SIMULTANEOUS REMEDIATION OF NO_X AND OXIDATION OF SOOT USING DIELECTRIC BARRIER DISCHARGES*

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AGENDA

- Introduction

- Description of the model – GLOBAL_KIN

- Reaction mechanisms

- Effect of soot particles on NO_x remediation

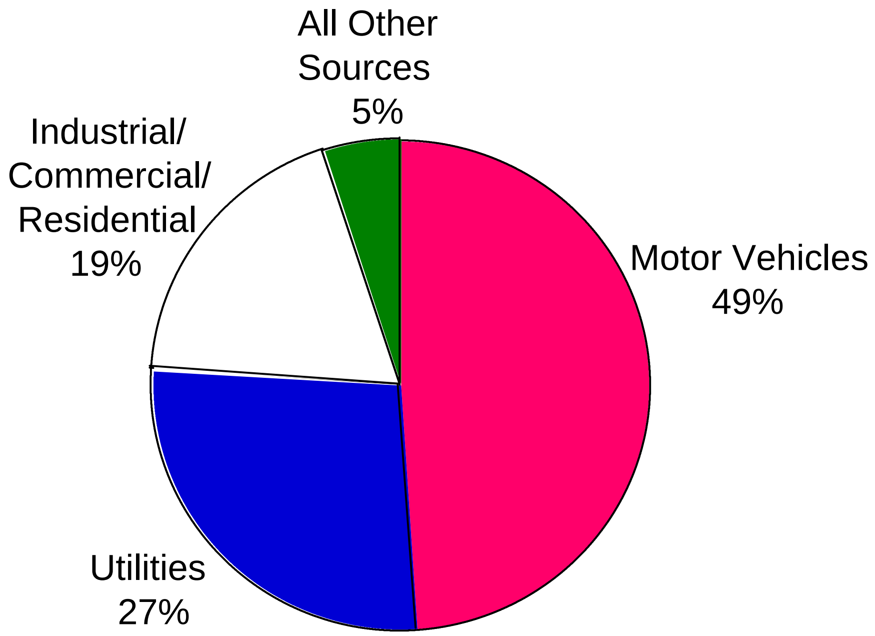
- Results
  - NO_x remediation
  - Soot oxidation
  - Effect of multiple pulses on NO_x chemistry

- Concluding remarks

INTRODUCTION

- **Nitrogen oxides (NO, NO_2) - NO_X, are one of the six major pollutants identified by the EPA, others being CO, Pb, SO_X, volatile matter and particulates. All emissions have decreased except for NO_x (EPA, 1998).**

- **Harmful effects of NO_X**
  - **Acid deposition**
  - **Formation of ozone**
  - **Eutrophication of water bodies**
  - **Inhalable fine particles**
  - **Visibility degradation**

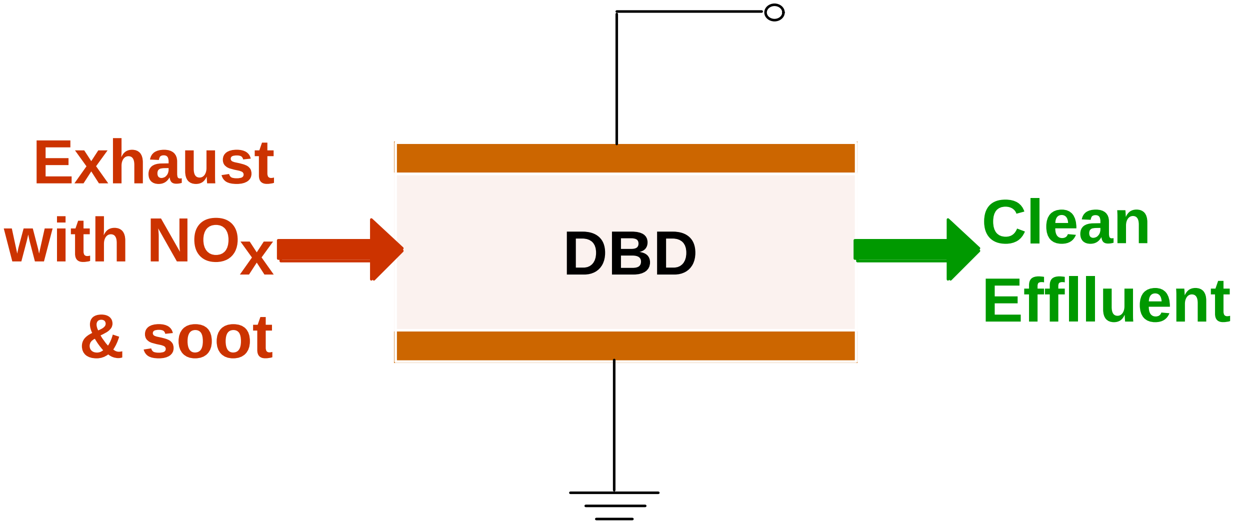


Major sources of NO_x (EPA, 1998)

