Environmental Aspects of Plasma Science

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Plasma Applications in Material Science, Greifswald 2010

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FROM THE IDEA TO THE PROTOTYPE

Content (1)

1. Introduction
   - Plasma technology as an environmental technology
   - Hot and thermal plasmas for environmental issues
   - Surface treatment and novel light sources
2. Exhaust treatment by non-thermal plasmas - Basics
   - Gas discharges for exhaust treatment
   - Discharge physics and plasma chemistry
   - Example for plasma chemistry: Ozone synthesis
   - Hybrid processes
3. Flue gas treatment (NOx and SOx removal)
   - Electron beam flue gas treatment (EBFGT)
   - Non-thermal plasmas flue gas treatment (NTPFGT)
   - Plasma enhanced/driven catalysis

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Content (2)

4. VOC and PM removal by means of non-thermal plasmas
   - Plasma VOC removal chemistry
   - Examples: Pulp mills and deodorization in gastronomy/food production
   - Removal of soot
   - Electrostatic precipitators

5. Water treatment by means of plasmas
   - Advanced Oxidation
   - Electro-hydraulic discharges
   - Antimicrobial treatment by indirect treatment of liquids

6. Summary and Outlook

1. Introduction

- Plasma technology as an environmental technology

Some selected aspects:

- Hot and thermal plasmas
- Surface treatment and novel light sources

1. Introduction
Plasma Technology = Environmental technology

Waste incineration
- Thermal plasma for burning of solid waste and hazardous gases

Energy and ressource saving technologies
- Substitution of wet chemical processes (surface processing)
- Use of solvent free products due to surface treatment

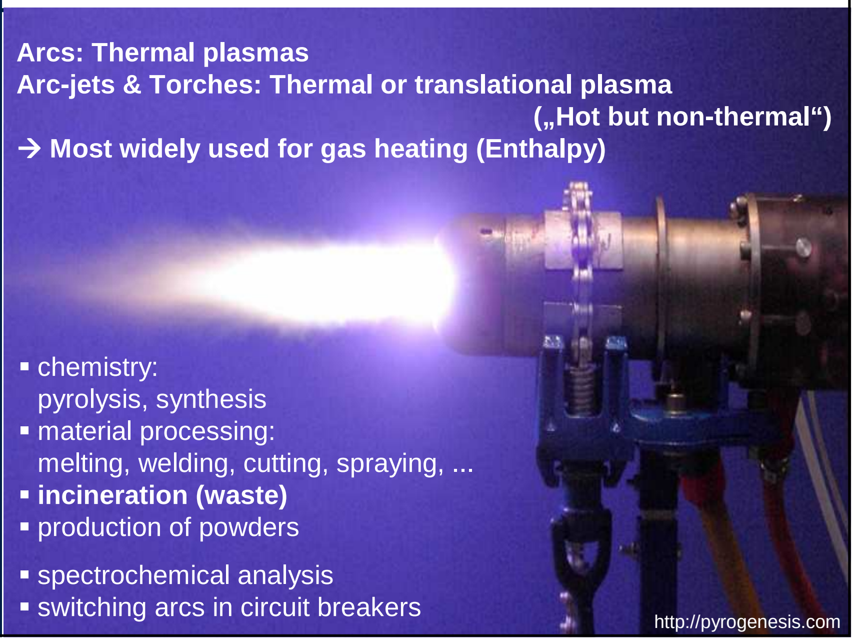
Depollution technologies
- Decomposition of pollutants
- Filtering of PM

Plasma based generation of active compounds
- Ozone for water treatment or chloride-free bleaching

Efficient lightsources
- Energy saving due to efficient light generation
- Plasma based UV-lightsources for surface processing and curing etc.

1. Introduction
„Hot plasmas“ application

Arcs: Thermal plasmas
Arc-jets & Torches: Thermal or translational plasma
(„Hot but non-thermal“)
→ Most widely used for gas heating (Enthalpy)



- chemistry:
  pyrolysis, synthesis
- material processing:
  melting, welding, cutting, spraying, ...
- **incineration (waste)**
- production of powders

- spectrochemical analysis
- switching arcs in circuit breakers

http://pyrogenesis.com

Plasma Technology = Environmental technology

Waste incineration

- Thermal plasma for burning of solid waste and hazardous gases

Energy and ressource saving technologies

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Depollution technologies

- Decomposition of pollutants
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Plasma based generation of active compounds

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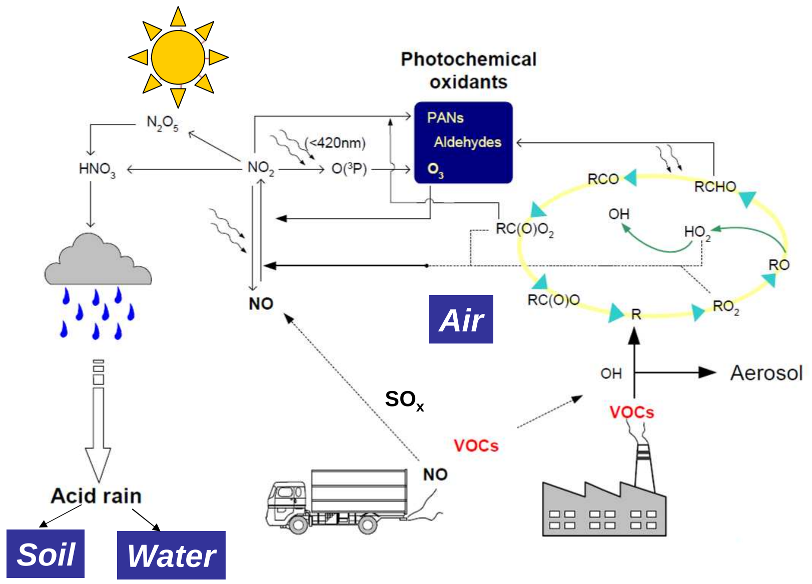
Efficient lightsources

- Energy saving due to efficient light generation
- Plasma based UV-lightsources for surface processing and curing etc.

2. Exhaust treatment by non-thermal plasmas

Introducing remarks to the problem

2. Exhaust treatment
Emission sites and effects



Kim, AIST JPN

2. Exhaust treatment
Emission sites and effects

Groups of pollution		Most important artificial emission sources (uncompleted)
Particulate Matter (PM)	Soot	Transportation; Energy supply by combustion
	Ash	Energy supply by combustion
Volatile organic compounds (VOCs)	Methane	Agriculture; Burning of biomass; Fuel emissions
	Non-methane VOCs (NMVOCs), e.g. aldehydes, ketones, aromatic and light hydrocarbons alcoholes, acetates, bencines, glykoles	Solvent use; Chemical processes; Transportation and fuel emissions; Offices and households (carpets, furnishings etc.)
Acid gases	NO_x	Transportation; Energy supply by combustion
	SO_x	
	HCl	
Ozone depletion substances	Halons	Industry; Cooling solvents
	Freons	
Toxic gases	Hg	Transportation; Energy supply by combustion
	Dioxins	
Greenhouse gases	CO_2	Transportation; Energy supply by combustion
	N_xO_y	
	Perfluorocarbons	
	Methane and other VOCs	See above
Radioactive Gases	Isotopes of C, Rn, I, Kr, …	Nuclear power supplies; Nuclear weapons; Medical devices

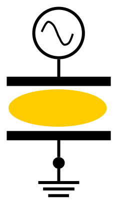
Kim, AIST Korea

2. Exhaust treatment by non-thermal plasmas

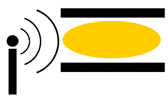
Generation of plasmas for exhaust treatment

Plasma generation

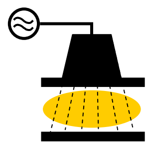
Electrical gas discharge
→ high voltage power supply
→ DC, AC, pulsed; frequency: Hz ... MHz
→ electrical breakdown according to Paschen law
(breakdown voltage dependent on pressure x distance)



Electromagnetic radiation
→ microwave excited plasmas (915 MHz, 2.54 GHz)
→ ignition structure needed
→ usually hot plasmas (plasma torches for incineration)



Electron beam
→ electron accelerating tubes
(beam gun, keV ... MeV)
→ extensive installations and therefore only suited for large gas flows

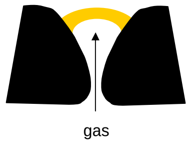


2. Exhaust treatment by non-thermal plasmas

Discharge generated plasmas @ 1 atm

Gliding "arc"

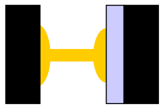
→ Expansion and cooling of plasma in increasing electrode gap by gas flow



Barrier discharge

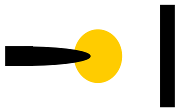
→ Isolator in discharge gap limits discharge duration, energy dissipation and thus spark formation

→ many sub-types (surface discharge, coplanar, packed bed



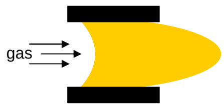
Corona

→ Inhomogeneous electric field enables discharge ignition at lower voltage and limits discharge duration and energy dissipation



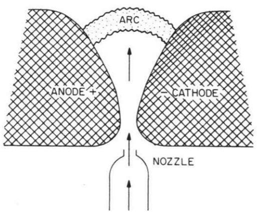
Plasmajet (APPJ)

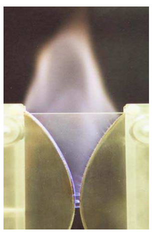
→ Plasma expanded outside electrode configuration by gas flow

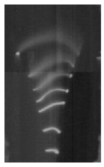


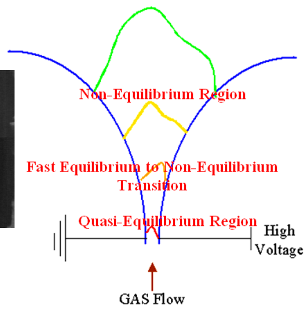
2. Generation of gas discharges

Gliding Arcs („Jacobs ladder“)

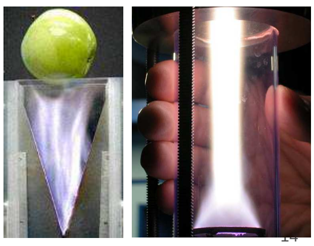








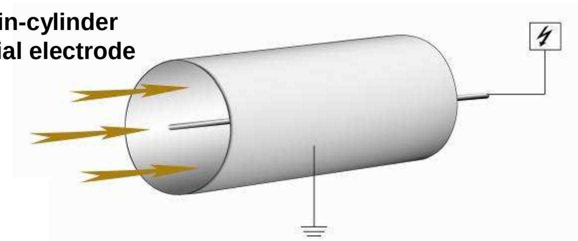
- arc (or spark) discharge in non-perpendicular discharge gap
- expansion cooling → non-thermal
- investigations on surface processing and volume chemistry (e.g. CH_4 conversion)



A. Gutsol et al.; Drexel University

2. Generation of gas discharges
Corona discharge

Wire-in-cylinder
Coaxial electrode



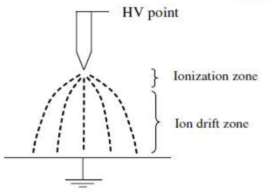
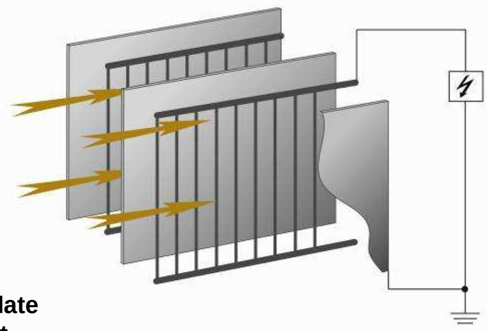
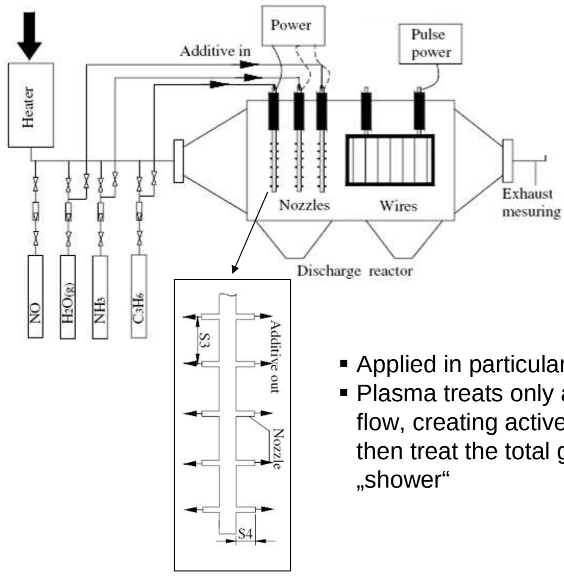


Figure 2. Schematic of a point-to-plate corona.



