

High Temperature Generation, Sampling, and Analysis of Inorganic Nano-Particles and their Health Effects

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Tele-seminar

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Manufacturing

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MARCH 31, 2005

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Scope of this lecture

- Inorganic nano-particles.
 - Generation in high temperature processes
 - Sampling and analysis
 - Particle size distributions and speciation of metals at high temperatures
 - Non-volatile metals
 - Semi volatile metals
 - In-flight sequestration of semi-volatile metals on sorbent powders
 - Health effects
 - Search for a “bad actor”
 - Mitigation of lung injury: Health Effects Engineering
- Organic diesel soot nano-particles
 - Persistent stable free radicals

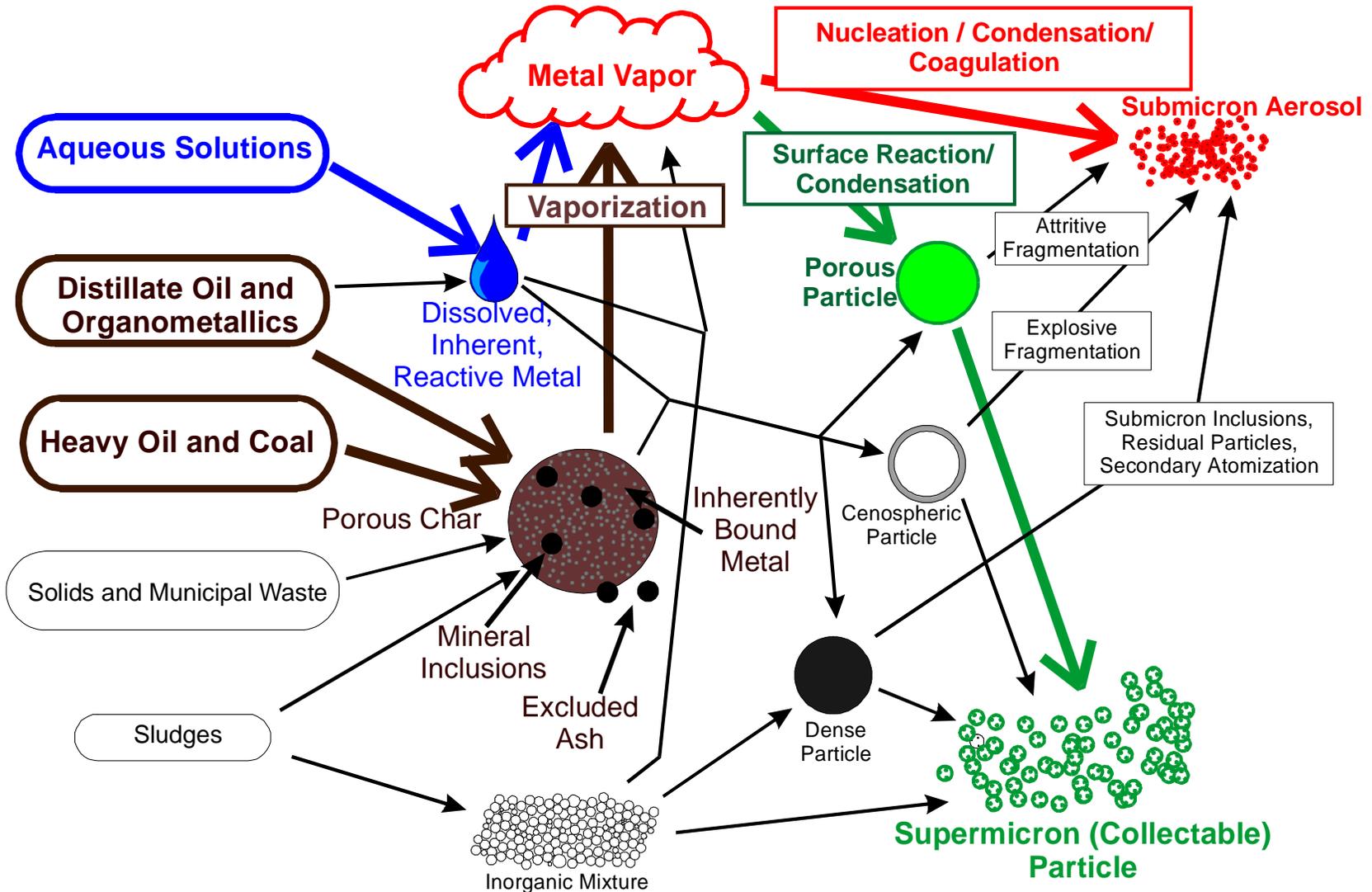


Metals considered

Volatility	Element	Dew point (at 100 ppmV, Natural gas or oil flame)	Form discussed in this paper
Low	Nickel	2000 K	Aq. solution, Fuel oil
	Strontium	2000 K	Aq. Solution
	Chromium	1900 K	Aq. solution
	Nickel w/ 1000ppm Cl	1800 K	Aq. solution
	Chromium w/ 1000ppm Cl	1800 K	Aq. solution
Medium	Strontium w/1000ppm Cl	1400 K	Aq. solution
	Cadmium	1225 K	Aq. solution
	Lead	1200 K	Aq. solution, Fuel oil
	Zinc	1350 K (no S) 1360 K (with S)	Fuel oil
	Cesium w/ 1000ppm Cl	900 K	Aq. solution
High	Cesium	675 K	Aq. solution
	Mercury	500 K	Coal
	Selenium	400 K	Coal