PLASMA REMEDIATION OF NO_X USING DBDs

- **Dielectric barrier discharges (DBDs) are well suited for generation of gas-phase radicals at atmospheric pressures.**

- **Electron impact processes in DBDs produce radicals and ions which initiate the plasma chemistry.**



Exhaust with NO_X & soot

DBD

Clean Efflluent

$e + N_2 \rightarrow N + N + e$

$e + O_2 \rightarrow O + O + e$

$e + H_2O \rightarrow OH + H + e$

Reduction

$NO + N \rightarrow N_2 + O$

Oxidation

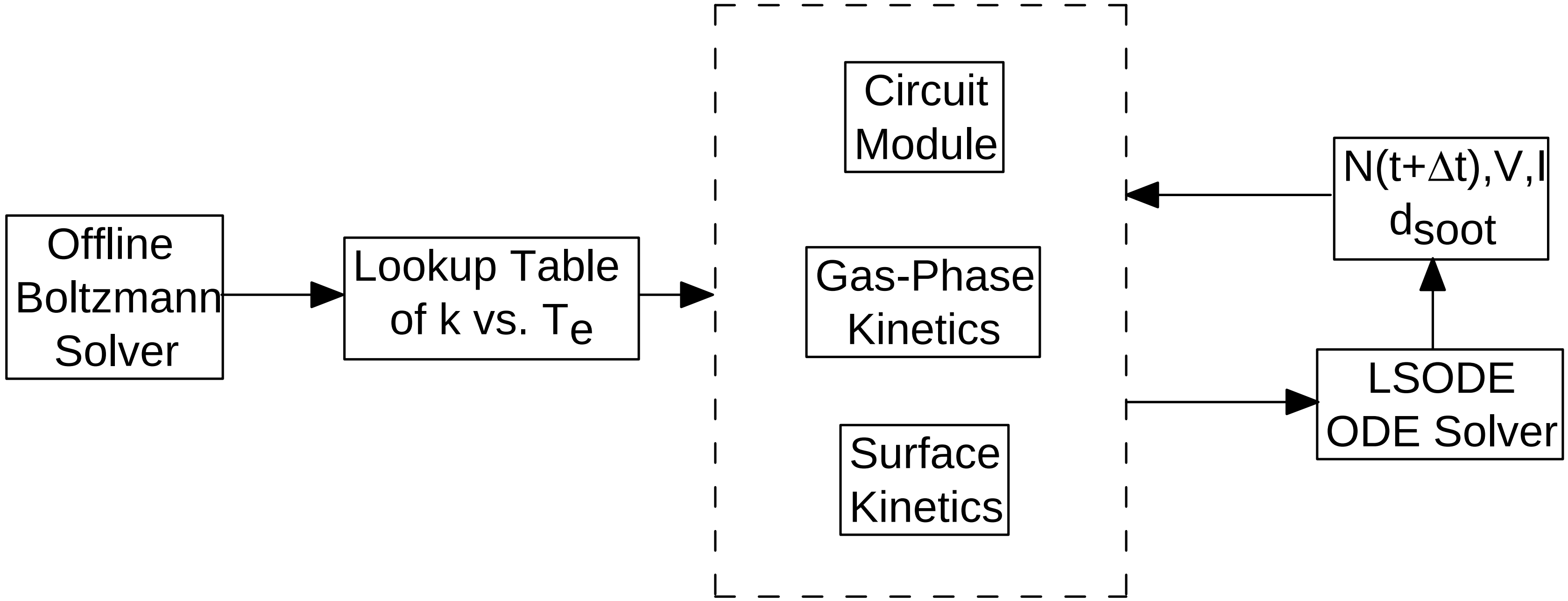
$NO + O \rightarrow NO_2$

$NO_2 + OH \rightarrow HNO_3$

DESCRIPTION OF GLOBAL-KIN

- **GLOBAL-KIN is a spatially homogeneous plasma chemistry simulation coupled with circuit and surface reaction modules.**

- **The model uses a lookup table generated by an offline Boltzmann solver to obtain the e-impact reaction rate coefficients.**



OPERATING CONDITIONS

- **Typical diesel exhausts contain N_2, O_2 (excess air); H_2O, CO_2 (products) and trace amounts of NO, CO, H_2 and unburned hydrocarbons (UHCs).**

- **To simulate actual exhausts, we have used propane (C_3H_8) and propene (C_3H_6) as representative of the UHCs.**

