Atmospheric Microwave Plasmas for the Abatement of Perfluorocompounds

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Agenda

- Greenhouse Effect & Greenhouse Gases
- PFC Emitters
- Methods for PFC Emissions Reduction
- Plasma types & Plasma Generation
- Atmospheric Microwave Plasmas
- BOC Edwards Zenith Etch Plasma
- Chemistry of PFCs Abatement in the Presence of Water: CF_4, C_2F_6, CHF_3 and SF_6
- Conclusions

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Greenhouse Effect

- The Kyoto Protocol calls for reductions in the emission of greenhouse gases, those gases with stronger global warming potential than CO_2

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Greenhouse Gas Emissions

Gases in the atmosphere can contribute to the greenhouse effect both

Directly: when the gas itself is a greenhouse gas

Example: H_2O, CO_2, CH_4, N_2O, O_3.

Indirectly: - when chemical transformations of the original gas produce other greenhouse gases;

- when a gas influences the atmospheric lifetime of other gases;
- when a gas affects atmospheric processes that alter the radiative balance of the earth;

Example: *perfluorocarbons* (PFCs), *hydrofluorocarbons* (HFCs), and *sulphur hexafluoride* (SF_6)

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Global Warming Potentials and Atmospheric Lifetime of Selected Greenhouse Gases

Global warming gas	GWP_{100}	Atmospheric lifetime, years
CO_2	1	50 – 200
CH_4	21	12
N_2O	310	120
CF_4	6,500	50,000
C_3F_8	7,000	2,600
C_2F_6	9,200	10,000
CHF_3	11,700	264
SF_6	23,900	3,200

GWP = Global Warming Potential - depend of IR-absorption and time horizon (hold up time) in the atmosphere

GWP_{100} = Integral about the time horizon 100 years

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PFC Emitters

- **Aluminium manufacture** – unintentional byproducts C_2F_6 and CF_4

- **Semiconductor industry** – largest emitter of intentionally produced PFCs

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Emission Reduction Targets

Fluoric gases like PFCs, HFCs and SF_6 are utilized to clean devices in semiconductor manufacturing processes

PFCs

Dielectric Etch CF_4, CHF_3, CH_3F, CH_2F_2, C_4F_8, C_5F_8

Polysilicon Etch CF_4, CHF_3, CH_2F_2, (HBr, Cl_2)

Dielectric Etch may also use toxic and corrosive species

NF_3, C_4F_6, SF_6

Target

A reduction in emissions to 90% of the baseline year levels by 2010.

- World Semiconductor Council, Okinawa, May 2001

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Methods for PFC Emissions Reduction

- DECOMPOSITION of PFCs to non-hazardous materials

  - Combustion
  - Plasma
  - Thermal-chemical → Direct thermal oxidation
  - Thermal-chemical → Catalytic oxidation

- RECYCLE & RECOVERY of the unused PFCs

- PROCESS OPTIMIZATION and/or REPLACEMENT of PFCs with other gases

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What is a Plasma?

- Mixture of electrons, ions, and neutrals in the ground state, excited species, and photons with negative and positive charges balance each other *(quasi-neutrality)*.
- Electrically conducting due to the presence of free charge carriers both negative (electrons and negative ions) and positive (positive ions).
- Affected by magnetic fields.

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Types of Plasmas

- Local Thermodynamic Equilibrium (LCT)

  $T_{\text{electrons}} = T_{\text{heavy particles}}$

- Non-equilibrium Plasmas

  $T_{\text{electrons}} >> T_{\text{heavy particles}}$

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Plasma Generation

Most energy for generating plasmas is supplied by electric sources:

- Electric discharges of high (MHz level) or very high (GHz level) frequency, in which an electromagnetic field is the source of energy
- Arc discharges, characterized by great concentrations of energy, originating from an electric arc.

Also, specific types of electric discharges: spark, corona, glow, silent or barrier

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Why Use a Microwave Atmospheric Plasma?

- Electron density and temperature is higher than in radio-frequency (RF) or direct current (DC)

  ⇒ Higher reactivity

- Electrons are primarily responsible for the absorption of energy from the electric field

  ⇒ The gas stream itself is used as the resistive medium for transferring electrical energy into heated gas molecules

- Intimate interaction between the wave and the plasma

  ⇒ The wave supplies energy to the plasma, but without the plasma, the wave could not exist ⇔ local balance between the power supplied by the wave and the power lost from the plasma

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Additionally….

