Nanoparticle Formation, Measurement and Capture in Coal Combustion Systems

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19th ETH Conference Combustion Generated Nanoparticles
Zurich, Switzerland
June 29, 2015

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School of Engineering & Applied Science

Acknowledgements

Results of work by
Graduate Students in AAQRL, Washington University in St. Louis

NSF, NIH, DOE
Consortium for Clean Coal Utilization
MAGEEP (McDonnell Academy Global Energy & Env. Partnership)

Consortium for Clean Coal Utilization

NNIN – A NSF NANOTECHNOLOGY NETWORK

NRF NANO RESEARCH FACILITY

MAGEEP

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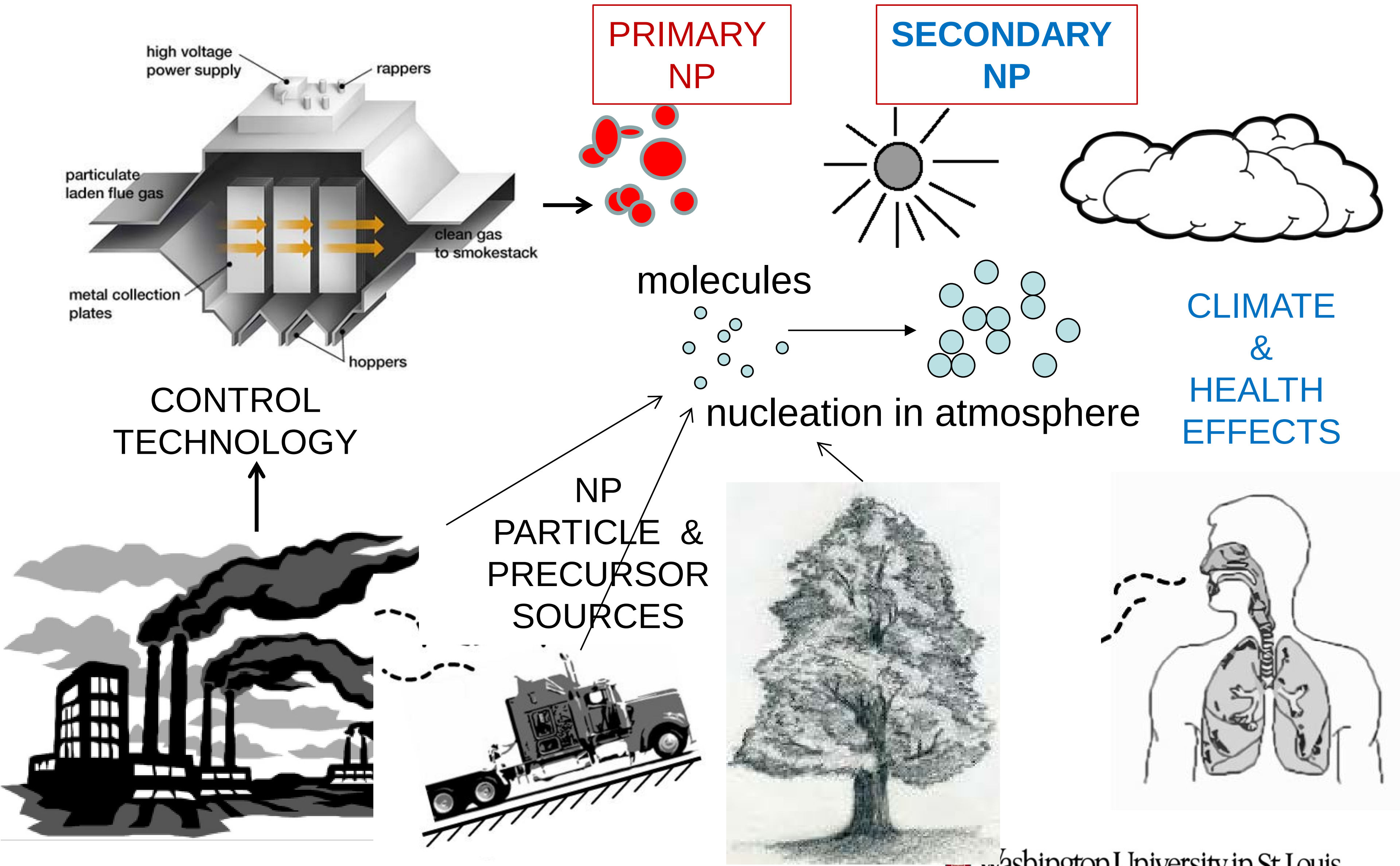
Life Cycle of Inadvertently Produced Nanoparticles



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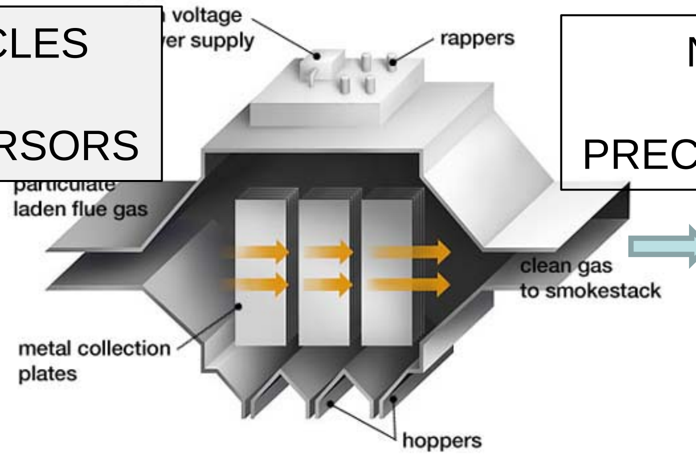
Outline of Presentation

ULTRA FINE PARTICLES
&
MOLECULAR PRECURSORS

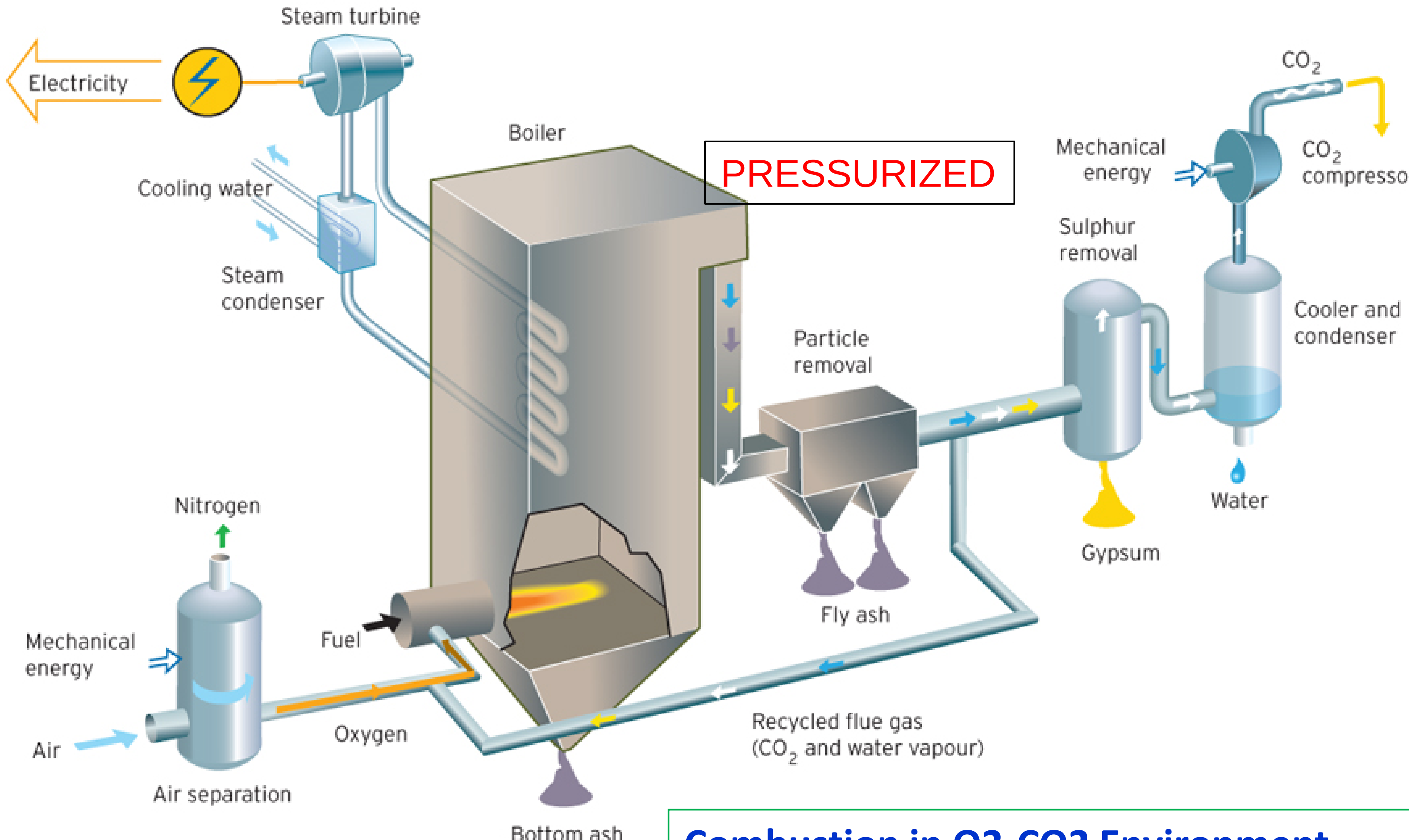


NPs
&
PRECURSORS

COAL COMBUSTION
- Formation of NP & Role of Precursors
- Size Distributions of NP
- Inorganic and Organic Species
- Charging of Coal Combustion NP

CONTROL TECHNOLOGY (ESPs)
- Penetration through ESPs
- Improvement of Collection Eff by Photoionizer
- Role of Pressure on Charging and Capture

Oxy-Coal Combustion System



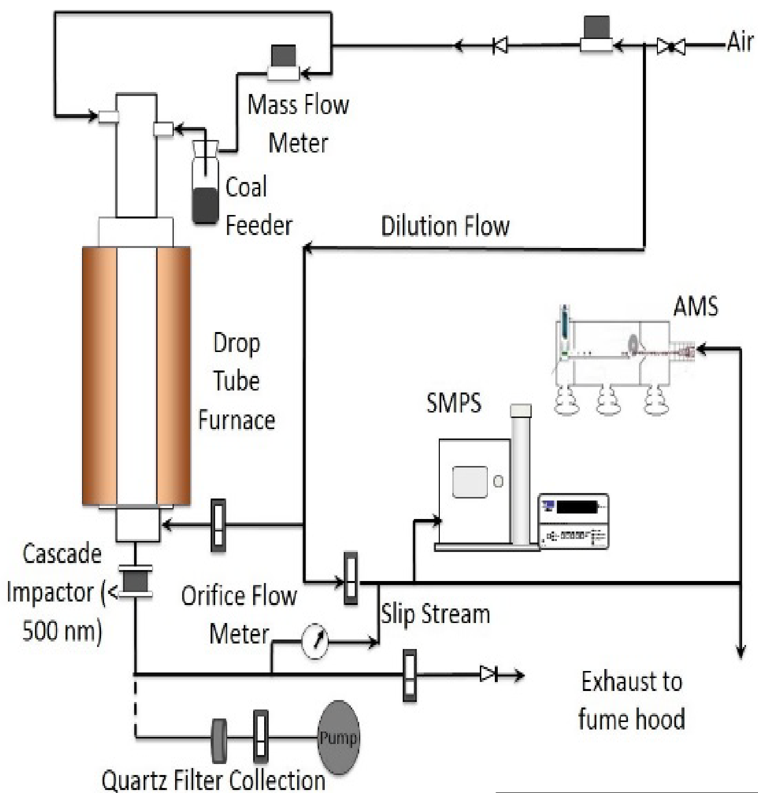
Adapted from Jordal, Anheden, Yan, Stromber,(Sweden)