- **Inlet gas composition**

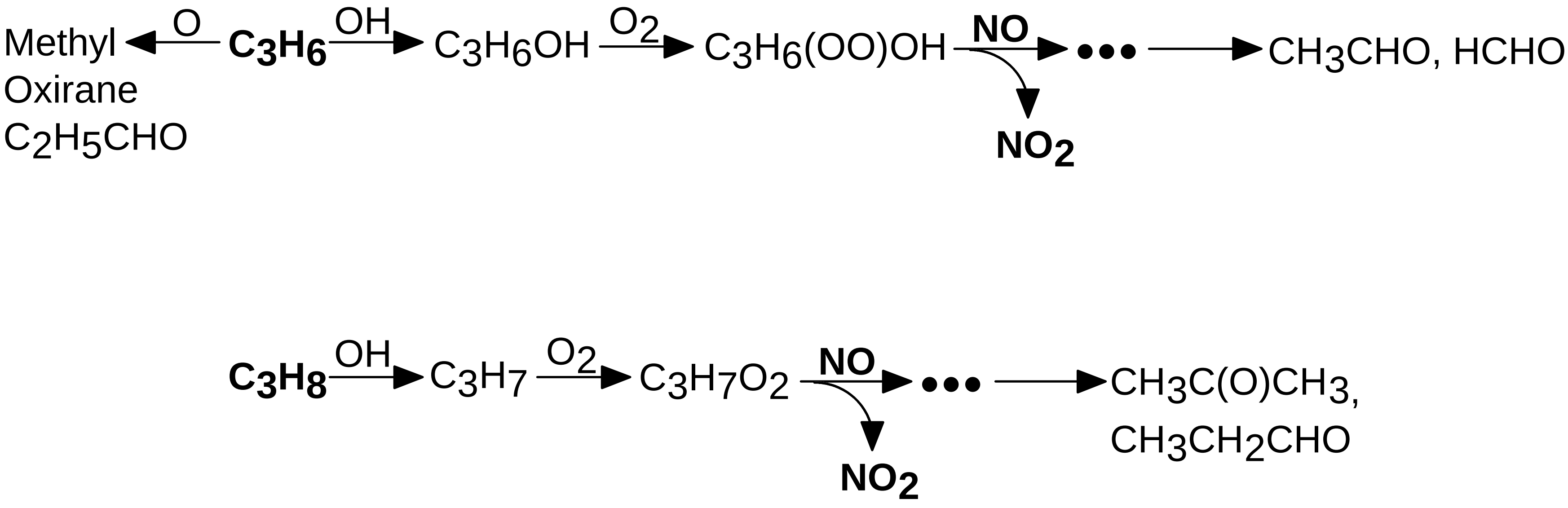
  $N_2/O_2/H_2O/CO_2$=78/8/6/7 NO=260 ppm, CO=400 ppm, H_2=133 ppm
  C_3H_6=500 ppm , C_3H_8=175 ppm

- **T=180 ^{o}C, P=1atm**
  τ = residence time of exhaust in DBD = 0.2 s

REACTION MECHANISMS : NO_X, C_3H_6, C_3H_8

- **In the presence of UHCs, the primary reaction is oxidation of NO by the peroxy radicals.**

- **Propene reactions are initiated both by O and OH whereas propane reactions are mainly OH initiated.**



$$\begin{array}{l}\text{Methyl}\\ \text{Oxirane}\\ C_2H_5CHO\end{array} \xleftarrow{O} \mathbf{C_3H_6} \xrightarrow{OH} C_3H_6OH \xrightarrow{O_2} C_3H_6(OO)OH \underset{\mathbf{NO_2}}{\xrightarrow{\mathbf{NO}}} \bullet\bullet\bullet \longrightarrow CH_3CHO,\ HCHO$$

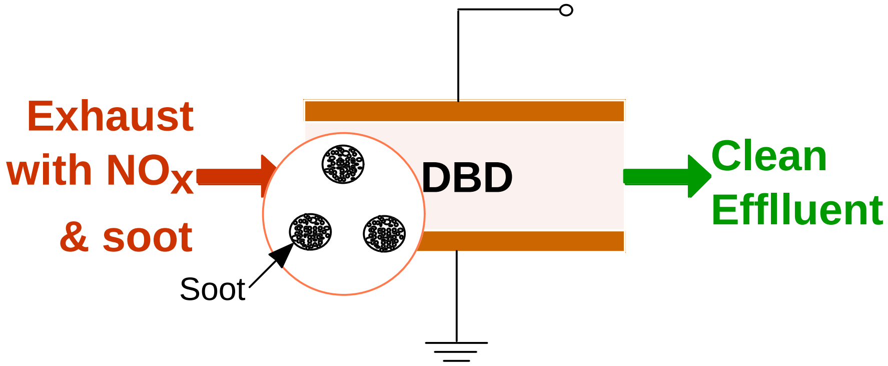
$$\mathbf{C_3H_8} \xrightarrow{OH} C_3H_7 \xrightarrow{O_2} C_3H_7O_2 \underset{\mathbf{NO_2}}{\xrightarrow{\mathbf{NO}}} \bullet\bullet\bullet \longrightarrow \begin{array}{l}CH_3C(O)CH_3,\\ CH_3CH_2CHO\end{array}$$