- Uses less energy than a burner or catalytic system
- Low operational risk compared to other thermal systems
  - No fuel gas
  - No electromagnetic emissions
- Post-pump install
- No foreline modifications required ↔ No risk of contamination/corrosion of pump & tool
- Maintenance does not require breaking of the vacuum lines

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BOC Edwards Solution

Zenith Etch Plasma

Integrated Vacuum & Abatement Technology

- Abatement: 2.45 GHz Microwave Atmospheric Plasma (PFCs, HFCs, SF_6 etc.) with Wet Scrubber (HAPs)
- Vacuum: 4-pump process

- ! Provides a non-fuel abatement alternative

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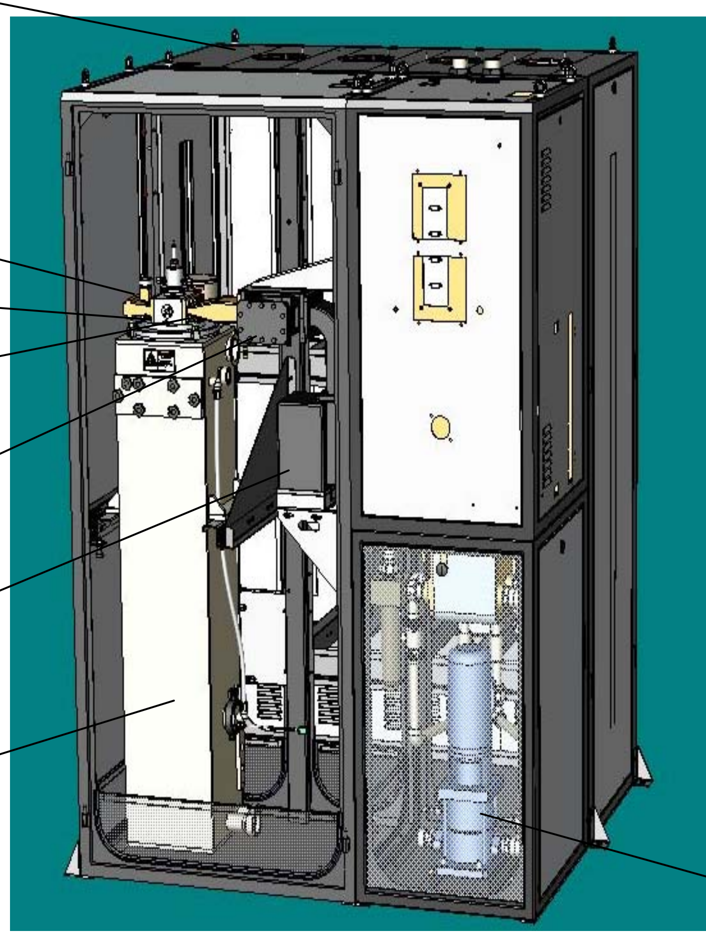
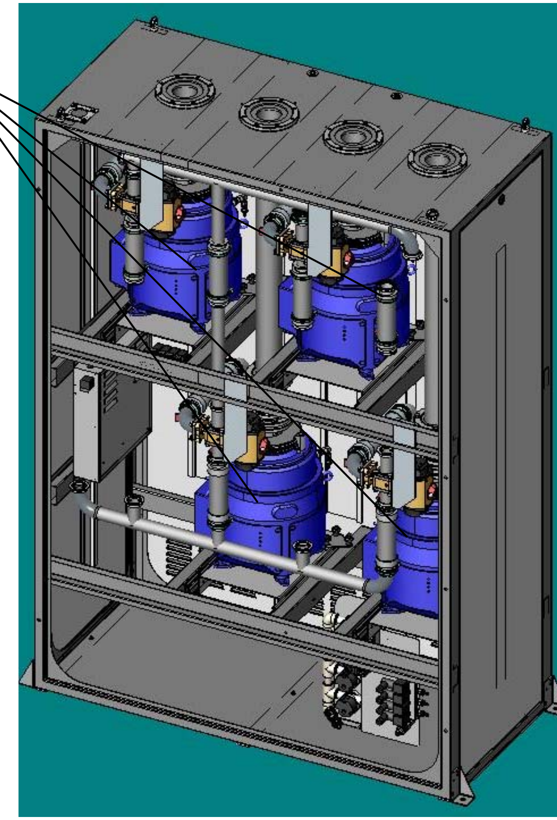
Zenith Etch Plasma Module





