

PFC Abatement in the Semiconductor Industry 2009

Joe Van Gompel
Glade Consulting, LLC

SESHA 31st International Symposium, Scottsdale AZ
May 19 – 22, 2009

Overview

- PFCs are stable and difficult to abate
 - Reactions and thermodynamics
- Approaches to abatement of PFCs
 - Burn-wet
 - Plasma
 - Catalytic
 - The HF Question
- Commercial Solutions
 - Applied Materials / Metron “Marathon”
 - Centrotherm CT-BW
 - DAS Escape
 - Edwards Atlas, TPU, Sirius, ERIX
 - Guild Trinity

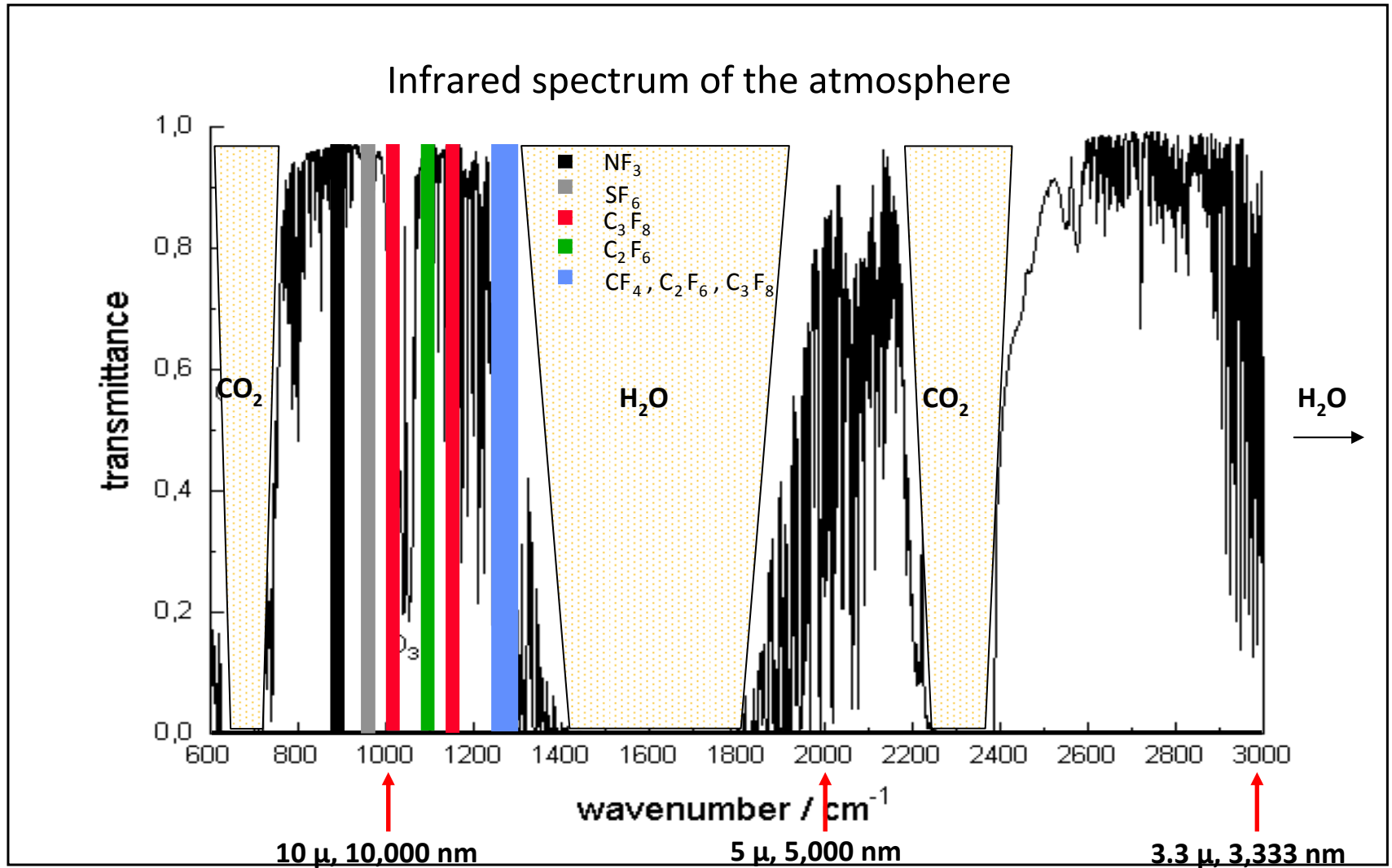
Glade Consulting, LLC

- Founded 2008, Austin TX
 - Joe Van Gompel, President
 - PhD, physical organic chemistry, University of Illinois
 - 12 years as POU abatement specialist at (BOC) Edwards
 - 5 Years, FTIR Specialist at (Thermo) Mattson/Nicolet
- Subfab operability consulting
 - Fabwide abatement strategies
 - PFC emissions reduction strategies
 - POU abatement – recommendations, uptime
 - Vacuum pumps
 - Emissions testing
 - PFC emissions audits
 - Training seminars

PFC Gases in the Semiconductor Industry

- The semiconductor industry phased in PFCs to replace chlorinated ODSs in the 1980s
 - PFCs were nontoxic and didn't deplete ozone
- PFCs were heavily used in chamber cleans since the early 1990s
 - Primarily C_2F_6 and CF_4 , mostly phased out in favor of NF_3
 - Still a global warmer, but well-utilized in chamber, so effect is minimized
 - Significant PFC consumption in etch, especially CF_4 and CHF_3
 - Etch is major emission component in most modern fabs
 - Difficult to optimize – need proper ratio of C, H, O, and F for anisotropic etch

Why PFCs are Such Potent Global Warming Gases



Visible light - red 0.7 μ , violet 0.36 μ



Relative Stabilities of PFCs

Lifetimes and Stabilities

| Fluorinated Gas | Lifetime (years) |
|---------------------------|------------------|
| CF_4 | 50,000 |
| C_2F_6 | 10,000 |
| SF_6 | 3200 |
| C_3F_8 | 2600 |
| c- C_4F_8 | 3200 |
| NF_3 | 740 |
| CHF_3 | 270 |
| CH_2F_2 | 4.9 |