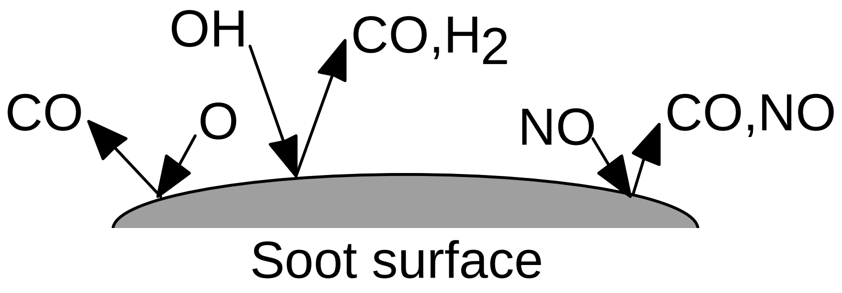
SOOT PARTICLES – EFFECT ON NO_X REMEDIATION

- **Soot particles found in diesel exhausts are typically 100 nm and containing C/H/O=89/1/10.**

- **The radicals produced in the plasma diffuse to the soot surface and react.**

$$O + Su \rightarrow O_{adsorbed} \rightarrow CO$$
$$OH + Su \rightarrow OH_{adsorbed} \rightarrow CO + H_2$$
$$NO_2 + Su \rightarrow NO_{2\ (adsorbed)} \rightarrow NO + CO$$





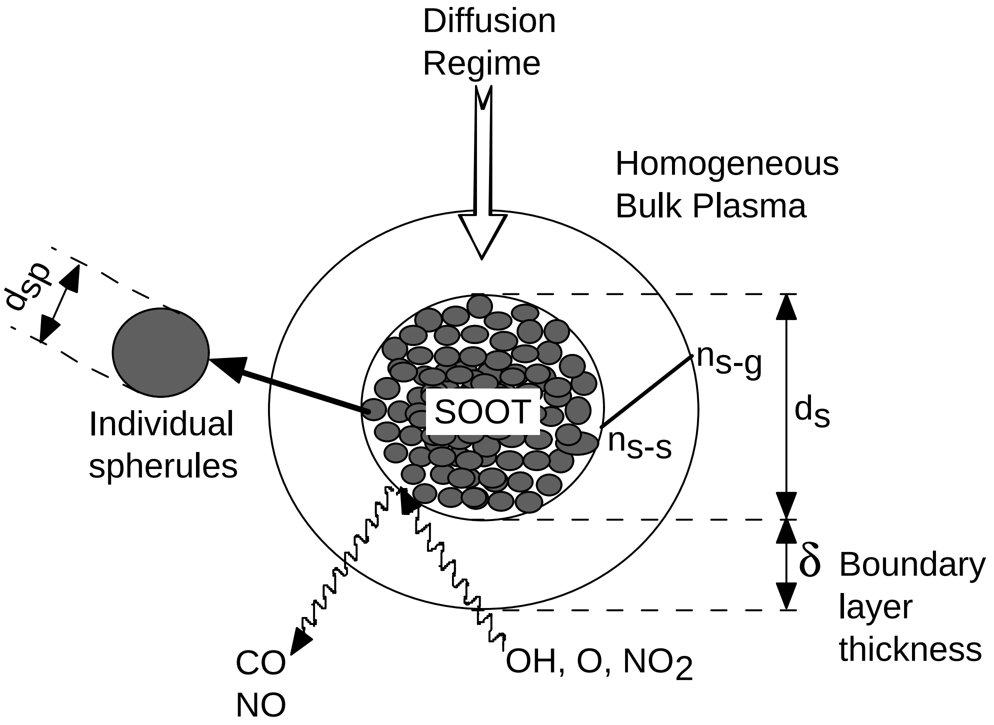
SOOT OXIDATION MODEL

- **Region surrounding soot is divided into two zones.**
  - **Diffusion regime**
  - **Homogeneous Bulk Plasma**

- **Species that react on the soot surface diffuse through the boundary layer.**

- **Boundary layer thickness, δ, is obtained from the Reynolds number. For low *Re*, $\delta \approx d_s/2$.**

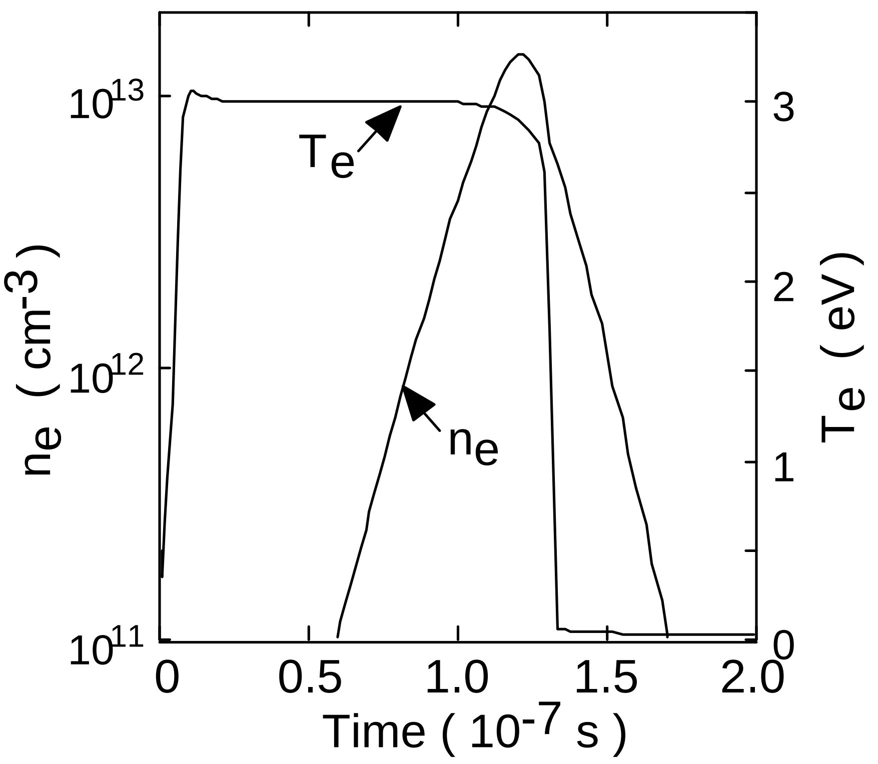
- **The diffusing species have a linear profile in the diffusion regime.**