Pump frame

4 ePX500P pumps

Short circuit

Plasma Reactor

Waveguide

Isolator + reflected power meter

2.45 GHz magnetron head

Wet scrubber

Water recirculation unit

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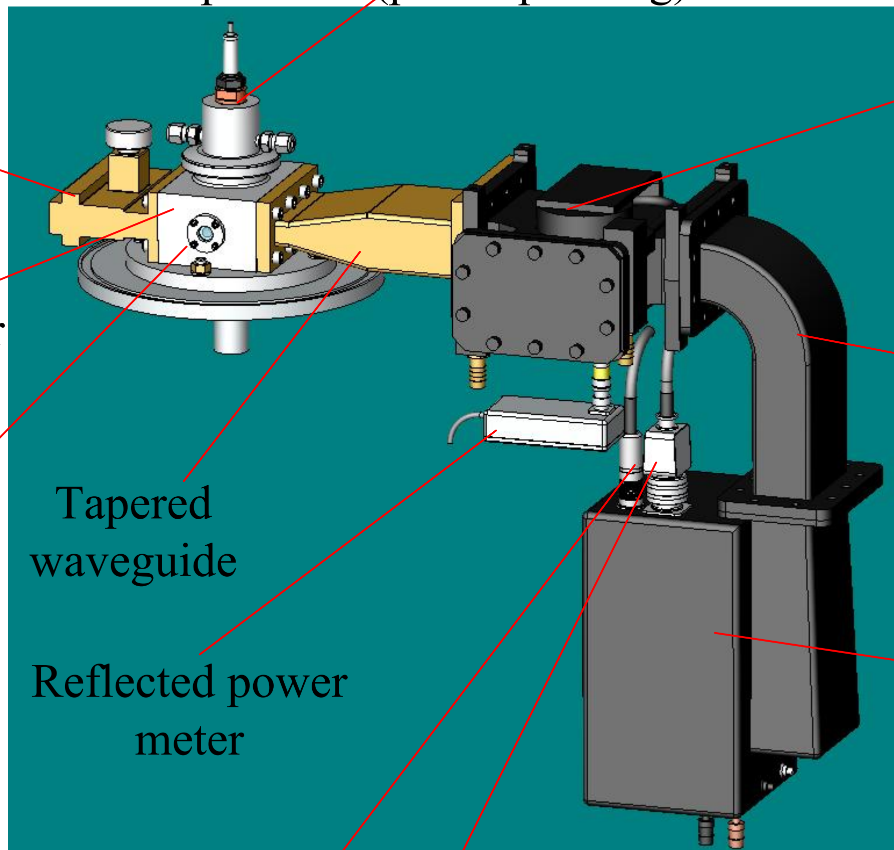
Microwave & Plasma System