Combustion in O2-CO2 Environment

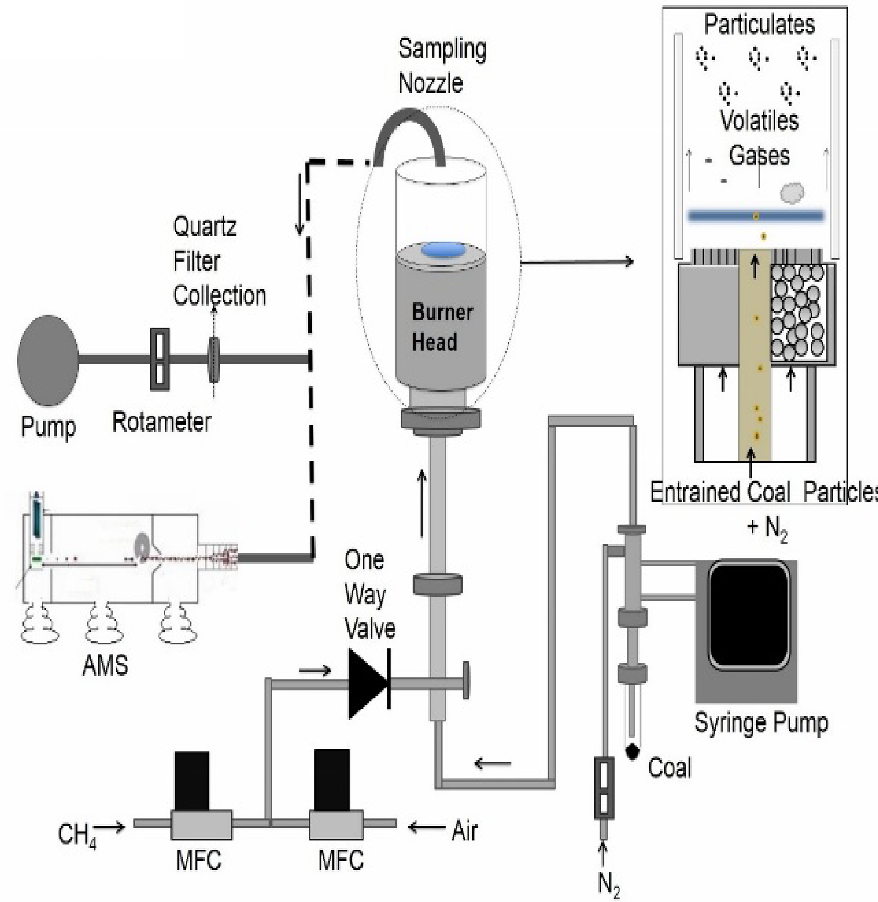
- Affects Flame Temperature
- Affects Volatilization Rates (Formation of Suboxides)

Detailed Understanding of Particle Formation

DROP TUBE FURNACE REACTOR



EARLY STAGE COMBUSTION / PYROLYSIS

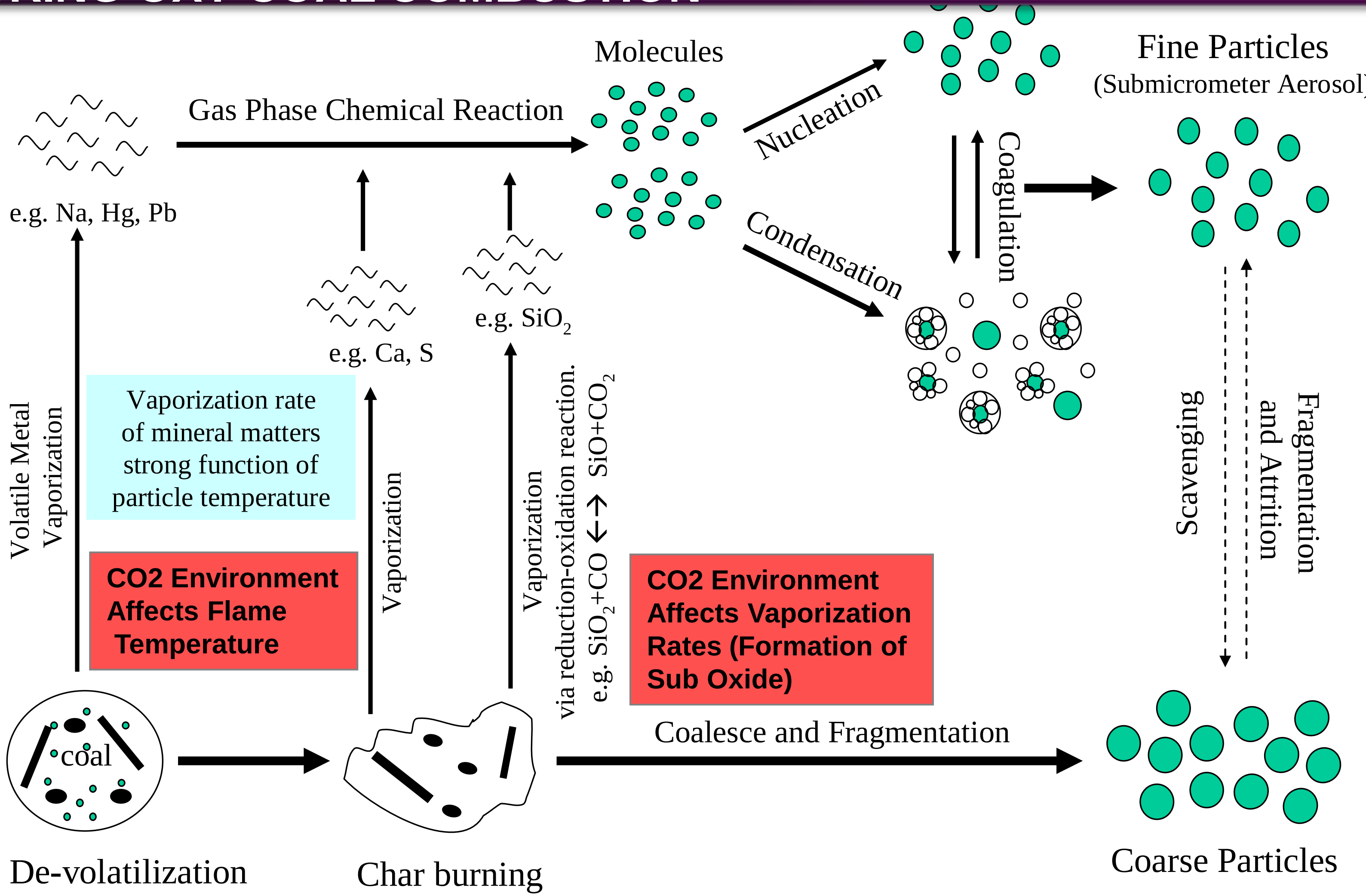


- SIZE DISTRIBUTION EVOLUTION
- AEROSOL MASS SPECTROMETRY

INSTRUMENTATION ENABLES NP STUDIES

- Workhorse Electrical Mobility Measurement (SMPS, NanoDMA: ~ 10 nm)
- Low size resolution CPCs (can count ~ 1 nm)
- Fast DMAs (down to sub 1 nm) [*Anal. Chem.*, 86: 7523-7529 (2014); *J. of Aerosol Sci.*, **71**(1): 52-64 (2014)]
- Portable Size Distribution Measurement: Nanoscan, PAMS, DISCmini
- Time of Flight Mass Spectrometers [*Atmos. Chem. & Phys.*, **13**(2): 3345-3377 (2013)]
- Tandem DMA – Mass Spectrometers
- LIBS, LII – Composition Analysis
- *Bring to bear Nanomaterials Characterization Tools (BET, AFM, HRTEM, SEM, XRD, Raman, etc)*

MECHANISTIC PATHWAY OF PARTICLE FORMATION DURING OXY-COAL COMBUSTION



Energy and Fuels, 20 (6), 2357-2363, 2006

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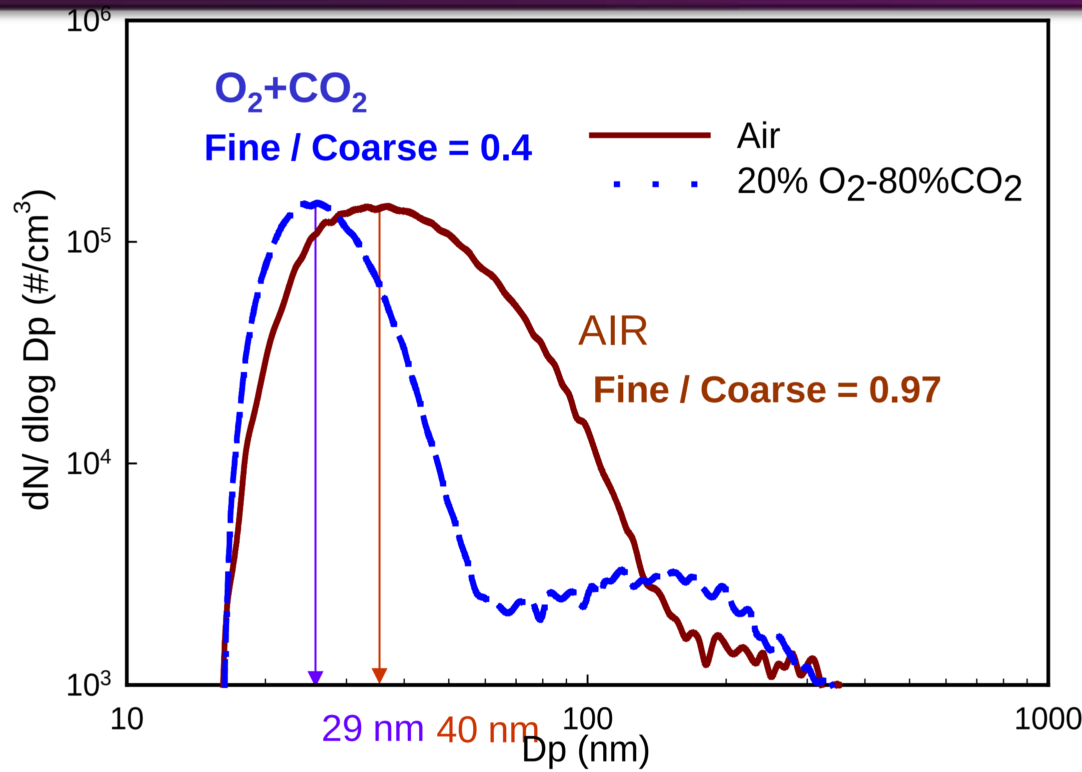
Oxy-Coal vs Air Combustion: Air vs. 21%O_2+79%CO_2

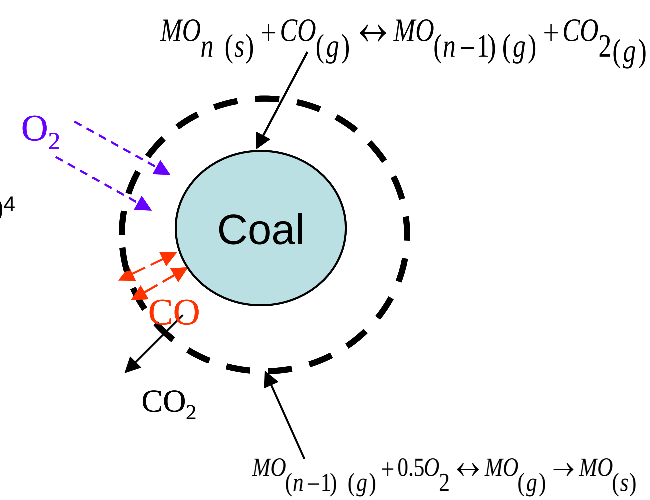


- **High CO_2 conc. delays devolatilization process due to thermophysical properties of N_2 and CO_2**
- **Flame temperature higher in Air (2311 K) vs CO2/O2 (1722 K)**
  - Cp: N_2=20.78 kJ/kmol-ºC, CO_2 = 58.84 kJ/kmol-ºC
  - $D_{O2/N2}$= 1.7x10^{-4} m^2/s; $D_{O2/CO2}$ = 1.3x10^{-4} m^2/s
- **High CO_2 conc. delays vaporization via reduction of metal oxide**

When AIR is replaced by 20%O_2+80%CO_2:

- □ Geometric mean particle size decreases from 40 nm to 29 nm
- □ Total number concentration decreases from 6.4 x10^4 to 3.9 x10^4
- □ No effects on particle shape

$$\left(\frac{Submicrometer\ Ash}{Coarse\ Ash}\right)_{AIR} = 2.5\left(\frac{Submicrometer\ Ash}{Coarse\ Ash}\right)_{O2-CO2}$$



