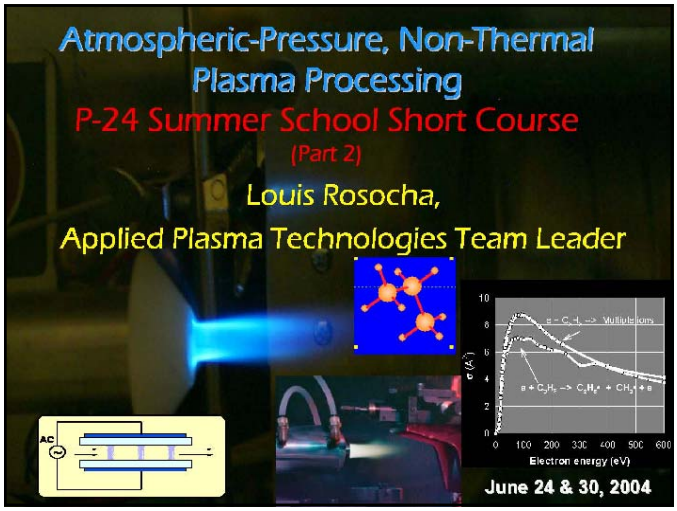
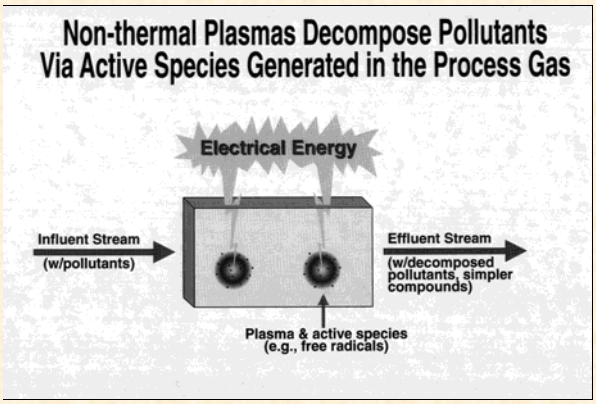


Our primary applications of non-thermal plasma processing

Pollutant/Hazardous Chemical Destruction	Surface Modification or Decontamination
Air pollutants •VOCs •NO_x, SO_x •Odors (H_2S, food processing) **Environmental remediation** •VOCs/haz chemicals in soil or groundwater	**Modification** •Adhesion •Stain resistance •Dye uptake **Decontamination** •Chem/bio warfare agents •Actinides
Combustion enhancement •IC engines (automotive) •Gas turbines •Burners	**Combined systems** •Thermal packed-bed reactor + NTP reactor for haz chem destruction



Example Radical Formation Mechanisms

Electron impact

$e + O_2 \rightarrow O + O^* + e$
$e + N_2 \rightarrow N + N + e$
$e + NO \rightarrow N + O + e$
$e + O_2 \rightarrow O + O + e$
$e + H_2O \rightarrow OH + H + e$
$e + N_2 \rightarrow N_2^* + e$
$e + NH_3 \rightarrow NH + H_2 + e$

Ionization/Clusters

$e + O_2 \rightarrow O_2^+ + e$
$O_2^+ + H_2O \rightarrow O_2^+ (H_2O)$
$O_2^+ (H_2O) + H_2O \rightarrow HO_3^+ + O_2 + OH$
$O_2^+ (H_2O) + H_2O \rightarrow HO_3^+ (OH) + O_2$
$HO_3^+ (OH) + H_2O \rightarrow HO_3^+ + H_2O + OH$

Quenching

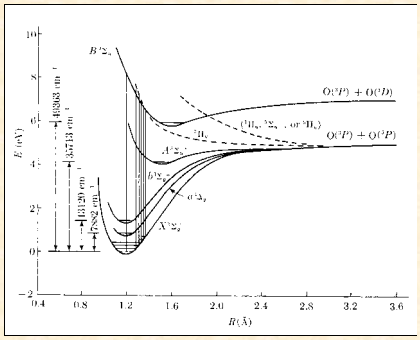
$O^* + H_2O \rightarrow 2OH$
$N_2^* + O_2 \rightarrow N_2 + O + O$

Others

$H + O_3 \rightarrow OH + O_2$
$HO_2 + NO \rightarrow OH + NO_2$
$H + O_2 + M \rightarrow HO_2 + M$

In chlorocarbon-containing mixtures, Cl and ClO radicals are also produced from reactions of radicals and other gas species with the entrained pollutants. These can further participate in decomposition chain reactions.