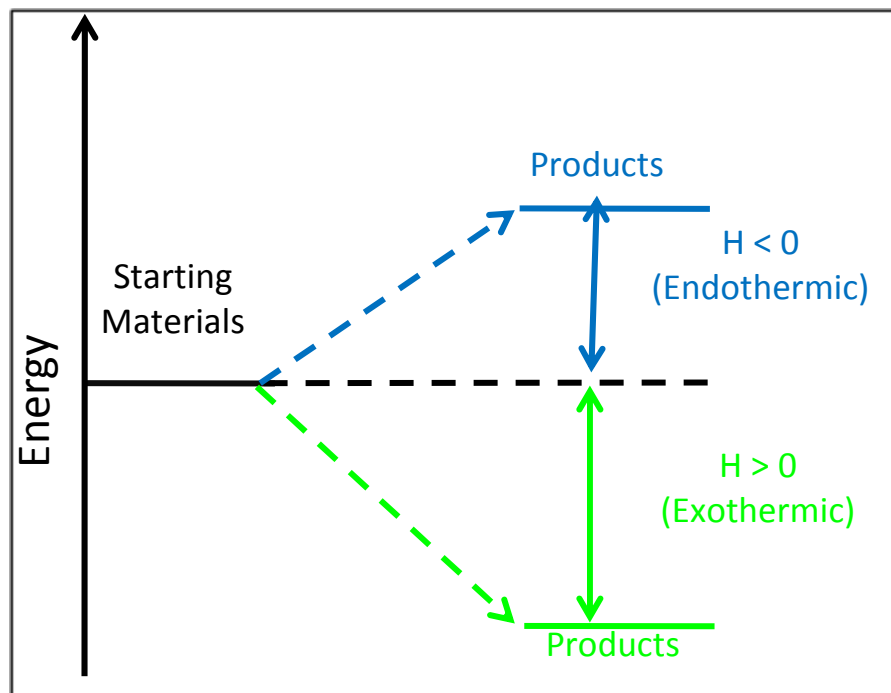
This is closely related to ease of abatement

PFC Gases are Very Stable Compounds

- Carbon-fluorine bond is strongest single bond in all of chemistry
 - Multiple C-F bonds on the same carbon enhance stability
 - C-C or C-H bonds are weaker and decrease stability
 - S-F bond is strong too
- Stability is reflected in atmospheric lifetimes
- Stability is closely related to ease of abatement
 - CF_4
 - C_2F_6 , SF_6
 - C_3F_8 , $\text{c-C}_4\text{F}_8$, NF_3
 - CHF_3 , CH_2F_2 , CHF_3 , C_5F_8 , C_4F_6

Thermodynamics in Chemistry

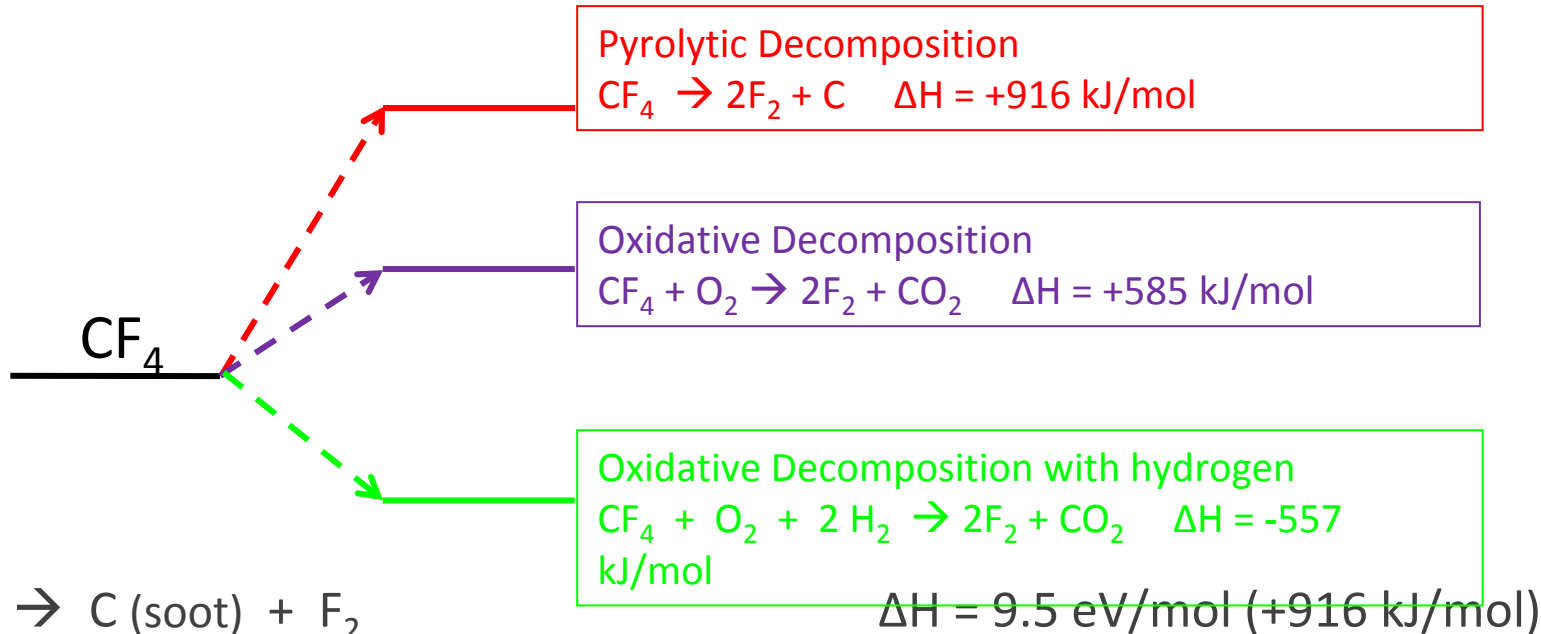
- Chemical reactions proceed preferentially “downhill” to lower energy products
 - These are exothermic reactions – they liberate heat
- Chemical reactions can be forced to proceed “up hill”, where the products have more energy than the reactants – energy or heat have to be put into them
 - These are endothermic reactions – they absorb heat (get cold)
- Thermodynamics simply tell if a reaction is favored or not. Thermodynamics are not always indicative of how fast a reaction will proceed (kinetics)