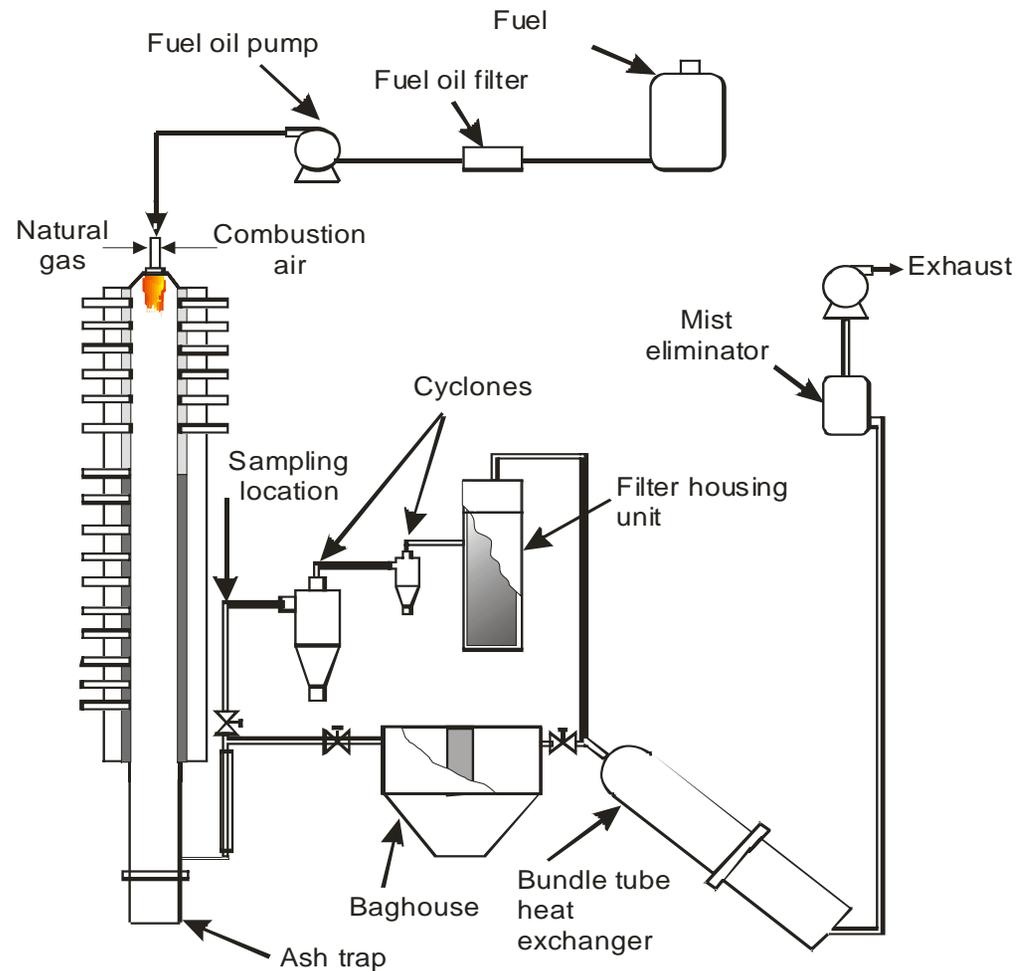


Mechanisms

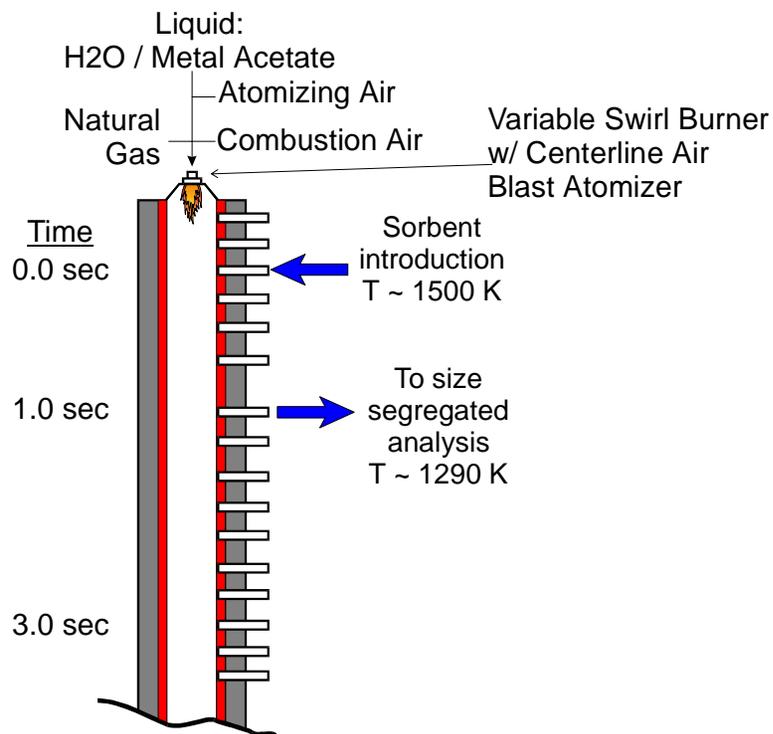


Generation and bulk collection of nano-particles in combustion facilities:

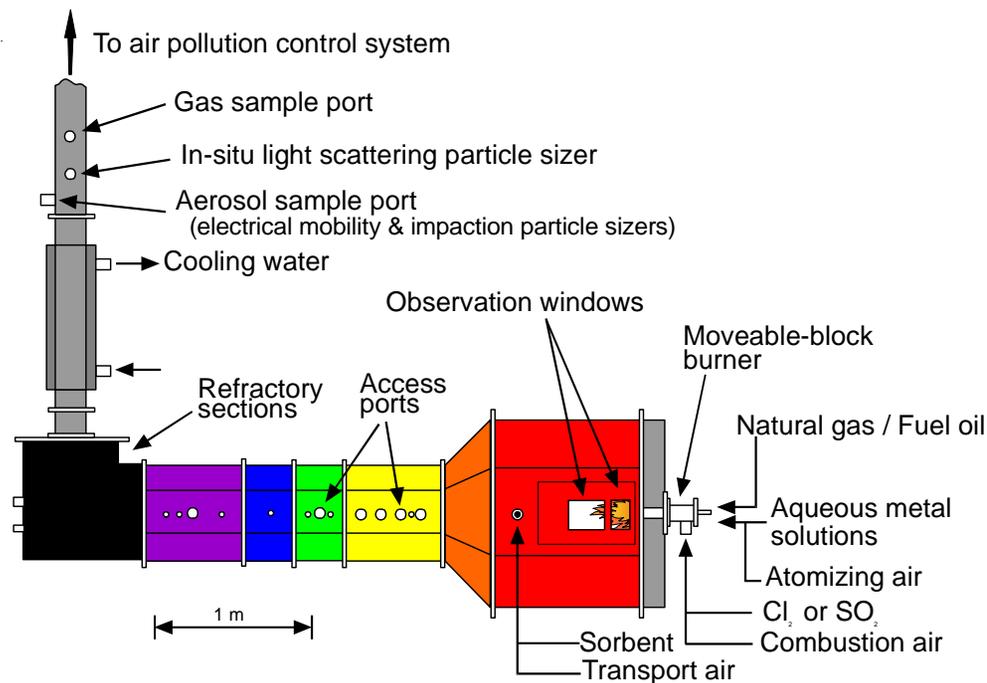
Metal doped liquid fuel or aqueous injection of metal salt solution through a gasflame.



Inorganic aerosol generation (continued)