Molecular Oxygen Potential Energy Diagram

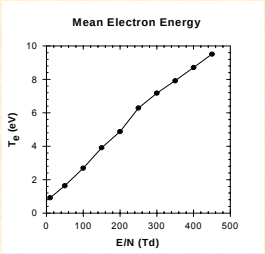


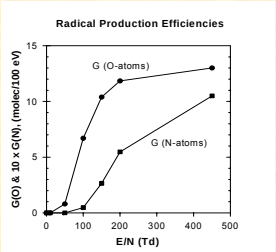
The radical production efficiency (G-value) depends on the gaseous electronics. Radical generation is mainly initiated by energetic-electron collisions.

$$G = f\left(\frac{k_{rad}}{v_d \frac{E}{N}}\right)$$

- E/N is the reduced field,
- V_d is the electron drift velocity, which depends on E/N, k_{rad} is the rate constant for radical formation (e.g., a dissociation rate constant, which depends on E/N), and/or other rate constants.

By increasing the plasma electron temperature, radical yields are increased.





Air-like mixture example - Left: Electron temperature vs E/N. Right: O-atom and N-radical yields. Common electrical-discharge nonthermal plasma reactors operate around 100 Td. T_e and the radical yields can dramatically increase at higher E/N.

The overall process efficiency can be effectively separated into two terms: the radical production efficiency and the radical utilization efficiency.

$$\eta_{net} = G_R\, \eta_u$$

- G_R is the radical-production efficiency (mainly depends on gaseous electronics/plasma chemistry)
- η_u is the radical utilization efficiency (mainly depends on chemical kinetics)

Gas-phase plasma chemical decomposition is driven by electron impact and radical attack.	Plasma chemical decomposition of VOCs produces a variety of terminal products.
(1) e + X → products **(2) O, OH, N, etc. + X → products** • **The first reaction is dominant at large pollutant mole fractions.** • **The second dominates at smaller mole fractions.** **(More energy is directly absorbed by pollutant at high mole fraction, hence electron channel dominates.)**	**e, O, OH, N, etc. + X → products** •**Manageable products:** CO_2, CO, Cl_2, HCl, $COCl_2$ •**Undesirable products:** Other halocarbons, hazardous byproducts (e.g., DCAC - CHCl2COCl); polymers •**Secondary treatment:** $CO_2 + NaOH \rightarrow NaHCO_3$ $CO + catalyst \rightarrow CO_2$ $Cl_2 + NaHCO_3 \rightarrow NaCl + HCl + ...$ $HCl + NaOH \rightarrow NaCl + H_2O$ $COCl_2 + H_2O \rightarrow 2HCl + CO_2$

Major de-NOx Reactions in Moist Gas Mixtures w/o HCs

$O + NO + M \rightarrow NO_2 + M$
$O + NO_2 \rightarrow NO + O_2$
$O + N_2 \rightarrow NO + N$
$O + O_2 + M \rightarrow O_3 + M$
$O_3 + NO \rightarrow NO_2 + O_2$
$O_3 + NO_2 \rightarrow NO_3 + O_2$
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$
$N(^2D) + O_2 \rightarrow NO + O$
$N + NO \rightarrow N_2 + O$
$N(^2D) + NO \rightarrow N_2 + O(^1D)$
$N + NO_2 \rightarrow N_2O + O$
$N + NO_2 \rightarrow 2NO$

$N(^2D) + H_2O \rightarrow NH + OH$
$NH + NO \rightarrow N_2 + OH$
$NH + O_2 \rightarrow NO + OH$
$NO + NO_3 \rightarrow 2NO_2$
$NO + OH + M \rightarrow HNO_2 + M$
$OH + HNO_2 \rightarrow NO_2 + H_2O$
$OH + NO_2 + M \rightarrow HNO_3 + M$
$N + NO_2 \rightarrow N_2 + O_2$
$N + N_2O \rightarrow NO + N_2$
$O(^1D) + NO_2 \rightarrow NO + O_2$
$O(^1D) + N_2O \rightarrow 2NO$ or $N_2 + O_2$
$N_2(A) + O_2 \rightarrow N_2 + 2O$
$N_2(A) + N_2O \rightarrow N_2 + N + NO$