Energy and Fuels, 20 (6), 2357-2363, 2006

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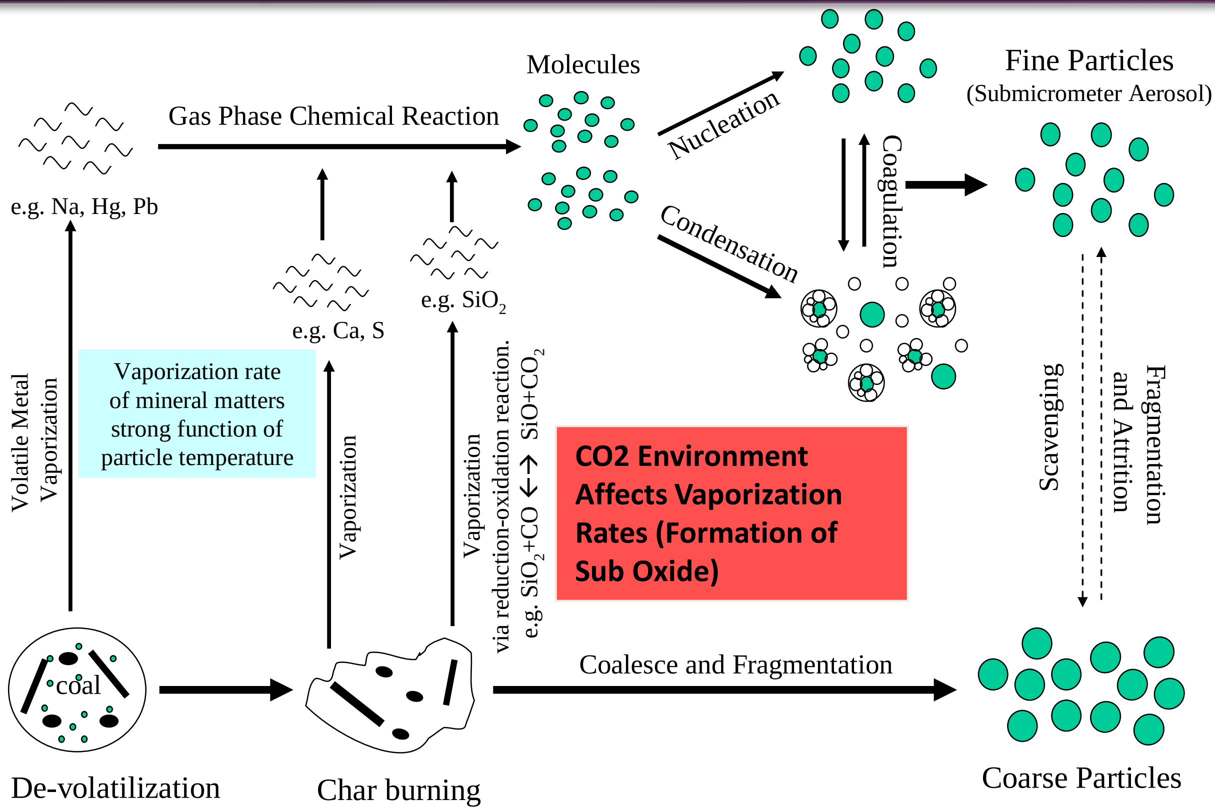
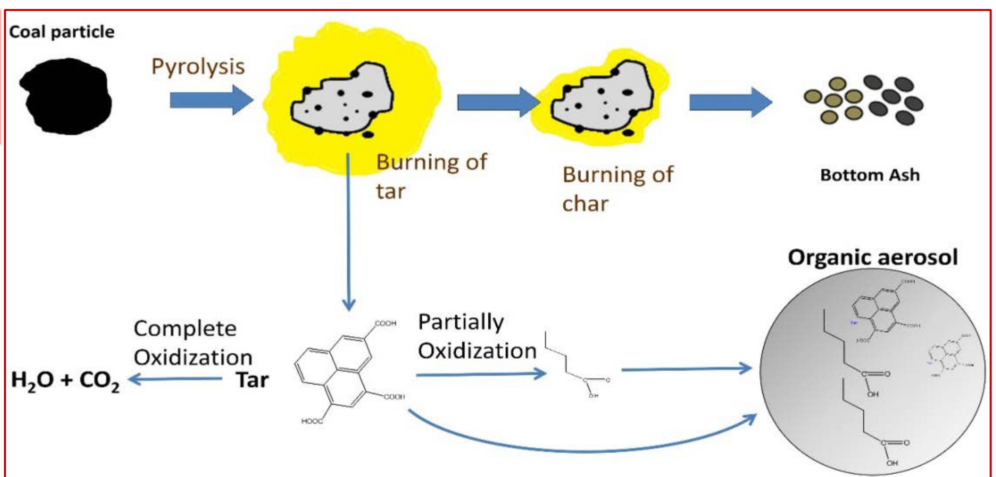
Pathway of Particle Formation: Organic & Inorganic



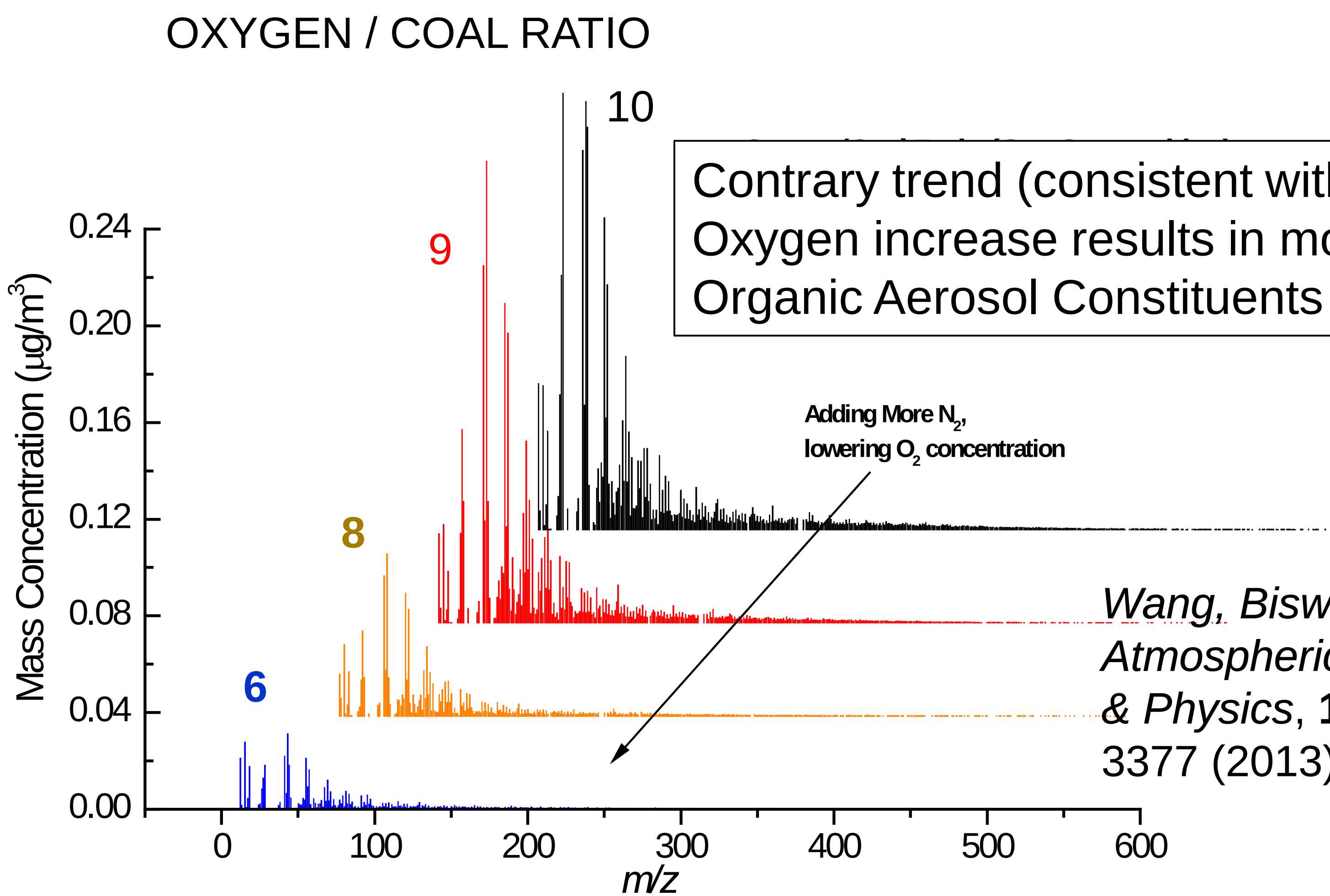
* Volatiles (organics) are released
* Small fraction is associated with Inorganic ash constituents
* Prevents from complete oxidation & released into atmosphere

CO2 Environment Affects Flame Temperature



Wang, Biswas et al. Atmospheric Chemistry & Physics, **13**(2): 3345-3377 (2013)

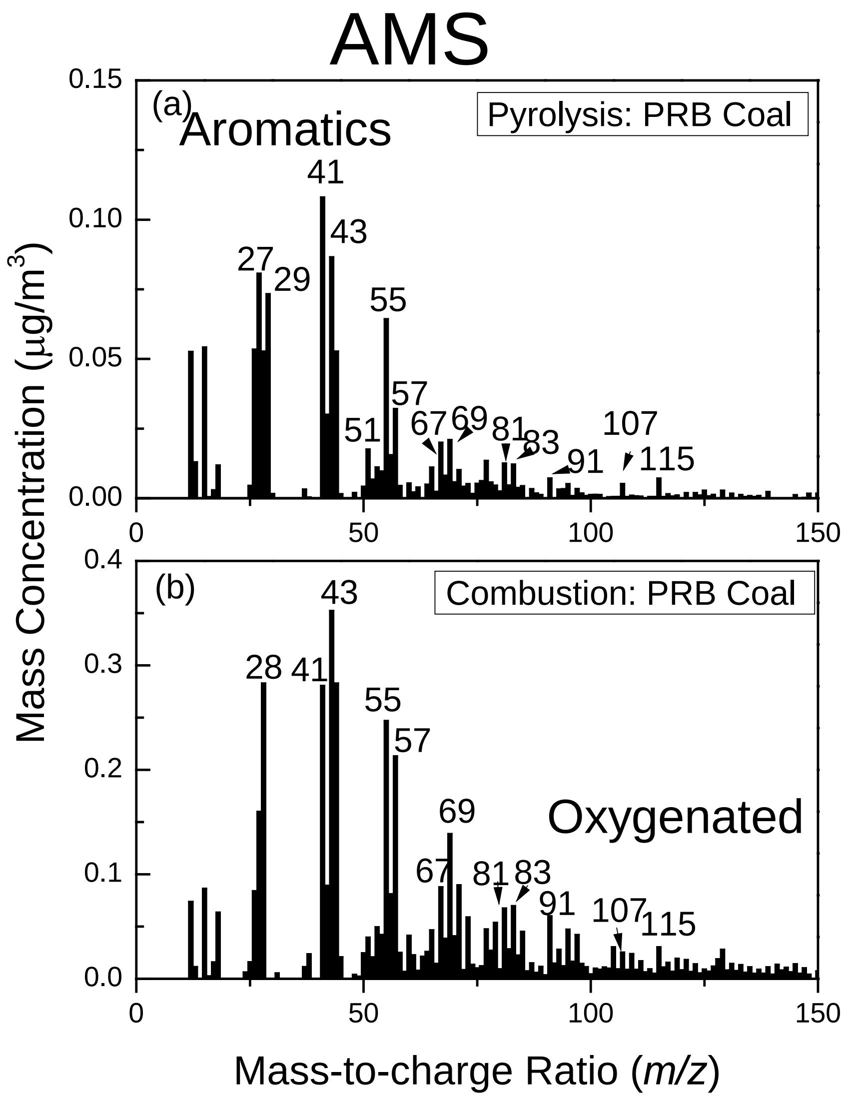
ORGANIC CONSTITUENTS IN NP FROM COAL

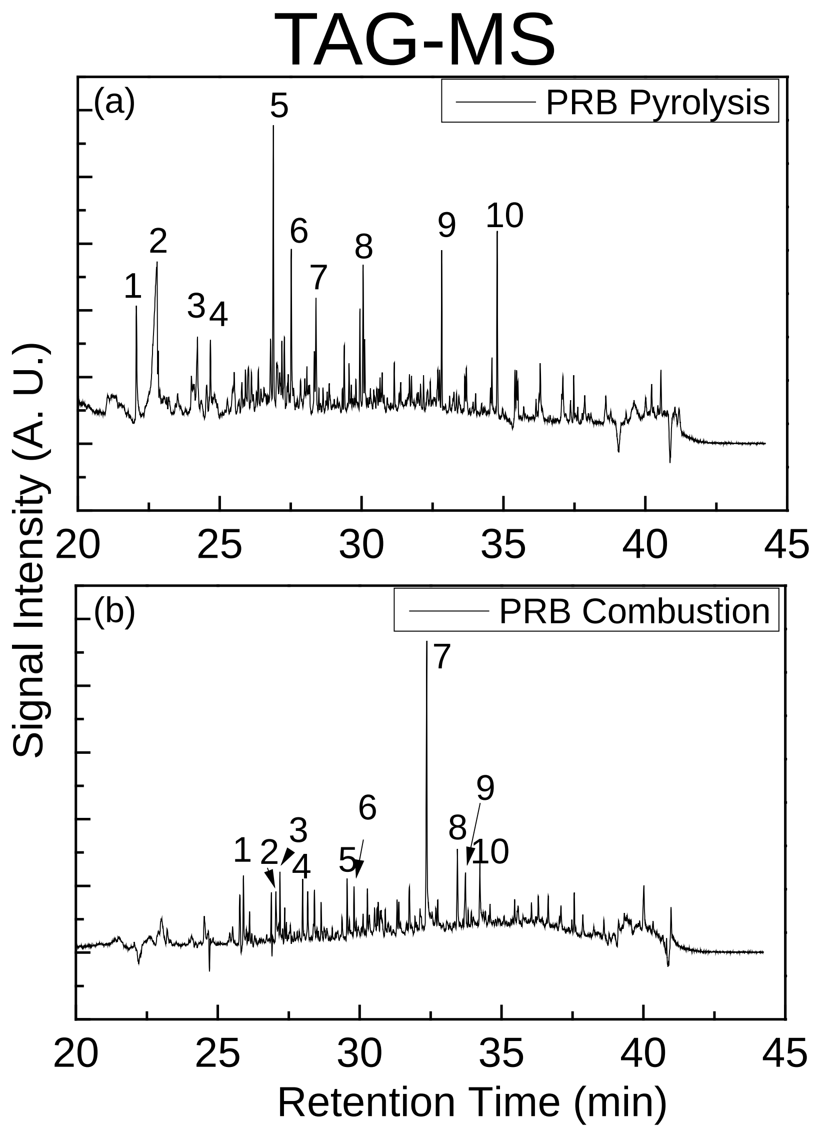


Contrary trend (consistent with Hypothesis)
Oxygen increase results in more
Organic Aerosol Constituents