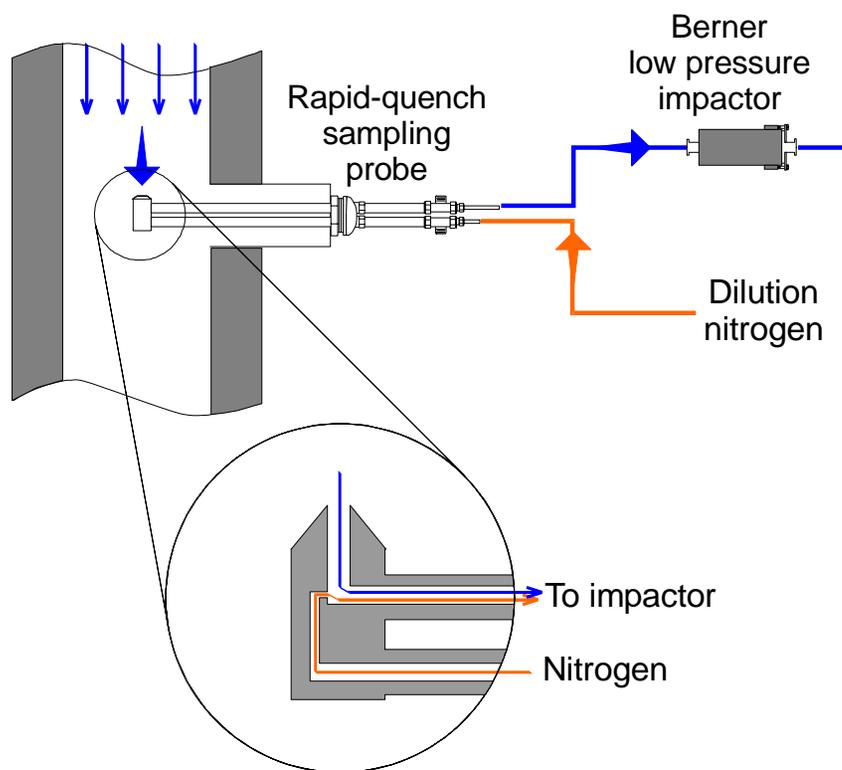
17kW downflow combustor



82kW refractory-lined furnace



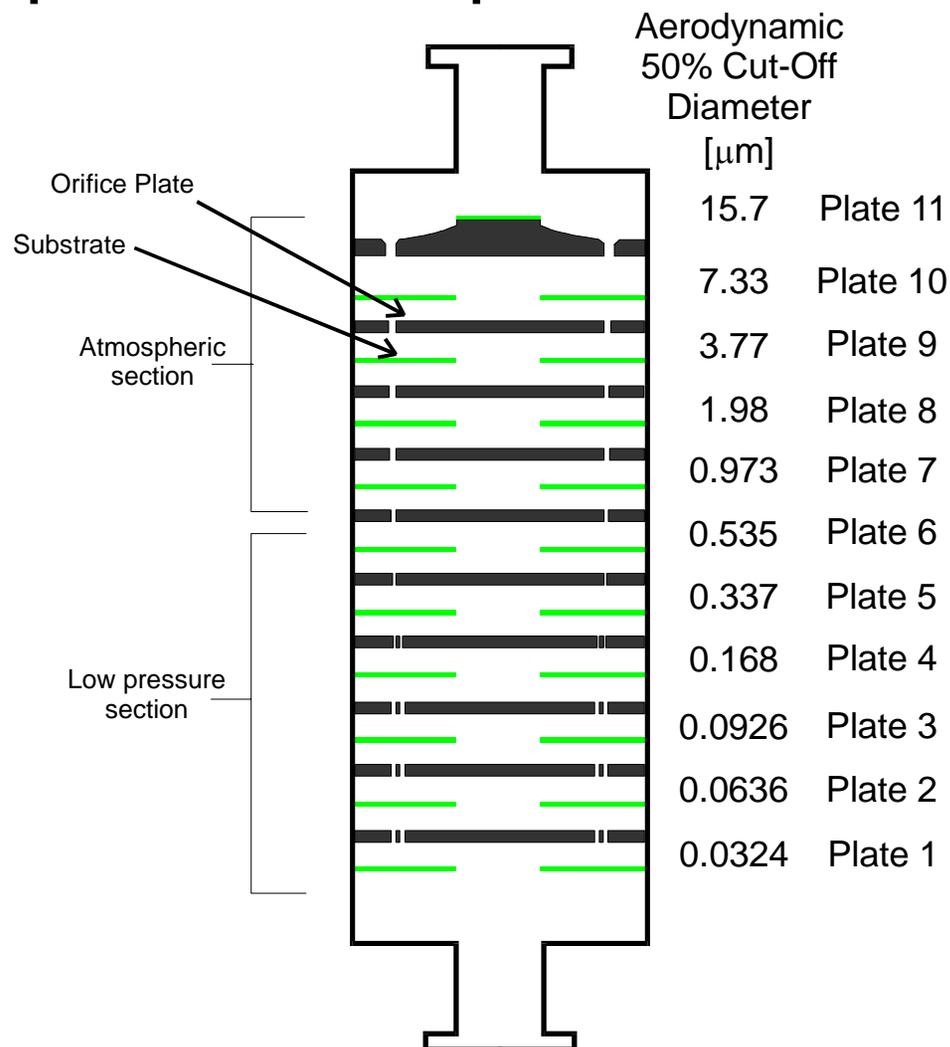
Approach: Rapid quench sampling



- Rapid quench near probe tip forces homogenous nucleation of metal vapor in presence of pre-existing particles
- Dilutions of ~10:1-20:1 generate cooling rates on the order of 25,000K/s
- Impactor has a sufficiently high resolution to discriminate between large sorbent particles and nucleated vapor

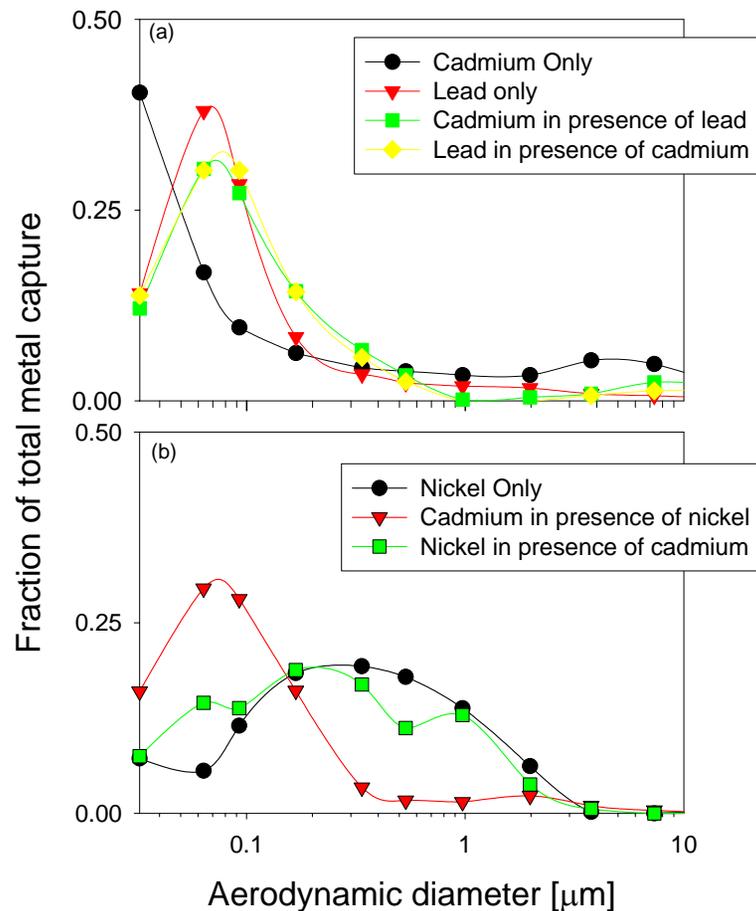
Berner low pressure impactor

- Excellent resolution for particulate size segregation
- Polycarbonate substrates
- Apeizon-L grease to diminish particle bounce-off
- Particle analysis by, atomic absorption (flame and graphite furnace), SEM, SAM as applicable



Probe sampling behavior

(~100ppm metal in exhaust)

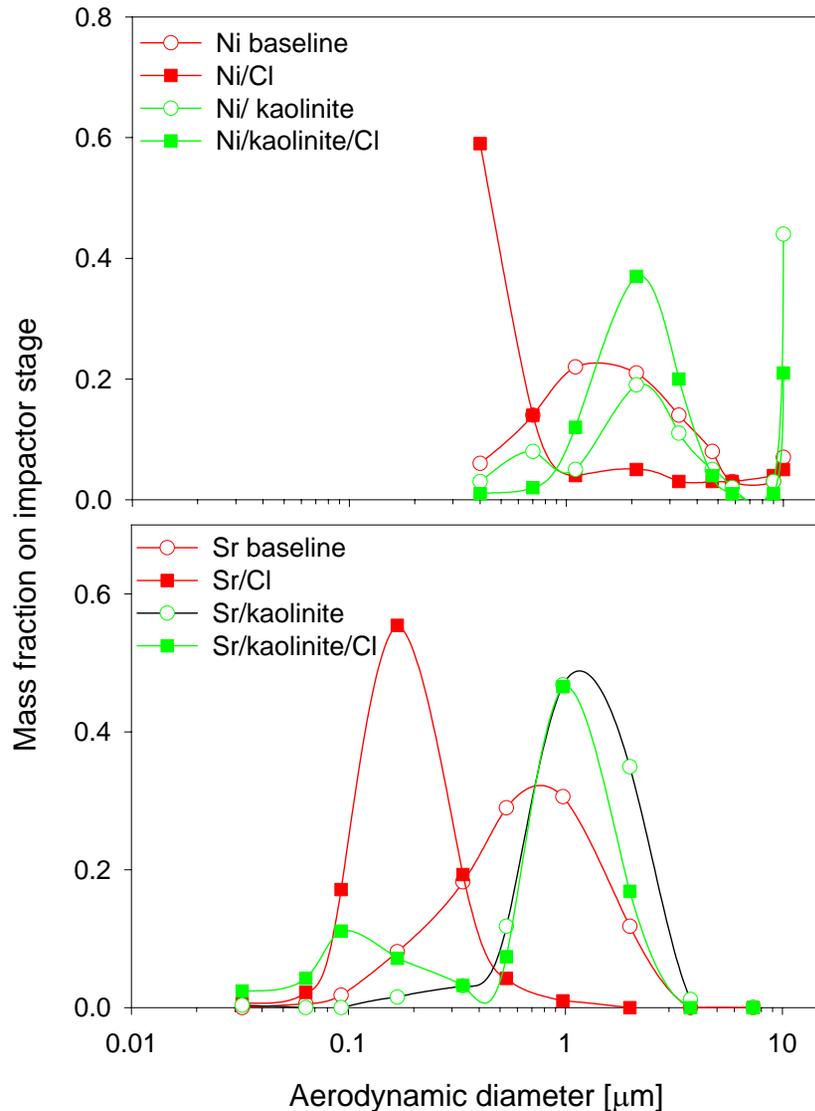


- Upper panel
 - All sampled particles predominantly below 100nm
 - Nucleation from sampled metal vapor in probe
 - Minimal coagulation in probe (Pb and Cd)
- Lower panel
 - Cd still nucleates in probe, even in presence of existing larger Ni particle population
 - Negligible interaction between Cd and Ni in probe
- Conclusion
 - Probe does not distort sampled nano-particle PSD



Low volatile metals: nickel and strontium

(~100ppm in exhaust)