Primary Acid-Formation Pathways:
$NO + OH + M \rightarrow HNO_2 + M$
$OH + NO_2 + M \rightarrow HNO_3 + M$

With ammonia (NH_3) addition, useful particulates (fertilizer) can be formed from NO_x

$e + NH_3 \rightarrow NH_2 + H + e$
$e + NH_2 \rightarrow NH + H + e$
$NH + H \rightarrow N + H_2$
$NH_2 + NO \rightarrow N_2 + H_2O$
$NH + NO \rightarrow N_2 + OH$
$N + NO \rightarrow N_2 + O$
$OH + NH_3 \rightarrow NH_2 + H_2O$
$OH + NO + M \rightarrow HNO_2 + M$
$OH + HNO_2 \rightarrow NO_2 + H2O$
$OH + NO_2 + M \rightarrow HNO_3 + M$

$NH_3 + HNO_3 \rightarrow NH_4NO_3$
(Ammonium Nitrate fertilizer)

Simple, first-order kinetics model gives exponential pollutant-removal function.

Chemical Reactions		Rate Equations
$e + A \rightarrow R^{\bullet} + A'$	(1)	$\frac{d[R\cdot]}{dt} = \frac{d[R\cdot]}{d\bar{E}} \cdot \frac{d\bar{E}}{dt} = G\bar{P}$
$R^{\bullet} + X \rightarrow$ Products	(2)	$\frac{d[X]}{dt} = -k[R\cdot][X]$
$R^{\bullet} + S_i \rightarrow$ Products	(3)	$\frac{d[R\cdot]}{dt} = -k_{S_i}[R\cdot][S_i]$

Assume steady state: $\frac{d[R\cdot]}{dt}(net) = G\bar{P} - k[R\cdot][X] - \sum_i k_{S_i}[R\cdot][S_i] = 0$.

Solve for $[R]_{ss}$ and insert into (2) to obtain generalized removal equation.

A generalized removal equation depends on plasma chemistry (radical yields), reaction chemistry, and applied plasma specific energy.

Generalized differential equation:

$$\frac{k[X]+\sum_i k_{S_i}[S_i]}{k[X]}\,d[X]=-G\,d\bar{E}$$

Integration with limits $[X]_0 \rightarrow [X]$ and $0 \rightarrow E$ gives:

$$\frac{[X]}{[X]_0}+\frac{\sum_i k_{S_i}[S_i]}{k\,[X]_0}\ln\frac{[X]}{[X]_0}-1=-\frac{G\bar{E}}{[X]_0}$$

For low degree of removal (i.e., $[X]/[X]_0 \sim 1 + \ln\{[X]/[X]_0\}$), an analytical solution is obtained:

$$[X]/[X]_0 = \exp(-\bar{E}/\beta)$$

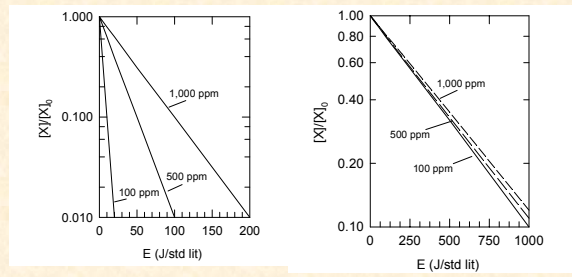
where

$$\beta=\frac{1}{G}\left([X]_0+\frac{\sum_i k_{S_i}[S_i]}{k}\right)$$

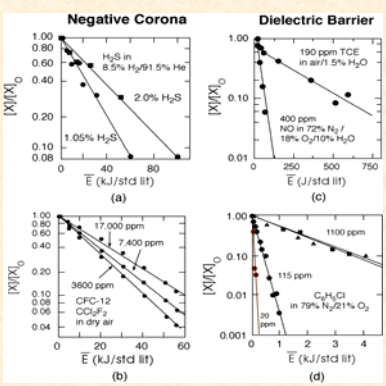
When $k[X] << \Sigma_i k_{Si}[S_i]$, the β-value and, hence the degree of removal $[X]/[X]_0$ shows no dependence on the initial concentration $[X]_0$.

The simple model predicts the form of the removal function (plot of degree of removal *vs* plasma specific energy).