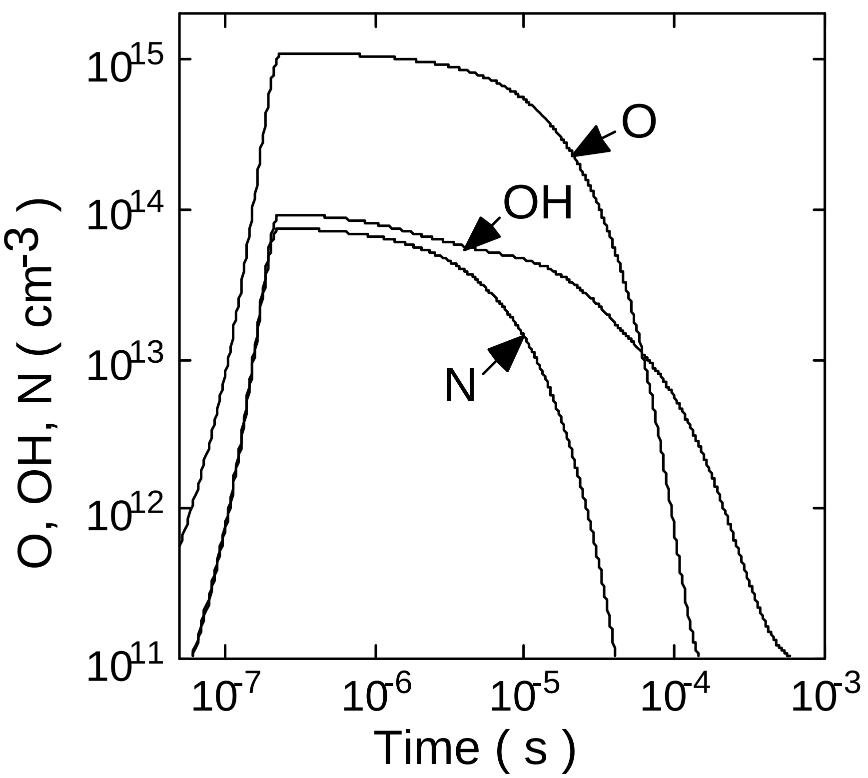


PLASMA CONDITIONS : n_e, T_e, [N], [OH], [O]

- Peak $n_e \approx 10^{13}$ cm^{-3} and $T_e \approx 3$ eV with $E_{dep} \approx 38$ J/L.

- Electron impact dissociation of N_2, O_2 and H_2O produce N, O and OH respectively.