Multi-wire-plate arrangement

2. Generation of gas discharges
(Corona) radical shower

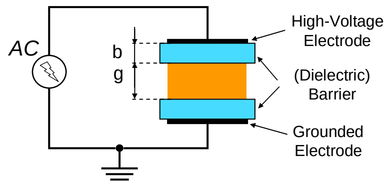


- Applied in particular to NOx-removal
- Plasma treats only a portion of gas flow, creating active species, which then treat the total gas flow as a „shower“

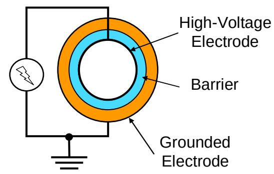
Chang et al, MacMaster Univ. CAN

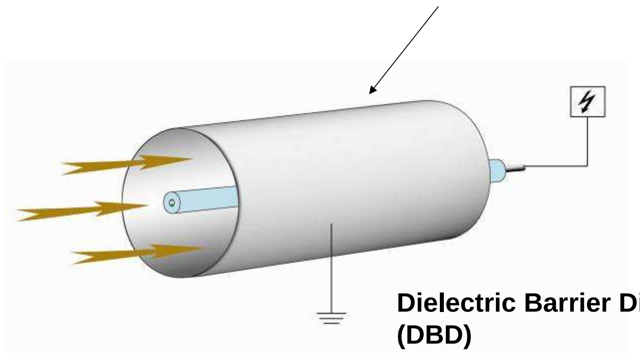
(Volume) Barrier discharge

Planar Geometry



Cylindrical Geometry

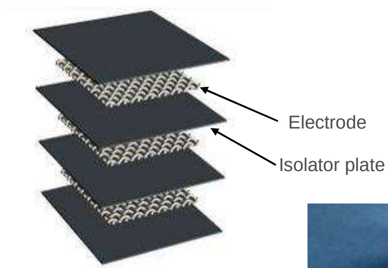


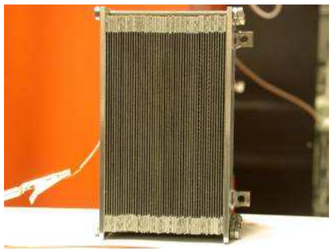


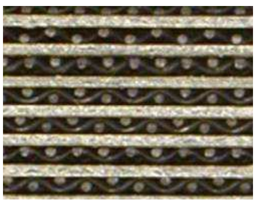
Dielectric Barrier Discharge (DBD)

Stack reactor DBD

Stack system with structured electrodes

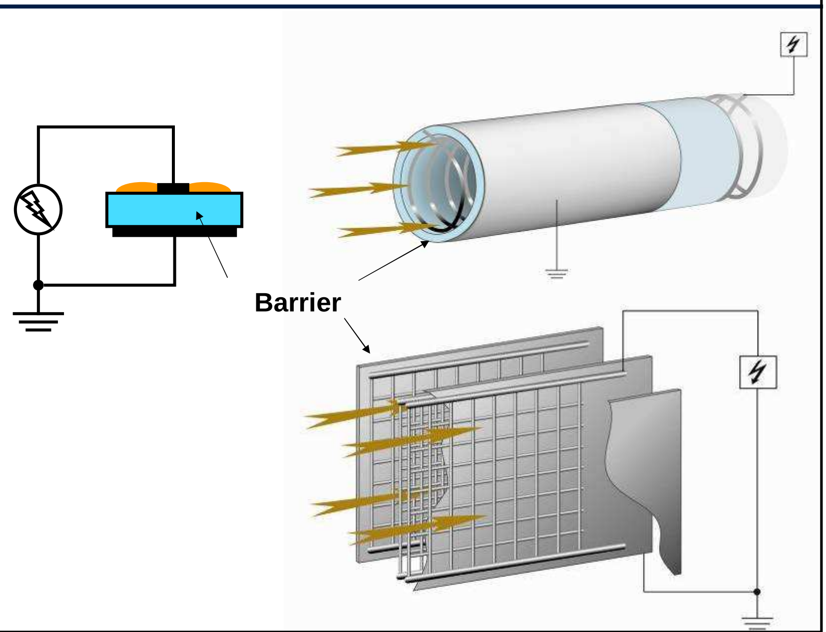




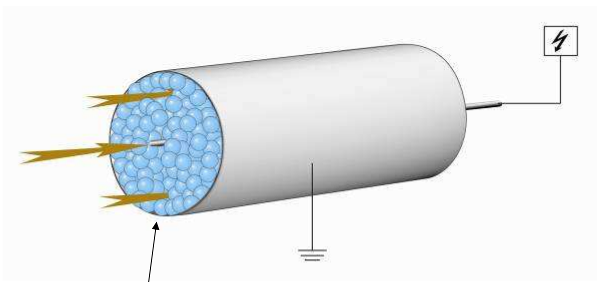


S. Müller, R.-J. Zahn; Contributions to Plasma Physics 47 (2007) 520-529

Surface (barrier) discharge



Packed bed reactors



Filling:
- Pellets
- Foams

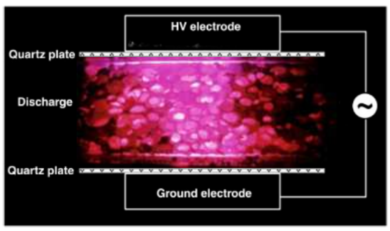
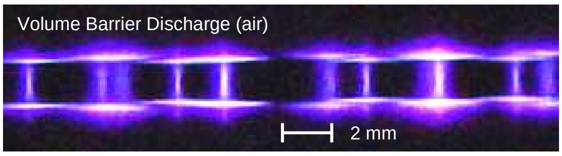


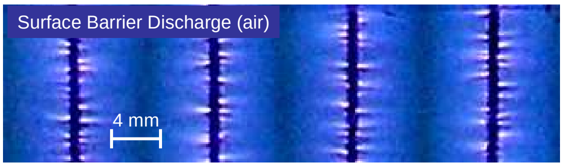
Fig. 2 DBD in the pores of a ceramic foam/schematic electrodes setup.

M. Kraus et al, ABB

Filamentary Plasmas

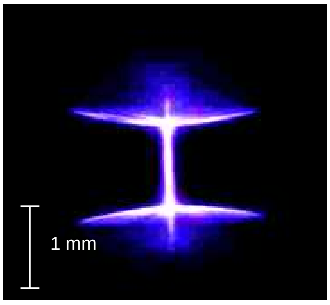
- Electrical breakdown in several individual ionization channels: filaments
- Filaments= repetitive, but transient Microdischarges (MDs)





- „Intrinsic“ miniaturisaton due to high pressure is common in most gases
  → non-thermal plasmas: barrier discharges, coronas, plasma jets etc.
  → high technological relevance

Filaments and microdischarges (MDs)



Single Filament=
10^2 ... 10^3 **Microdischarges**

- non-stationary, transient, non-homogeneous plasmas
- small dimension (0.1 ... 1 mm)
- short duration (10 ns ... 1 µs)
- statistical occurrence

→ MDs = tiny chemical reactors
→ Multitude of MD determine overall chemistry of plasma

2. Exhaust treatment by non-thermal plasmas

Hybrid processes for exhaust treatment

Hybrid NTP / Wet Processes

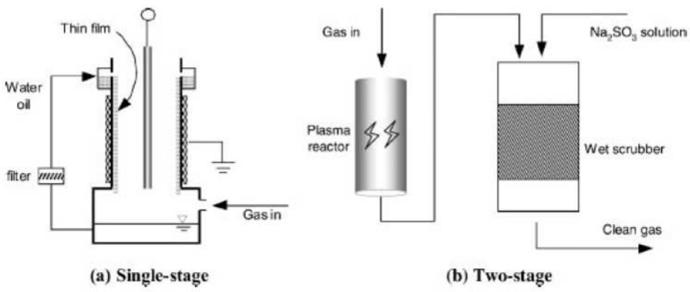
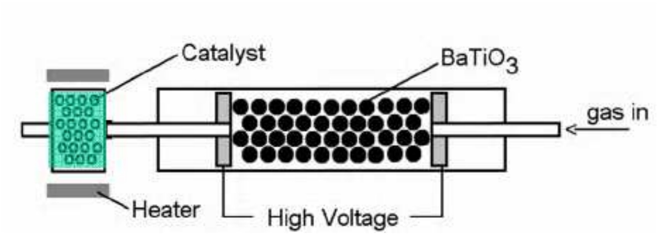


Figure 4. Hybrid NTP reactors combined with a wet process: (a) single stage, (b) two stage.

- Removal of reaction intermediates or final products from gas phase by adsorption and/or chemical reaction
- Gas-phase NTP enhance liquid-phase chemical reactions
- Electrical discharge over a liquid surface → modify mass-transfer characteristics

Kim, AIST JPN

2. Plasma enhanced and hybrid processes
Plasma enhanced (assisted) catalyst (PEC)



Plasma: **O_3 formation**
Partial oxidation

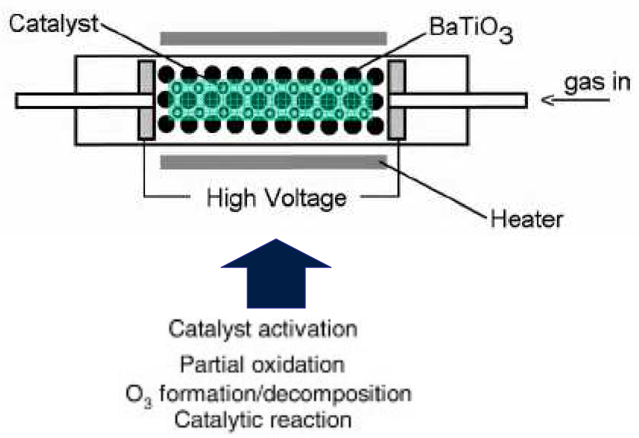
Catalyst: Catalytic reaction

Activation

Gas conditioning

Whitehead et al, Manchester Uni.

2. Plasma enhanced and hybrid processes
Plasma driven catalyst (PDC)



Whitehead et al, Manchester Uni.