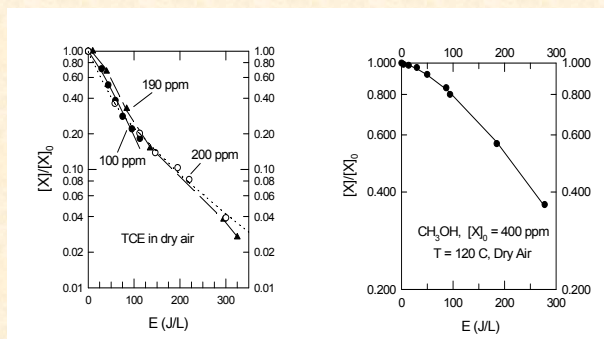
- $\Sigma_i k_{Si}[S_i] << k[X]_0$
- $\Sigma_i k_{Si}[S_i] >> k[X]_0$



Example removal data for various compounds



Example removal data for sample compounds



After Falkenstein; Korzekwa & Rosocha

After Hsiao et al

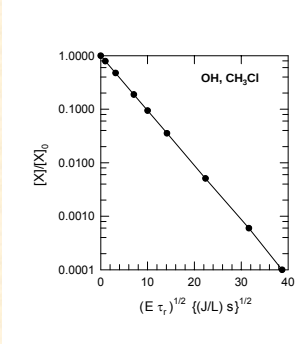
Example recombination-dominated removal plot (calculated)

Additional example case (explicit residence-time dependence):
$\Sigma_i k_{Si} [S_i] >> k [X]_0$ and dominant scavenging pathway is recombination of the radicals, e.g., $[R^\bullet] = [S]$, where S represents the primary scavenger

$$[R^\bullet] = (G\bar{P}/k_s)^{1/2}$$

$$\frac{d[X]}{[X]} = -k\left(\frac{G\bar{P}}{k_S}\right)^{1/2} dt$$

$$[X]/[X]_0 = \exp\{-k\,(G\bar{E}/k_s)^{1/2}\,\tau_r^{1/2}\}$$



Ballpark β-value calculation for TCE (C_2HCl_3) in a dry, air-like gas mixture

Simple Chemical Model

1) $e + O_2 \rightarrow O + O + e$
2) $O + TCE \rightarrow Products$
3) $O + O_2 + M \rightarrow O_3 + M$

G (O) ~ 10 molec/100 eV
$k_2 = 5.3 \times 10^{-13}$ cm^3/s
$k_3 = 6.1 \times 10^{-34}$ cm^6/s (for M = O_2)
$k'_3 = 5.9 \times 10^{-34}$ cm^6/s (for M = N_2)

β-Value Estimates

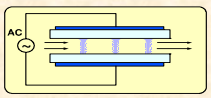
Without Chain Reactions

$\beta = 1/G\,\{[X]_0 + 1/k_2\,(k_3\,[O_2]^2 + k'_3\,[O_2]\,[N_2])\}$
β ~ 260 J/liter

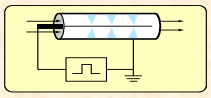
With Cl Chain Reactions

Chain length 2: **β ~ 130 J/liter**
Chain length 5: **β ~ 52 J/liter**
Chain length 10: **β ~ 26 J/liter**

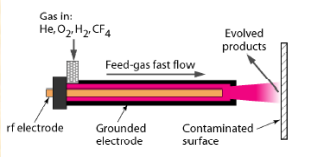
We mainly employ four types of NTP reactors



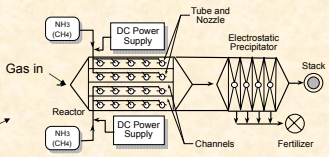
Silent discharge (dielectric-barrier discharge)



Pulsed or DC corona



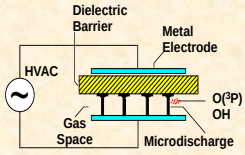
Atmospheric pressure plasma jet



Corona radical shower

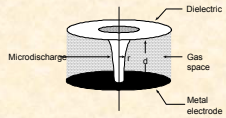
Silent Discharge Plasma (SDP) or Dielectric-Barrier Discharge Fundamentals

Illustration of SDP Reactor



- Dielectric-Barrier Discharge (DBD) inventen by W. von Siemens in 1857
- Referred to as Silent Electrical Discharge by Andrews & Tait, 1860
- Used for over 150 years to produce ozone
- Is a non-thermal plasma (electrons are 'hot', while ions & neutrals are 'cold')