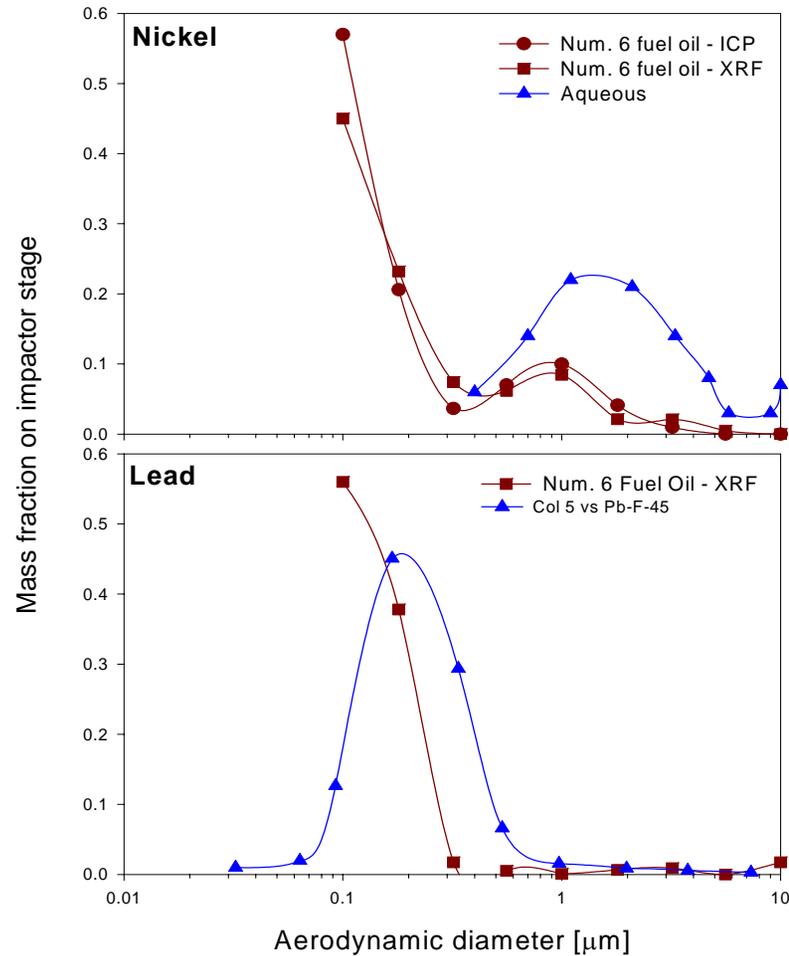


- Chlorine enhances vaporization of both nickel (upper panel) and strontium (lower panel)
- Kaolinite will reactively scavenge vaporized nickel (upper panel) and strontium (lower panel)
- No evidence of scavenging of either metal by kaolinite *in absence of chlorine*

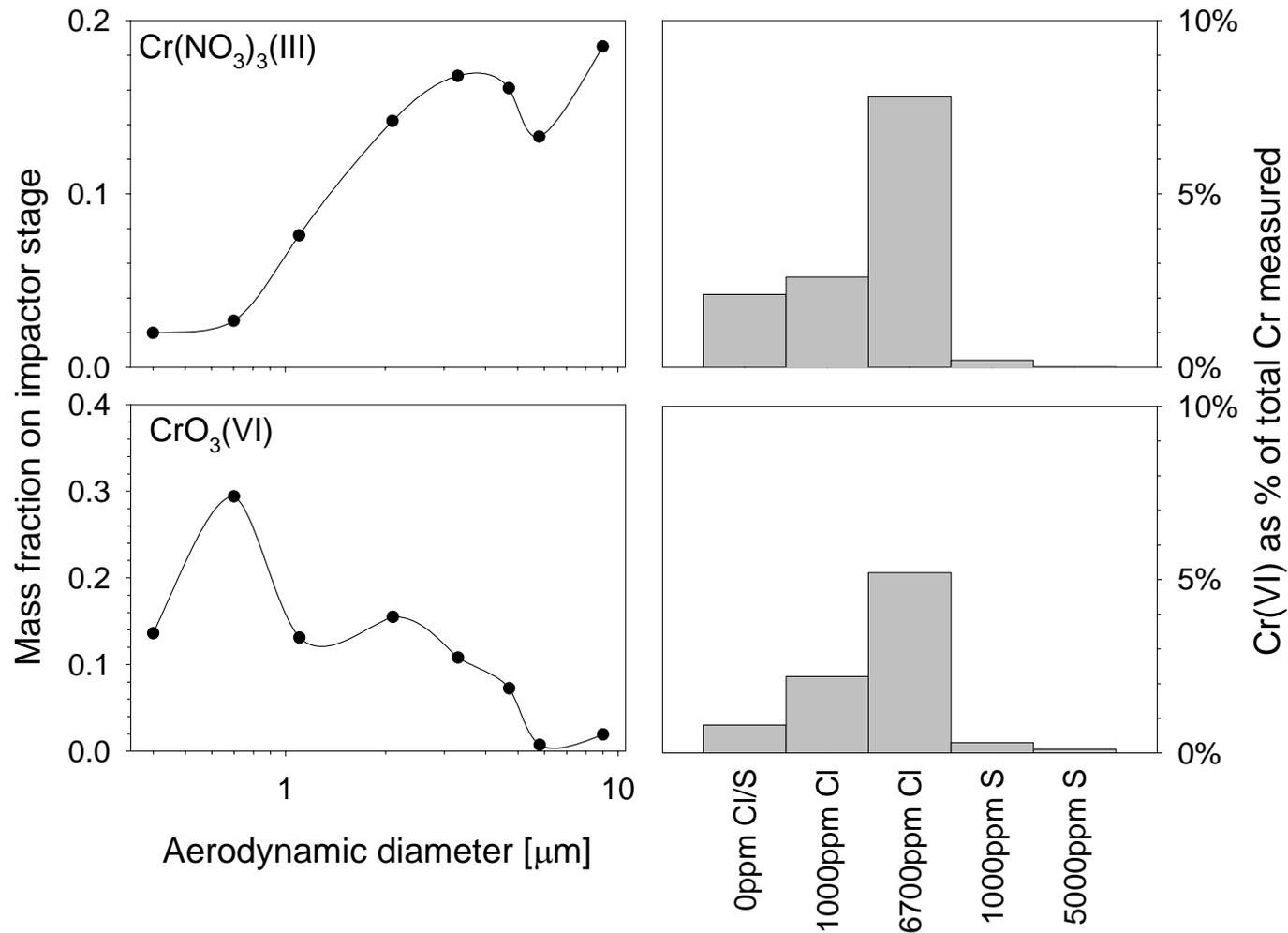


Effect of inlet form and conc. of metal (Ni and Pb):

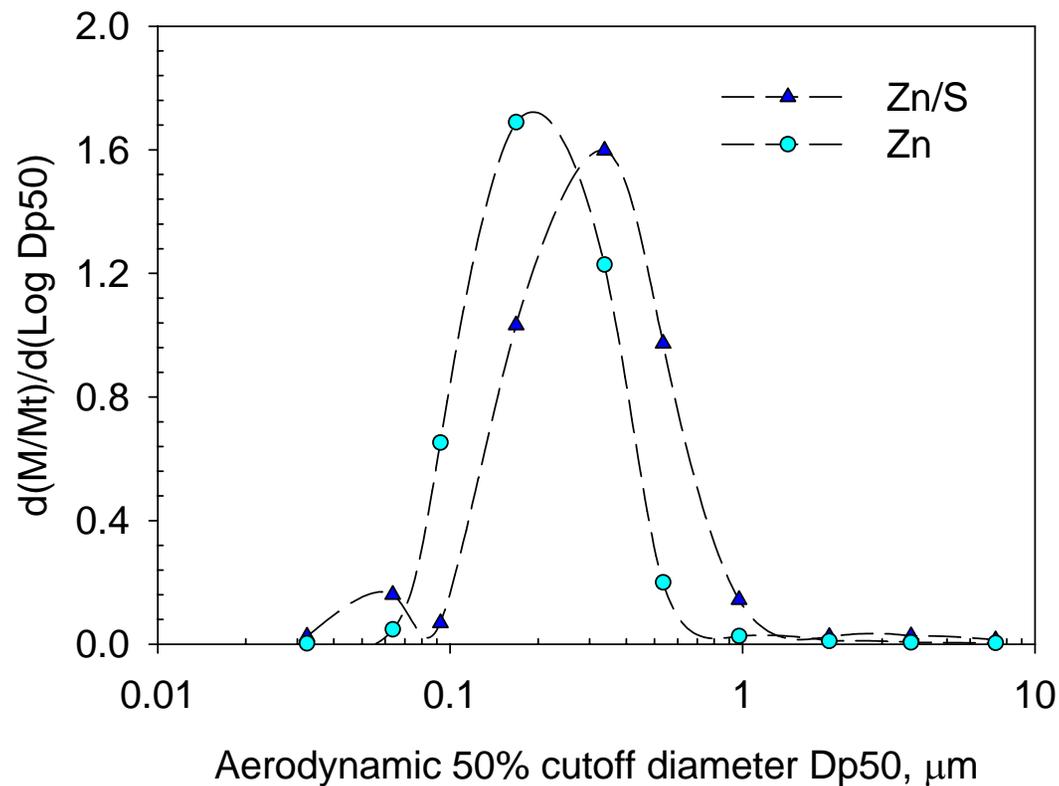
Fuel oil (low concs.) versus aqueous salt solution (high concs):