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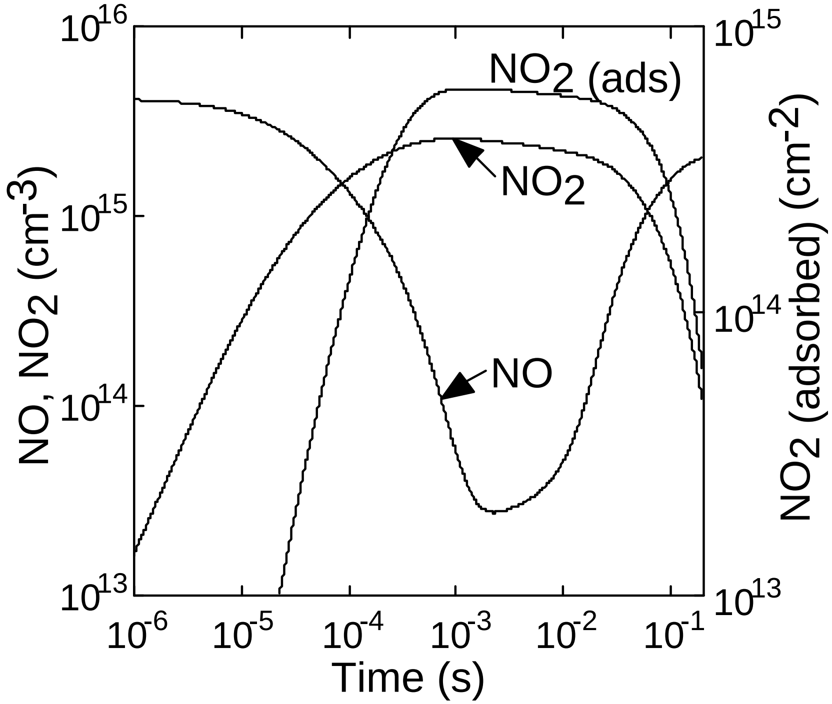
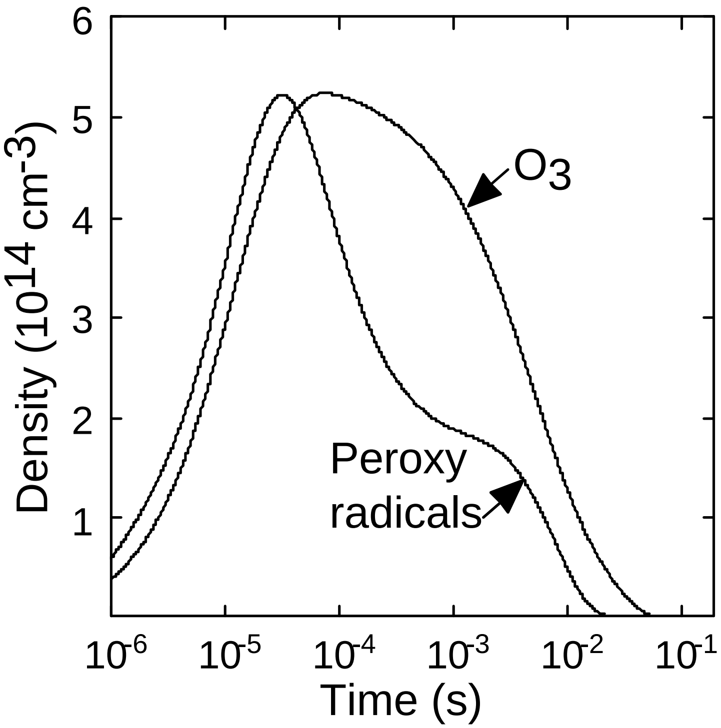
NO_X REMEDIATION : SINGLE PULSE

- **With a single pulse, exit NO densities are high because of the depletion of O_3 and peroxy radicals by the time of desorption of $NO_{2(ads)}$.**

$$NO + O_3 \text{ (or peroxies)} \rightarrow NO_2 \rightarrow NO_{2(ads)} \rightarrow NO$$





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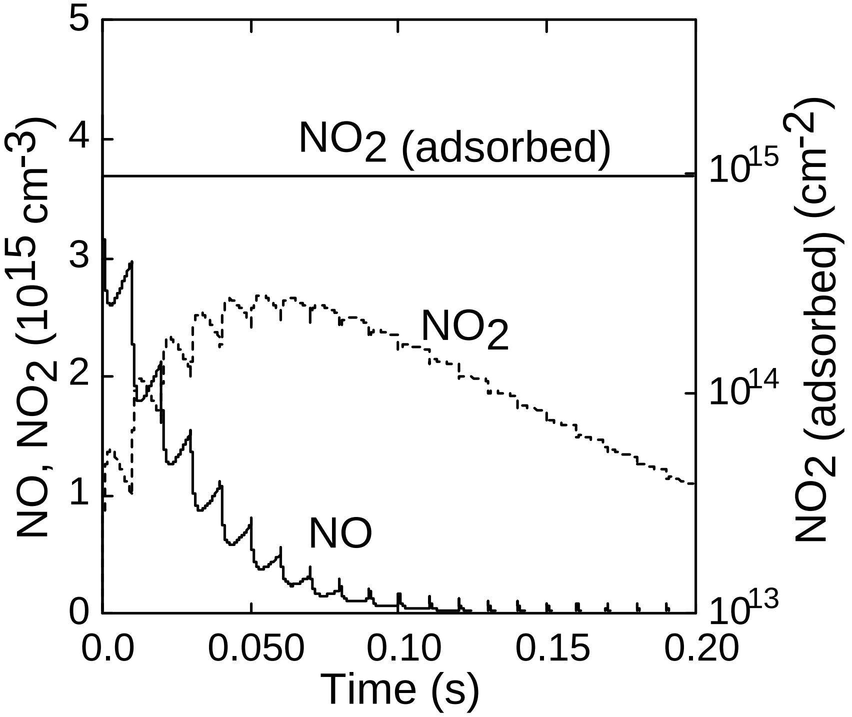
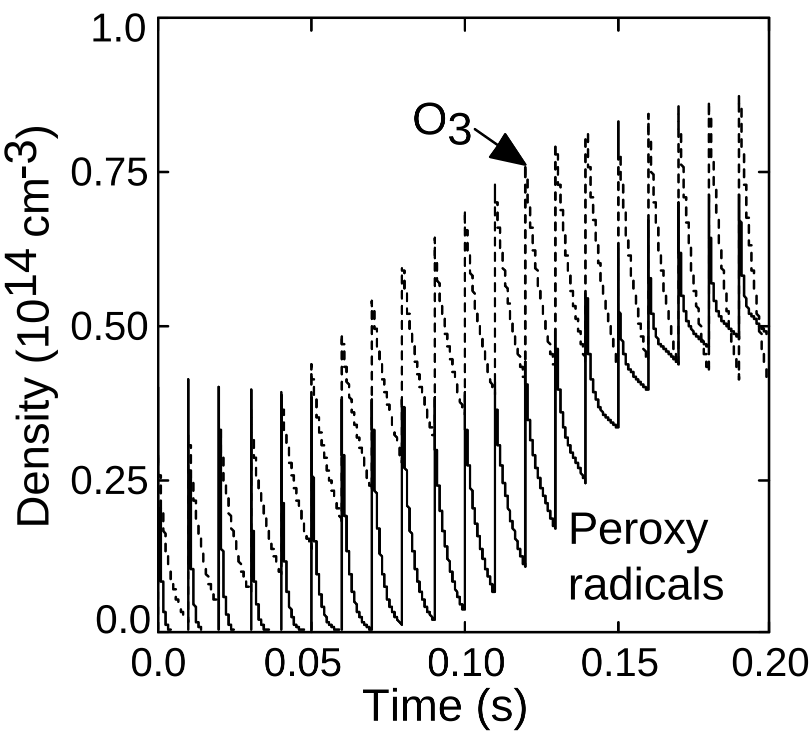
NO_X REMEDIATION : MULTIPLE PULSE