Illustration of Microdischarge

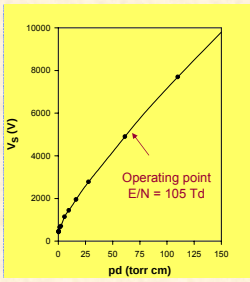


Microdischarge Properties

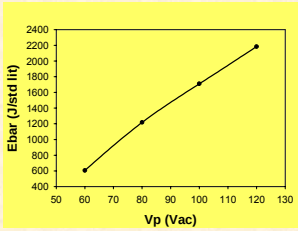
Parameter	Symbol	Typical value
Channel radius	r	~ 100 μm
Microdischarge duration	t_d	2-3 ns
Electron density	[e]	~ 10^{14} cm^{-3}
Reduced electric field	E/N	100-200 Td (or 10^{-17} V-cm^2)
Average electron temperature	T_e, D/m	4-5 eV
Current density	J	~ 1 kA/cm^2
Electron drift velocity	v_d	~ 2 x 10^7 cm/sec

Typical operating parameters: E/N and E_{bar}

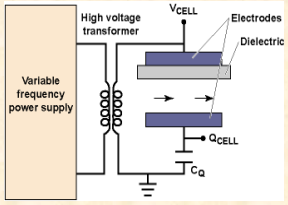
Sparking Voltage (from Heylen, 2001)

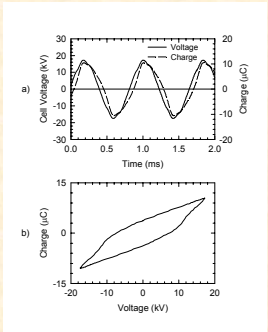


Plasma Specific Energy (measured)

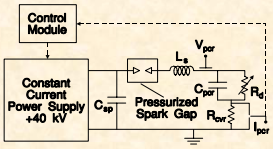


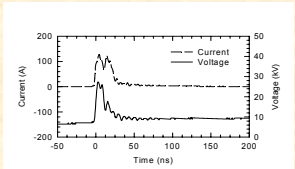
Silent Electrical Discharge Reactor Schematic & Electrical Waveforms



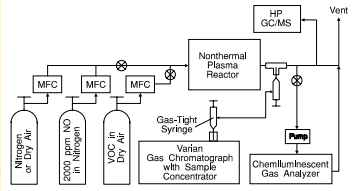


Pulsed corona reactor (PCR) circuit schematic and waveforms

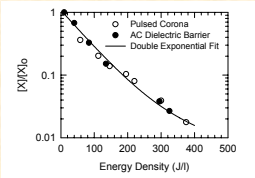




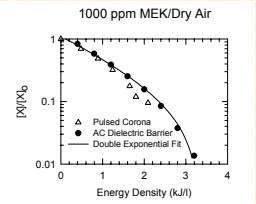
Example SDP & PCR Destruction Results



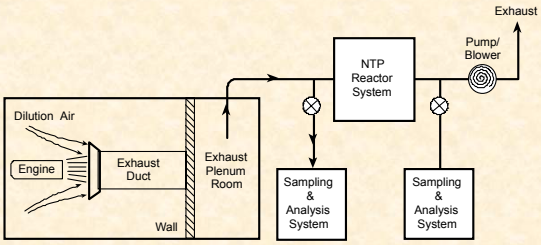
200 ppm TCE/Dry Air



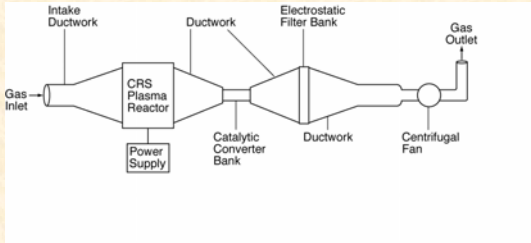
1000 ppm MEK/Dry Air



Cruise Missile Engine Test Cell De-NO_x Demo at Tinker AFB Employing CRS System

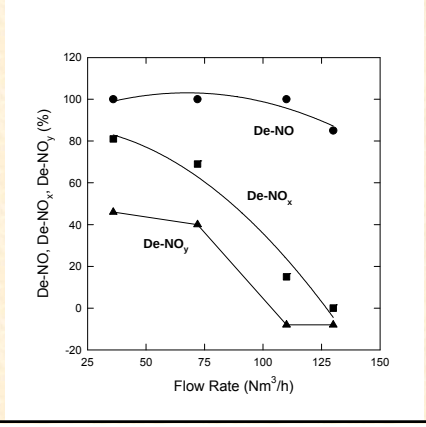


Schematic diagram of small, pilot-scale Corona Radical Shower (CRS) non-thermal plasma (NTP) reactor for NO_x abatement from jet-engine test cells