Bond Strengths

| BOND | kcal/mol | kJ/mol |
|--|----------|--------|
| $\text{F}_3\text{C} - \text{F}$ (CF_4 , Freon 14) | 130 | 543 |
| $\text{F}_3\text{C}-\text{CF}_2 - \text{F}$ (C_2F_6 , Freon116) | 127 | 531 |
| $\text{H}_3\text{C} - \text{F}$ | | 108 |
| | 452 | |
| $\text{F}_3\text{C} - \text{H}$ (Freon 23) | 106 | |
| | | 444 |
| $\text{H}_3\text{C} - \text{H}$ (methane) | 105 | |

CF₄ Decomposition Mechanisms



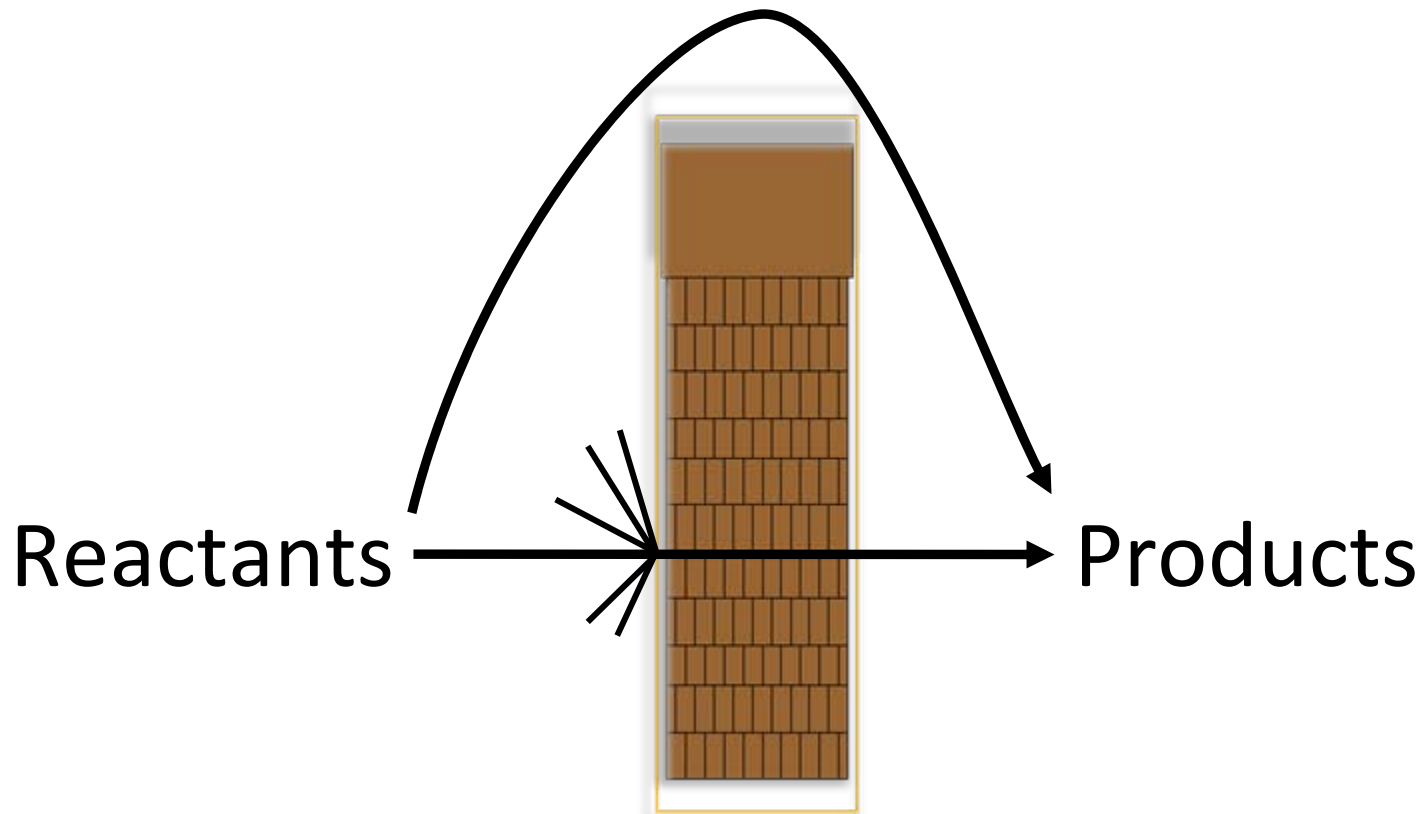
Plasma Chemistry, Alexander Fridman, Cambridge University Press, 2008. ISBN 0521847354, 9780521847353



ΔH is the “Heat of Reaction” ; how much heat is given off or must be added

- Thermodynamics is “chemistry as the crow flies” – independent of the pathway. Getting to the oxidative decomposition with hydrogen is still difficult
 - Plus, now we have to dispose of HF ...