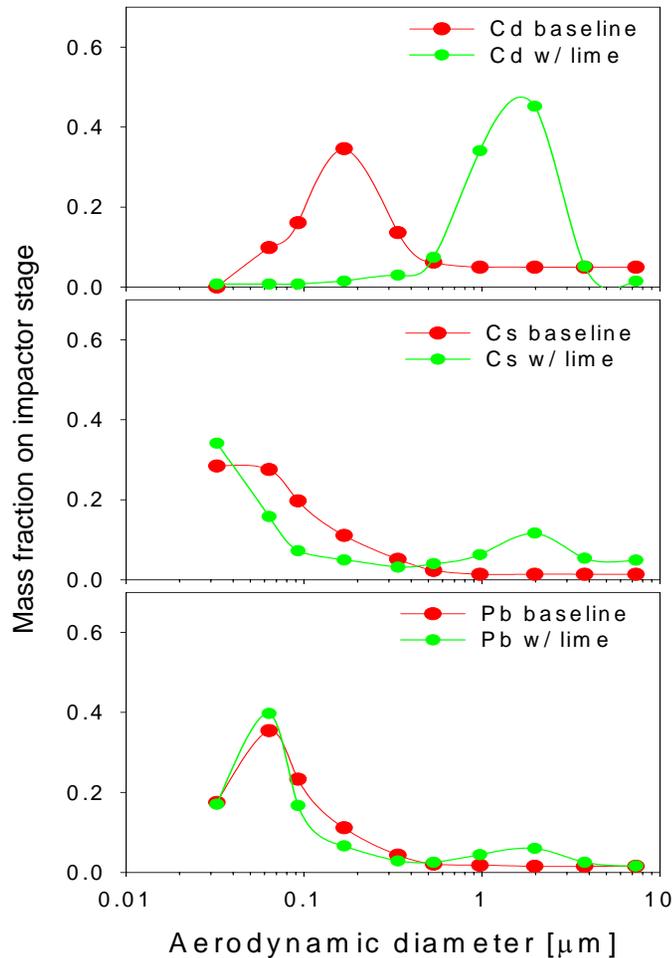
Chromium speciation in high temperature systems: PSD from aqueous/Cr systems and Cr(VI)/Cr(Total) partitioning



Semi-volatile metal, Zn, sampled in exhaust after some coagulation in furnace.



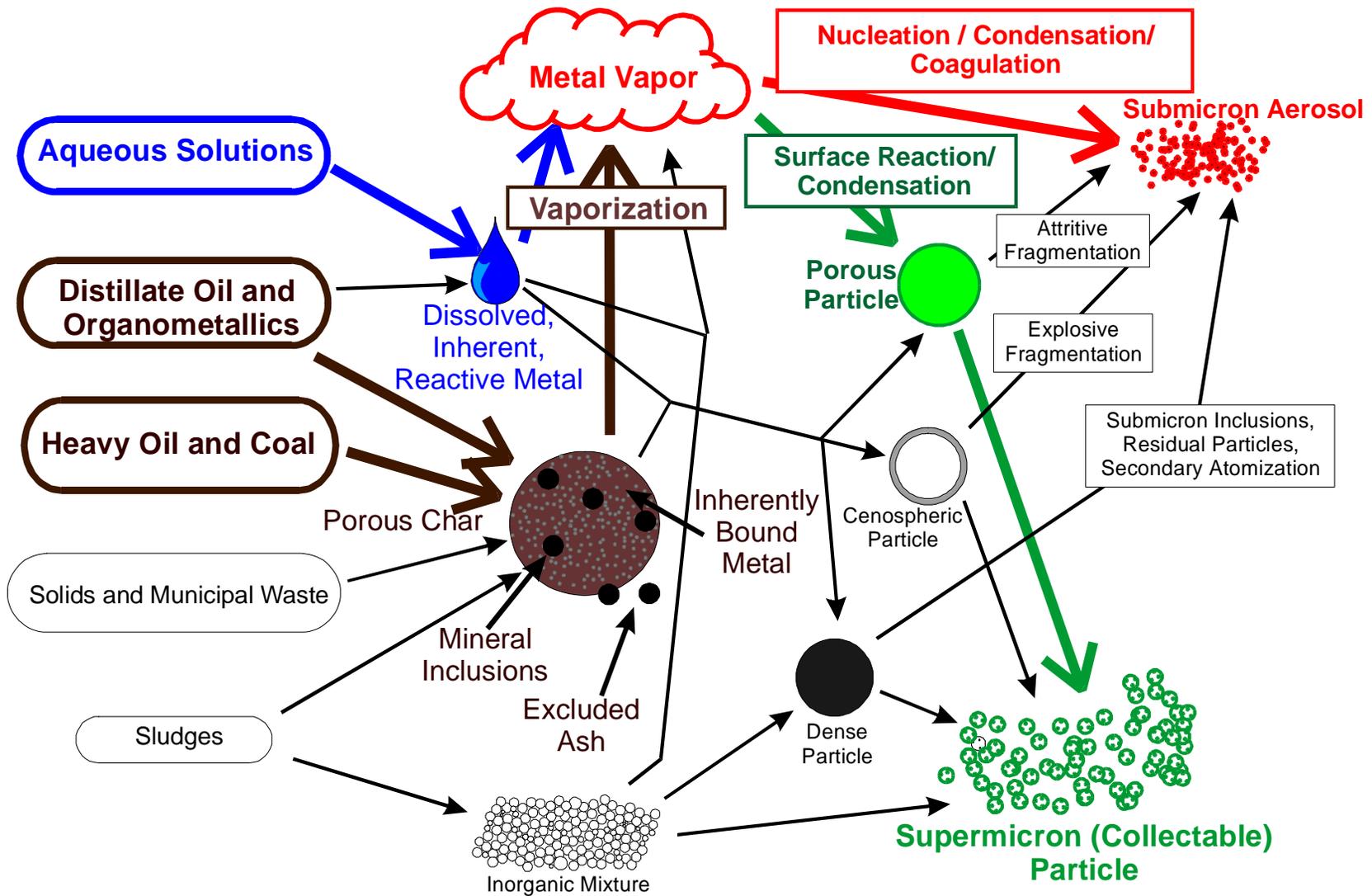
Semi-volatile metals, Cd, Cs, and Pb, with and without lime added downstream



- Without lime, PSD in exhaust determined by nucleation temperature and coagulation time prior to sampling.
- With lime, Cd tracks lime sorbent PSD. Cd is sequestered.
- With lime, Cs and Pb PSD's are unaffected. Cs and Pb are NOT sequestered.



Sequestration mechanisms



Sorbents to capture semi-volatile (and some volatile) metals

Sorbent	Kaolinite [Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O]	Calcium Hydroxide [Ca(OH) ₂]	Calcium Carbonate [CaCO ₃]	Major Impurities
Kaolinite	97%			1-2% TiO ₂
Hydrated Lime		99%		0.2 FeO 0.3 Al ₂ O ₃
PWDS	45%	1% (22% CaO)	33%	0.1 TiO ₂

PWDS= Paper Waste Derived Sorbent. It is made from paper waste recycling sludge

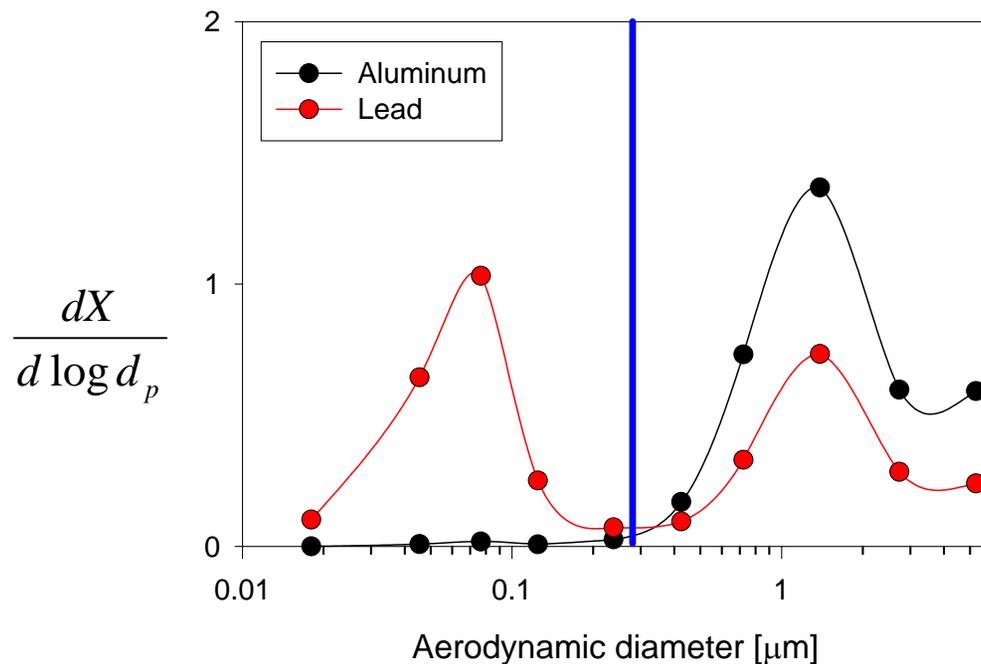


Semi-volatile metals suitable for sequestration by sorbents dispersed into the post-flame region

