Atmospheric Microwave Plasmas for the Abatement of Perfluorocompounds

Dr Marilena Radoiu
BOC Edwards
Kenn Business Park
Clevedon, North Somerset, UK

E-mail: Marilena.Radoiu@bocedwards.com
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: CF₄, C₂F₆, CHF₃ and SF₆
- Conclusions
The Kyoto Protocol calls for reductions in the emission of greenhouse gases, those gases with stronger global warming potential than CO\textsubscript{2}
Gases in the atmosphere can contribute to the greenhouse effect both 

**Directly:** when the gas itself is a greenhouse gas
  Example: $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{CH}_4$, $\text{N}_2\text{O}$, $\text{O}_3$.

**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$_6$)
## Global Warming Potentials and Atmospheric Lifetime of Selected Greenhouse Gases

<table>
<thead>
<tr>
<th>Global warming gas</th>
<th>GWP&lt;sub&gt;100&lt;/sub&gt;</th>
<th>Atmospheric lifetime, years</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>50 – 200</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>21</td>
<td>12</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>310</td>
<td>120</td>
</tr>
<tr>
<td>CF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>6,500</td>
<td>50,000</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;F&lt;sub&gt;8&lt;/sub&gt;</td>
<td>7,000</td>
<td>2,600</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;6&lt;/sub&gt;</td>
<td>9,200</td>
<td>10,000</td>
</tr>
<tr>
<td>CHF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>11,700</td>
<td>264</td>
</tr>
<tr>
<td>SF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>23,900</td>
<td>3,200</td>
</tr>
</tbody>
</table>

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

**GWP<sub>100</sub>** = Integral about the time horizon 100 years
PFC Emitters

- **Aluminium manufacture** — unintentional byproducts
  $C_2F_6$ and $CF_4$

- **Semiconductor industry** — largest emitter of intentionally produced PFCs
Fluoric gases like PFCs, HFCs and SF$_6$ are utilized to clean devices in semiconductor manufacturing processes.

**Dielectric Etch**  CF$_4$, CHF$_3$, CH$_3$F, CH$_2$F$_2$, C$_4$F$_8$, C$_5$F$_8$

**PFCs**

**Polysilicon Etch**  CF$_4$, CHF$_3$, CH$_2$F$_2$, (HBr, Cl$_2$)

Dielectric Etch may also use toxic and corrosive species

NF$_3$, C$_4$F$_6$, SF$_6$

**Target**

A reduction in emissions to 90% of the baseline year levels by 2010.
- World Semiconductor Council, Okinawa, May 2001
Methods for PFC Emissions Reduction

- DECOMPOSITION of PFCs to non-hazardous materials
  - Combustion
  - Plasma

- Direct thermal oxidation
  - Thermal-chemical

- Catalytic oxidation

- RECYCLE & RECOVERY of the unused PFCs

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

- **Local Thermodynamic Equilibrium (LCT)**
  \[ T_{\text{electrons}} = T_{\text{heavy particles}} \]

- **Non-equilibrium Plasmas**
  \[ T_{\text{electrons}} \gg T_{\text{heavy particles}} \]
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
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
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 \(\leftrightarrow\) No risk of contamination/corrosion of pump & tool
- Maintenance does not require breaking of the vacuum lines
Zenith Etch Plasma

Integrated Vacuum & Abatement Technology

- Abatement: 2.45 GHz Microwave Atmospheric Plasma (PFCs, HFCs, SF₆ etc.) with Wet Scrubber (HAPs)
- Vacuum: 4-pump process

! Provides a non-fuel abatement alternative
Zenith Etch Plasma Module

- Pump frame
- Short circuit
- Plasma Reactor
- Waveguide
- Isolator + reflected power meter
- 2.45 GHz magnetron head
- Wet scrubber
- Water recirculation unit
- 4 ePX500P pumps
Microwave & Plasma System

- Ignition electrode - atmospheric pressure (patent pending)
- Short circuit
- Plasma reactor
- Sight window
- Tapered waveguide
- Reflected power meter
- Isolator
- Waveguide
- 2.45 GHz magnetron head (2 kW)
- To the power supply

Slide 16
Plasma ‘Circuit Diagram’

- Pumps
- Process Gas
- Humidifier
- Plasma Reactor
- Water Heater
- Cold Water In
- Exhaust
- Wet Scrubber

The content of this presentation is confidential and should not be distributed to a third party without prior authorization from BOC Edwards.
Target!
Convert PFCs to less harmful substances to the environment

\[ \text{CF}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{HF} \]

\text{CF}_4 \text{ abatement provides the highest challenge}

- PFCs produce CF\textsubscript{4} as by-product
- D(CF\textsubscript{3}-F) \sim 130 \text{ kcal/mole}
- Large infrared absorption cross-section \Leftrightarrow \text{Large GWP (5700)}

Reagent H\textsubscript{2}O – source of hydrogen and oxygen
**Plasma**
- Atmospheric pressure plasma
- Discharge @ 2.45 GHz microwave
- Nitrogen-based gas flow

**Reagents**
- Water
- Non-toxic

**Wet Scrubber**
- Water removal of HAPs
Abatement Performance

- Total flow rate 20 L/min
- Total Microwave Power 1.9 kW

- DRE > 90% for CF₄
- DRE > 99% for all other PFC gases used in Dielectric Etch processes
DRE of CF$_4$ vs. Microwave Power

Total flow rate = 20 L/min
Molar ratio H$_2$O/CF$_4$ = 2.5/1
CF$_4$ = 0.8 L/min
DRE of CF₄ vs. Initial CF₄ Concentration

Total flow rate = 20 L/min
Molar ratio \( \text{H}_2\text{O}:\text{CF}_4 = 2.5:1 \)
\( P_{\text{MW}} = 1.9 \text{ kW} \)
DRE of CF₄ vs. total flow rate

CF₄ = 0.8 L/min
Molar ratio H₂O:CF₄ = 2.5:1
P_MW = 1.9 kW
DRE of CF$_4$ vs. H$_2$O amount

- CF$_4$ = 0.8 L/min
- $P_{MW}$ = 1.9 kW
$$C_2F_6 + 3H_2O + \frac{1}{2}O_2 \rightarrow 2CO_2 + 6HF$$

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

$$SF_6 + 3H_2O \rightarrow SO_3 + 6HF$$
DRE vs. Total Flow Rate

CHF₃ = 0.4 L/min; C₂F₆ = 0.4 L/min; SF₆ = 0.4 L/min

Molar ratio H₂O:CHF₃ = 2.5:1; H₂O:C₂F₆:O₂ = 3.5:1:0.5; H₂O:SF₆ = 3.5:1

P_MW = 1.9 kW
By-products

- HF
- CO₂

! OF₂ NOT DETECTED
! NO SOOT FORMATION
**Conclusions**

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

Example:

**Zenith Etch Plasma**
- Microwaves: 1.9 kW
- Water Recirculation Unit: 1.6 kW
- Pumps (EPX500) 4 x 1.6 kW: 6.4 kW

Total: 9.9 kW

Nitrogen 20 L/min: - 59%

---

**Commercially available**
- Microwaves: 12 kW
- Post Scrubbing Unit: Unknown
- Pumps (iH-600) 4 x 3 kW: 12 kW

Total: > 24 kW

Nitrogen 120 L/min: - 83%
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.