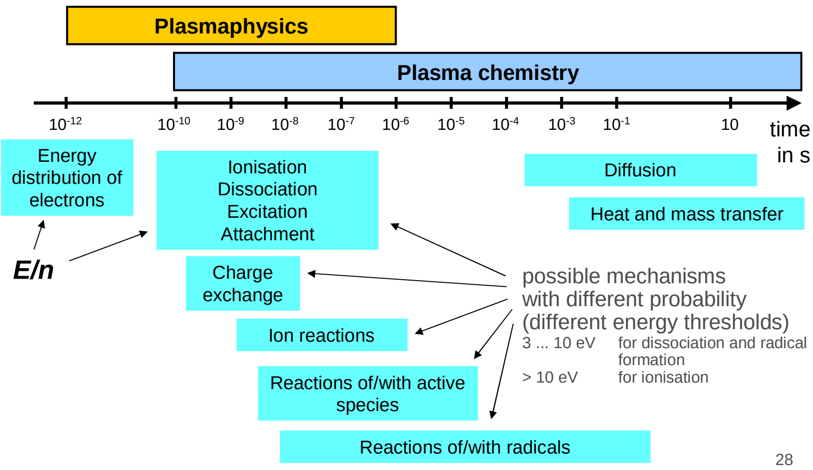
2. Exhaust treatment by non-thermal plasmas

Plasma chemistry - Example: Ozone generation

Processes and time scales

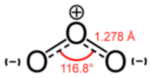
Plasma chemistry based on non-thermal activation of particles via collisions

→ quality and quantity determined by kinetic parameters (v_{mean}, ν_{coll})



Ozone synthesis

1. Dissociation of O_2



1.a Direct

$e + O_2 \rightarrow O^- + O$

$\rightarrow O + O + e$

$\rightarrow O + O^* + e$

1b. Indirect (Penning-Diss.)

$e + N_2 \rightarrow N_2^* + e$

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

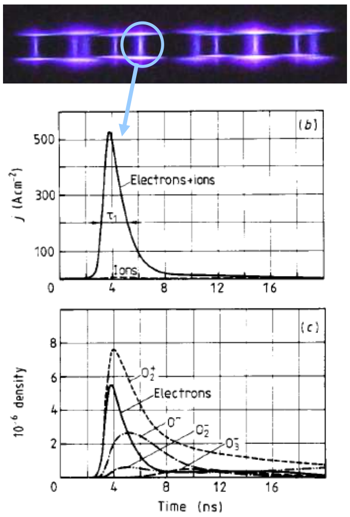
2. Formation of O_3

$O + O_2 + M \rightarrow O_3 + M$ (M= N_2, O_2)

Christian Schönbein

Werner Siemens

Ozone synthesis



Discharge

Chemistry

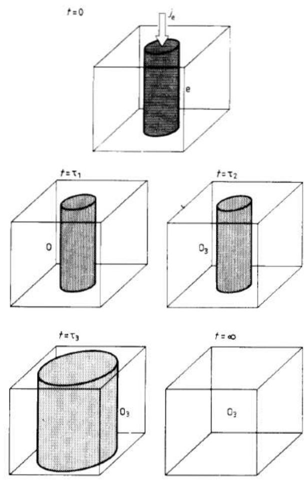
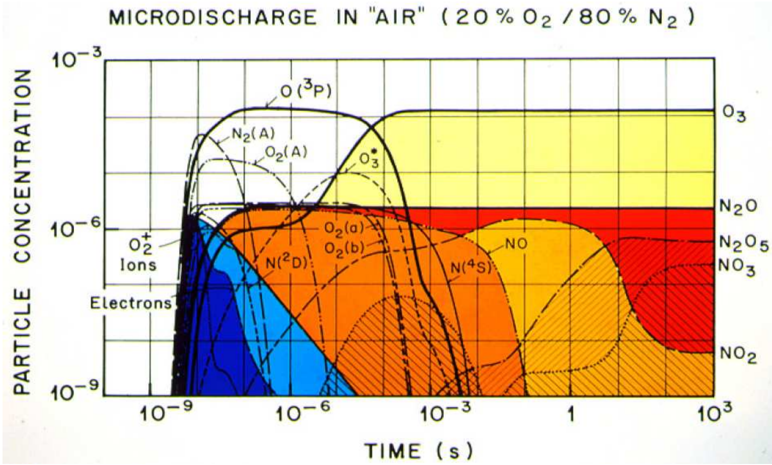


Figure 3. A schematic diagram of the spatial distribution of electrons, oxygen atoms and O_3 molecules at different times.

Hirth et. al; J. Phys. D. (1986)

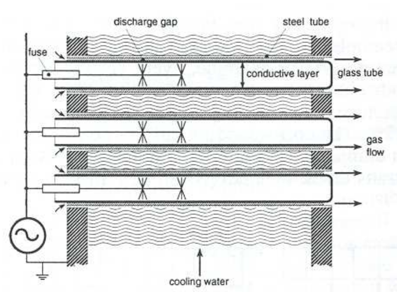
2. Plasma chemistry
Air chemistry in NTP

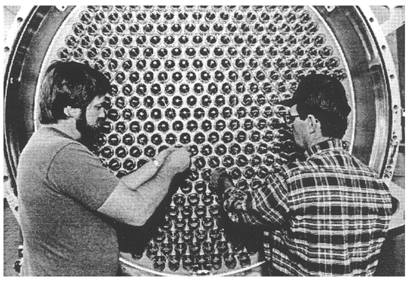


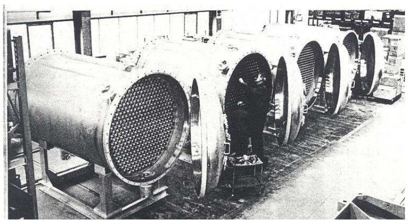
Homogeneous model (143 reactions, 30 reacting species)

U. Kogelschatz, B. Eliasson

2. Plasma chemistry
Modern ozonisers







O_3 (g/kWh)	oxygen	air
U_{sinus}	150– 80	80 - 95
U_{impuls} (kV/ns)	240-290	130-140
Theory:	430-450	200-220

Hirth et. al; J. Phys. D. (1986)

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2. Exhaust treatment by non-thermal plasmas

Plasma chemistry for removal of gaseous contaminants

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NO_x-conversion

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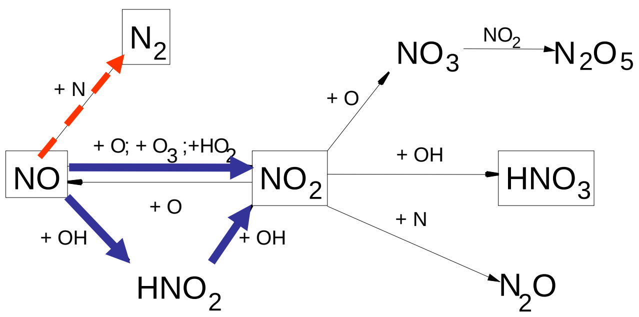

- **Oxidative pathways dominate (espacially in case of humid conditions)**
- **Reduction at (to) high energy input**

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2. Plasma chemistry
SO_x-conversion

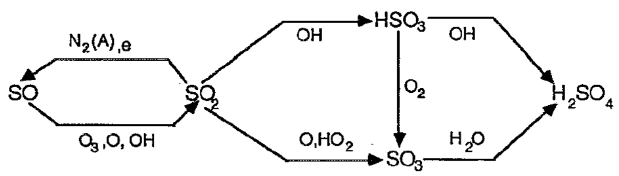


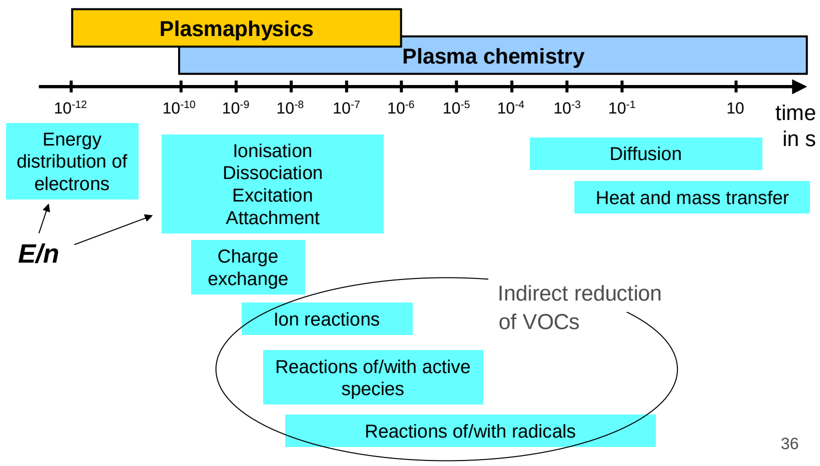
FIG. 2. Schematic of the dominant direct and chemical reaction pathways to remove SO_2 from gas streams. Direct removal results primarily in producing other SO_x species. Chemical removal is optimized by generation of OH radicals.

- **Oxidative pathways dominate (espacially in case of humid conditions)**
- **Reduction at (to) high energy input**

M.B. Chang et al., 1991

2. Plasma chemistry
VOC removal in NTP

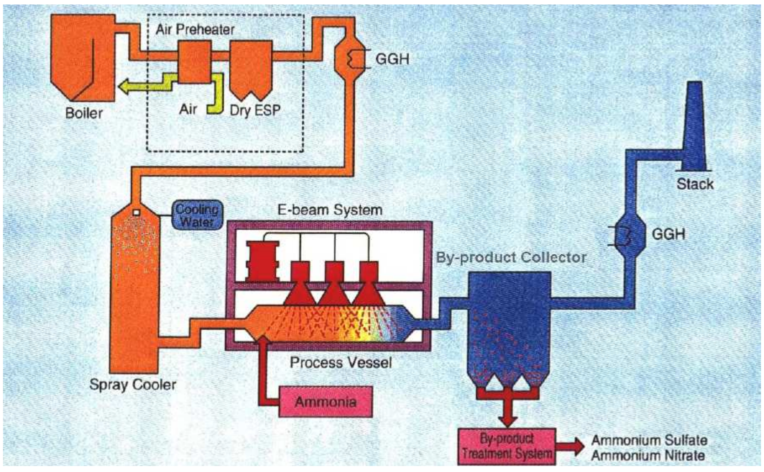
- no direct dissociation of VOC molecules
  (low density of contaminants, short duration of electron current)
- reduction via reactions with radicals and other active species



3. Flue gas treatment

Electron beam flue gas treatment (EBFGT)

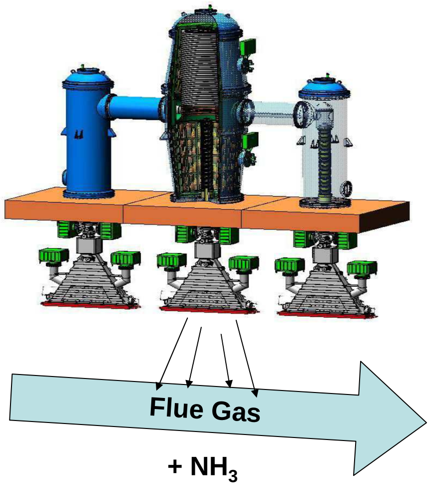
NO_x and SO_x removal from large gas streams (> 50.000 Nm^3/h)