- Zinc on kaolinite
- Sodium on kaolinite
- Lead on kaolinite, hydrated lime and PWDS
- Cadmium on kaolinite, alumina, hydrated lime, and PWDS
- Arsenic on calcium and iron
- Selenium on calcium and iron

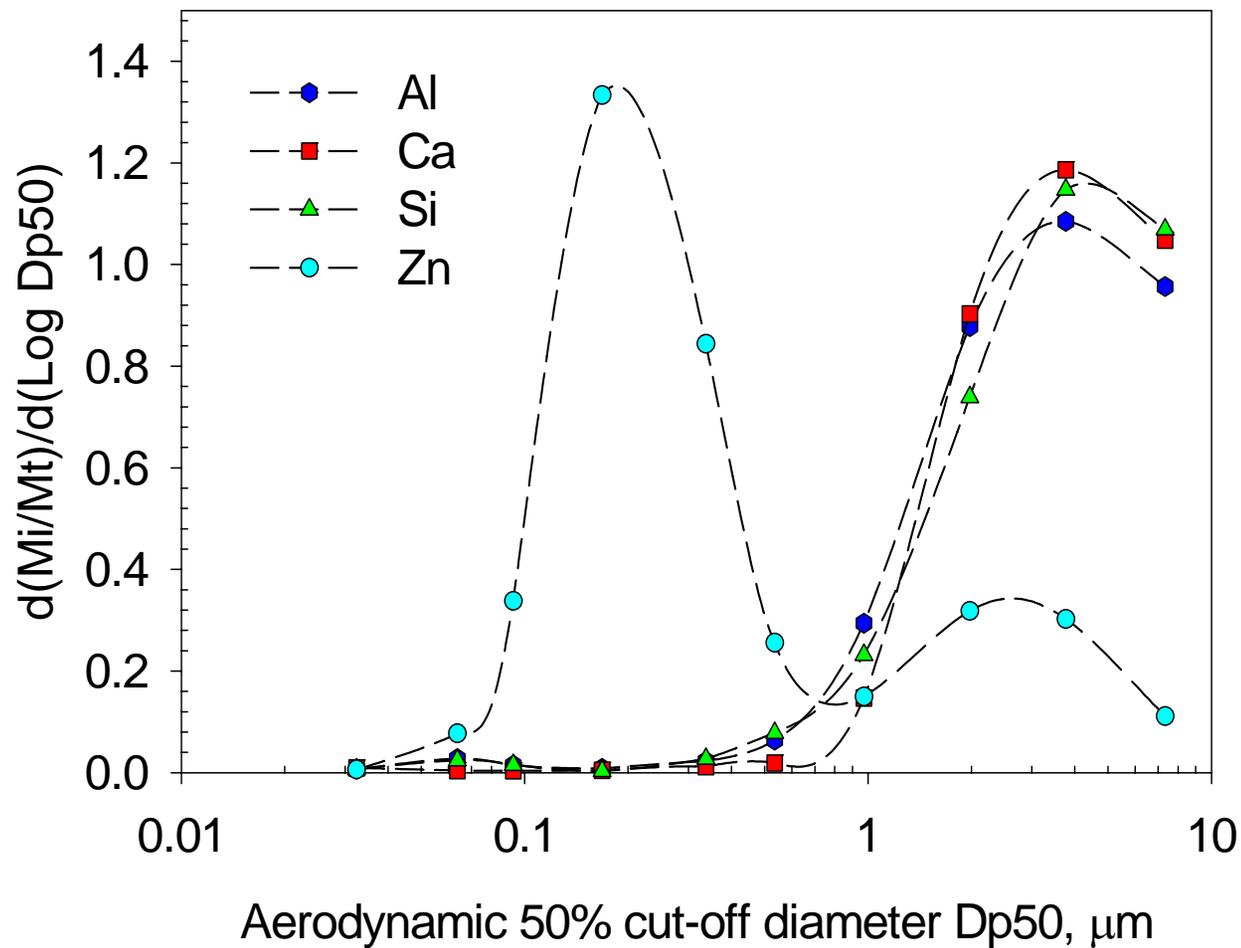


Aerosol size fractionation to measure reacted or adsorbed lead

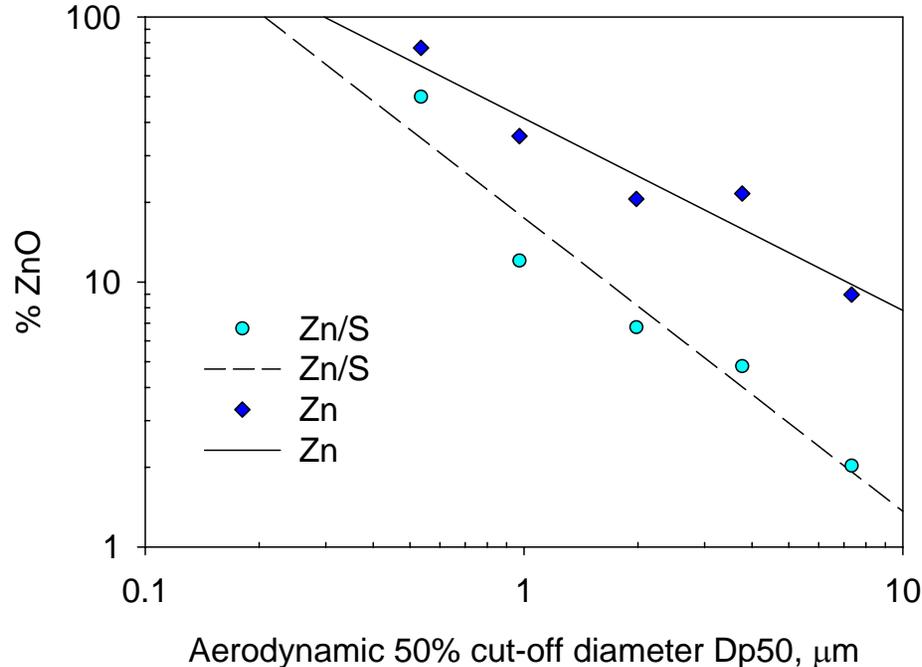


- Crude analogy to chromatographic techniques
- Total area under curve represents normalized mass of lead or aluminum
- Fraction of lead captured by sorbent is area under curve to the right of line.

Elemental size segregated compositions with sorbent

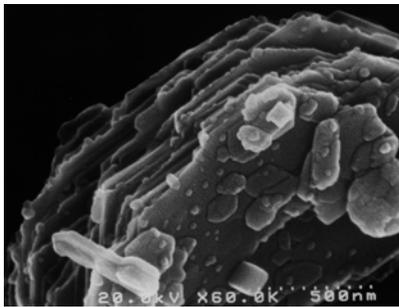


Composition/particle size dependence for large particles containing sequestered Zn after sorbent injection.