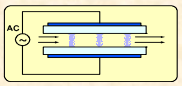


Cruise Missile Engine Test Cell Exhaust De-No_x Demonstration at Tinker AFB Using Corona Radical Shower NTP Reactor
Mar/Apr 2000

Removal of NO_x species, CRS NTP catalytic hybrid system field-pilot tests on a CMTC at Tinker AFB



Environmental restoration field-pilot demonstration at McClellan AFB



Silent discharge (dielectric-barrier discharge)

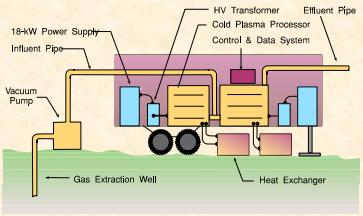
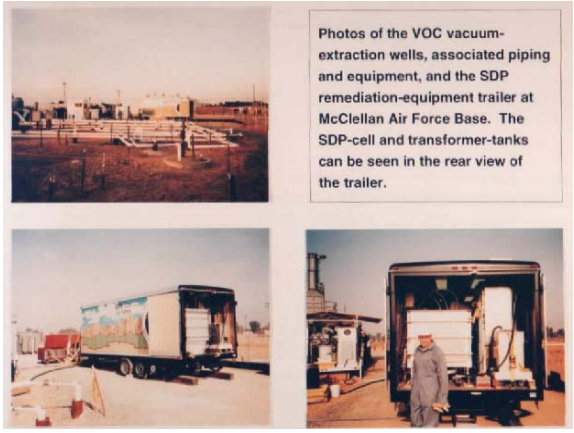


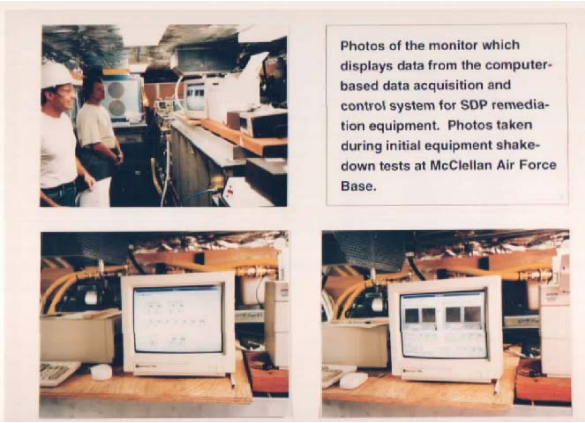
Illustration of mobile dielectric-barrier NTP reactor system employed for VOC decomposition tests at McClellan AFB. Each plasma reactor tank operated at up to 10 kW of plasma power.

CRADAs with the Electric Power Research Institute (EPRI) & High Mesa Technologies (HMT) were an essential part of the development & fielding of this equipment.



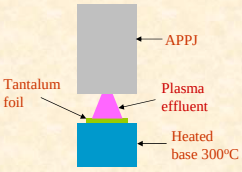
Photos of the VOC vacuum-extraction wells, associated piping and equipment, and the SDP remediation-equipment trailer at McClellan Air Force Base. The SDP-cell and transformer-tanks can be seen in the rear view of the trailer.

Assembling two 5-SCFM (142 lit/min) SDP processor units, each containing two 10-cell modules, in the equipment trailer at McClellan Air Force Base. The plasma power for each 5-SCFM unit is about 10 kW.



Photos of the monitor which displays data from the computer-based data acquisition and control system for SDP remediation equipment. Photos taken during initial equipment shake-down tests at McClellan Air Force Base.

