) method SPE 1/RM/2. These samples were then analyzed and quantified by the external laboratory.
- The flow rate of off-gas was measured continuously using a pitot tube.
- Particulates, acid gases (HCl, HF, HBr, P_2O_5), and mercury were collected over 3 hours using isokinetic sampling according to EC method EPS/1/RM/8. These samples were then analyzed and quantified by the external laboratory.
- O_2, CO_2, CO, SO_2, and Total Organic Carbon (TOC) were measured continuously using a CEMS according to US EPA method 3A/3A/10.

Industrial-purity R-11 (CCl_3F) and R-12 (CCl_2F_2) were used in the pilot tests. The R-11 sample was 73% pure and contained significant R-141B ($C_2H_3Cl_2F$). The R-12 sample was 97% pure and contained significant R-124 (C_2HClF_4) and R-22 ($CHClF_2$).

RESULTS OF PILOT TESTS

Table 2 below presents the composition of the stack gas as certified by the external laboratory while treating R-12 feed and the stack discharge limits for each component.

Table 2: Summary of stack gas composition from pilot tests

	R-12 feed	**Discharge limit**[*]
HCl (mg/Rm^3) [†]	0.4	50
HF (mg/Rm^3)	0.01	5
HBr (mg/Rm^3)	< 0.05	5
P_2O_5 (mg/Rm^3)	< 0.02	10
SO_2 (mg/Rm^3)	12.2	150
Dioxins and furans (ng-TEQ/Rm^3)	0.011	0.08
Mercury Hg (µg/Rm^3)	0.07	50
Destruction and Removal	>99.9999%	99.9999%

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[*] The limits of HCl, HF, SO2, dioxins and furans, and mercury correspond to Quebec *Règlement sur la qualité de l'air*, with a correction to 11% oxygen. The limits of HF, HBr, and P2O5 correspond to Quebec *Règlement sur la qualité de l'atmosphère Q2 R20*, with a correction to 50% excess air.

[†] Rm^3 means that the gas volume is corrected to 101.3 kPa and 25°C.

Efficiency, DRE		

These results show that the amount of pollutants is well below the applicable regulations and that the target DRE of 99.9999% was achieved.

DEMONSTRATION PLANT SCALE-UP

Context

The first commercial-scale SPARC system is installed at the Recyclage ÉcoSolutions (RES) plant in Laval, Canada. RES is a company that specializes in the management and recycling of appliances and equipment containing ODS, especially domestic or commercial refrigerators and freezers. The placement of the SPARC system at the RES plant allows RES to avoid the expense and risk of shipping ODS to an off-site destruction system.

Process simulation results

The plant was scaled up using the data collected from the pilot scale system. A complete computer process simulation model (detailed mass and energy balances linked with free-energy-minimization calculations) with 100 process streams was developed using the software METSIM. This was used to simulate each kind of feed material to be destroyed. Process parameters such as the plasma torch power and the quench water flow rate were derived from this simulation.

The conditions in the reactor were adjusted to minimize the amount of pollutants such as carbon monoxide or chlorine. The flow rate and composition of the off-gas for each of the different feed materials was calculated. Typical off gas parameters of the system are:

- Off gas flow rate 100 Nm^3/h (62 scfm)[‡]
- Bulk composition: almost entirely carbon dioxide, nitrogen, oxygen, argon, and water
- Anticipated pollutants:

Table 3: Anticipated pollutants in gas effluent from 50 kg/h ODS destruction

Pollutant	**Calculated amount**	**Legal limit**[§]
carbon monoxide (CO)	less than 50 ppmv	54 ppmv
hydrogen chloride (HCl)	less than 20 ppmv	36 ppmv
hydrogen fluoride (HF)	less than 4 ppmv	7 ppmv

Atmospheric dispersion model results

[‡] In comparison, the exhaust from an automobile is 10 to 120 scfm.