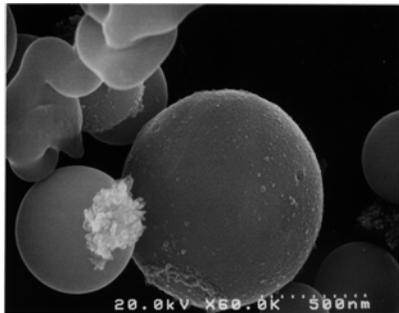


- No sulfur:
 - $\text{Wt\% Zn} \sim d_p^{-0.88}$
- With sulfur
 - $\text{Wt\% Zn} \sim d_p^{-1.1}$
- $d_p^{-1.0}$ dependence indicates external surface reaction, or pore diffusion control, not film diffusion controlled condensation
- Sorption of Zn is reactive sorption

Mechanisms Governing the High Temperature Scavenging of Alkali and Trace Metals in Combustion Flue Gases



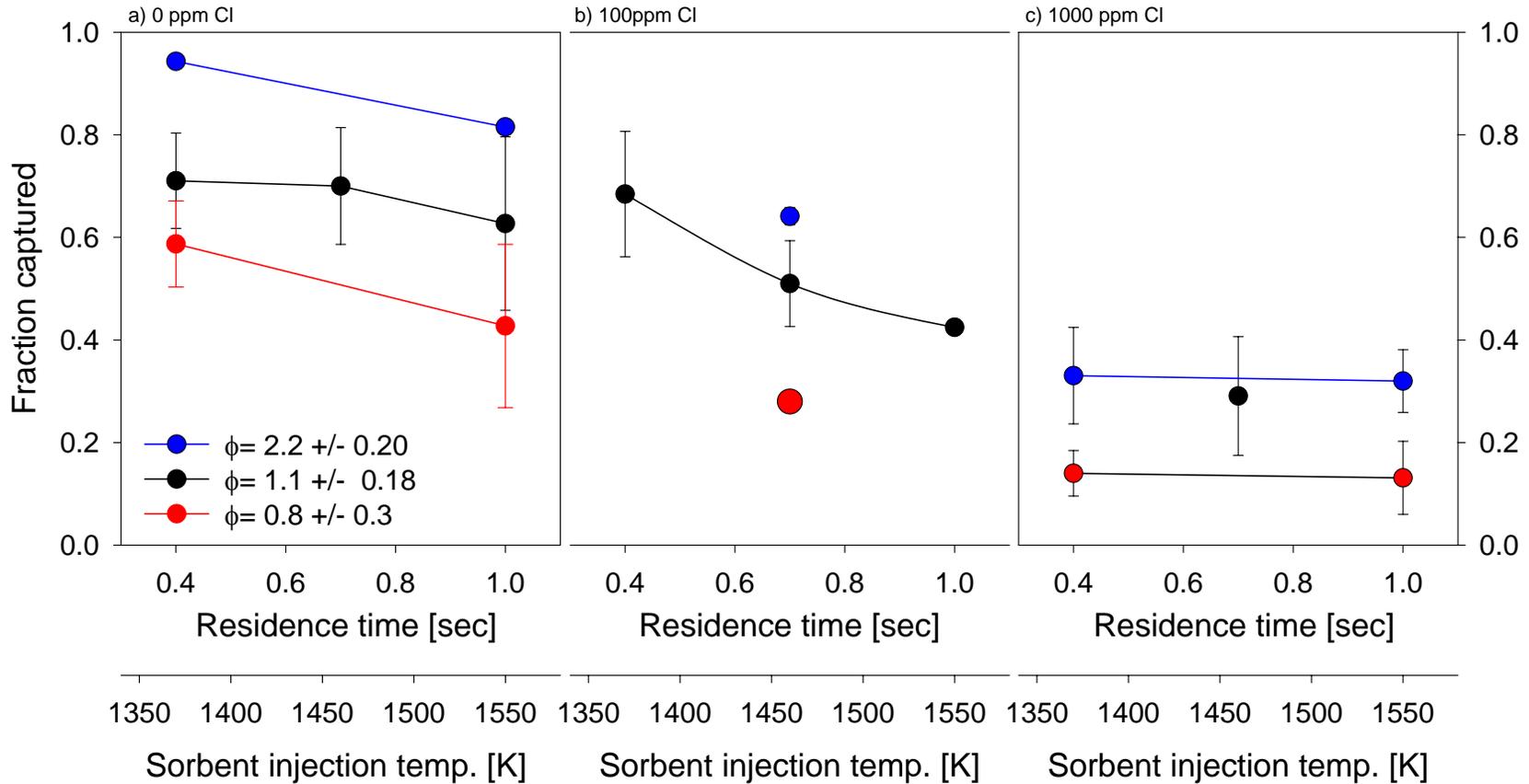
Kaolinite after injection at 1530K



Kaolinite reacted with lead at 1530K
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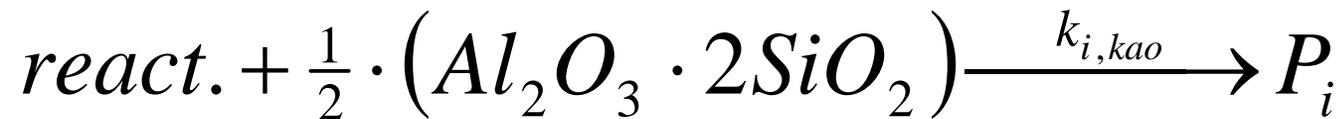
- Quantified high temperature mechanisms of interaction between **dispersed kaolinite** and **sodium, lead**, and **cadmium vapor** in combustion flue gases.
- Temperature range $1600\text{K} < T < 1350\text{K}$
- Global mechanism only - includes surface reaction and substrate de-activation steps.
- Sodium + kaolinite and lead + kaolinite mechanism very similar. Na surface reaction faster, deactivation step identical.
- Cadmium + kaolinite surface reaction slowest of all, but little deactivation within temperature range above.

Lead/kaolinite kinetics: Summary of experimental results



Global mechanism for Na, Pb, and Cd sorption on kaolinite

For Na and Pb, the sorption step:



is followed by de-activation step:



For Cd, there is only the sorption step, no de-activation.



Global kinetics: Na, Pb, and Cd sorption

A_i , E_i sorption, A_D , E_D de-activation step

Rate coefficients for Na, Pb and Cd reaction with dispersed kaolinite $1350 \text{ K} < T < 1600 \text{ K}$, according to global reaction mechanism, reactions (1), (2),(3),(4) and (8)

	A_i	E_i	A_D	E_D	α
	cc/mol.s	J/mol	cc/mol.s	J/mol	
sodium	3.72E9	0.0	7.93E13	1.1E5	0.9
lead	2.95E9	0.0	7.93E13	1.1E5	1.0
cadmium	3.11E26	4.8E5	NA	NA	NA

$$\text{MARCH } k_i = A_i \exp\{-E_i / RT\}$$



What is “health effects engineering”?

- Seeks to establish a connection between the particle generation process and the health effects of the by-products generated.
- Requires collaboration between engineers and toxicologists.
- Has special application to particulate releases, where intent is to modify combustion process in order to change emissions such that potential for human injury is minimized.
- Investigates effects on mouse model through changes in inhaled particle composition, speciation, and surface properties.



Motivation: Fine particles

- Acute lung and cardiovascular injury due to particles in the air.
 - Solubility?
 - Surface free radicals?
- Can we be specific about the inhalation health risk?
 - What fine particles are the problem?
 - Ultrafines (less than $0.1 \mu\text{m}$)? Acid? Transition metals? Primary? Or Secondary?
- Can we modify the chemistry inside the pertinent process to manage the health risk?
 - Change reactant composition.
 - Add sorbents for- zinc, lead, cadmium, arsenic, selenium sorption.
 - Modify stable free radicals on soot (or inorganic?) aerosols.



Health Effects: The search for “bad actors” in combustion generated particulates

- Health effects screening studies
 - *In-Vivo, mouse model, measure lung permeability, bronchial alveolar lavage fluid (BALF) cell count*
 - Ash from biomass/coal mixtures.
 - Coal ash particles.
 - Ash from laboratory combustor tests.
 - *In-Vitro, Type II epithelial lung cells*
 - Effects on cell growth
 - Effects on cell metabolism
 - Other biomarkers