Wang, Biswas et al. Atmospheric Chemistry & Physics, **13**(2): 3345-3377 (2013)

AMS and TAG-GC ANALYSIS

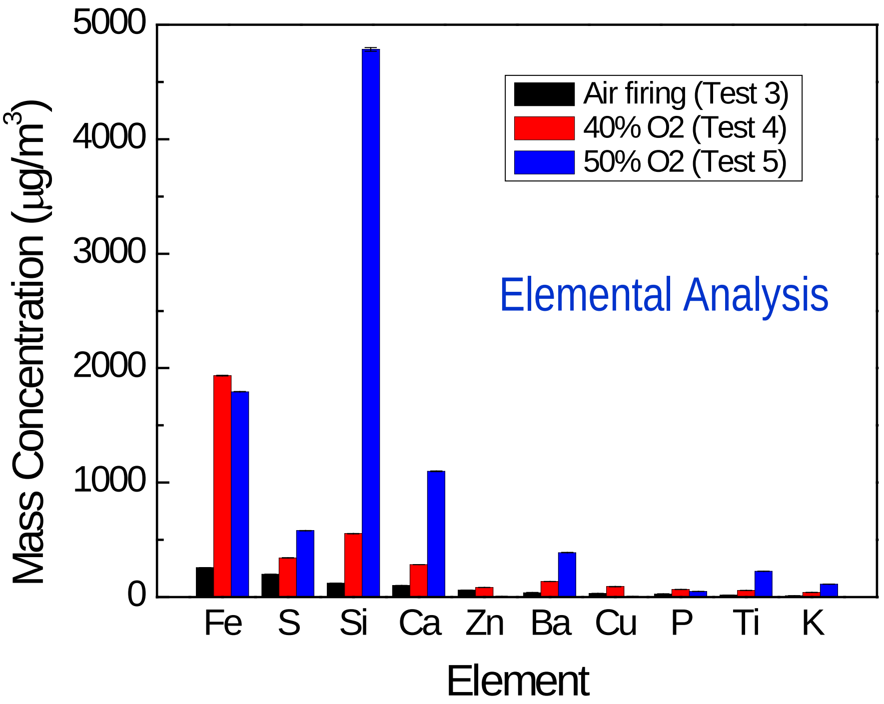




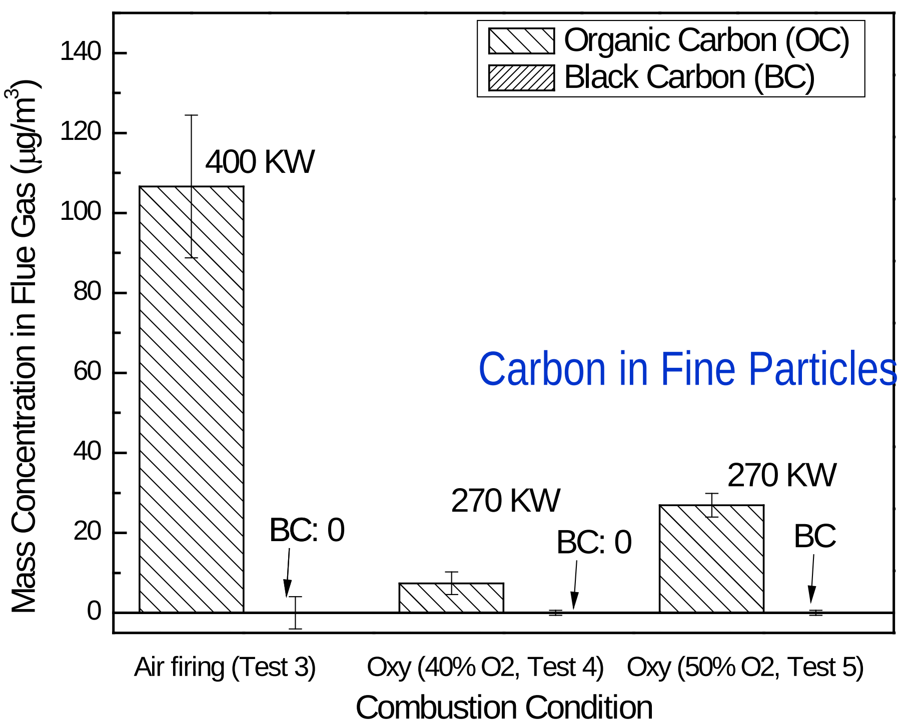
Both cases: non-aromatic hydrocarbons carboxylic acids and aromatics

Wang, Biswas: Proc.Combustion Institute , **35**, 2347-2354 2 (2015).

Chemical Composition of Particles: Coal Combustion



Inorganic Constituents of Ash Dominate NPs



Organic Carbon & Brown Carbon Exceeds Black Carbon in NPs

ESPS: How good are they to remove NPs ?

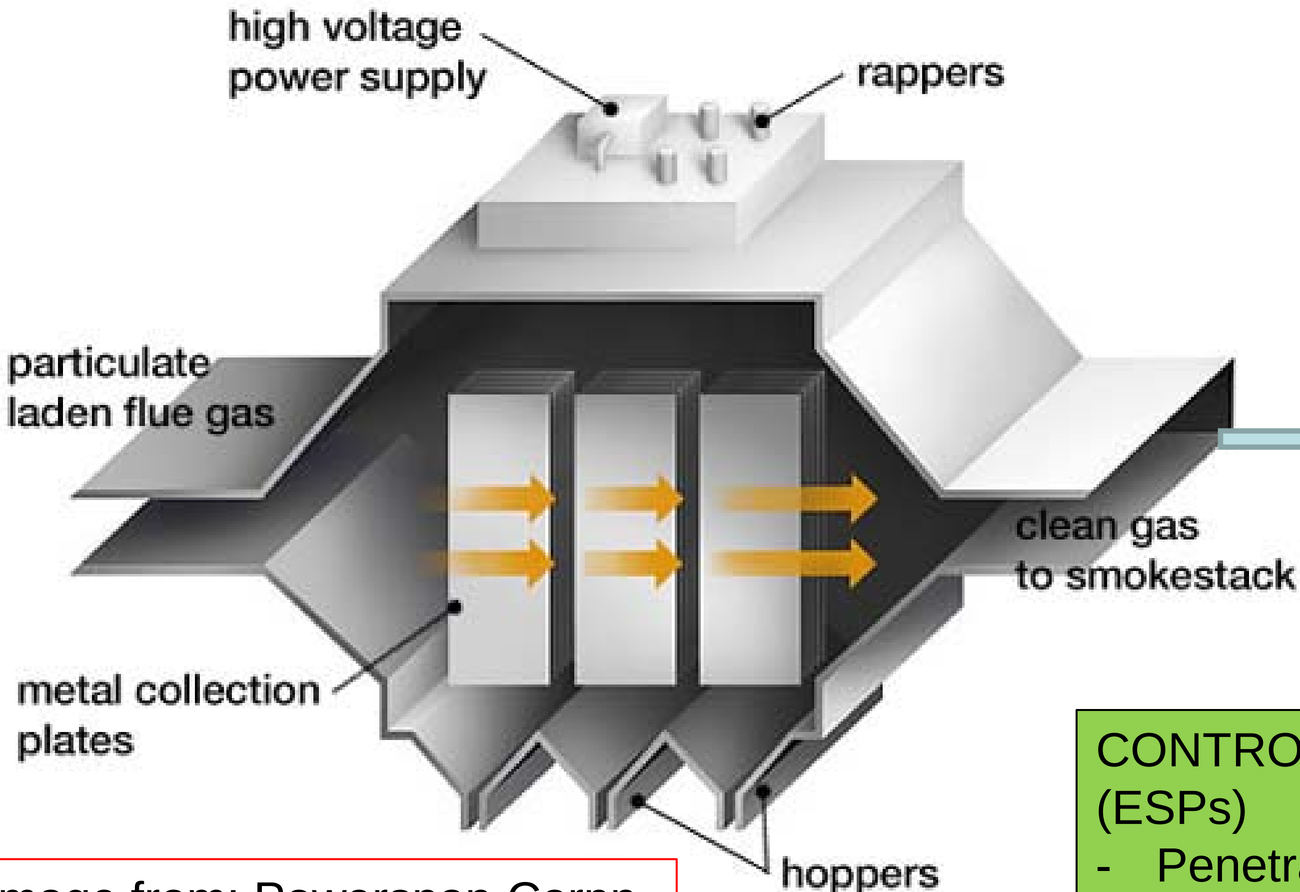


Image from: Powerspan Corpn.

NPs
&
PRECURSORS

CONTROL TECHNOLOGY (ESPs)
- Penetration through ESPs
- Improvement of Collection Eff
- Co-Pollutant Removal