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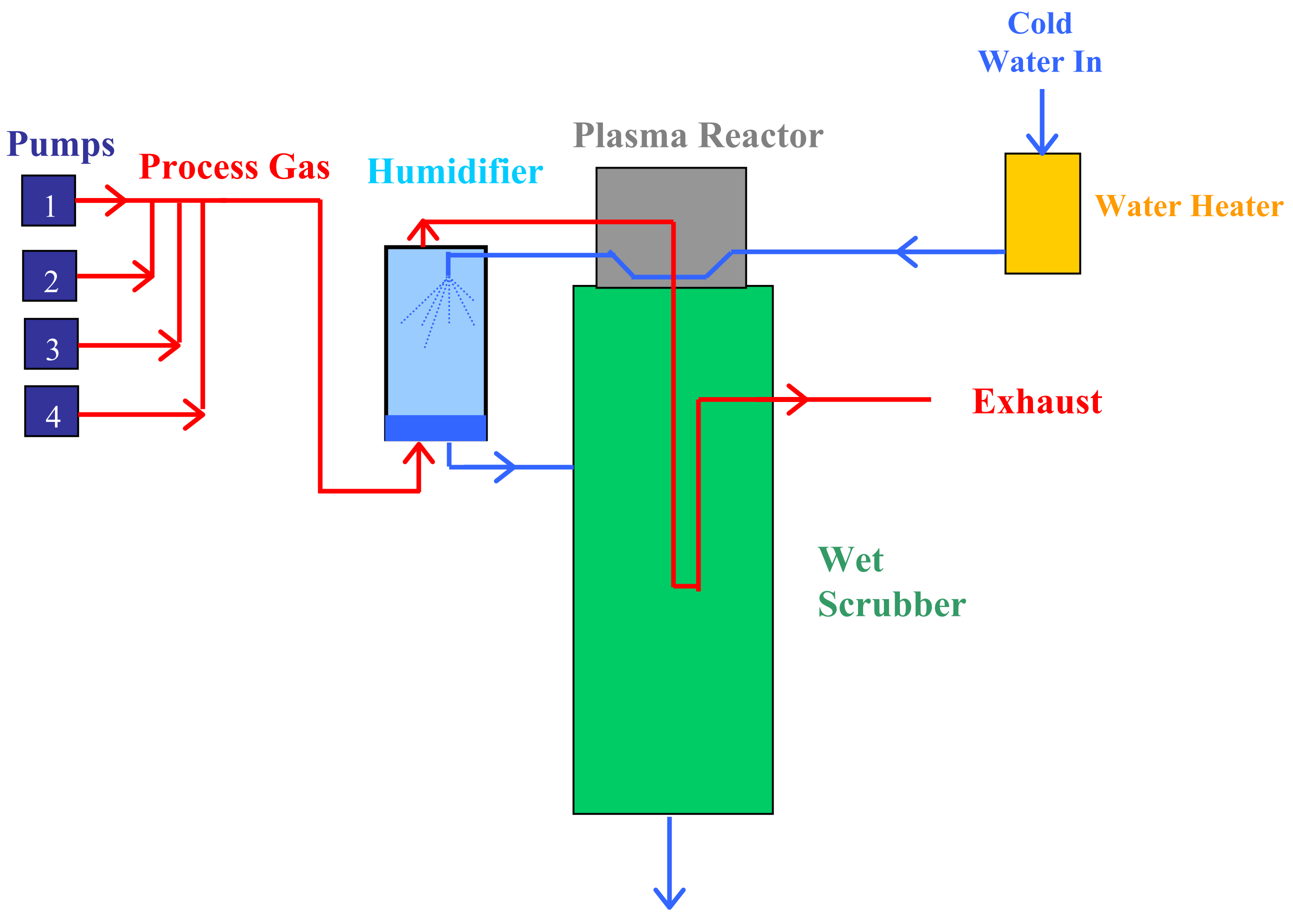
Plasma 'Circuit Diagram'



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Target!

Convert PFCs to less harmful substances to the environment

$$CF_4 + 2H_2O \rightarrow CO_2 + 4HF$$

CF_4 abatement provides the highest challenge

- PFCs produce CF_4 as by-product
- $D(CF_3\text{-}F) \sim 130$ kcal/mole
- Large infrared absorption cross-section ⇔ Large GWP (5700)

Reagent H_2O – source of hydrogen and oxygen

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Abatement System – Basic Technology

Plasma

- Atmospheric pressure plasma
- Discharge @ 2.45 GHz microwave
- Nitrogen-based gas flow

Reagents

- Water
- Non-toxic

Wet Scrubber

- Water removal of HAPs

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Abatement Performance

Total flow rate 20 L/min

Total Microwave Power 1.9 kW

- DRE > 90% for CF_4
- DRE > 99% for all other PFC gases used in Dielectric Etch processes