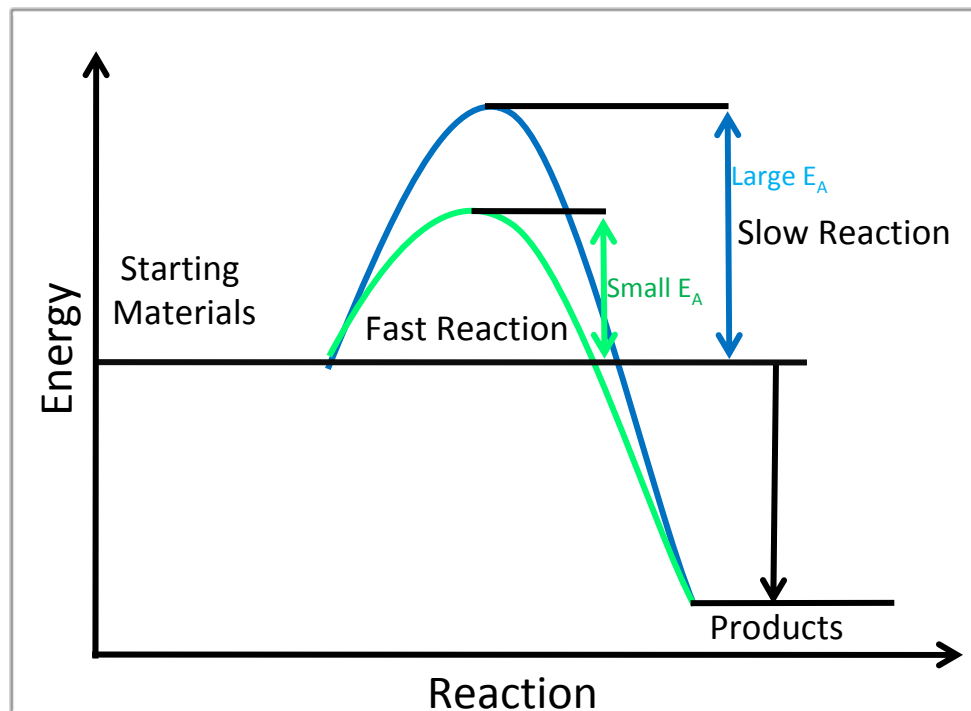
Bond Energies are Not the Whole Story



- Going directly to the products (HEAT) may not be the best solution. Chemical environment will greatly affect reaction path and energy required.

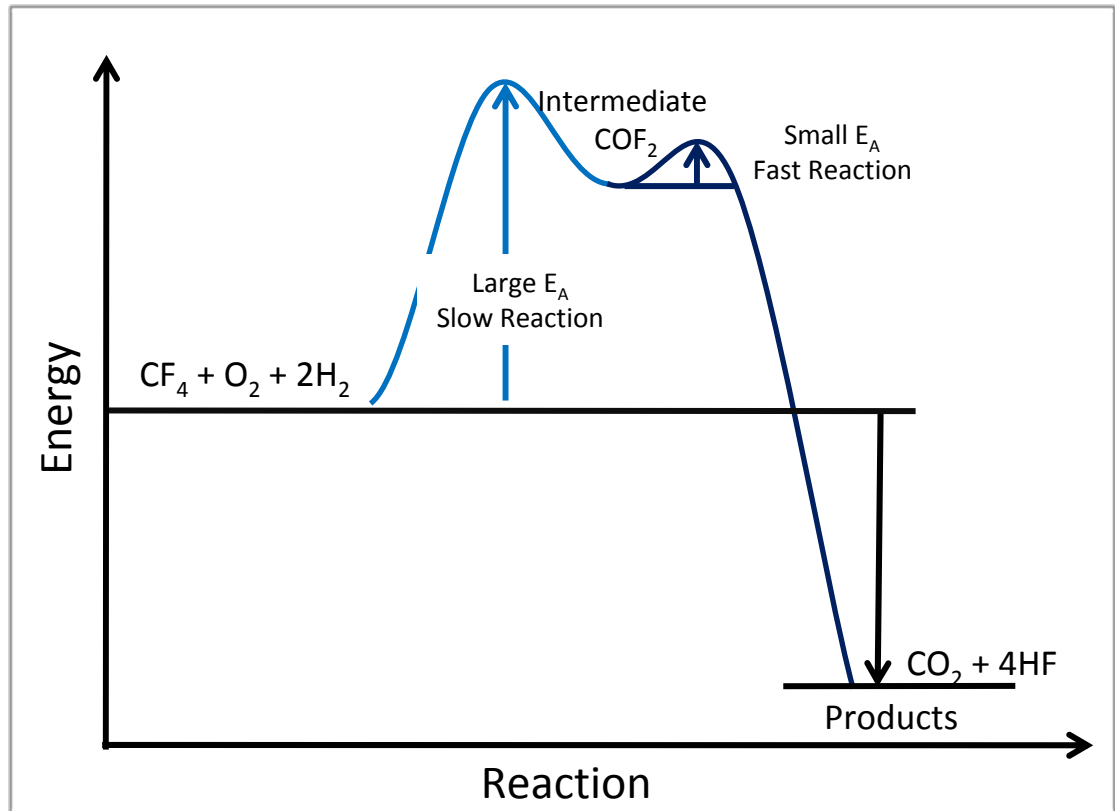
Kinetics in Chemistry

- Every reaction requires an activation energy E_A to push reactants to change to products
- Lower E_A means less energy must be put into a reaction for it to proceed.
 - Lower E_A means a faster reaction
- E_A is strongly dependent on the reaction “mechanism”.
 - Mechanism is the “roadmap” of how the reaction actually proceeds



Kinetics of CF₄ Decomposition

- Reaction of CF₄ to CO₂ and HF is very exothermic, but also requires a big push to break the very strong C-F bonds
 - This is why CF₄ abatement is so difficult
- Actual reaction is much more complicated than shown



Note that hydrogen can come from CH₄ or from H₂. CH₄ has a better reaction mechanism.