[§] The limits of CO, HCl, and HF correspond to Quebec *Règlement sur la qualité de l'air*, with a correction to 11% oxygen.

In order to study the dispersion of the pollutants from the newly designed plant, a third party was commissioned to create a detailed atmospheric dispersion model using AERMOD 12060 and AERMET 11059. This model includes meteorological data from nearby Trudeau airport from the period 2006-2011. It covers a grid of 1000 points within a 5 km radius, and it calculates hourly, daily, and annual averages. This grid includes a topographical map with 10 m graduations, and nearby buildings were also added. The contaminants studied were NO_x, dioxins and furans, CO, non-destroyed ODS, HCl, and HF.

The atmospheric dispersion model shows that the SPARC system will meet the ambient air quality for all contaminants at ground level as shown in Table 4 below. The limits below correspond to the Quebec Clean Air Regulations, except for the limit of residual ODS which corresponds to the Ontario ambient air quality criteria. (Table 3 above lists the discharge limits from an industrial point source, whereas Table 4 lists the maximum concentrations in the nearest residential or commercial area.)

Table 4: Results of atmospheric dispersion model

Contaminant	% of ambient air limit (background level)	% of ambient air limit (during operation)
NOx (1h limit)	36	39
NOx (24h limit)	48	50
NOx (1 year limit)	29	30
Dioxins and furans (1 year limit)	67	67
CO (1h limit)	8	8
CO (8h limit)	14	14
Residual ODS (24h limit)	0	~0
HCl (1h limit)	0	~0
HCl (1 year limit)	0	~0
HF (1h limit)	0	16
HF (24h limit)	0	6
HF (1 year limit)	0	11

Advantages of steam hydrolysis over conventional technology

Based on the pilot-scale tests and the detailed simulations, the SPARC system offers two major advantages over conventional incineration systems: lower off-gas volumes and lower amounts of pollutants.

(a) The flow rate of off-gas from a commercial-scale SPARC system is expected to be more than 60 times lower than that of an ODS incinerator of the same capacity. This is less than the effluent from a single automobile. As a result, the gas cleaning equipment will be more compact and less costly than an incinerator system.

(b) Destruction using steam plasma will also have an important impact of reducing the amount of pollutants. Typically, incinerator systems have a long list of byproducts resulting from incomplete combustion and other gaseous pollutants such as dioxins and furans, chlorine gas

(Cl_2) and fluorine gas (F_2)[3]. Cl_2 and F_2 result from the reaction of ODS with oxygen; when steam is used in the destruction reaction, it forms hydrogen chloride (HCl) and hydrogen fluoride (HF) gases, which can be scrubbed much more easily than Cl_2 and F_2.

SUMMARY AND CONCLUSION

Over the past three years, PyroGenesis Canada Inc. has developed and patented the SPARC™ (Steam Plasma Arc Refrigerant Cracking) technology which uses steam plasma to hydrolyze CFC's and HFC's into CO_2, HCl and HF. The acid gases are neutralized in a wet scrubber. A 2 kg/h pilot system was designed, built, and tested, and a 50 kg/h demonstration plant is installed in Laval, Quebec.

Steam hydrolysis offers two major advantages over incineration: a lower flow rate of flue gas and a lower amount of pollutants. This offers a compact and economical system which can be installed directly at an ODS stockpiling facility.

A series of third-party tests on the 2 kg/h system proved that the process can achieve a DRE of 99.9999%. At the same time, the pollutants (acid gases, dioxins and furans, NO_x, and mercury) are orders of magnitude below the applicable discharge limits.

Based on the results of the pilot-scale tests, several improvements were incorporated into the demonstration plant design. These include better ODS pre-heating and feeding system, more automation, and more optimal reactor geometry.

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[3] Springsteen, B.; Ho, L.; Kryder, G. *Experimental Investigation of PIC Formation During the Incineration of Recovered CFC-11*; US EPA Air and Energy Engineering Research Laboratory; National Technical Information Service: Springfield, VA, 1994.