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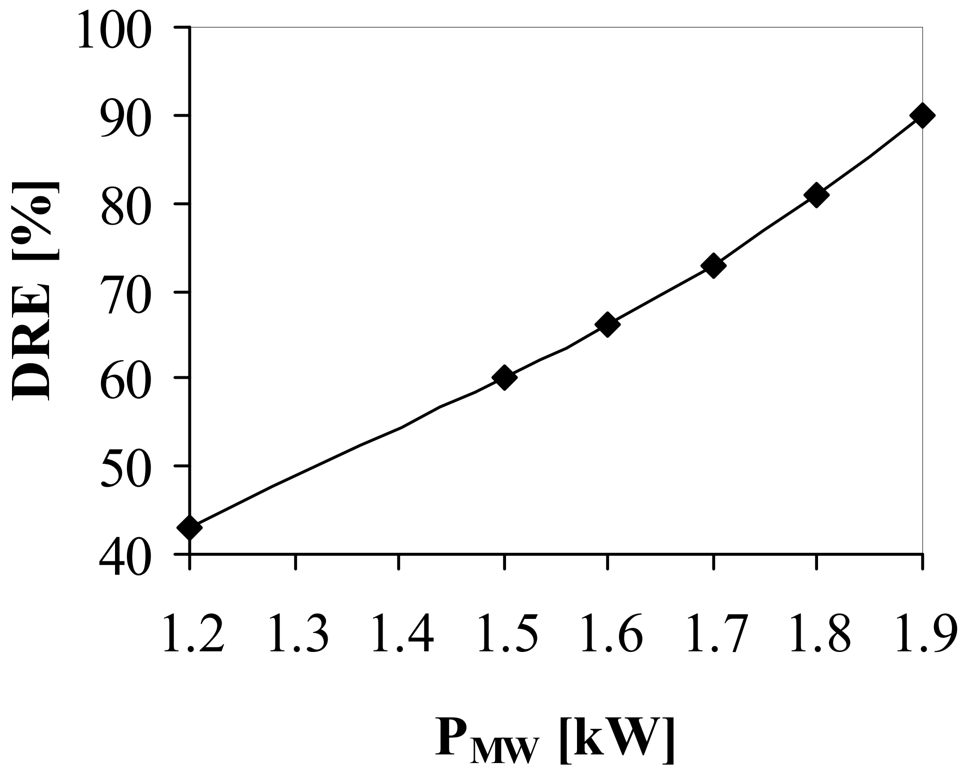
DRE of CF_4 vs. Microwave Power



Total flow rate = 20 L/min
Molar ratio H_2O/CF_4 = 2.5/1
CF_4 = 0.8 L/min

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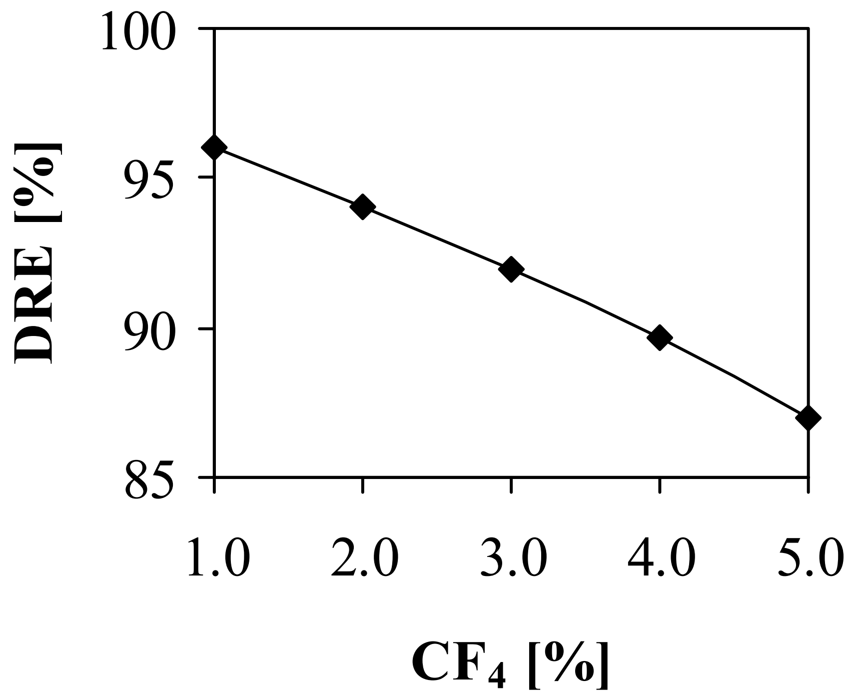
DRE of CF_4 vs. Initial CF_4 Concentration