CAPTURE CHARACTERISTICS IN THE ESP

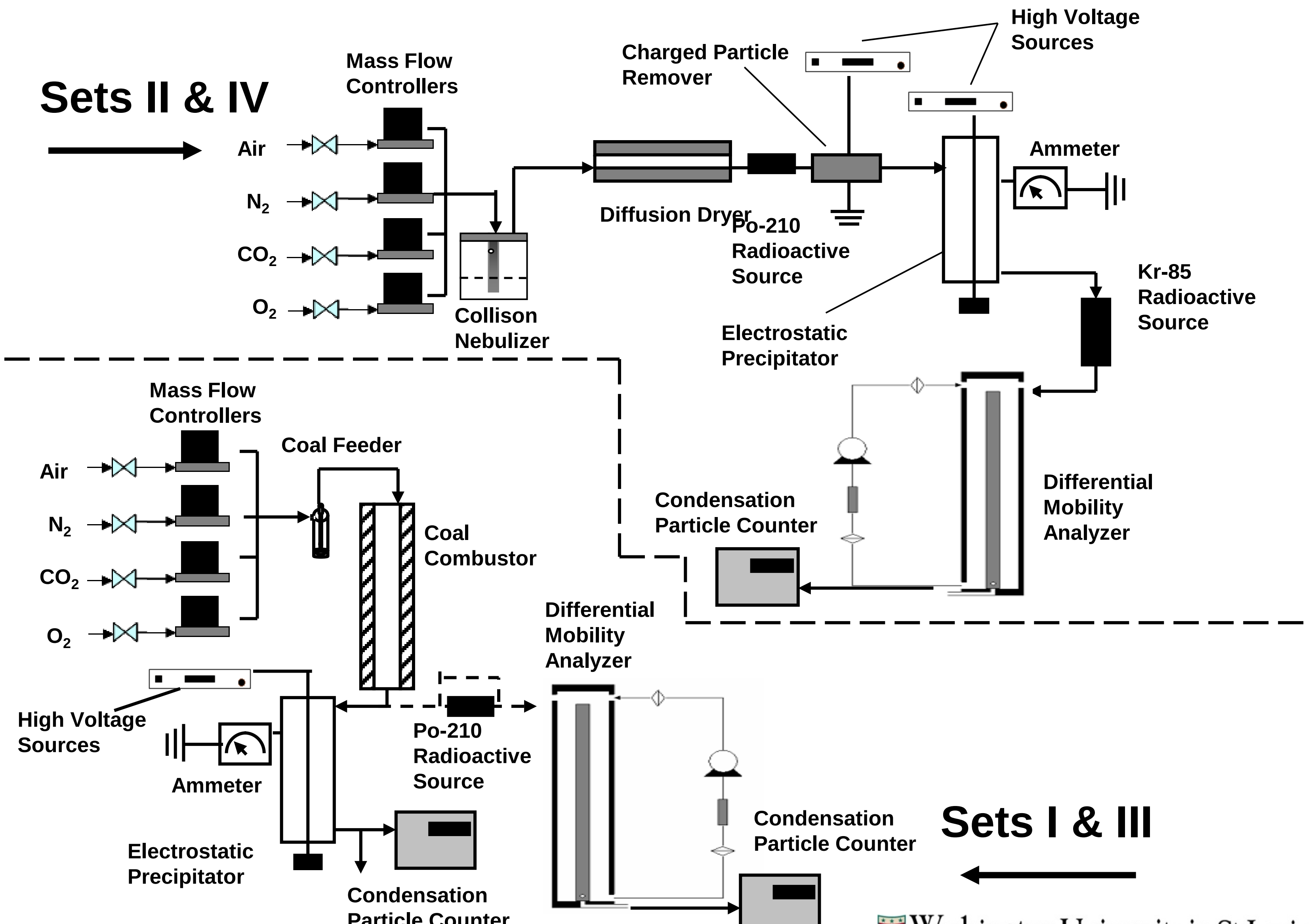
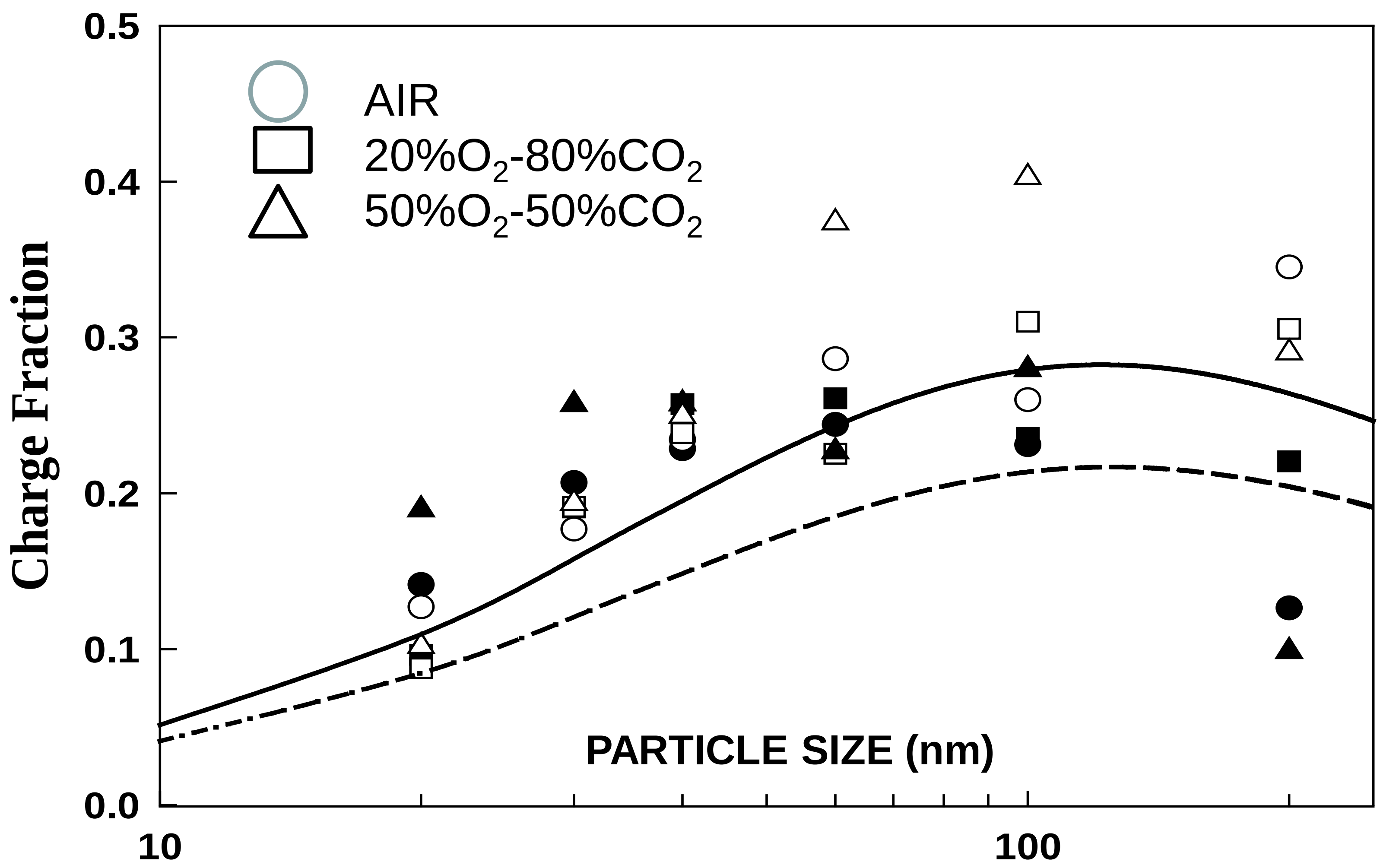


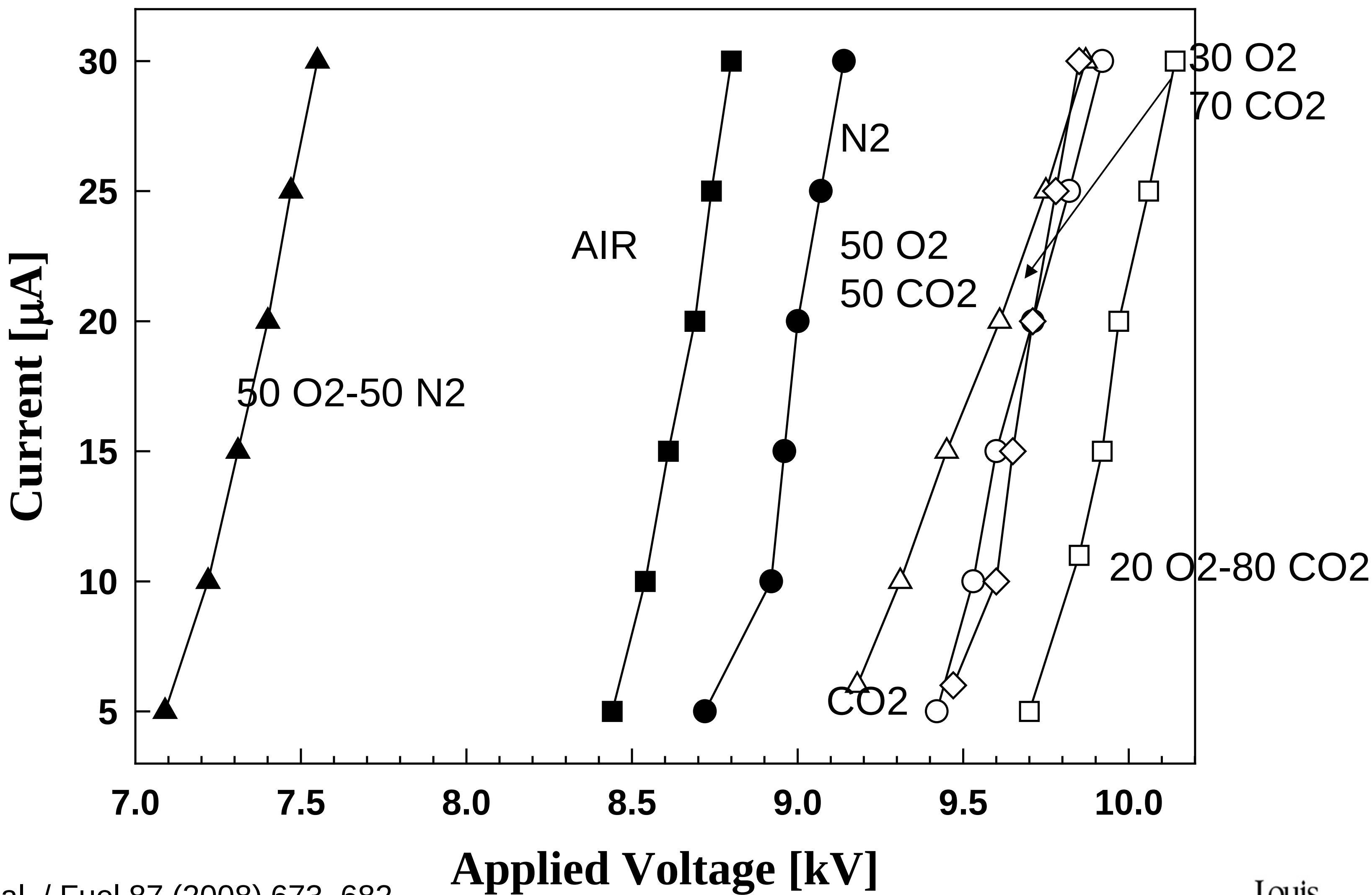
Figure 1

CHARGED FRACTION OF COAL COMBUSTION PARTICLES



Fraction of +1 and -1 charged particles Legend: Air (-1), Air (+1), 20%O_2-80%CO_2 (-1), 20%O_2-80%CO_2 (+1), 50%O_2-50%CO_2 (-1), 50%O_2-50%CO_2 (+1).
Equilibrium lines: Weidensohler, 1988. Solid Line (-1), Dashed Line (+1).

CORONA INITIATION VOLTAGE (POSITIVE VOLTAGES) (LARGER WHEN CO2 CONCENTRATIONS ARE HIGHER



Suriyawong et al. / Fuel 87 (2008) 673–682

Comprehensive Charging Model: Apply to ESP

Attachment coefficient

$$\beta^{\pm}(v,q)=\frac{\pi\theta c_{ion}^{\pm}\delta^2\exp(-U(\delta)/k_BT)}{1+\exp(-U(\delta)/k_BT)\dfrac{\theta c_{ion}^{\pm}\delta^2}{4D_{ion}^{\pm}a}\int_0^{a/\delta}\exp(U(a/y)/k_BT)dy}$$

Photoelectric yield coefficient

$$\alpha^{+}(v,q)=K_c(h\upsilon-\Phi(v,q))^m\frac{I\pi a^2}{h\upsilon}$$

Thermionic yield coefficient

$$\gamma^{+}(v,q)=BT^2\exp\left(-\frac{\Phi(v,q)}{k_BT}\right)\frac{4\pi a^2}{e}$$

Spatio-temporal number concentration of particles with size (volume) *v* and *q* elementary charges at location $\vec{x}$ and time *t*

$$\begin{aligned}\frac{\partial}{\partial t}(n(v,q,\vec{x},t)) &= \beta^{+}(v,q-1)N_{ion}^{+}n(v,q-1,\vec{x},t)-\beta^{+}(v,q)N_{ion}^{+}n(v,q,\vec{x},t)\\
&+\beta^{-}(v,q+1)N_{ion}^{-}n(v,q+1,\vec{x},t)-\beta^{-}(v,q)N_{ion}^{-}n(v,q,\vec{x},t)\\
&+\alpha^{+}(v,q-1)n(v,q-1,\vec{x},t)-\alpha^{+}(v,q)n(v,q,\vec{x},t)\\
&+\gamma^{+}(v,q-1)n(v,q-1,\vec{x},t)-\gamma^{+}(v,q)n(v,q,\vec{x},t)-\nabla\cdot n(v,q,\vec{x},t)\vec{u}\\
&-\nabla\cdot n(v,q,\vec{x},t)\overrightarrow{u_{ext}(v,q)}+\nabla\cdot n(v,q,\vec{x},t)\left[\tau_p(v)(\nabla\cdot\vec{u})\vec{u}\right]+D(v)\nabla^2 n(v,q,\vec{x},t)\\
&+\frac{1}{2}\sum_{s=-\infty}^{\infty}\int_0^{v}\beta^{s,q-s}(v',v-v')n(v',s,\vec{x},t)n(v-v',q-s,\vec{x},t)dv'\\
&-n(v,q,\vec{x},t)\sum_{s=-\infty}^{\infty}\int_0^{\infty}\beta^{q,s}(v,v')n(v',s,\vec{x},t)dv'\end{aligned}$$

Jiang, Lee, Biswas: J. of Electrostatics,65, 209-220, 2007.