A. Chmielewski et al., ICHTJ Warzsawa

3. Electron beam flue gas treatment (EBFGT)

Electron gun



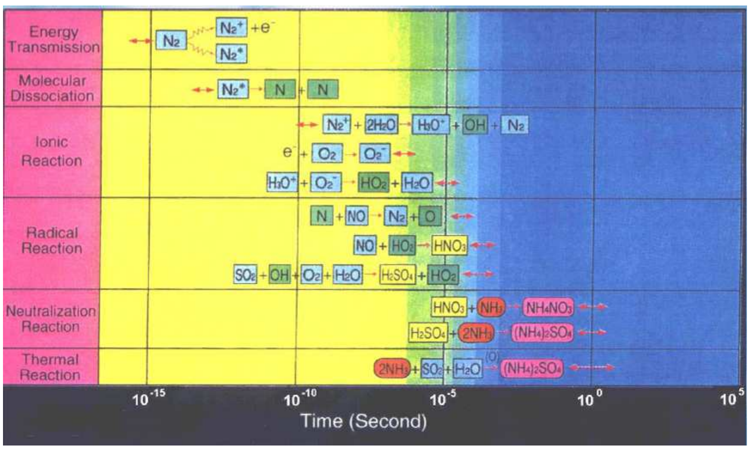
+ NH_3
(reducing agent)

Electron gun
→ 300 keV ... 1 MeV

A. Chmielewski et al., ICHTJ Warzsawa

3. Electron beam flue gas treatment (EBFGT)

EBFGT-chemistry



A. Chmielewski et al., ICHTJ Warzsawa

3. Electron beam flue gas treatment (EBFGT)

EBFGT removal efficiency

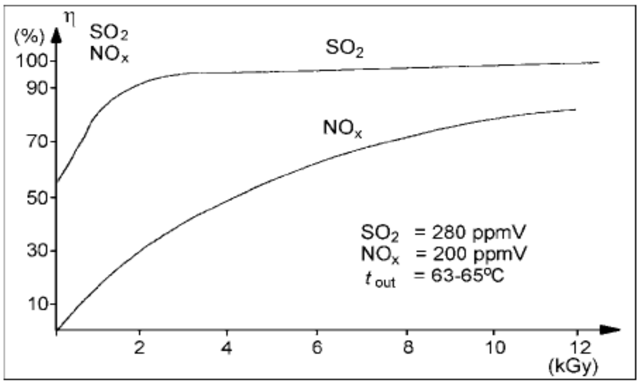


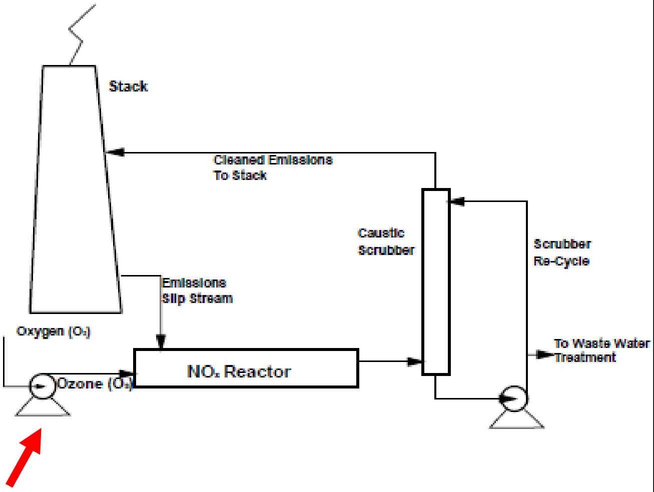
Fig. 1. SO_2 and NO_x removal efficiency *vs*. dose. The results obtained in the pilot plant experiments.

A. Chmielewski et al., ICHTJ Warzsawa

3. Flue gas treatment

Non-thermal plasma based or assisted flue gas treatment (NTP-FGT)

3. NTP-FGT
LOTOX (Low Thermal Oxidation)



Belco

3. NTP-FGT
LOTOX-chemistry

Ozone injection and NO-conversion to N_2O_5

$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_2 + NO_3 \rightarrow N_2O_5$

„Post-Plasma“
O_3

N_2O_5 conversion to nitric acid

$N_2O_5 + H_2O \rightarrow 2\ HNO_3$

Nitric acid conversion to nitrate

$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

Nitrate and SO_2 removal with scrubber purge

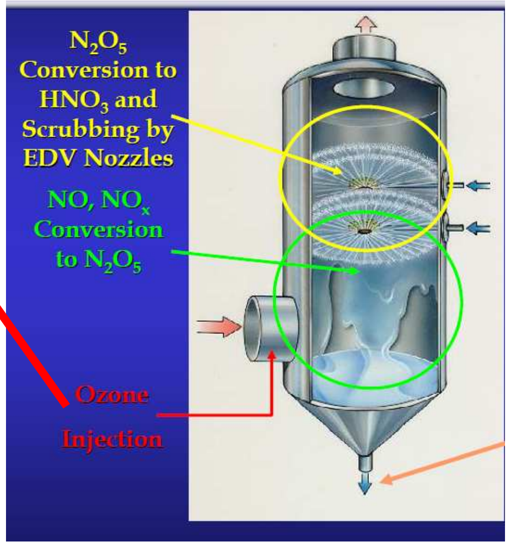
$SO_2\ (g) \leftrightarrow SO_2\ (l)$
$SO_2(l) + H_2O(l) \leftrightarrow H_2SO_3\ (l)$
$H_2SO_3(l) + 2NaOH \rightarrow Na_2SO_3(l) + 2H_2O$
$2Na_2SO_3(l) + O_2 \rightarrow 2Na_2SO_4$
$HCl + NaOH \rightarrow NaCl + H_2O$

Wet Scrubbing
H_2O
NaOH
HCl

Belco/Dupont

3. NTP-FGT

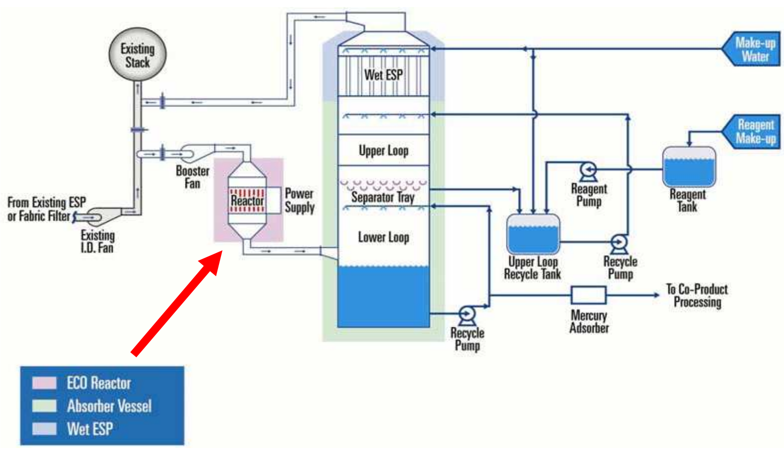
LOTOX - wet scrubbing combination



Belco

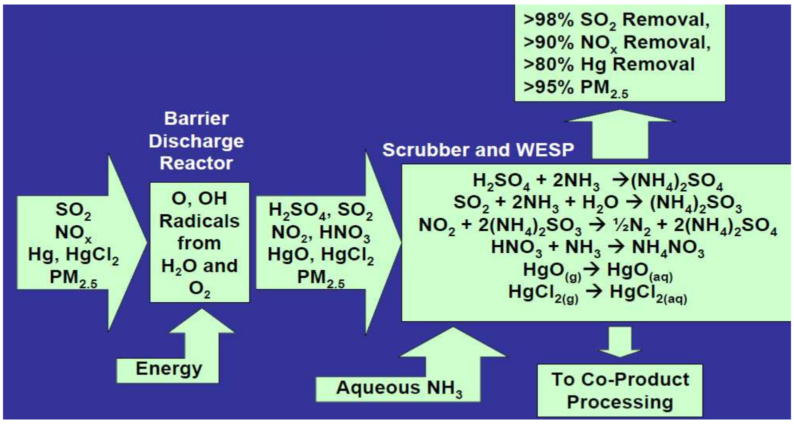
3. NTP-FGT

ECO-process



Powerspan

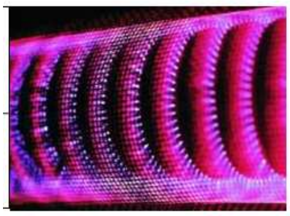
ECO chemistry

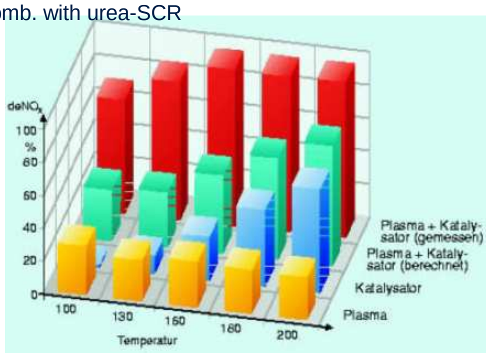


Powerspan

Plasma-enhanced SCR (selective catalytic reduction)

Volume Barrier Discharge comb. with urea-SCR





- up to 85% NO*x* reduction under cold start and urban driving conditions
- less than 300 W of plasma power applied
- model studies: fuel penalty introduced estimated to be below 2%.

T. Hammer; Plasma Sources Sci. Technol. 2002

INP Greifswald

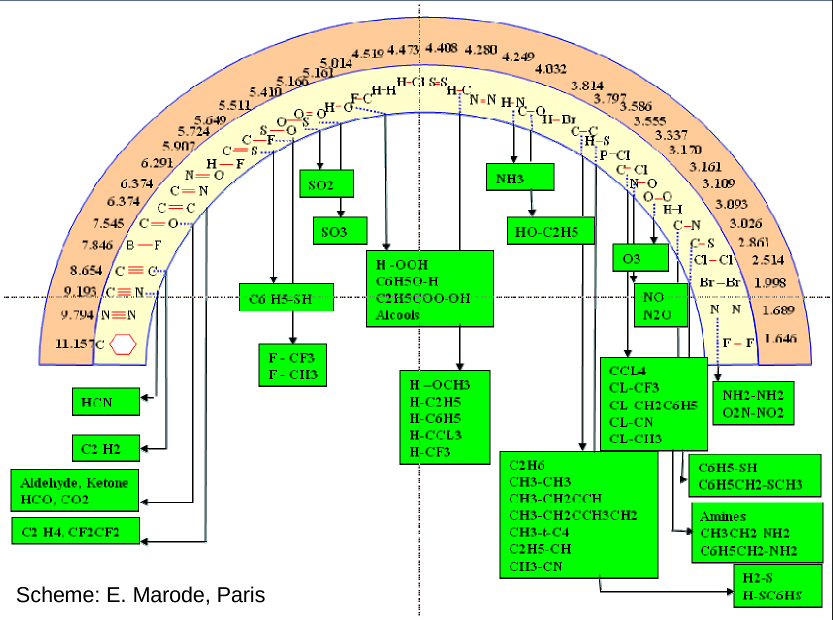
4. Removal of volatile organic compounds (VOC) and particulate matter (PM)

VOC-removal chemistry and examples

INP Greifswald

Molecular Bond Energies (in eV)