Plasma Decomposition of CF₄


Table 2. Contribution of individual reactions to kinetic processes in the plasma region.

| Process | Rate (particles cm ⁻³ s ⁻¹) | | |
|---|--|--|--|
| | Pure CF ₄ | 25% O ₂ / 75% CF ₄ | 80% O ₂ / 20% CF ₄ |
| Main reactions for CF₂ radicals | | | |
| CF ₂ + F → CF ₃ | -3.183 x 10 ¹⁶ | -4.052 x 10 ¹⁴ | -4.963 x 10 ¹² |
| CF ₂ + O (³ P) → COF + F | zero | -2.016 x 10 ¹⁶ | -5.416 x 10 ¹⁵ |
| CF ₂ + O (³ P) → CO + 2 F | zero | -5.760 x 10 ¹⁵ | -1.547 x 10 ¹⁷ |
| CF ₂ + COF → CO + CF ₃ | zero | -3.695 x 10 ¹¹ | -1.191 x 10 ⁹ |
| CF ₂ + COF → CF + COF ₂ | zero | -3.695 x 10 ¹¹ | -1.191 x 10 ⁹ |
| Main reactions for CF₃ radicals | | | |
| CF ₃ + F + M → CF ₄ + M | -3.904 x 10 ¹⁶ | -1.198 x 10 ¹⁵ | -1.591 x 10 ¹³ |
| 2 CF ₃ → C ₂ F ₆ * | -7.665 x 10 ¹⁵ | -4.752 x 10 ¹¹ | -1.7181 x 10 ⁹ |
| CF ₃ + F ₂ → CF ₄ + F | -2.142 x 10 ¹⁵ | -1.669 x 10 ¹⁴ | -1.022 x 10 ¹² |
| CF ₃ + F* → e ⁻ + CF ₄ | -5.641 x 10 ² | -1.753 x 10 ² | -1.109 x 10 ⁰ |
| CF ₃ + O (³ P) → COF ₂ + F | zero | -9.794 x 10 ¹⁵ | -2.853 x 10 ¹⁵ |
| CF ₃ + O ₂ + M → CF ₃ O ₂ + M | zero | -1.970 x 10 ¹⁴ | -3.782 x 10 ¹³ |
| CF ₃ + COF → CO + CF ₄ | zero | -2.703 x 10 ¹² | -9.441 x 10 ⁹ |
| CF ₃ + COF → CF ₂ + COF ₂ | zero | -2.703 x 10 ¹² | -9.441 x 10 ⁹ |
| CF ₃ → CF ₃ (s) | -8.295 x 10 ¹⁴ | -6.531 x 10 ¹² | -3.927 x 10 ¹¹ |
| CF ₃ + CF ₃ (s) → C ₂ F ₆ (s) | -9.308 x 10 ¹¹ | -1.612 x 10 ⁸ | -1.233 x 10 ⁶ |
| Main reactions for F atoms | | | |
| CF ₃ + F + M → CF ₄ + M | -3.904 x 10 ¹⁶ | -1.198 x 10 ¹⁵ | -1.591 x 10 ¹³ |
| 2 F + M → F ₂ + M | -4.791 x 10 ¹⁵ | -1.099 x 10 ¹⁷ | -5.362 x 10 ¹⁵ |
| CF ₂ + F → CF ₃ | -3.183 x 10 ¹⁶ | -4.052 x 10 ¹⁴ | -4.963 x 10 ¹² |
| F + COF + M → COF ₂ + M | zero | -1.152 x 10 ¹⁵ | -1.479 x 10 ¹³ |
| F + CO + M → COF + M | zero | -1.564 x 10 ¹⁴ | -9.228 x 10 ¹² |
| F + O ₂ + M → FO ₂ + M | zero | -5.052 x 10 ¹⁴ | -3.563 x 10 ¹⁴ |
| F + FO ₂ → F ₂ + O ₂ | zero | -2.087 x 10 ¹⁴ | -1.107 x 10 ¹³ |
| F → F(s) | -8.852 x 10 ¹⁵ | -3.450 x 10 ¹⁶ | -7.620 x 10 ¹⁵ |
| F + CF ₃ (s) → CF ₄ (s) | -9.929 x 10 ¹³ | -8.512 x 10 ¹² | -2.390 x 10 ¹¹ |
| F + Si → SiF/Si | -2.526 x 10 ⁵ | -6.350 x 10 ¹⁴ | -3.949 x 10 ¹⁵ |
| F + SiF/Si → SiF ₂ /Si | -2.526 x 10 ¹⁵ | -6.351 x 10 ¹⁴ | -3.949 x 10 ¹⁵ |
| F + SiF ₂ /Si → SiF ₃ /Si | -2.526 x 10 ¹⁵ | -6.351 x 10 ¹⁴ | -3.949 x 10 ¹⁵ |
| F + SiF ₃ /Si → SiF ₄ /Si | -2.526 x 10 ¹⁵ | -6.351 x 10 ¹⁴ | -3.949 x 10 ¹⁵ |

Bauerfelt, G. F. and Arbilla, G. "Kinetic Analysis of the Chemical Processes of the Decomposition of Gaseous Dielectrics by a Non-equilibrium Plasma – Part 1: CF₄ and CF₄/O₂". *Journal of the Brazilian Chemical Society*, Vol. 11, No. 2, Mar-Apr 2000.

CF₄ as a Byproduct

- Recombination of various plasma species to CF₄ is common in plasma reactors
 - CF₄ is most stable product of reaction between carbon and fluorine
 - Recombination is circumvented by presence of hydrogen
- C₂F₆, C₃F₈, C₄F₈, etc have all been shown to generate significant CF₄ from plasma reactions
 - Some POU devices have also been shown to form CF₄, but that is from F₂ in a rich CH₄ flame
- CF₄ abatement is a major consideration for any PFC emissions reduction strategy



Technological Approaches to PFC Abatement

Burn-Wet Abatement

- Burn-wet is the primary POU abatement technology
 - Fuel-fired combustor (generally methane) followed by a wet scrubber to capture HF
- Combustor settings for deposition gases is generally inadequate for PFC abatement
 - Silane, H₂, TEOS, WF₆, NH₃ burn much more readily
 - PFC combustion generally requires additional fuel O₂ enrichment
 - Added expense
- Recall that PFCs also have different stabilities
 - CF₄ < C₂F₆, SF₆, C₃F₈ < C₄F₈, C₅F₈, CHF₃, C₄F₈O, C₄F₆

Burn-Wet Configurations

- Most burn-wet POU scrubbers can be configured to abate C_2F_6 , C_3F_8 , NF_3 , and SF_6 relatively well (>95% in all cases).
 - Little C_2F_6 and C_3F_8 used in 300-mm fabs these days
- Etch processes use CF_4 , SF_6 , CHF_3 , and C_4F_8 in significant quantities
 - Keep in mind that CF_4 may be a significant byproduct of plasma decomposition of other PFCs