PENETRATION AS A FUNCTION OF SIZE

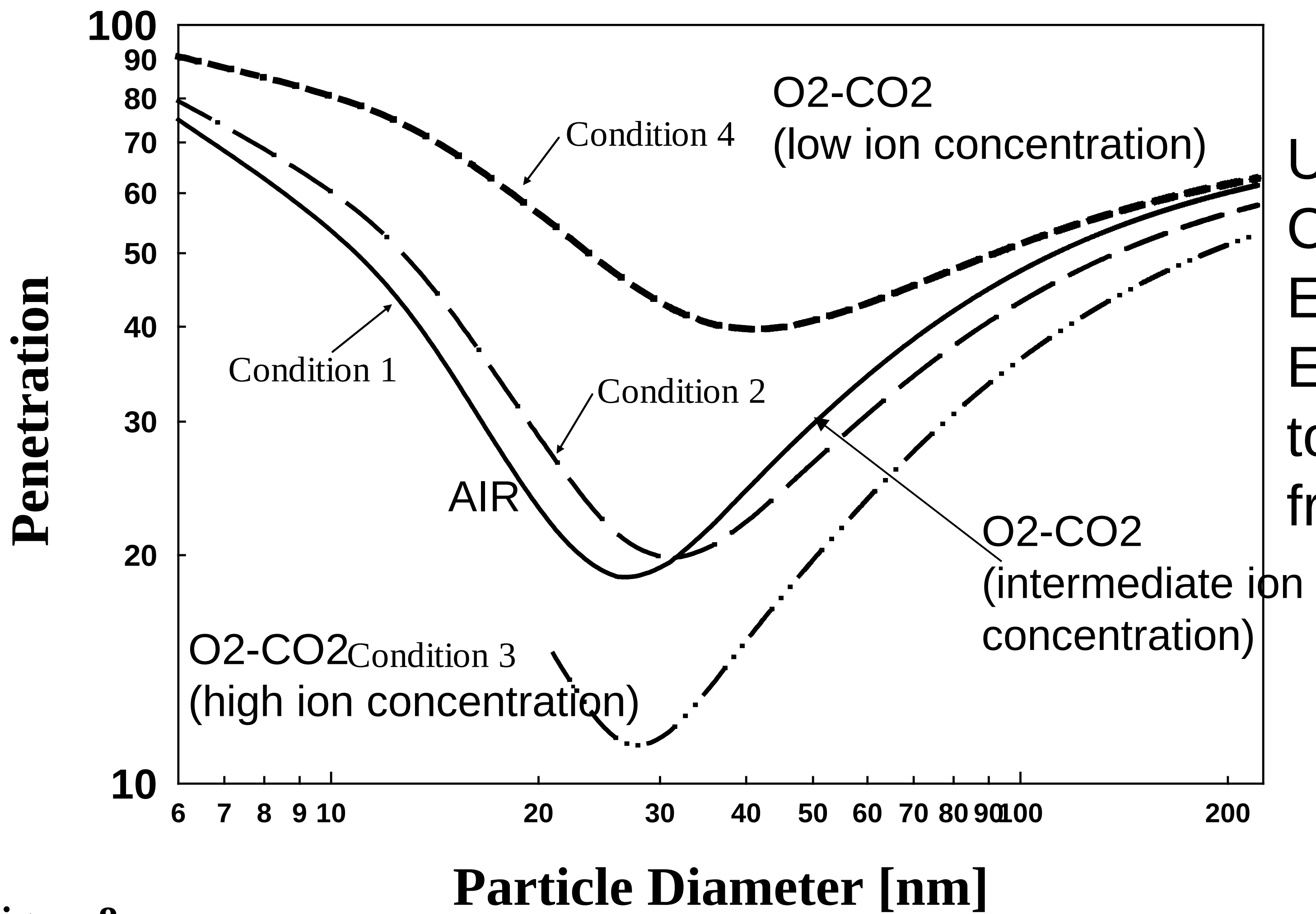


Figure 8

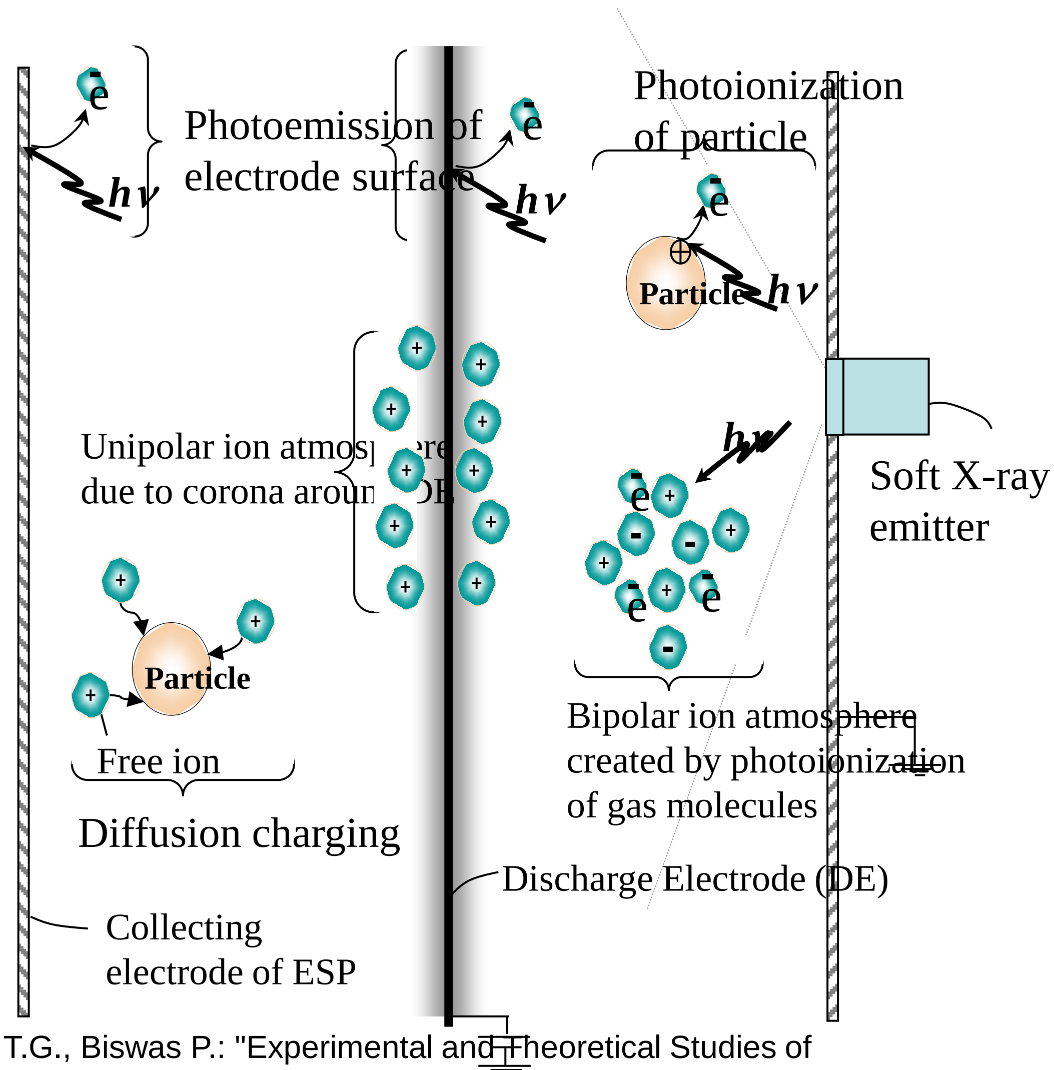
UFPs are not Captured Efficiently in ESPs. Difficult to charge large fraction