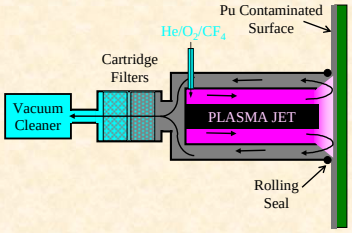
Pu Surrogate Etching Studies



- $Ta(s) + 5F(g) \Rightarrow TaF_5(g)$

- Ta used as surrogate for Pu due to thermodynamic similarities
- Typical etch rates > 10 mg/min over ~ 1.1 cm² area (equivalent to ~ 5.5 μm/min)

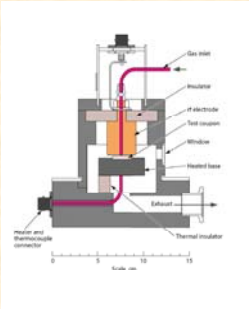
Concept for Decontamination of Actinides, such as Plutonium and Uranium

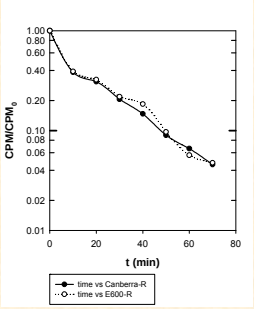


Decon Benefits:
- Dry- no secondary waste stream
- Actinides recoverable
- Endpoint detection possible

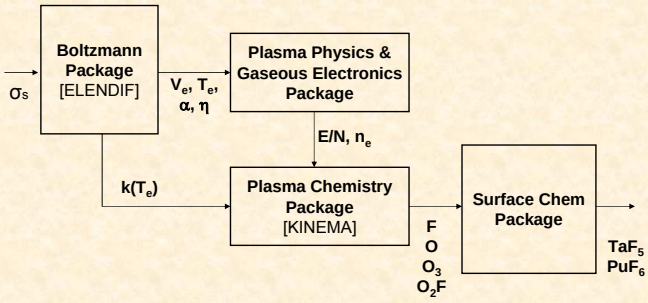
- **Decon Concept ⇒ Volume Reduction**
- Energetic plasma electrons dissociate CF_4/NF_3 forming F atoms
- Atomic Fluorine etches contamination: $Pu(s) + 6F(g) \Rightarrow PuF_6(g)$
- Volatile byproducts (e.g., PuF_6) captured in reactive or adsorbent filters

Pu is quickly etched by APPJ plasma

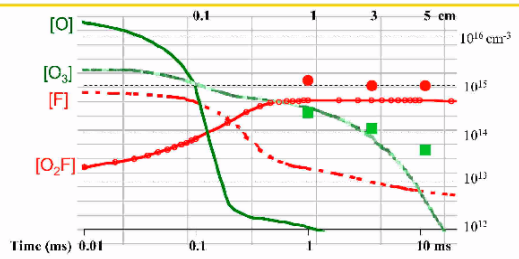




Modeling for Benchmarking & Optimization



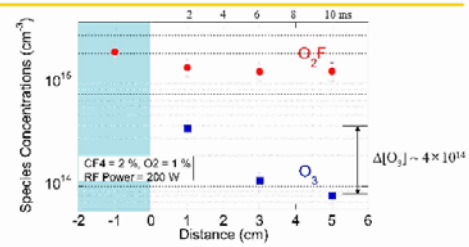
Comparison with Post-Plasma Chemistry Simulation (at 300 K calculated by Hilary Teslow)



- At room temperature calculation (cf. measured T_{gas} ~ 35 °C), F decays fast, order of 2, within 1 ms producing O_2F ($F + O_2 \rightarrow O_2F$).
- F can be short-lived metal etching agent. O_2F can be a newly found long-lived etching agent.

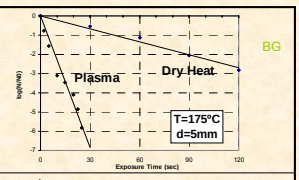
1st Measurements of $[O_2F]$ in APPJ (by Y. Kim)

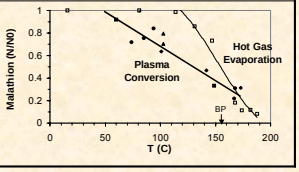
$[O_2F]$ in $He/O_2/CF_4$ Discharge (CF_4 = 2 %)



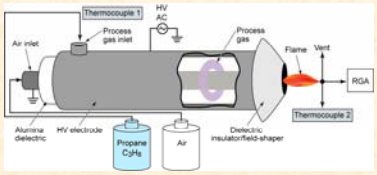
- $[O_2F]$ was around 10^{15} at 2 % CF_4 ➔ O_2F is long-lived species
- O_2F may be etching agent → O_2F may be decomposed on Ta surface to O_2 and F, then F etches Ta ($Ta - O_2F \rightarrow TaF - O_2$).
- $[O_3]$ decreases by $O_3 + F \rightarrow OF + O_2$ ➔ $[F] < \Delta[O_3]/(k[O_3]\,\Delta t) \sim 10^{14}$ cm^{-3}