INP Greifswald

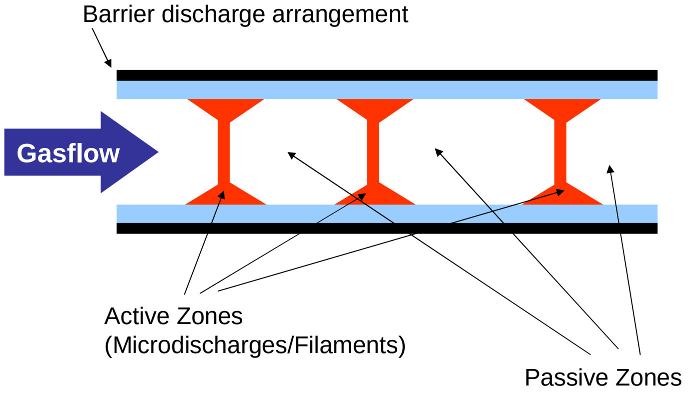


Scheme: E. Marode, Paris

INP Greifswald

4. VOC-reduction plasma chemistry

VOC-conversion

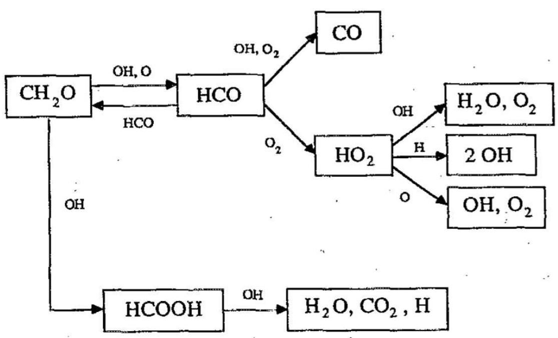


1. **Electron initiated plasma generation stage**
2. **Radical particle formation and removal stage**
3. **Aerosol particle formation stage**

4. VOC-reduction plasma chemistry

Example: Formaldehyde (CH_2O)

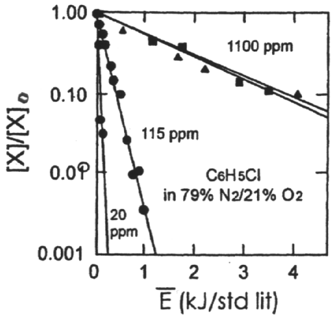
- destruction of CH_20 results dominantly from chemical attack by OH and O radicals
- primary end products: CO, H_2O
- destruction rates typically 2-8 ppm/(1 J/l)



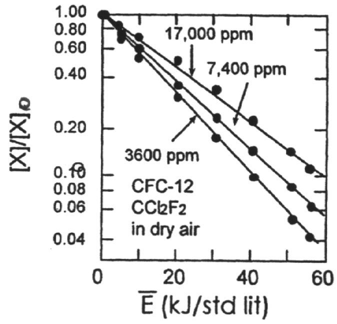
Storch and Kushner, J. Appl. Phys. 1993

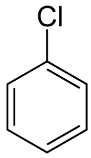
4. VOC-reduction plasma chemistry
Examples: CVOCs

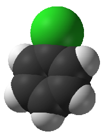
Chlorobenzene

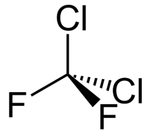


CFC-12



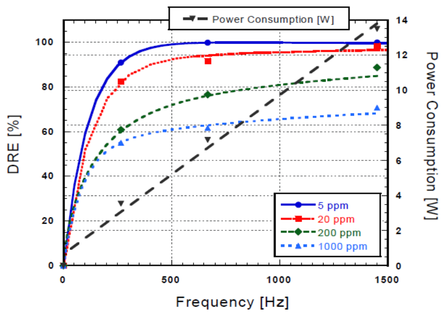


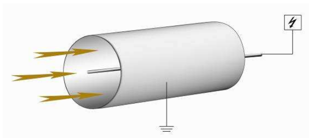


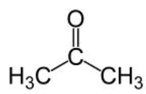


Veldhuizen, TU Eindhoven

4. VOC-reduction plasma chemistry
Acetone removal by pulsed negative corona







- Wire-in-cylinder coaxial electrode configuration
  1 – 20 W; 9 -12 kV; 0.2 … 2 kHz
  100 ns duration; 10 ns rise time
- 2 slm → 13 s residence time
- T= 200 ℃
- By.product: methanol (only for $[CH_3COCH_3]_0$= 200 … 1000 ppm)

Gutsol and Fridman, Drexel University

Evaluation

- Specific Energy Density (Spec. Input Energy SIE)

$$SED\ (J/L) = P_{dis} / Q$$

P_{dis} … dissipated plasma power; Q … gas flow

- CO_2-Selectivity S_{CO2}

$$S_{CO_2}(\%) = \frac{[CO_2]}{[CO_2]+[CO]} \times 100$$

- Carbon balance CB

$$CB\,(\%) = \frac{[CO]+[CO_2]+[HCOOH]}{n([VOC]_0-[VOC])} \times 100$$

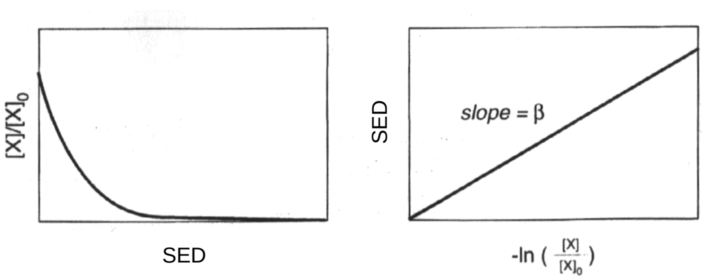
- Decomposition efficiency η (Destruction and removal efficiency, DER)

$$\eta\ (\%) = \frac{[VOC]_0-[VOC]}{[VOC]_0} \times 100$$

$[VOC]_0$ … inlet concentration;
n … number of C-atoms

Kim, Plasmas and Polymers 2004

Evaluation



$[VOC] = [VOC]_0 \exp(-SED/\beta)$ $\quad$ $SED = -\beta \ln([VOC]/[VOC]_0)$

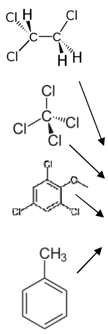
$1/\beta = k_E$ ... energy constant

$k_E = f($ Temp, gas comp., $[VOC]_0$, ...$)$

Veldhuizen, TU Eindhoven

Energy constants

$$[VOC] = [VOC]_0 \exp(-SED/\beta)$$

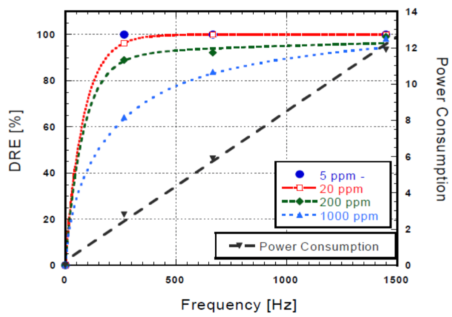


Exponential-folding values β for example gas mixtures (straight-line removal plot approximations).

Gas mixture	β value (J/std l)
TCE in dry Ar–O_2	12
TCE in humid Ar–O_2	95 (at 3 exp. folds)
CCl_4 in dry Ar–O_2	520
CCl_4 in humid Ar–O_2	1824
TCA in dry N_2	208 (at ≤4 exp. folds)
Toluene in dry N_2	300

Veldhuizen, TU Eindhoven

Energy cost



$$DRE = A \cdot \left(1 - e^{-\left(SEI/\alpha\right)}\right)$$

limit value of removal efficiency increasing supplied power

Energy cost

Gutsol and Fridman, Drexel University

4. VOC-reduction plasma chemistry
Energetic efficiency

$$\text{Energy Cost} = \frac{\text{J/L}}{\Delta[\text{C}]} \times 250\ (\text{eV/molecule})$$

$$G\text{-value} = \frac{\Delta[\text{C}]}{\text{J/L}} \times 0.4\ (\text{molecules/100 eV})$$

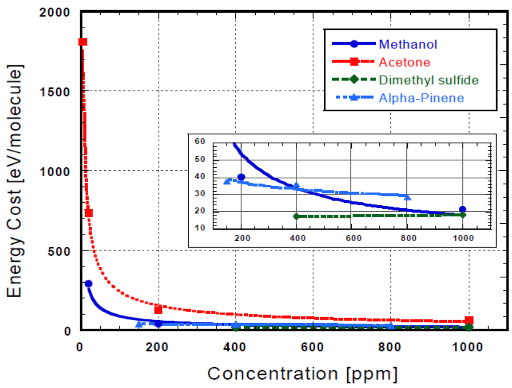
$$\text{Energy Yield} = \frac{\Delta[\text{C}]m}{\text{J/L}} \times 0.15\ (\text{g/kWh})$$

where m is molecular weight of the gas compound. The factors of 250, 0.4 and 0.15 in the equations are the conversion factors at 20 °C and 1 atm.

Δ[C] … removed amount of molecules in ppm

Kim, Plasmas and Polymers 2004

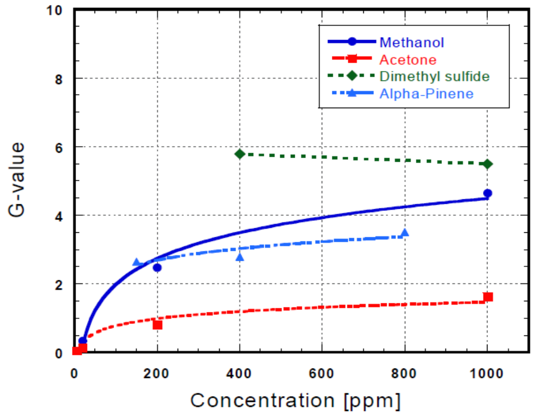
4. VOC-reduction plasma chemistry
Energy cost



- Energy Price significantly depends on initial concentration
- Few ppm: energy price reaches very high values (not all active species can target VOC molecules)
- Higher concentrations: fraction of energy for removing pollutant molecules higher and energy spent for elimination of each single molecule decreases

Gutsol and Fridman, Drexel University

4. VOC-reduction plasma chemistry
G-value



- G-value: number of VOC molecules attacked and destroyed by active species per 100 eV of energy input

Gutsol and Fridman, Drexel University

4. VOC-reduction plasma chemistry
G-values

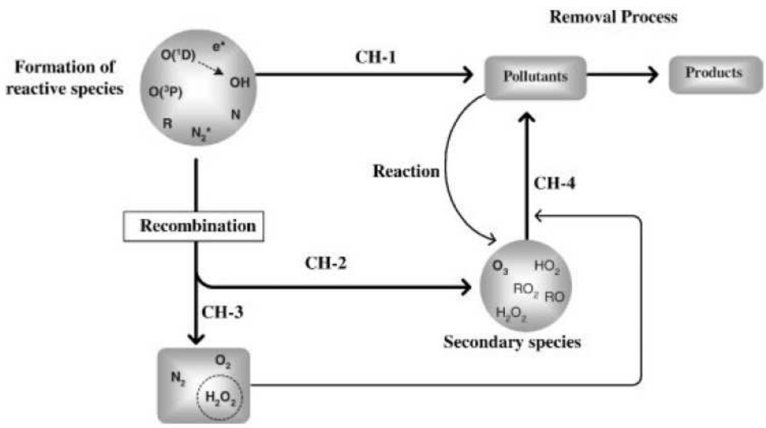
- G-value: number of VOC molecules attacked and destroyed by active species per 100 eV of energy input

Radicals	Reactor	Td	Gas	*G*-Value molecules/ 100 eV	EC eV/molecules
$O(^1D)$	DBD		Humid air (H_2O 2.2 wt.-%)	1.4	
	DBD	150	6% O_2, 5% H_2O, 9% CO_2	1.1	
$O(^3P)$	Pulsed	200	19% H_2O, 0.5% O_2, 9.5% CO_2, 71% N_2	3.3	
	Streamer	800[a)]	5% O_2, 16% H_2O, 8% CO_2	0.25	
$O(^3P)+O(^1D)$	DBD		air	3.4–3.8	
	DBD		6% O_2, 5% H_2O, 9% CO_2	1.0	
OH	DC (impulse)		5% O_2, 6% H_2O, 15% CO_2	0.2	
	DBD		Humid air (H_2O 2.2 wt.-%)	1.4	
	DBD	150	6% O_2, 5% H_2O, 9% CO_2	0.6	
	Pulsed	150	NO–N_2	0.21	238
N	Streamer	800	5% O_2, 16% H_2O, 8% CO_2	0.37	
	Pulsed		NO–N_2		70
	Pulsed	205	345 Torr		80–180[b)]
	Pulsed		Dry air (assuming electron mean energy of 4 eV)		1 440
electron	Streamer	800	5% O_2, 16% H_2O, 8% CO_2	0.7	

a) Reduced electric field at streamer head (E_h/n).
b) Measured value. Td $= 10^{-17}$ V $\cdot$ cm^2.