Suriyawong, et al. Fuel, 673-682, 2008

Zhuang, Biswas:J. Electrostatics, 245-260,2000

SXC – ESP: ENHANCES NP CAPTURE

SOFT X-RAY ENHANCED CORONA SYSTEM
ENHANCES NANOMETER SIZE PARTICLE CAPTURE

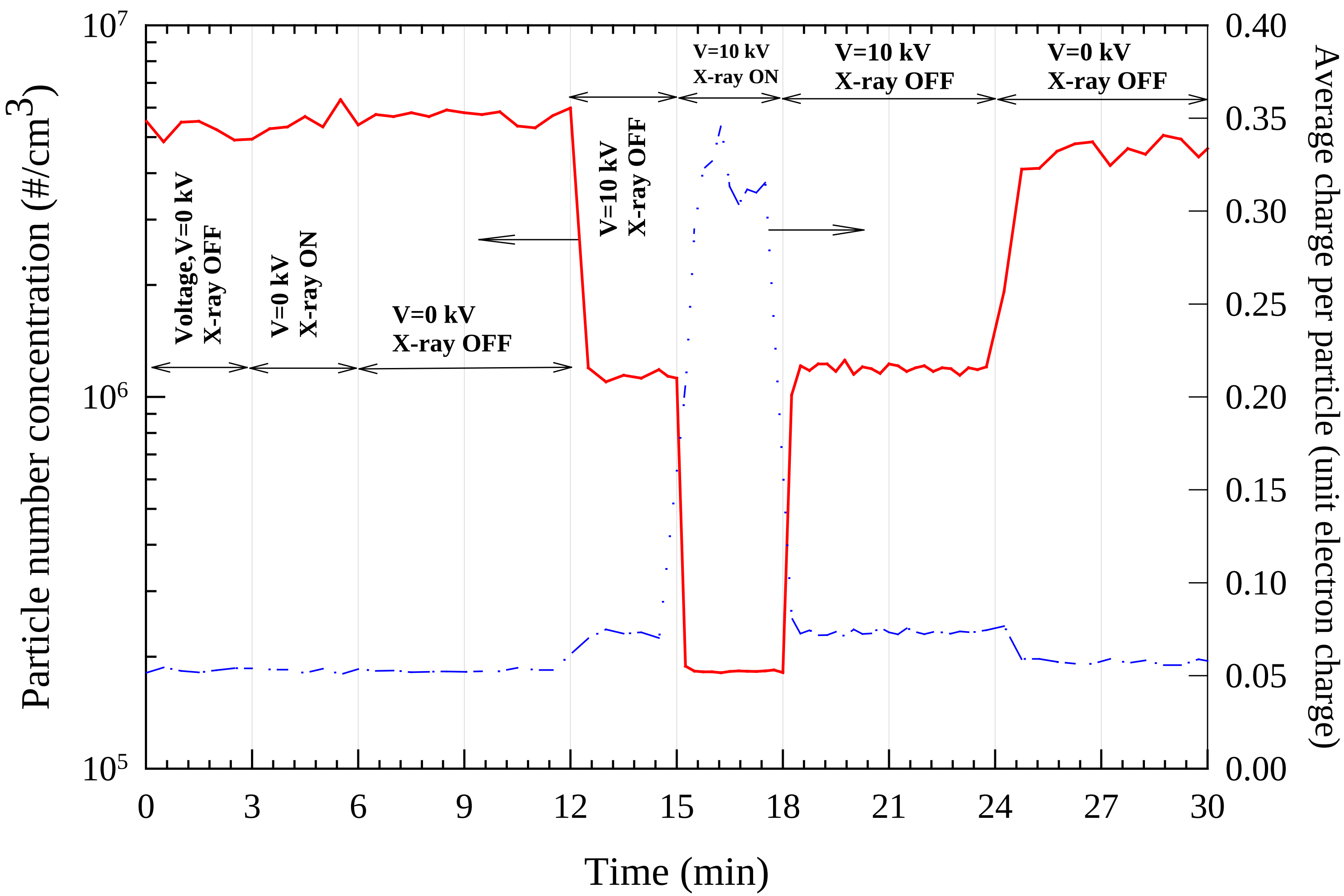


Biswas P., Namiki N. & Kulkarni P.
US Patent 6,861,036

Aerosol & Air Quality Res

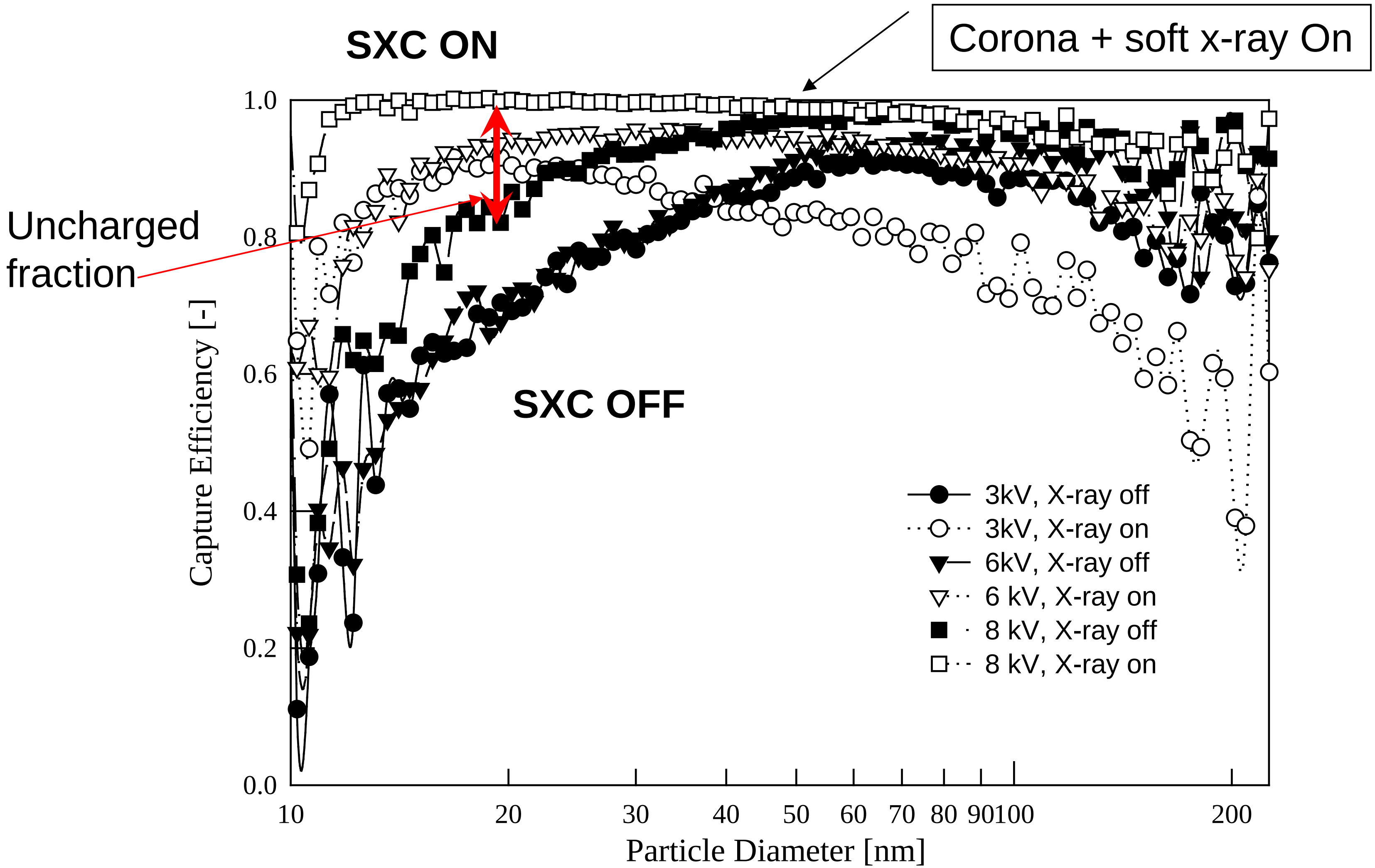
Zhuang Y., Kim Y.J., Lee T.G., Biswas P.: "Experimental and Theoretical Studies of Ultra-Fine Particle Behavior in Electrostatic Precipitators", J. of Electrostatics, 48, 245-260, 2000.

SXC-ESP COLLECTION EFFICIENCY

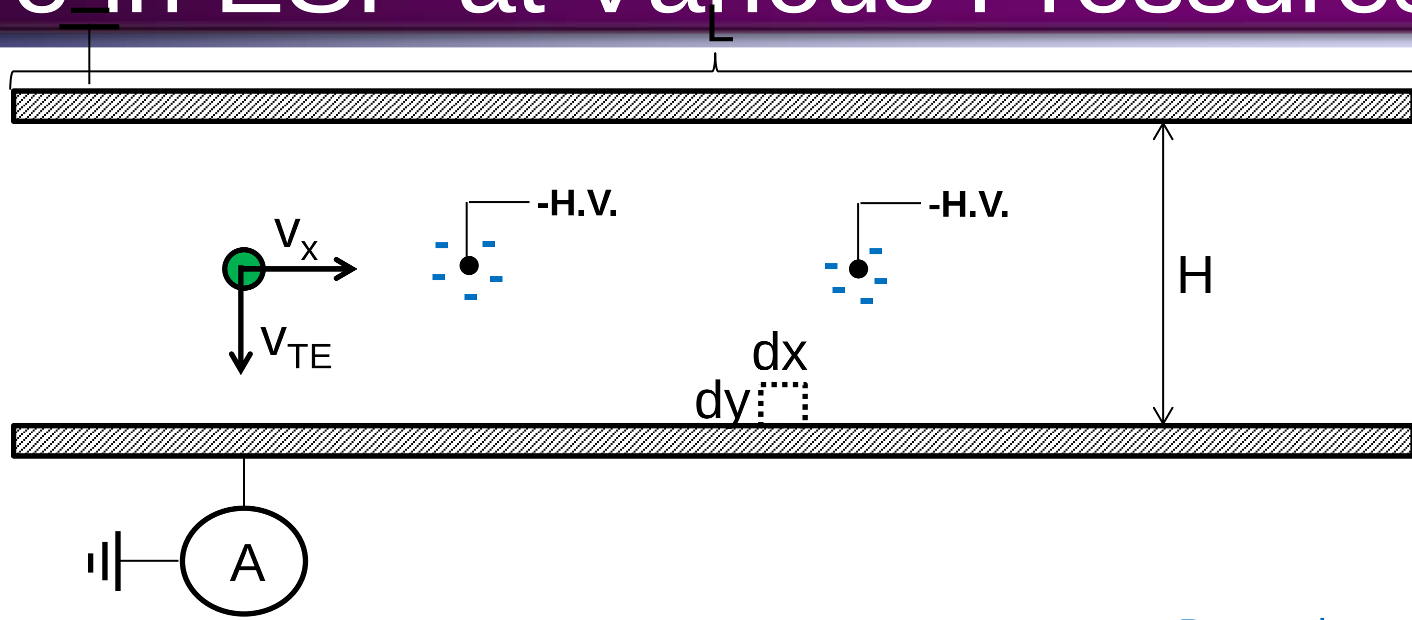


Kulkarni P., Namiki N., Otani Y. and Biswas P.: "Charging of particles in unipolar coronas irradiated in-situ soft X-rays: Enhancement of Capture Efficiency of Ultrafine Particles", J. Aerosol Sci., 33 (9), 1279-1298, 2002.

Capture efficiency at different particle diameters from 10 –225nm (Q=10 lpm).



Capture in ESP at Various Pressures



- Deutsch-Anderson equation

Dependent on gas pressure

ESP collection surface area

Particle migration velocity

$$\boldsymbol{\eta = 1 - \exp\left(-\frac{A_c v_{TE}}{Q}\right) = 1 - exp\left(-\frac{A_c\left(\frac{neEC_c}{3\pi\mu d_p}\right)}{Q}\right)}$$

Capture efficiency

Volumetric flow rate

$$n = n_{diff} + n_{field}(\lambda)$$

$$C_c = 1 + \frac{\lambda}{d_p}\left(2.34 + 1.05\, exp\left(-0.39\frac{d_p}{\lambda}\right)\right)$$

$$\lambda = \frac{RT}{\sqrt{2}\pi {d_m}^2 P N_A}$$

Robinson. *Air pollution control*. 1970 *Lab (AAQRL)*

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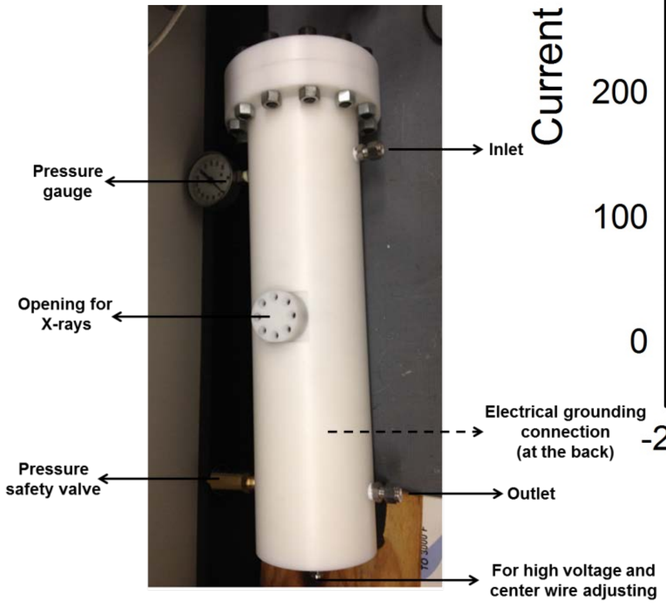
Fine Particle Capture in a Pressurized ESP

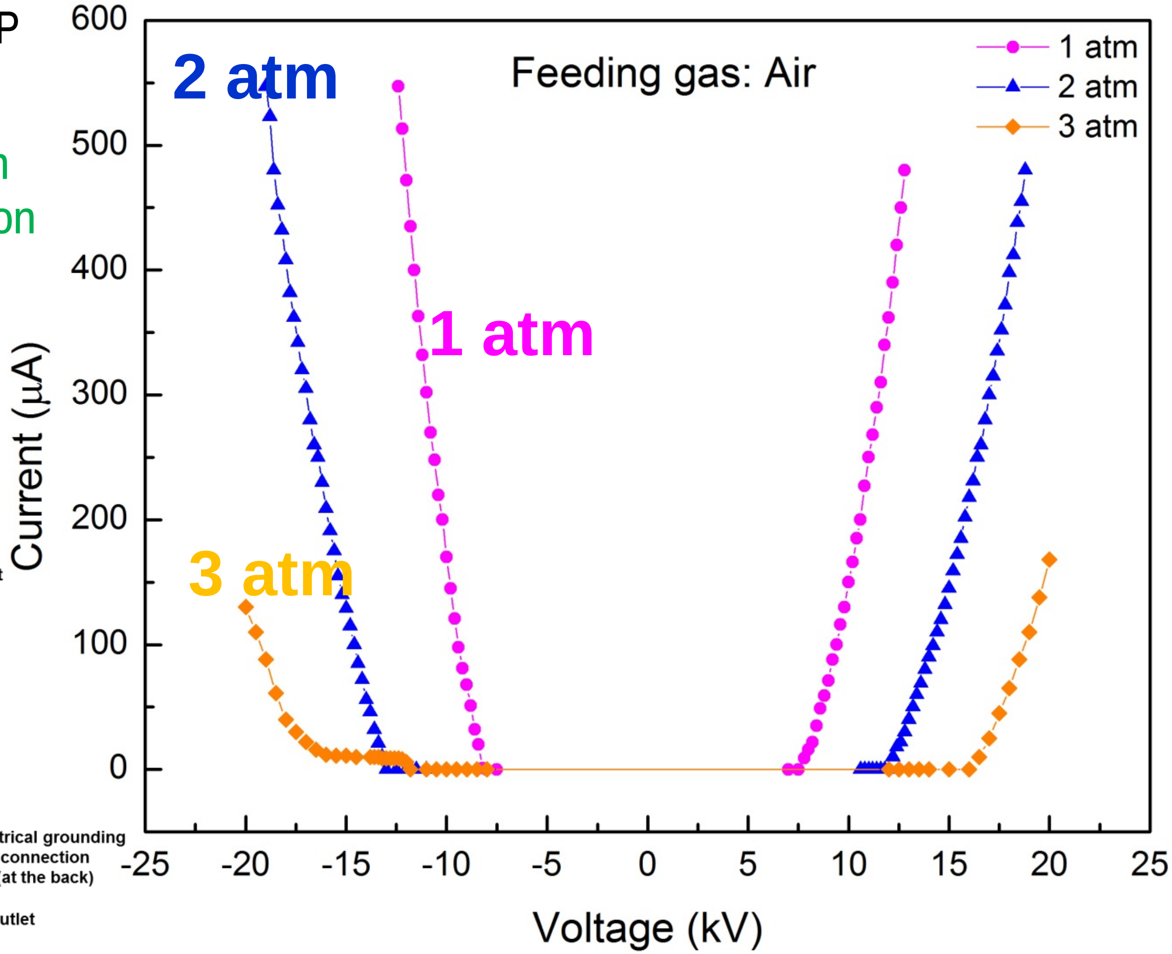
Application of pressurized ESP

Gas cleaning for
- Pressurized combustion
- Coal/biomass gasification

Benchtop pressurized ESP



V-I Characteristics



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Fine Particle Capture in a Pressurized ESP