Total flow rate = 20 L/min
Molar ratio $H_2O:CF_4$ = 2.5:1
P_{MW} = 1.9 kW

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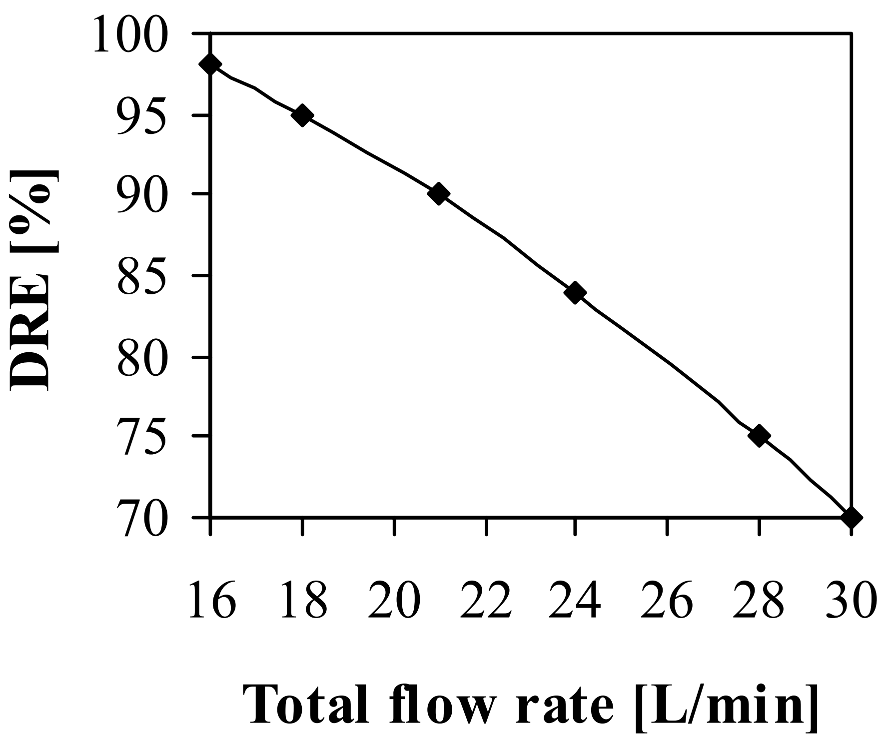
DRE of CF_4 vs. total flow rate



CF_4 = 0.8 L/min
Molar ratio $H_2O:CF_4$ = 2.5:1
P_{MW} = 1.9 kW

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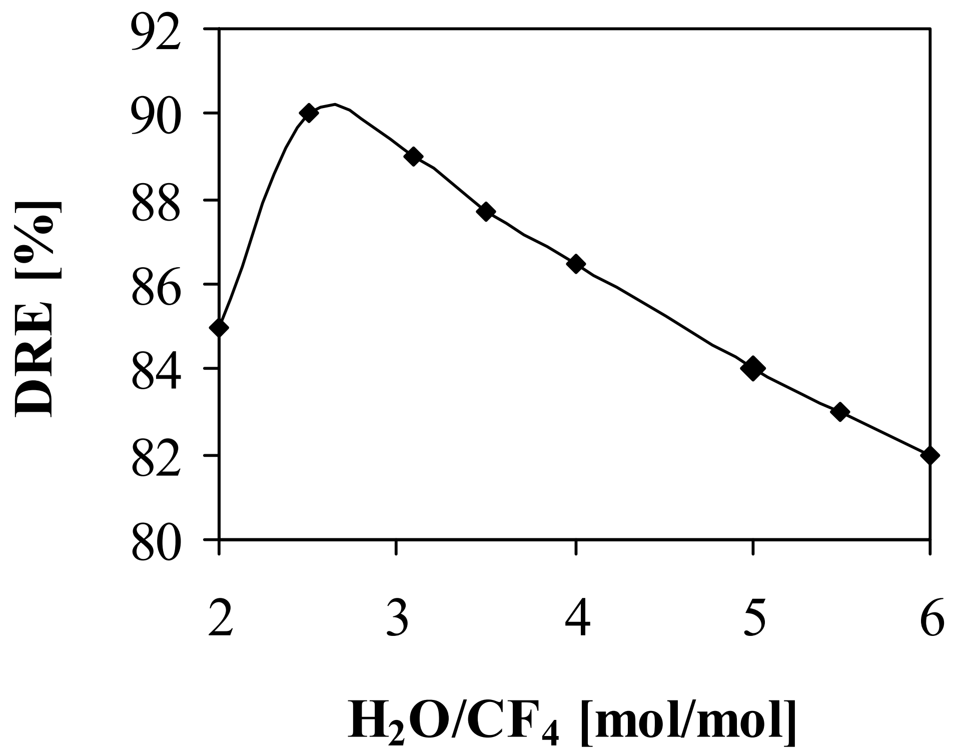
DRE of CF_4 vs. H_2O amount