PFC Abatement Efficiency

- Burn-wet POU abatement must be used within manufacturer's recommended specifications for efficient PFC destruction
 - Total PFC flow
 - Specific PFC flow (e.g. CF_4 limitations)
 - Total exhaust gas flow
 - N_2 purge flow
 - Fuel flow to combustor
 - Fuel flow to nozzle
 - O_2 flow
 - O_2 quality (99%, 60%, 20% (air))
 - Proper interface to tool
- CF_4 abatement tends to be most sensitive to conditions
 - Some manufacturers achieve 95-99% under ideal conditions

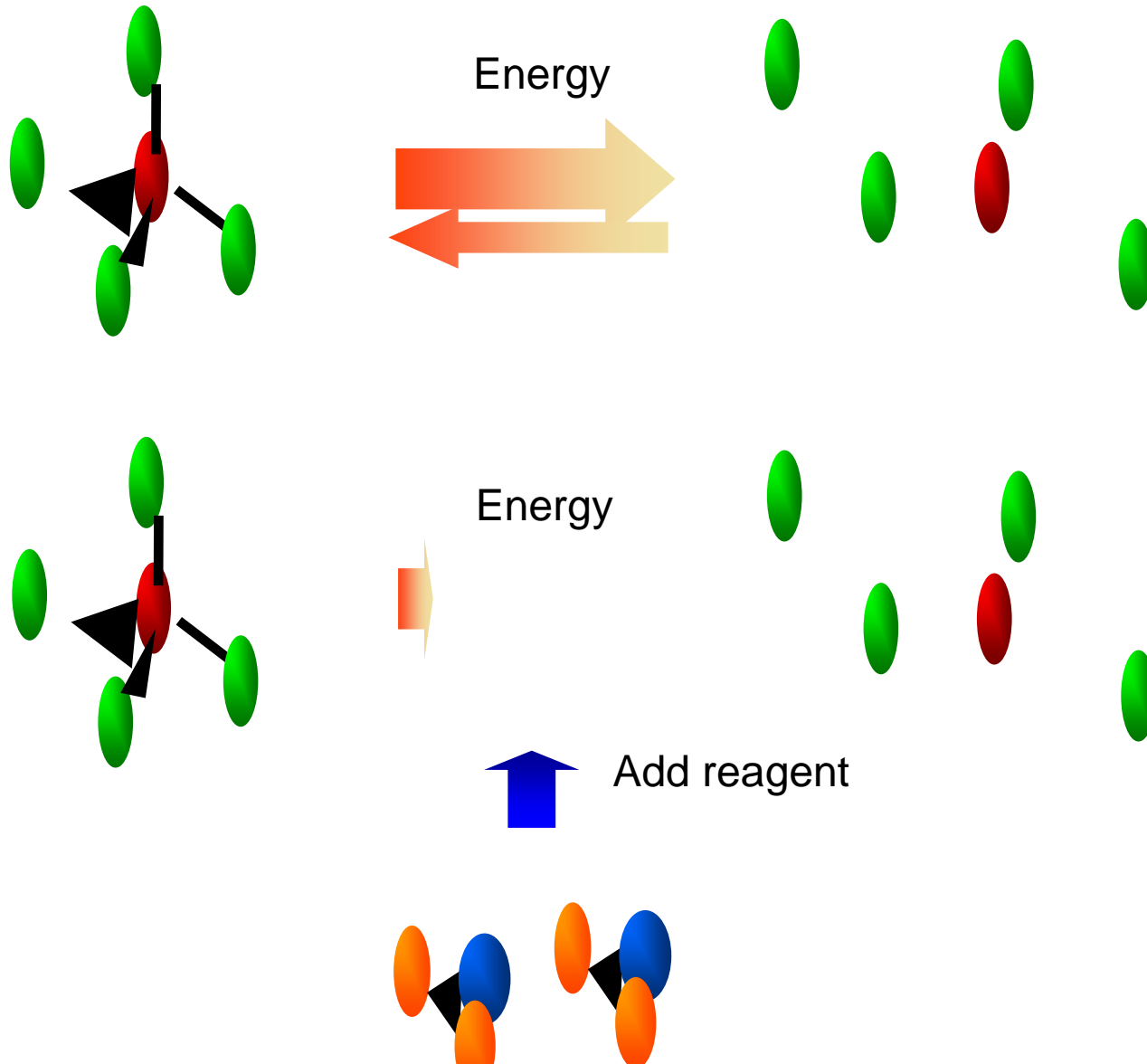
Fuel Considerations

- Methane, CH₄, Natural Gas
 - Superior flame chemistry, higher calorific content
 - Generates appropriate free radicals to attack C-F bonds
 - Slow flame front velocity and denatured for smell; safer
 - Narrow flammable range
 - Inexpensive
 - Readily available
- Hydrogen, H₂
 - Very expensive (only high purity H₂ is found in fabs)
 - No smell or taste
 - Very high flame front velocity
 - Very wide flammable range
 - Poor flame chemistry for PFC abatement

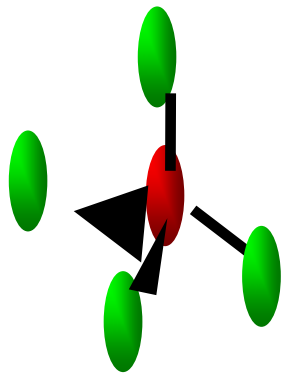
Plasma Decomposition of PFCs

- PFCs are decomposed all the time in plasma etchers
 - Low pressure, low process flows, low efficiency (for CF_4)
 - Plasma as an abatement device is much less common
- Plasma POU abatement can be pre-pump (high vacuum) or post-pump (atmospheric or near-atmospheric pressure)
 - Plasmas are very sensitive to pressure and total flow of gases
- In the absence of fuel (vs. burn – wet), overall carbon footprint is very small despite high electrical usage