Kim; Plasmas and Polymers 2004

4. VOC-reduction plasma chemistry
Reactivity vs. Selectivity



Kim; Plasmas and Polymers 2004

4. VOC-reduction plasma chemistry
NTP vs. Electron beam

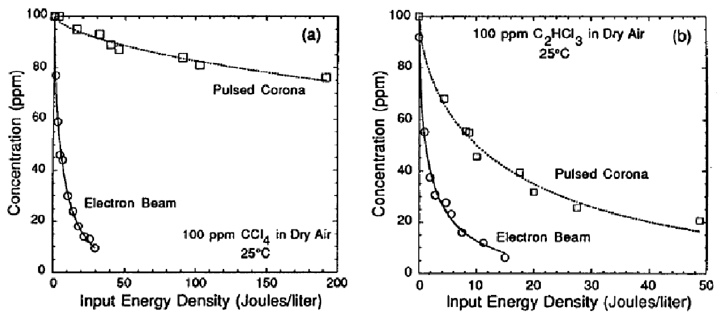


Fig. 1. Comparison between electron beam and pulsed corona processing of 100 ppm of (a) carbon tetrachloride and (b) trichloroethylene, in dry air at 25°C.

Kim; Plasmas and Polymers 2004

4. VOC-reduction plasma chemistry
NTP vs. RTO

NTP-VOC removal:

10 – 30 eV/VOC-molecule

Regenerative Thermal Oxidation:

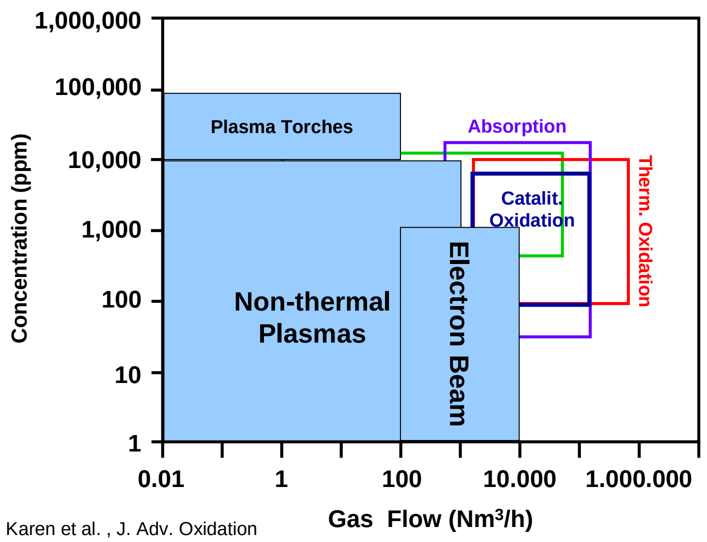
0.1 eV/molecule

per molecule of air

Lower energy consumption in NTP if VOC-concentration > 0.3 … 1% (3.000 – 10.000 ppm)

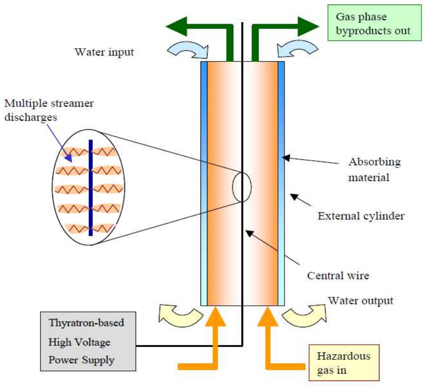
Fridman, Drexel University

4. VOC-reduction plasma chemistry
Ranges of application



nach Karen et al. , J. Adv. Oxidation Technol. 1997; Hammer, Contrib. Plas. Phys. 1999

4. VOC-reduction plasma chemistry
Heterogeneous pulsed corona discharge

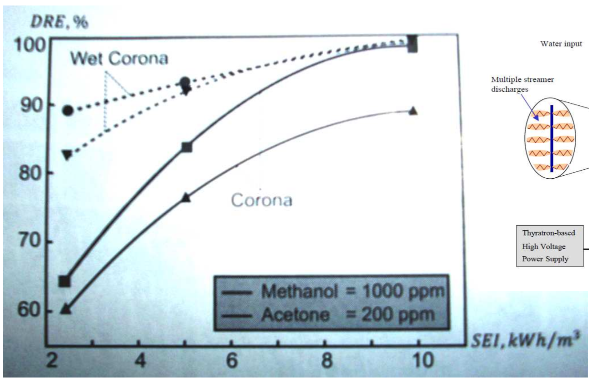


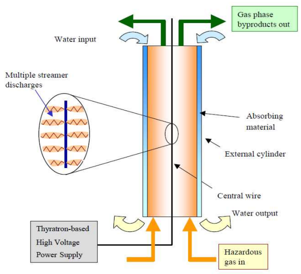
1. **Scrubbing/Adsorption of soluble VOCs in liquid phase**
2. **Plasma-induced conversion of non-soluble VOCs in soluble VOCs (RO_2, RO_2H)**
3. **Scrubbing of plasma-induced soluble compounds**

- power requirements for NTP-conversion reduced (smaller amount of pollutants needs to be removed by plasma induced oxidation)
- Plasma stimulated oxidation continues after adsorption and increases capacity of water droplets
- VOCs not completely removed → converted to liquid phase (waste water)

Gutsol et al, Drexel Uni.

4. VOC-reduction plasma chemistry
Effect of wet corona





Gutsol et al, Drexel Uni.

4. VOC-reduction plasma chemistry
Example: Pulp and Paper Mills Emissions

- converts wood chips or other plant fibre source into a thick fibre board which can be shipped to a paper mill
- vent stream from brownstock washers (High volume – Low concentration HVLC):

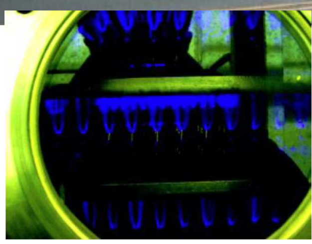
Methanol	83 ppm
Acetone	3 ppm
α-Pinene	209 ppm
Dimethyl Sulfide	2 ppm
Humidity	100%RH
Temperature	110°F

- Major traditional techniques for VOC removal: biological filters, two stage adsorbers, regenerative thermal incineration or RTO
  → relatively high energy consumption
  → high treatment costs
- alternative: heterogeneous non-equilibrium gas discharge
  → negative pulsed corona discharge and liquid phase

Gutsol et al, Drexel Uni.

4. VOC-reduction plasma chemistry
Mobile laboratory for paper/pulp mills

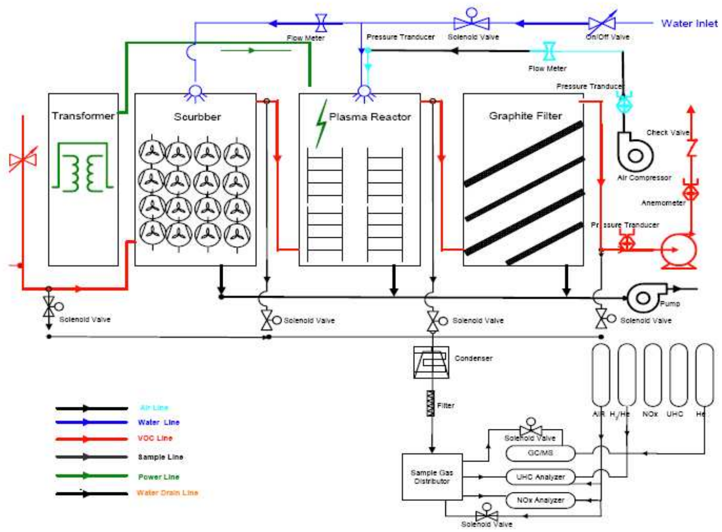
10 kW
750 m³/h



A. Fridman, A. Gutsol (Drexel) 2005

4. VOC-reduction plasma chemistry

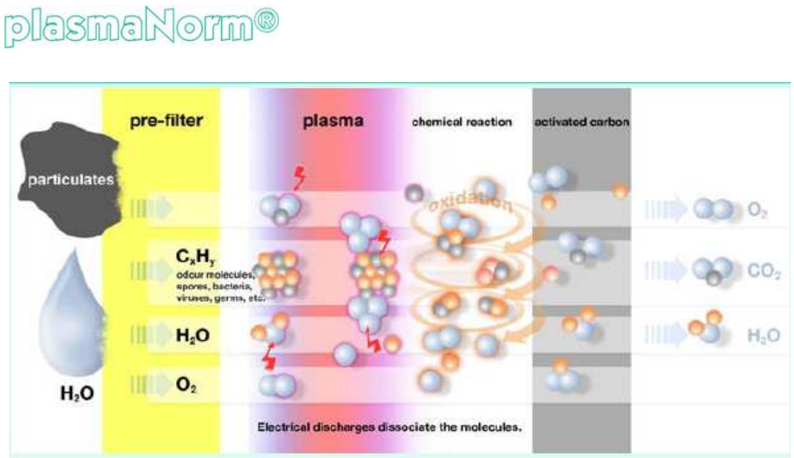
Mobile laboratory for paper/pulp mills



A. Fridman, A. Gutsol (Drexel) 2005

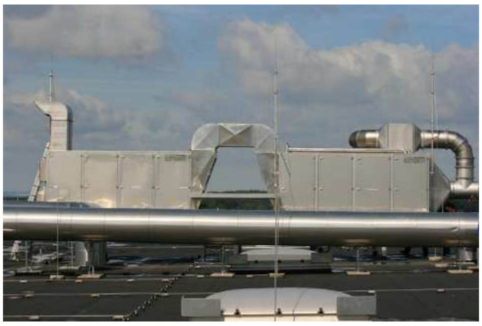
4. VOC-reduction plasma chemistry

Deodorization



M. Langner; Airtec competence GmbH

4. VOC-reduction plasma chemistry
PlasmaNorm-Technology



Deodorization of exhaust from ovens for convenience products made of meat (1.5 MW ovens; exhaust stream of 8000 Nm^3/h)