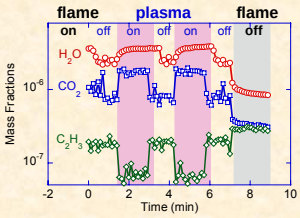
CBW Agent Decon with APPJ - Surrogate Tests: BG ↔ Anthrax, Malathion ↔ Nerve Agents

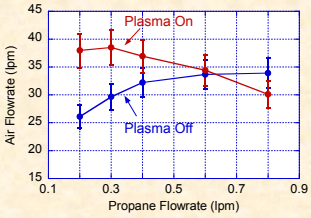




Preliminary experiments have proven the NTP combustion enhancement concept





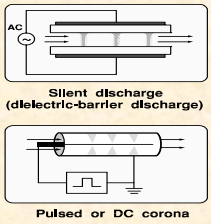


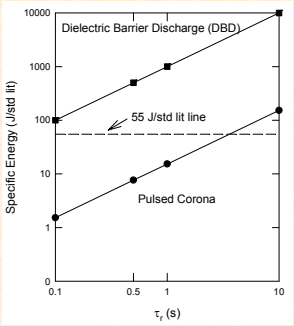
Flow (C_3H_8) = 0.3 lpm, Flow (Air) = 4.6 lpm

0 4 6 8 10 12 W

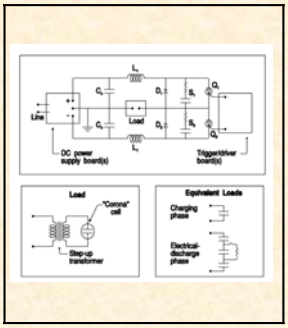
Kim, Stange, Ferreri (6/2004)

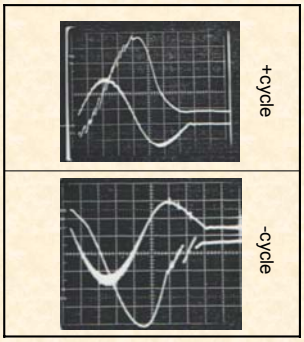
SDP reactor outperforms PCR in terms of plasma energy density





Series inverter powers SDP reactors effectively & efficiently





Technology-development motivators are regulatory, economic, and social

Regulatory
New and/or more stringent regulations
Clean Air Act Amendment of 1990, Clean Water Act
Attendant MACT standards
Enforcement of regulations
New NO_x/SO_x regulations (2007 – 2010)

Economic
Impact of regulations
Costs associated with conventional methods

Social
Environmental consciousness
Health risks

The CAAA 1990 contains three titles closely related to new technologies (e.g., NTPs)

Title III (Air Toxics)
Directly concerned with emission of hazardous air pollutants (HAPs)
Established standards for 189 listed chemicals

Title IV (Acid Rain)
Reduction of SO_x/NO_x emissions

Title VI (Stratospheric Ozone)
Phase out of VOCs

MACT (Max Achievable Control Technology) Standards
Calls for state-of-art pollution control equipment
Require changes in equipment, processes, treatment

Outline

Overview of Applications of NTPs for Air Pollution Control and Surface Decontamination
Stack emissions (VOCs, NOx/SOx)
Environmental remediation (hazardous chemicals in soil and/or groundwater)
Surface decontamination (actinides, chemical/biological warfare agents)
Combustion enhancement

Applied Electrical Discharge Physics
Streamers/microdischarges (corona and silent electrical discharges)
Atmospheric pressure RF-driven discharges

Plasma Chemistry and Gas-Phase Reaction Chemistry
Electron-energy distribution functions, transport coefficients, and rate coefficients
Active Species (Free Radical) Yields in Electrical-Discharge Driven NTPs
Electron/radical attack mechanisms
Simple reactions/scaling laws

Power Conditioning & Electrical Measurements for NTP Applications
Power supplies/modulators for NTP processing
Voltage and power measurements for corona processing
Voltage and power measurements for silent discharge processing

Example Laboratory and Field Demonstrations
Soil/groundwater remediation
Engine test facility exhaust
Surface decontamination
Combustion enhancement of propane-air flames

Summary and Future Outlook
Regulatory factors
Social/health factors
Energy efficiency