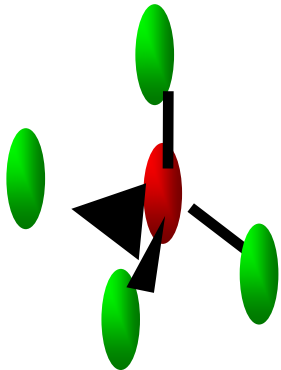
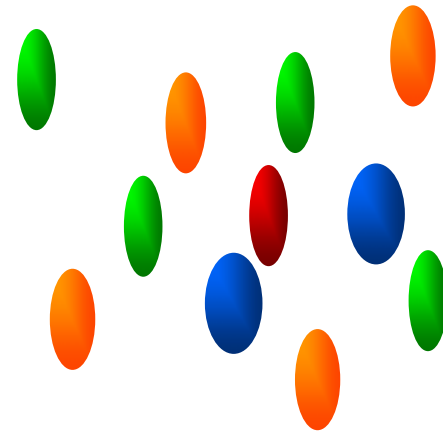
Plasma Details



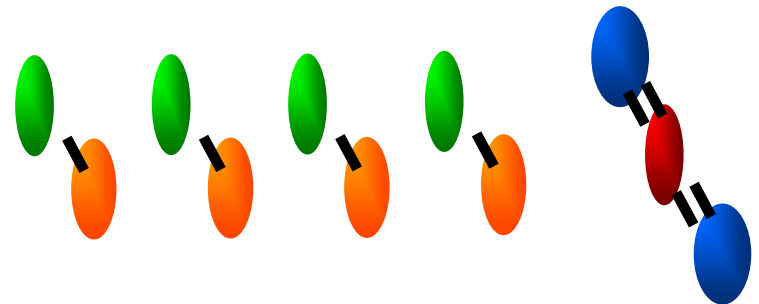
Plasma Details



Energy



Energy



Pre-Pump Plasma Abatement

- Sematech Technology Transfer 98093561A-ENG, Surface Wave Plasma (Texas A&M)
- Sematech Technology Transfer 98123605A-ENG, Litmas “Blue” POU Plasma
- Both of these were vacuum-side abatement
- Reagents (typically H₂O) added to foreline to form CO, CO₂, COF₂, and HF
 - CF₄ DRE 90 – 99%
 - Addition of materials to foreline made tool engineers nervous
 - Particles, backstreaming
 - Few if any commercial sales

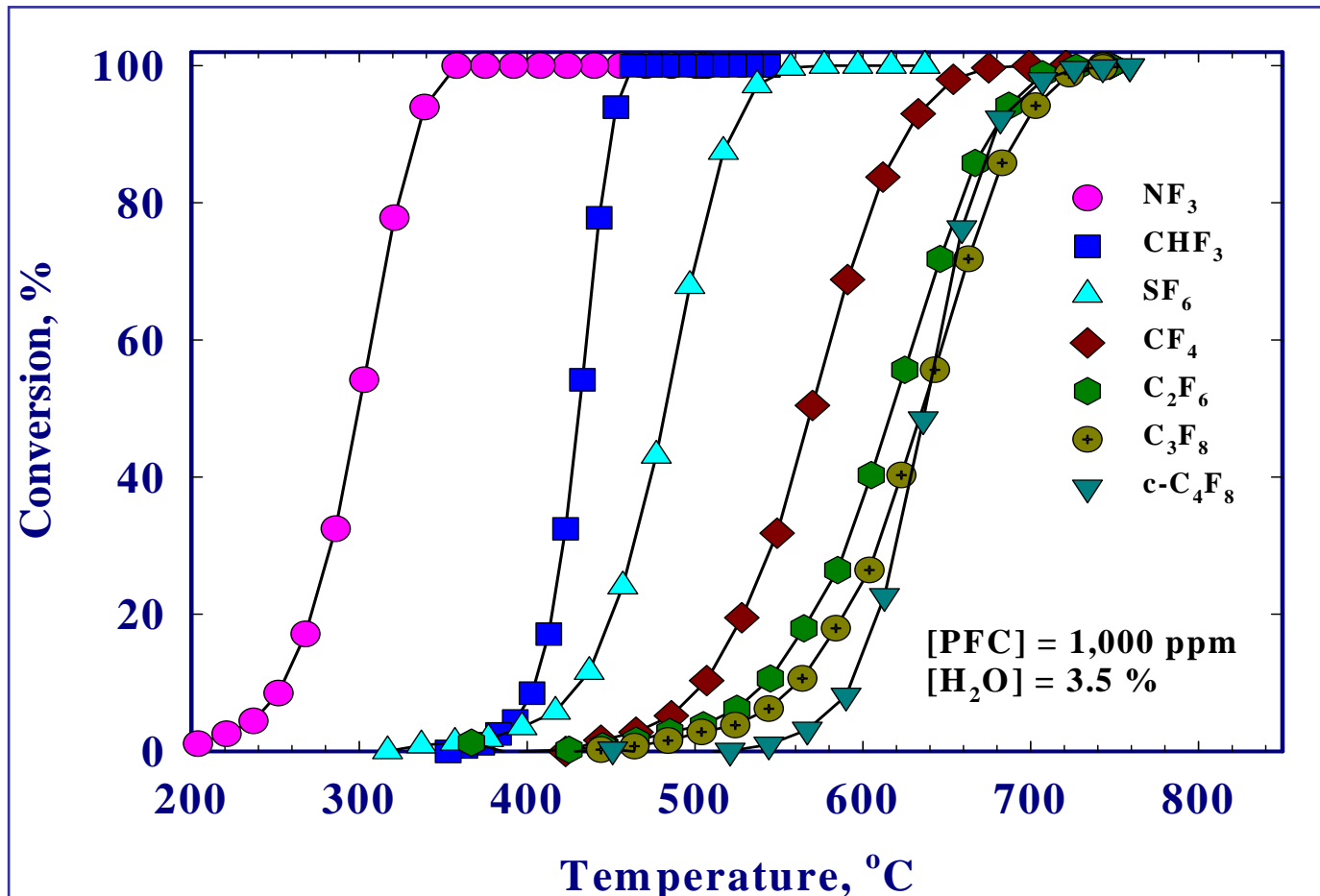
Post-Pump Plasma Abatement

- Vacuum pump becomes very important
 - N₂ vacuum pump purge must be minimized to prevent blowing out the plasma
 - Approx. 1 kW of plasma power is needed per 10 slm total flow
 - Feedback between pumps and plasma abatement is useful
- Water vapor is easy to add (small water scrubber pre-plasma)
 - Eliminates concerns about backstreaming as pump is a natural barrier
- Unlike burn-wet, plasma POU is strictly for PFC abatement