Cooker hoods for large-scale kitchens, gastronomy and private hausholds

M. Langner; Airtec competence GmbH

4. VOC-reduction plasma chemistry
PlasmaNorm-Technology

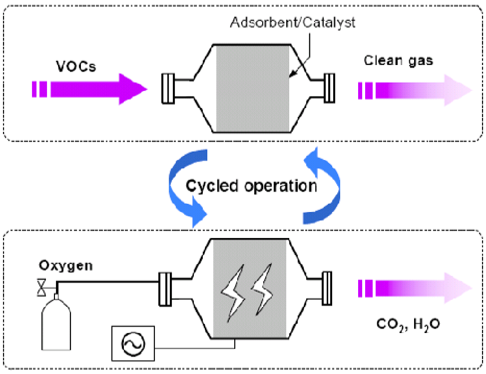
Gastronomy & Kittchen | Private | Industry & Trade

aereus | aereus arco | plasmaNorm

M. Langner; Airtec competence GmbH

4. VOC-reduction plasma chemistry
Cycled process

- Adsorption (Plasma OFF)



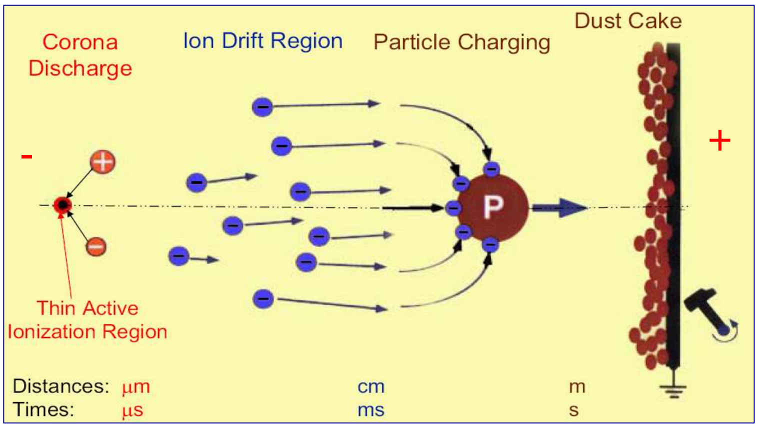
- VOC decomposition by O_2 Plasma

Kim, AIST JP

4. **Removal of volatile organic compounds (VOC) and particulate matter (PM)**

PM-removal by non-thermal plasmas and electrostatic precipitators (EPSs)

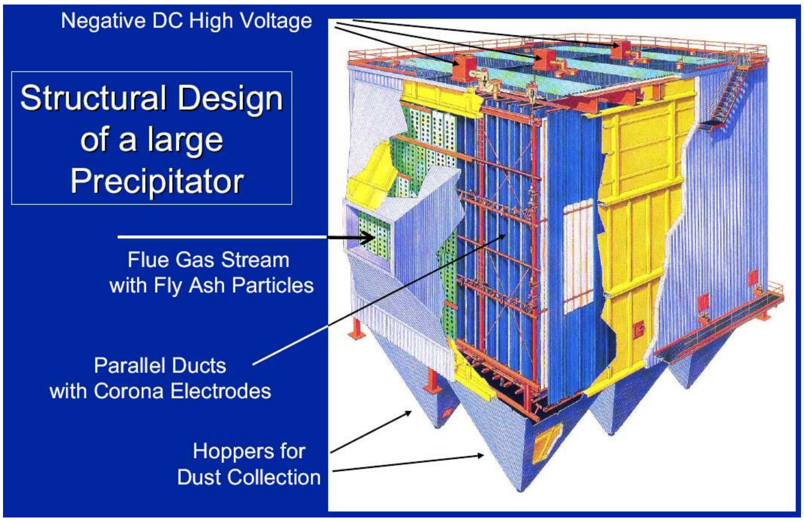
4. PM-reduction
Electrostatic Precipitators (ESPs)



- Voltage: 30–80 kV
- Down to PM of 1 µm diameter
- Up to 100.000 Nm^3/h and 450 ℃

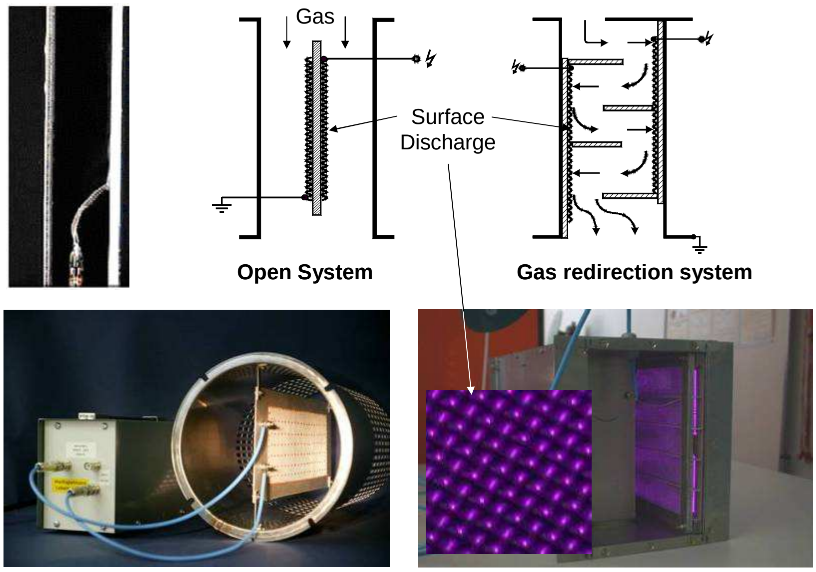
U. Kogelschatz, ABB

4. PM-reduction
Electrostatic Precipitators (ESPs)



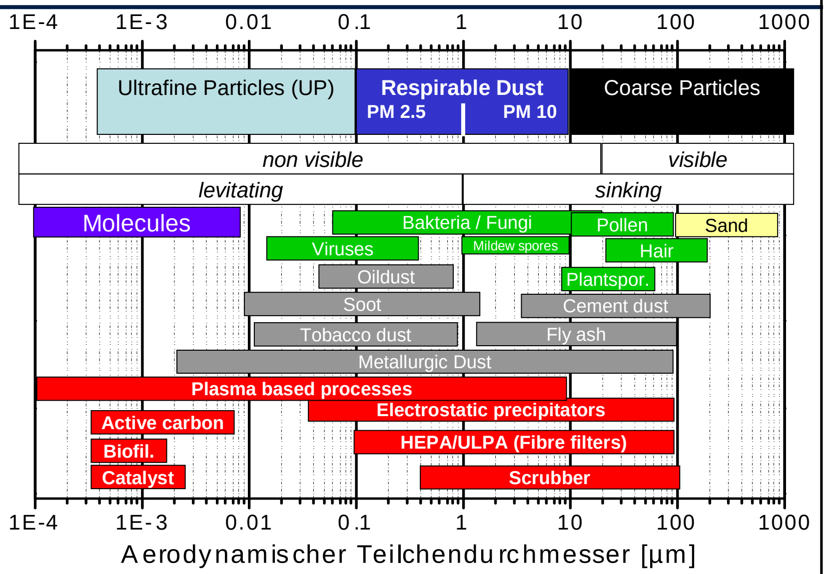
U. Kogelschatz, ABB

4. PM-reduction
Surface DBD with ion-extraction



S. Müller, R.-J. Zahn, J. Grundmann; Plasmas and Polymers 4 (2007) S1004

4. PM-reduction
Overview



nach S. Müller et al.

PM: Particulate Matter; UP: Ultrafine Particles

Environmental Aspects of Plasma Science

5. Water treatment

- ***Overwiew on water treatment and plasma techniques for liquids***
- ***Advanced Oxidations Processes ("Plasma and Water")***
- ***Indirect Treatment of Liquids ("Plasma on/at Water")***
- ***Electro hydraulic discharges ("Plasma in Water")***

5. Water treatment
Overview

Water cleaning

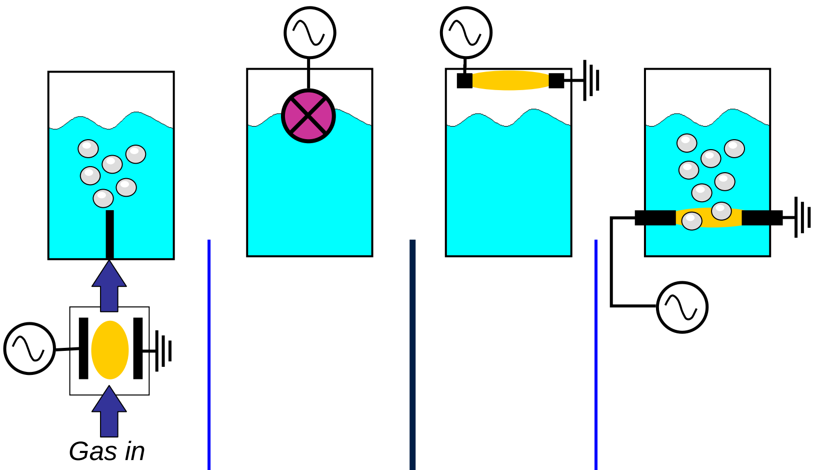
Physical methods
- Sedimentation
- Filtering
- Flotation

Biological methods
- Biochemical Ox.
- Anaerobic cleaning

Chemical methods
- Oxidation
- Disinfection

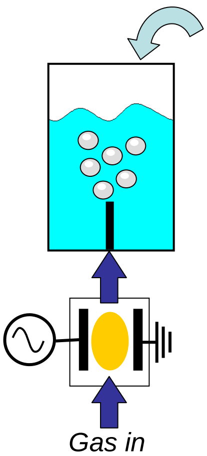
Plasma

5. Water treatment
Overview on plasma methods



Remote treatment | **UV-treatment** | **Indirect plasma treatment** | **Direct plasma treatment**

5. Water treatment
Post discharge / remote treatment



Additional reactants (e.g. H_2O_2)

→Ozonization

$O_3 + H_2O \rightarrow 2\ OH + O_2$

→Advanced Oxidation Processes (AOP)

Peroxon

O_3 and H_2O_2:

$H_2O_2 \rightarrow H^+ + HO_2^-$

$HO_2^- + O_3 \rightarrow HO_2 + O_3^- \rightarrow O_2^- + HO^\bullet$

→Catalytic Ozonisation (+ TiO_2/Fe)

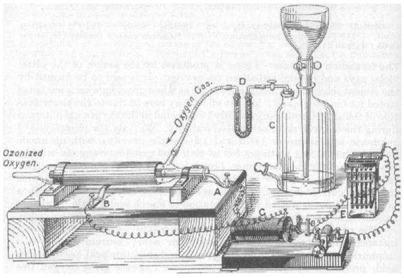
Fenton-mech.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet$

5. Water treatment
Ozonisation

O_3: important oxidant
- water cleaning and advanced oxidation
- paper bleaching
- required: “on-site” production, high pressure but low temperature

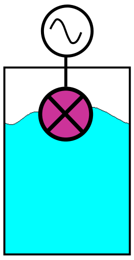
Werner von Siemens, 1875



Largest facility (Brazil): 500 kgO_3/h

U. Kogelschatz et. al; Journal de Physique **7** (1997) C4-47

5. Water treatment
(V)UV-treatment



→ **Photocatalytic Oxidation**
→ **Photochemical Oxidation**
→ **Photo-Fenton Oxidation**