- **With multiple pulses, NO is converted to NO_2 by O_3 and peroxy radicals produced during each pulse.**

$$NO + O_3 \rightarrow NO_2 + O_2$$

- **The rate of adsorption of NO_2 being higher than the rate of desorption, the NO_x remains adsorbed on the surface of soot.**





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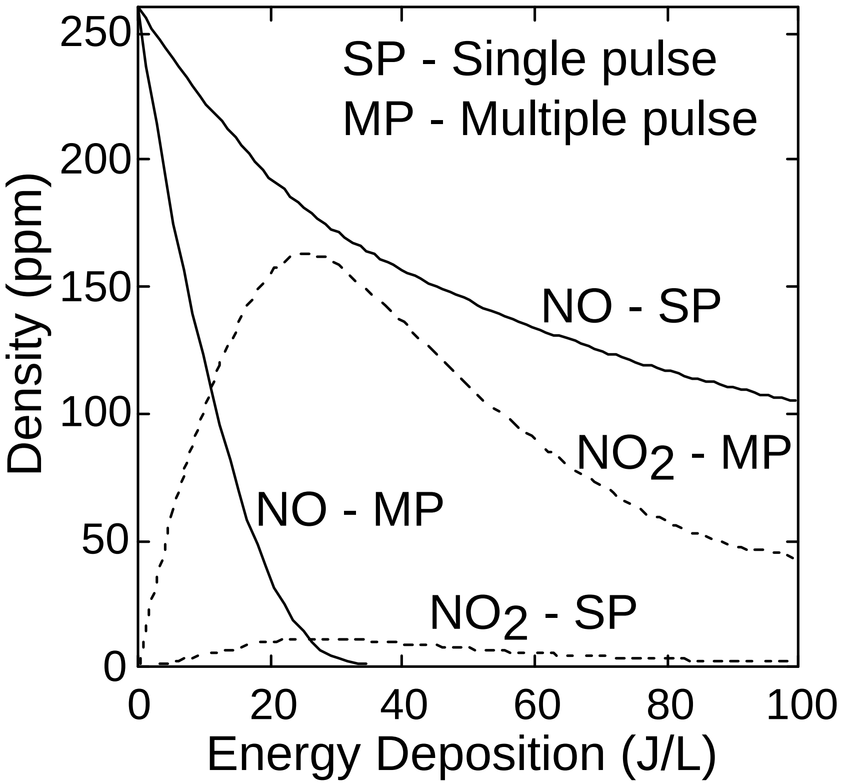
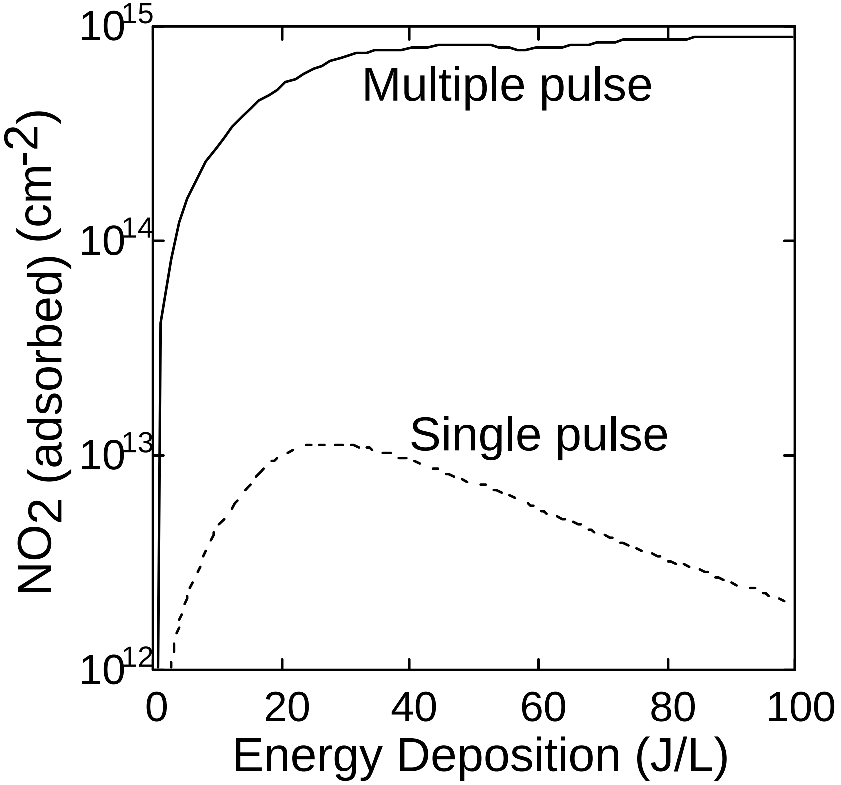
EFFECT OF ENERGY DEPOSITION

