## MHI Gas Abatement Principle and Physics of Operation

With the ever growing menace of perflourocompound emissions, MHI has pioneered an energy efficient way to abate these materials through a plasma process.

**Background of the problem:** 

- More operations per chip
- Perflourocarbons are popular for F and C source required in etching
- These are high lifetime gasses and cause GWP and absorb infrared throughout their life
- PFC's replaces CFC's as they did not deplete ozone but caused a different and more serious problem
- Main suppliers of PFC's have indicated that they may not sell PFC's unless abatement procedures were in place.

## Scope of the supply

The scope of the supply will include the following:

- Plasma processor for efficient abatement
- Integrated Reaction chamber
- Controls for easy setting. Power read outs.
- Fractal mixer in reaction chamber
- Training at MHI site if required.

## Salient features of the MHI plasma abatement of C<sub>2</sub>F<sub>6</sub> and other toxic gas abatements.

- One of the advantages for the proposed plasma over the other methods is the elimination of electrodes that are known in D.C. plasma to be subject to corrosion.
- All done at one atmosphere. No need for vacuum
- The proposed plasma also has a adjusted gas flow rate and a larger plasma discharge that results in higher residence time.
- The proposed plasma process is expected to be 99.99% efficient while destroying CFC at a rate as high as 80 kg/h for low energy usage.
- Emissions from the proposed plasma process are very low.
- High C<sub>2</sub>F<sub>6</sub> abatement is obtained at good flow rates and high powers.

- No requirement for diluting with nitrogen and subjecting to plasma abatement. If nitrogen diluted systems are used the plasma will still function effectively. Both possibilities are allowed by the MHI abatement system.
- We recommend that the resultant products should be treated in a scrubber prior to disposing off to atmosphere in order to remove fluorine.

The abatement of  $C_2F_6$  gas is carried out in plasma. Several opportunities exist for such abatement (see reference 1), for instance:

• Oxidizing hexafluoroethane C<sub>2</sub>F<sub>6</sub> by mixing with oxygen, or air and subjecting it to plasma abatement inside a chamber. Therefore, C<sub>2</sub>F<sub>6</sub> abatement can be characterized as proceeding via two competing reactions:

$$\begin{array}{cccc} C_2F_6 + 2O_2 \to 2 \ CO_2 + 3 \ F_2 & & \dots \ (1) \\ C_2F_6 + \ O_2 \to 2 \ COF_2 + \ F_2 & & \dots \ (2) \end{array}$$

Mohindra (reference 1) has carried out thermodynamic equilibrium calculations for the following reactions to estimate the potential for thermal decomposition to  $C_2F_6$  abatement.

$C_2F_6 \rightarrow CF_3 + CF_3$	(3)
----------------------------------	-----

$$O_2 \rightarrow O + O \qquad \dots (4)$$

$$C_2F_6 + O_2 \rightarrow 2 \operatorname{COF}_2 + F_2 \qquad \dots (5)$$

$$C_2F_6 + 2O_2 \rightarrow 2 CO_2 + 3 F_2 \qquad \dots (6)$$

The first two reactions are for the decomposition of  $C_2F_6$  and  $O_2$  respectively, while the last two are for the overall reactions. The respective extents of reactions are:  $\epsilon_{DC2F6}$ ,  $\epsilon_{DO2}$ ,  $\epsilon_{RCOF2}$ ,  $\epsilon_{RCO2}$ . Thus if an extent equals 1, then the reaction essentially goes to completion for the conditions at which the extent is calculated. The extents were calculated at four temperatures – 1000 °C, 1200 °C, 1500 °C and 2000 °C. The thermodynamic data used in the calculations is summarized in the following Table. The mean heat heat capacity  $C_{pm}$  at other temperatures were determined from Burgess et al (1955) (reference 2). The standard heat of formation  $\Delta H^0_{f, 298K}$  for COF<sub>2</sub> was taken from the calculations of the Schneider and Wallington (1994) (reference 3).

Species	$\Delta H^0_{f, 298K}$	$S^{0}_{f, 298K}$	C <sub>pm</sub> , 800 K
	(kJ/mol)	(J/mol.K)	(J/mol, K)
$C_2F_6$	-1343.9	332.1	160.34
O <sub>2</sub>	0	205	33.75
CO <sub>2</sub>	-393.5	213.7	51.54
COF <sub>2</sub>	-607.9	258.8	70.82
F	78.9	158.7	21.46

The extent reactions at various temperatures are summarized in the following Table.

Table. Extents of reaction if one the modynamic equilibrium calculation $-0.216 + 0.2$							
	$1000 {}^{0}\mathrm{C}$	1200 <sup>0</sup> C	1500 <sup>0</sup> C	2000 <sup>0</sup> C			
EDC2F6	4%	33%	97%	100%			
ε <sub>DO2</sub>	0	0	1%	19%			
E <sub>RCOF2</sub>	100%	100%	100%	100%			
ε <sub>RCO2</sub>	0	0	0	76%			

Table: Extents of reaction from the thermodynamic equilibrium calculation -  $C_2F_6 + O_2$ 

The calculations show that  $C_2F_6$  may decompose at about 1000  $^{0}$ C, while  $O_2$  could not start decomposing till about 1500  $^{0}$ C. However, the decomposition product of  $C_2F_6$  (CF<sub>3</sub>) could spontaneously react with  $O_2$  at lower temperatures (all equilibrium  $K_p$  are greater than 10<sup>5</sup>). The extent of reaction for COF2 formation is 100% for all temperatures (>1000  $^{0}$ C); however, a significant barrier prevents the spontaneous reaction of  $C_2F_6$  with  $O_2$  from COF<sub>2</sub>. The formation of CO<sub>2</sub> is not favored thermodynamically until the temperature is in excess of 1500  $^{0}$ C. It is important to point out that these calculations are thermodynamic <u>equilibrium</u> calculations only and do not consider kinetic effects.

MHI plasma are highly stable.

Optional scrubber unit.

## **References:**

- 1. Vivek Mohindra, '*Characterization of Perfluorocompound Emission and Abatement Kinetics in Plasma Process*', Ph.D. thesis submitted to the department of chemical engineering, MIT, December 1995.
- 2. Burgess, D.R.F. Jr., M.R. Zachariah, W. Tsang, and P.R. Westmoreland, *'Thermochemical and Chemical Kinetics Data for Fluorinated Hydrocarbons'*, NIST document (1995).
- 3. Schneider, W.F., and T.J. Wallington, 'Thermochemistry of COF<sub>2</sub> and Related Compounds', J. of Physical Chemistry, **98** (31), 7448 (1994).