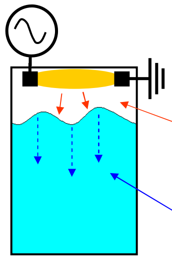
UV-Oxidation
$H_2O_2 + h\nu$ (210-240 nm) $\rightarrow 2\ HO^\bullet$
$O_3 + h\nu$ (200-300 nm) $\rightarrow O_2 + O(^1D)^\bullet$
$O(^1D)^\bullet + H_2O \rightarrow 2\ HO^\bullet$

VUV-Oxidation
$H_2O + h\nu$ (<190 nm)
$H^\bullet + {}^\bullet OH + H^+ + e^-$

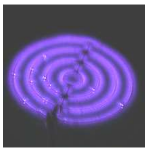
Fenton- Reaction
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet$

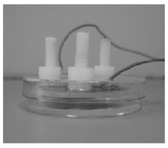
UV: Regeneration of Fe^{2+}
$Fe^{3+} + H_2O + UV \rightarrow Fe^{2+} + H^+ + HO^\bullet$

5. Water treatment
Indirect plasma treatment



- Use of “classical gas discharge” for water treatment, no special efforts (power supply, independent on water conditions, …)
- Indirect interaction of atmospheric pressure plasma with liquids mainly based on reactions at gas/plasma-liquid interface
- Bulk effects based on diffusion processes
- Biological (bactericidal) effects of plasma treatment mainly based on changes of liquid: resulting in generation of more or less stable reactive species



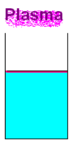


5. Water treatment
Bulk effects by indirect treatment

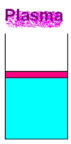
Generation of H⁺ → pH change
(methyl orange as pH indicator)

Generation of nitrite
(Spectroquant® – nitrite test)

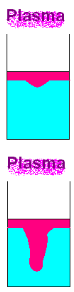
Phases of spreading:



surface reaction
directed gas phase-liquid interaction



spreading phase
formation of a diffusion front



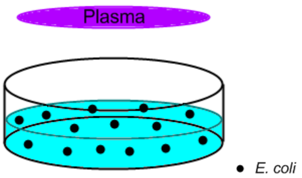
Diffusion influenced by gradients
e. g. temperature, magnetic fields

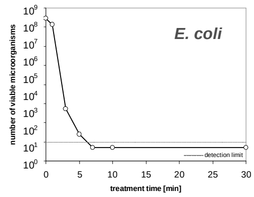
⇩

„Drop and structure formation“

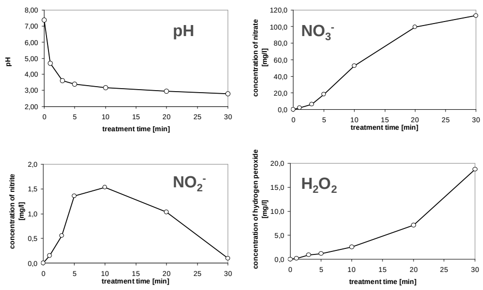
5. Water treatment
Indirect treatment of non-buffered liquid

Inactivation of suspended vegetative microorganisms





Acidification and generation of nitrate, nitrite and hydrogen peroxide



K. Oehmigen et al., Plasma Process. Polym. 7 (2010) 250-257

5. Water treatment
Electrohydraulic discharges

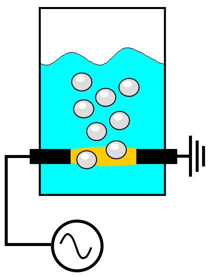


Table 1. Characteristics of Different Electrohydraulic Discharges[a]

parameter	Value: pulsed corona	pulsed arc
operating frequency	10^2–10^3 Hz	10^{-2}–10^{-3} Hz
current (peak)	10–10^2 A	10^3–10^4 A
voltage (peak)	10^4–10^6 V	10^3–10^4 V
voltage rise	10^{-7}–10^{-9} s	10^{-5}–10^{-6} s
pressure wave generation	weak to moderate	strong
UV generation	weak to moderate	strong

[a] Data taken from Chang et al.[1]

→ Driven by short HV-pulses (high currents)
→ Majority of discharge types (corona … arc, hybrid)
→ Generation of shockwaves additional to radicals, ions and radiation

Breakdown in water

Water:

- highly polar, high electrical permittivity (ε_r= 80) and non zero electrical conductivity σ
- Much denser then gases
- Water being exposed to an electric field E for a time t:
  → behaves as a dielectric for t << ε/σ,
  → behaves as ion semiconductor for t >> ε/σ
  (@ σ = 100µS/cm: $\tau = \varepsilon/\sigma$ = 72 ns)
- In most of real experiments water solution behaves as an ion semiconductor with a low mobility of ions
  (H^+ with highest mobility μ=315 $cm^2/V.s$ (its velocity $v= \mu.E$))
- Electric field E of the order of 1MV/cm needed for discharge initiation (to compare: DC breakdown E in air: 30 kV/cm)

Breakdown in water

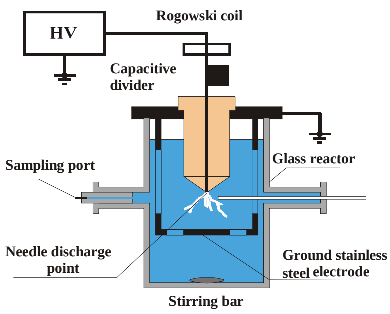
Two different theories:

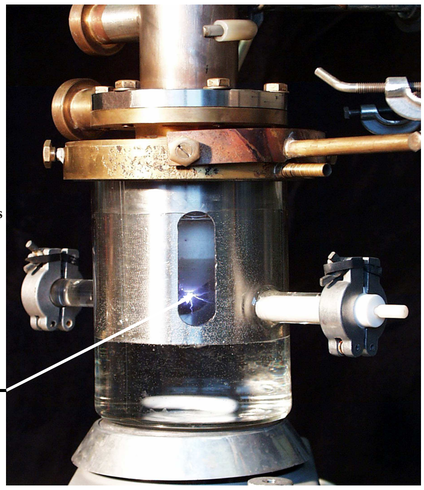
1) Electron multiplication theory
2) Bubble mechanism breakdown theory
   (= Phase change mechanism breakdown)

→ Even up to now there is no single comprehensive theory!

→ General acceptance of importance of pre-existing bubbles (dissolved gases) and field enhancement effects in near electrode region

5. Water treatment
Point-to-plane reactor



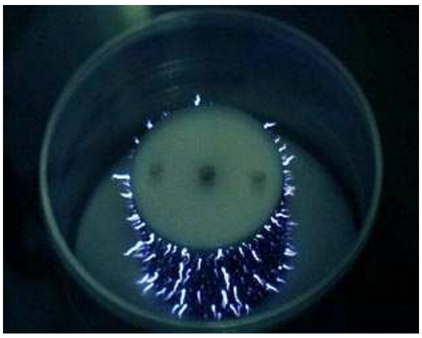


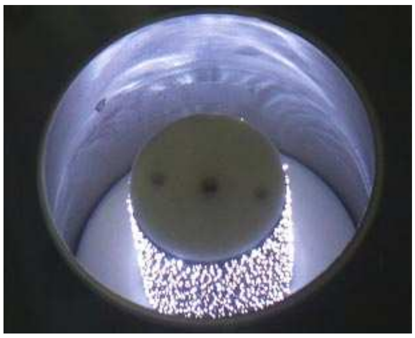
Corona-like discharge

A-K gap
28 mm

P. Sunka et al, IPP Prague

5. Water treatment
Reactor with composite anode





Solution conductivity:

σ = 0,6 mS/cm **σ = 15 mS/cm**

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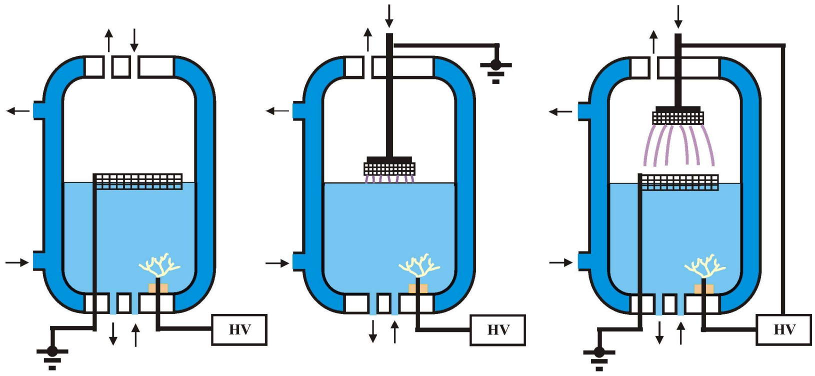
5. Water treatment
Hybrid reactors (Tallahassee)



Reference reactor   Hybrid-series reactor   Hybrid-parallel reactor

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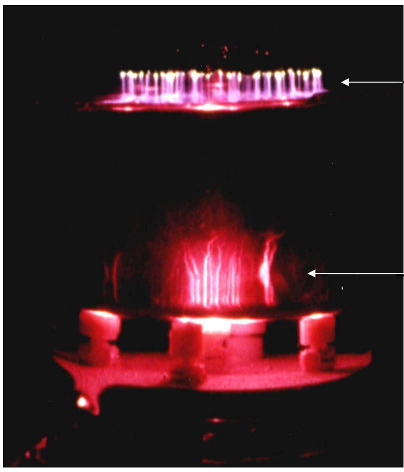
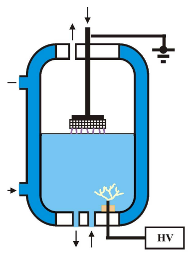
5. Water treatment
Hybrid reactors (Tallahassee)



Gas Phase Discharge
- intense bright arc-like discharge

Liquid Phase Discharge



Hybrid-series reactor

P. Sunka et al, IPP Prague

5. Water treatment
Electro hydraulic discharges

Pulse electrical discharges produced in water combines action of:

- high electric fields
- chemically active species (H, O, OH, H_2O_2)
- UV light (at higher conductivity)
- acoustic or shock waves (at high conductivity)

Potential applications depend on basic understanding

- combination of effects for given application
- optimization of discharge

P. Sunka et al, IPP Prague

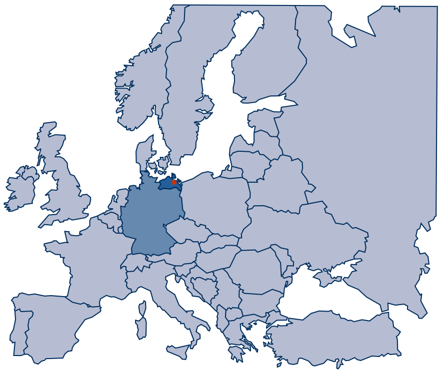
6. Summary and Outlook

- Plasma technolgy is (already) an environmental technology at all!

- NOx, SOx, VOCs and other gaseous contaminants can be decomposed in non-thermal plasmas (NTPs) via „radical based“ plasma chemistry.
- Exhaust treatment by means of NTP is especially suited for low concentrations in small and medium gas flows.
- Applicability/feasibility is determined by the specific situation (type and amount of contaminants, properties of gas flow) and has to consider effectivity and selectivity.

- There is a large potential for hybrid/catalytic/heterogenous methods.
- Generation of plasma at or in water is possible and leads to antimicrobial and chemical effects.

Contact



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