Challenging aerosols: NaCl Particles

Current controlled

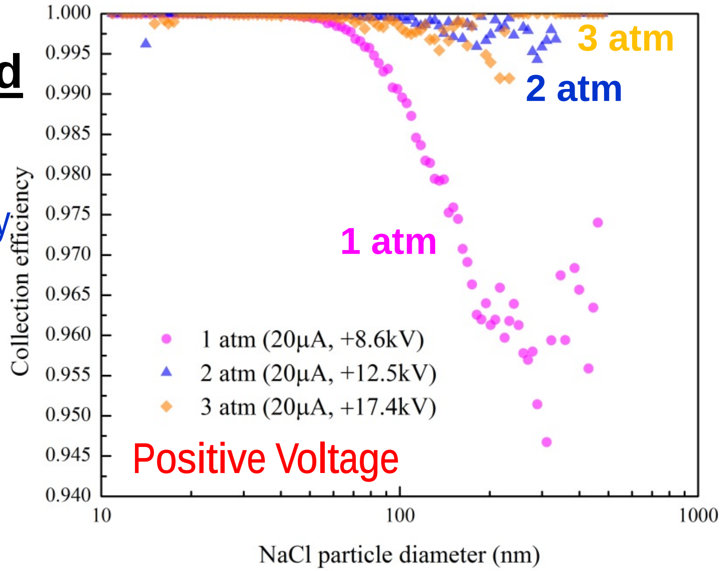
Higher pressure

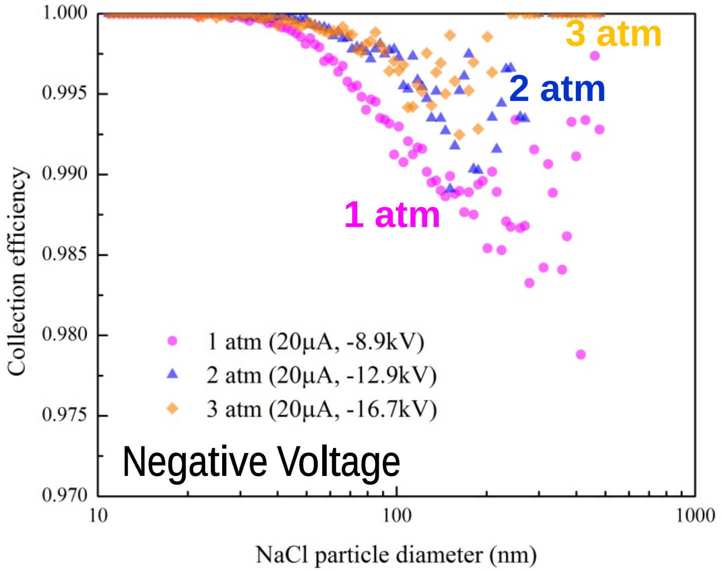
Higher collection efficiency

Due to combined effect of

Slower particle migration

and Higher filed intensity





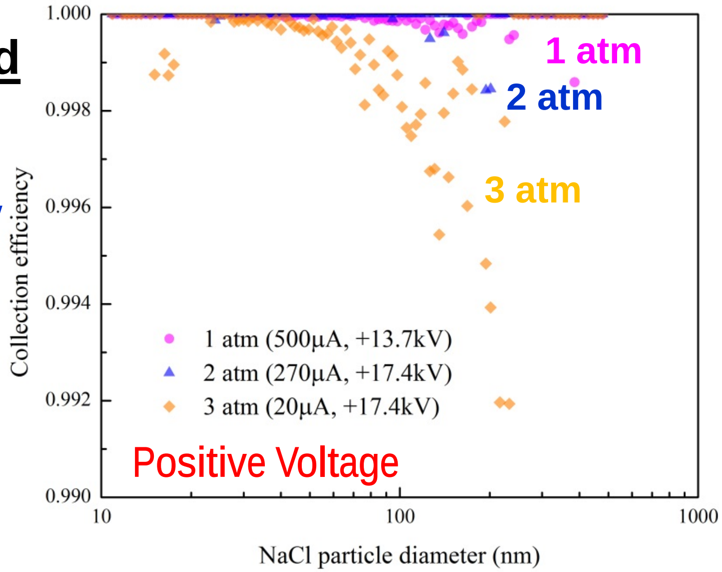
Voltage controlled

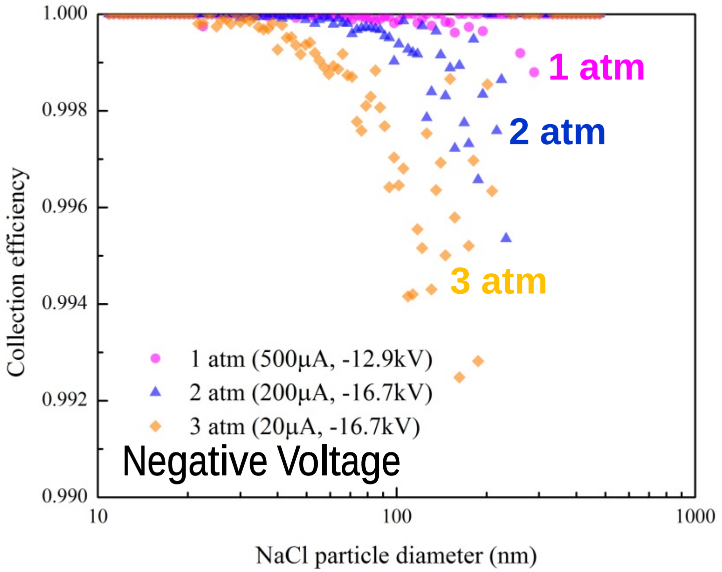
Higher pressure

Lower collection efficiency

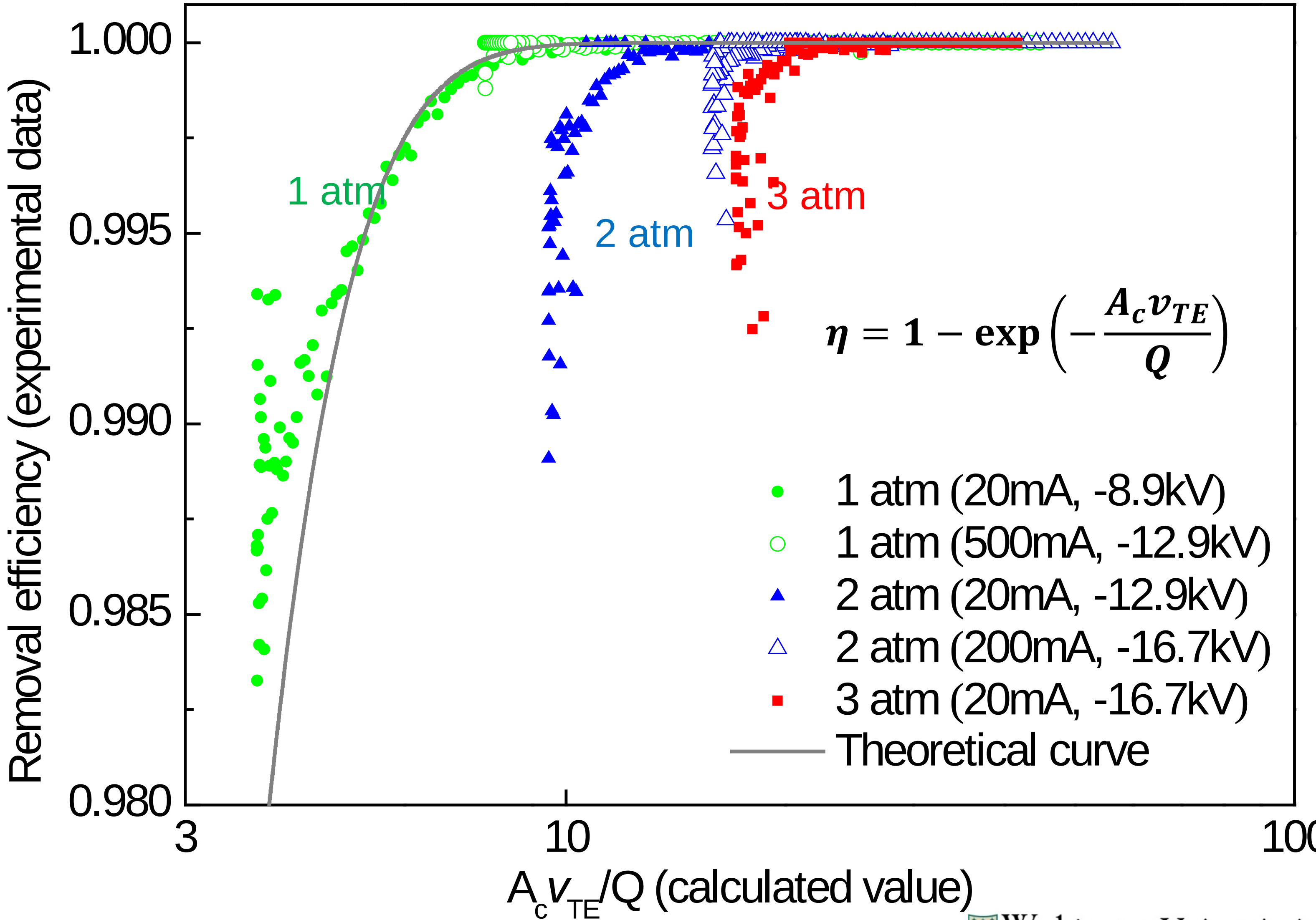
Due to

Lower ion concentration





Capture Efficiency at Different Pressures



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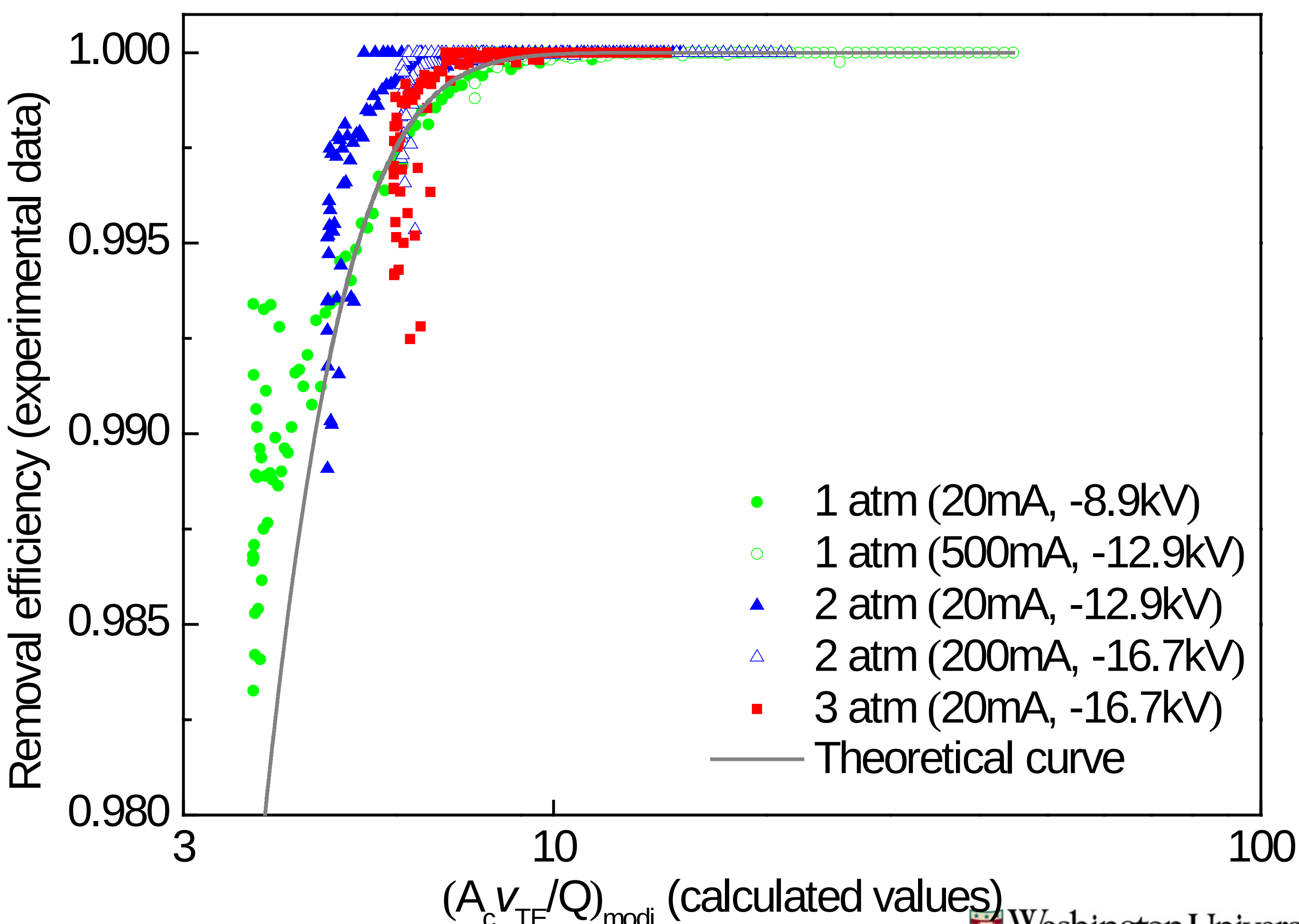
Modified Capture Efficiency Equation

$$\eta = 1 - \exp\left(-\frac{A_c v_{TE}}{Q} \times f\,(P)\right)$$



SUMMARY

- Detailed source and control technology studies for NP are essential
- New instrumentation enables detailed studies which will help tackle potential NP problem (design new systems)
- Timing for NP study due to changing energy source mix is now
- Coal combustion aerosols complex: cannot ignore organic constituents (related to inorganic constituents)
- Performance of ESP can be improved by using photo-ionizer charging systems
- Effect of pressure on charging NPs and capture efficiency elucidated