- **For a single pulse, exit NO densities are higher because of the larger time available for NO_2 desorption from the soot surface.**

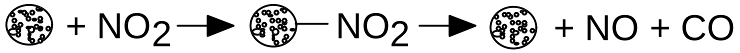
- **The peroxy radicals available for NO consumption are lost by the time NO is regenerated from NO_2.**





SOOT OXIDATION

- **With increasing energy deposition, the diameter of the soot decreases due to the oxidation by NO_2.**

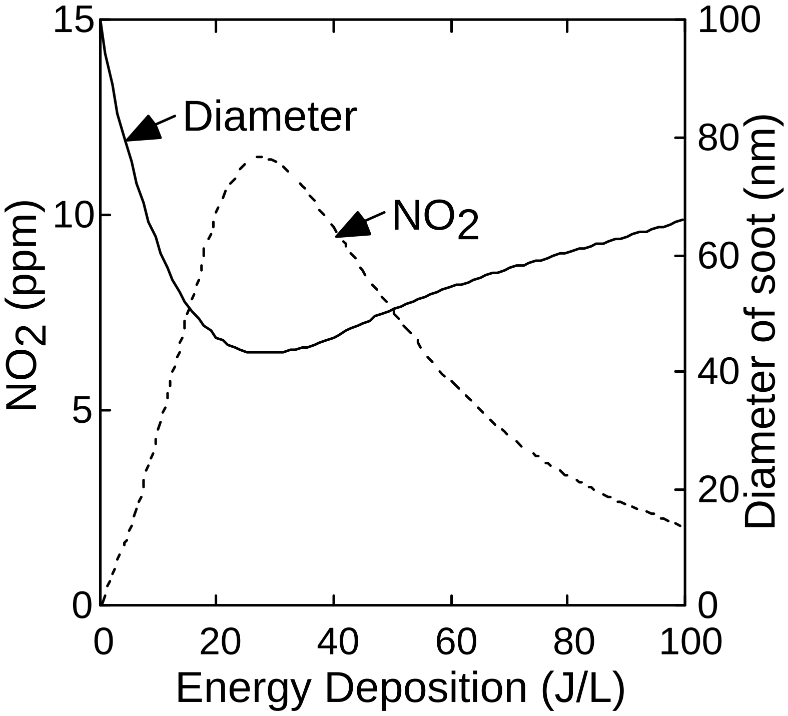


$\text{soot} + NO_2 \rightarrow \text{soot}-NO_2 \rightarrow \text{soot} + NO + CO$

- **At higher energies, the final diameter of soot increases because the density of NO_2 decreases due to the gas-phase reconversion to NO.**

$$NO_2 + O \rightarrow NO + O_2$$

- **Note that the oxidation of soot is partial and results in CO and not CO_2.**
  - **CO – poisonous**
  - **CO_2 – greenhouse gas**



CONCLUDING REMARKS

- **Plasma remediation of NO_x, by itself is not sufficient to completely remove NO_x.**

- **Soot chemistry significantly affects the NO_x composition in plasma remediation of NO_x.**

- **Soot can be oxidized by plasma and as high as 30% soot removal can be achieved at 60 J/L.**

- **Multiple pulse input results in *apparent* NO_x removal because of the increased adsorption onto the soot surface.**

- **With single pulse energy deposition, the exit-NO_x is primarily NO because of the reconversion of NO_2 to NO on soot surface.**