Catalytic PFC Abatement

- Catalytic PFC abatement utilizes a pre-scrubber and a heated catalyst to convert PFCs to HF and CO or CO₂
- Catalyst runs in 600°C – 750°C range
 - Much cooler than burn-wet or plasma
 - Different reaction mechanism
 - C₂F₆, C₃F₈, c-C₄F₈ more difficult to abate than CF₄
 - Probably related to pore-size of catalyst
- Catalytic PFC Abatement requires pre-scrubber (typically included) to protect catalyst from silicon halides or other materials
 - These can poison or mask catalyst
- In the absence of fuel (vs. burn – wet), overall carbon footprint is very small despite high electrical usage

Catalytic PFC Abatement vs Temperature

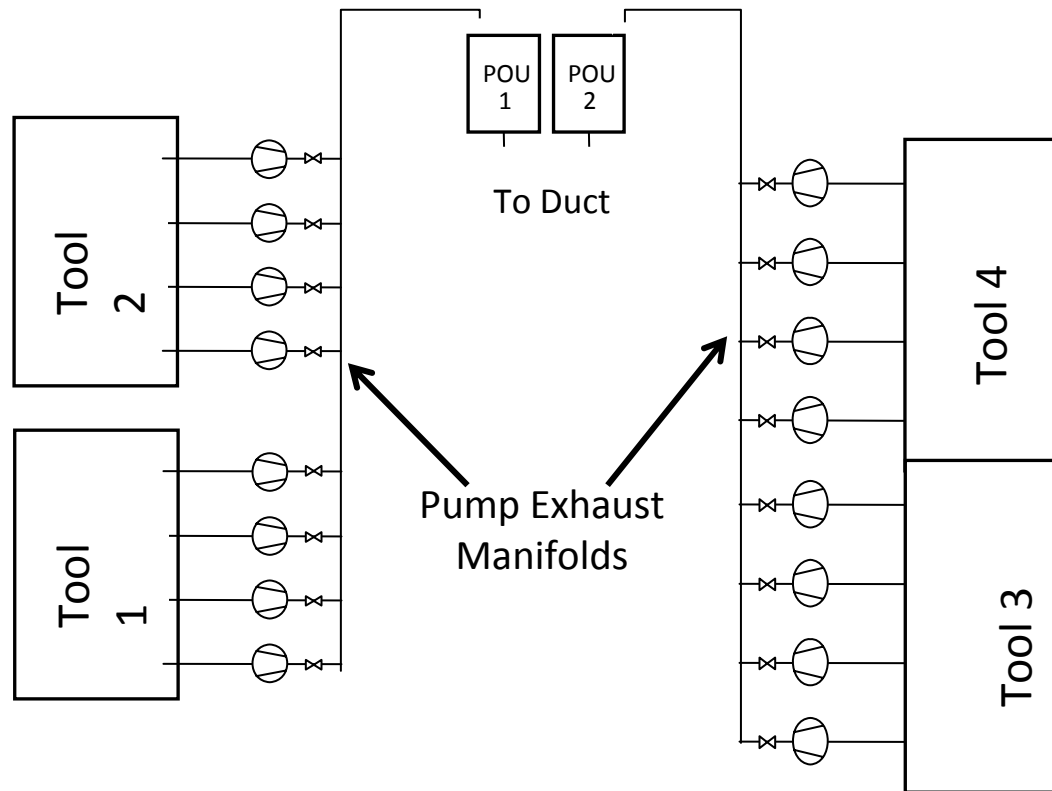


- Small molecules require lower temperatures than larger molecules (Courtesy Guild Associates)

Multiple Chambers per POU Device

- CVD processes are typically restricted to a single process chamber per inlet
 - Prevents combination of SiH_4 and NF_3 in pipework
- Etch chambers may be combined if the process is the same
 - No incompatible gas issues
 - Must be wary of total N_2 flows from pump purges
- Assume 4 inlets in Burn-wet device, 50 slm max capacity per inlet.
 - Set N_2 pump purges to 15 slm; could abate 4 inlets x 3 chamber/inlet = 12 chambers
 - Redundant configuration recommended

Multiple Chambers per POU Device



- Eight etchers are abated per single burn-wet POU device
 - This number is limited by inlet capacity of POU device

Hydrogen Fluoride Byproduct

- One liter of CF_4 generates 4 liters of HF

| PFC | Liters HF | Kg HF |
|---------------------------|------------------|--------------|
| CF_4 | 4 | 0.91 |
| C_2F_6 | 6 | 0.87 |
| c- C_4F_8 | 8 | 0.80 |
| SF_6 | 6 | 0.82 |
| NF_3 | 3 | 0.85 |

- Abatement of PFCs requires an HF treatment facility be sized appropriately
 - Requires careful consideration of annual usage
 - Must also consider hydraulic capacity – lower concentration of HF means higher overall volume



Commercial Approaches to PFC Abatement

Air Liquide UPAS Plasma

- Universal Plasma Abatement System

Applied Materials / Metron Marathon

Centrotherm CT – BW

CSK Burn – Wet

DAS ESCAPE Burn – Wet

Edwards TPU Burn – Wet

Edwards Atlas Burn – Wet

Edwards Sirius Plasma

Edwards ERIX HF Treatment

GST Burn – Wet

Guild Trinity Catalytic

Summary

- PFC gases are chemically stable, making them difficult to abate
- Abatement technologies include
 - Burn – Wet (combustor followed by a water scrubber)
 - Plasma
 - Catalytic
- Burn – Wet is most prevalent
 - Dedicated PFC Abatement doesn't sell well
 - Plasma, catalytic systems are not common
 - Burn – Wet can be adapted to abate multiple etch chambers
- HF treatment capacity should not be overlooked