CF_4 = 0.8 L/min
P_{MW} = 1.9 kW

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$$C_2F_6 + 3H_2O + \frac{1}{2}O_2 \rightarrow 2CO_2 + 6HF$$

$$CHF_3 + H_2O \rightarrow CO \ \ + 3HF$$

$$SF_6 + 3H_2O \rightarrow SO_3 + 6HF$$

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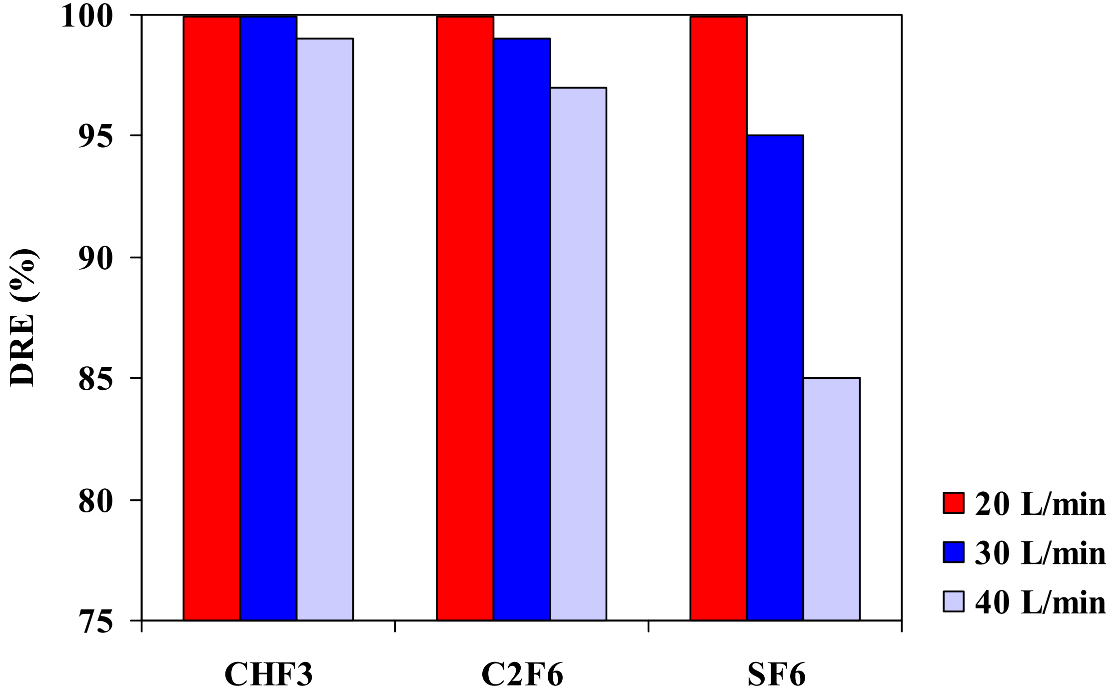
DRE vs. Total Flow Rate



CHF_3 = 0.4 L/min; C_2F_6 = 0.4 L/min; SF_6 = 0.4 L/min

Molar ratio $H_2O:CHF_3$ = 2.5:1; $H_2O:C_2F_6:O_2$ = 3.5:1:0.5; $H_2O:SF_6$ = 3.5:1

P_{MW} = 1.9 kW

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By-products

- HF
- CO_2

! **OF_2 NOT DETECTED**

! **NO SOOT FORMATION**

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Conclusions

- Effective PFC emission reduction by integrating the atmospheric plasma abatement with wet scrubbing
  ~ 60% utilities savings

Example:

Zenith Etch Plasma		**Commercially available**	
Microwaves:	1.9 kW	Microwaves:	12 kW
Water Recirculation Unit:	1.6 kW	Post Scrubbing Unit	Unknown
Pumps (EPX500) 4 x 1.6 kW	6.4 kW	Pumps (iH-600) 4 x 3 kW	12 kW
	9.9 kW		> **24 kW**

9.9 kW ← - 59% — > **24 kW**

Nitrogen 20 L/min ← - 83% — **Nitrogen 120 L/min**

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Additional Benefits

- Good plasma stability proven for a wide range of operating conditions – total gas flows and PFCs concentration;
- Chemical flexibility – can be used as oxidizing as well as reduction processes;
- Efficient energy transfer – the gas stream itself is used as the resistive medium for transferring electrical energy into heated gas molecules;
- Efficient energy usage – plasma can be instantly ignited or extinguished via simple electrical control, so that the energy is only consumed when PFCs are flowing.

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