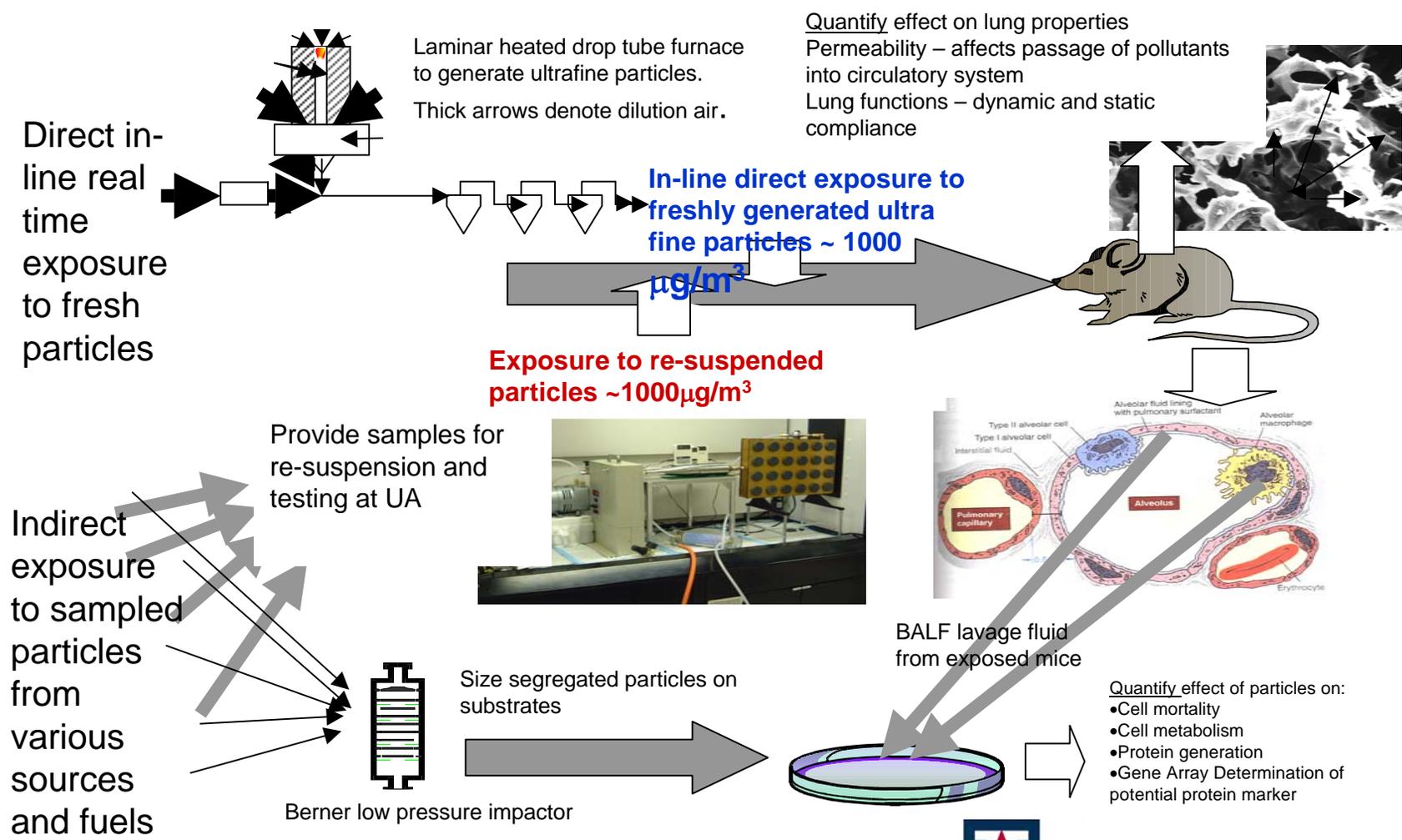


Engineering issues

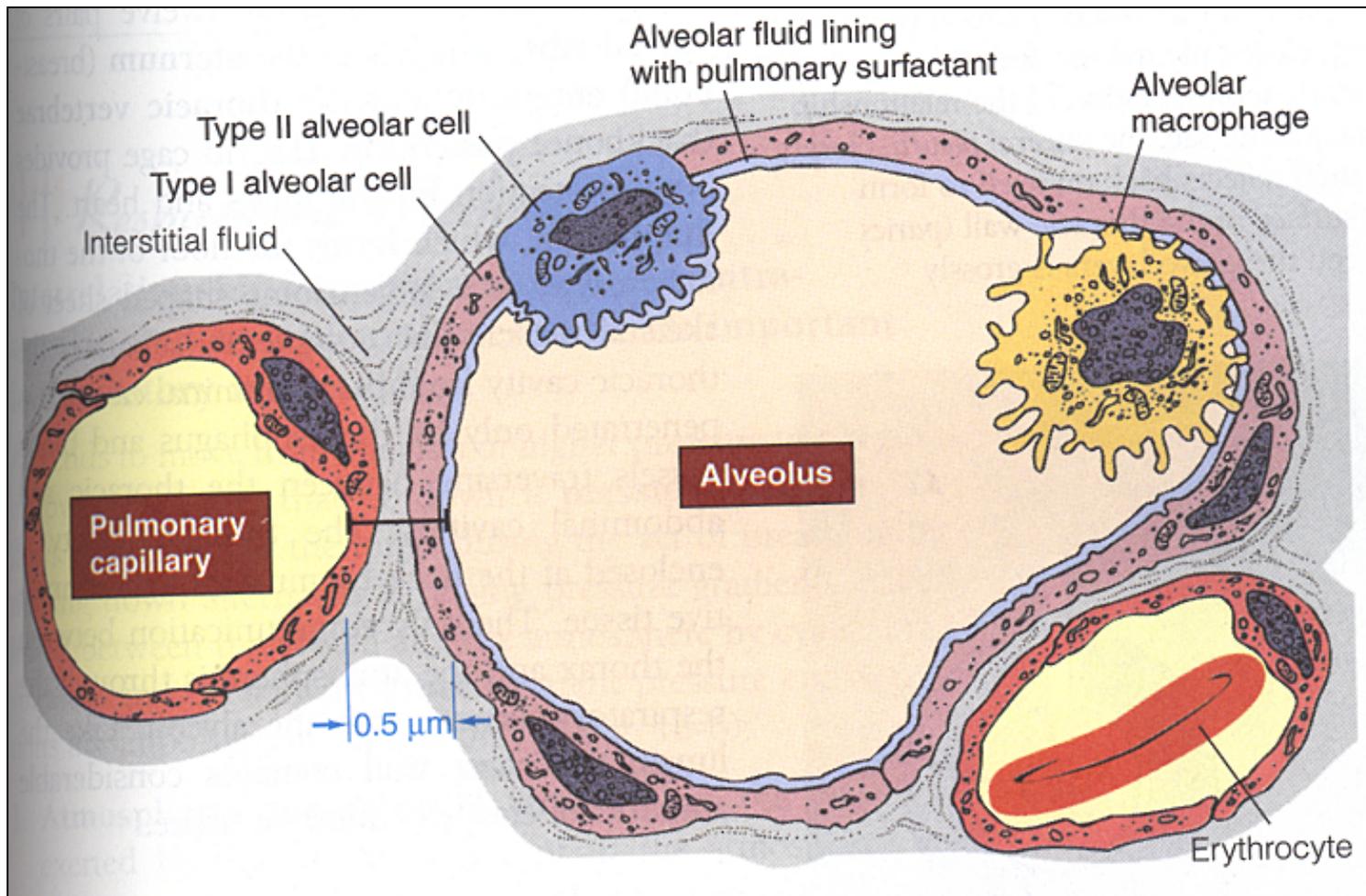
- *In-Vivo* whole animal test
 - with **particle inhalation**, requires
 - resuspension of collected particles (large amounts)
 - difficult for ultrafine particles $\sim 0.1 \mu\text{m}$ in diameter
 - alternative, real time, in line exposure system from combustor, through plume and atmospheric simulator
 - or uses **particle instillation** (direct placement into lungs)
 - good for all particles that can be suspended in a saline solution
 - does not mimic actual exposure route
 - can be used to measure effects on whole lung properties
 - permeability (an increase denotes incipient lung damage)
 - compliance (flexibility, ability to breathe)
 - can be used to measure effects on other bodily organs
 - body weight
 - heart etc
 - or measures bio-indicators in cells washed out from lungs (Bronchial Alveolar Lavage Fluid)



Health effects engineering research



Detail of alveolus space of the lung where fine particle effects are likely to be found



Particle re-suspension, dilution and exposure system



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Mouse chambers with mice inside showing nose exposure configuration



Mouse exposure procedure

- 8 mice (pathogen free, C57BL/6)
 - Exposure
 - 1 day
 - 3 days
 - 12 days
 - 24 days
 - 1 exposure per day
 - 1 hour per exposure
 - 2 day recovery
- Coal plus MSS,
 - 1000 $\mu\text{g}/\text{m}^3$
 - 3000 $\mu\text{g}/\text{m}^3$
 - Coal ash alone,
 - 1000 $\mu\text{g}/\text{m}^3$
 - MSS ash alone,
 - 1000 $\mu\text{g}/\text{m}^3$
 - Ash from oil doped with organic zinc (100ppm Zn in flue)
 - 1000 $\mu\text{g}/\text{m}^3$
 - Ash from oil doped with organic zinc and thiophene (100ppm Zn and S, in flue)
 - 1000 $\mu\text{g}/\text{m}^3$
 - Sequestered zinc
 - 1000 $\mu\text{g}/\text{m}^3$

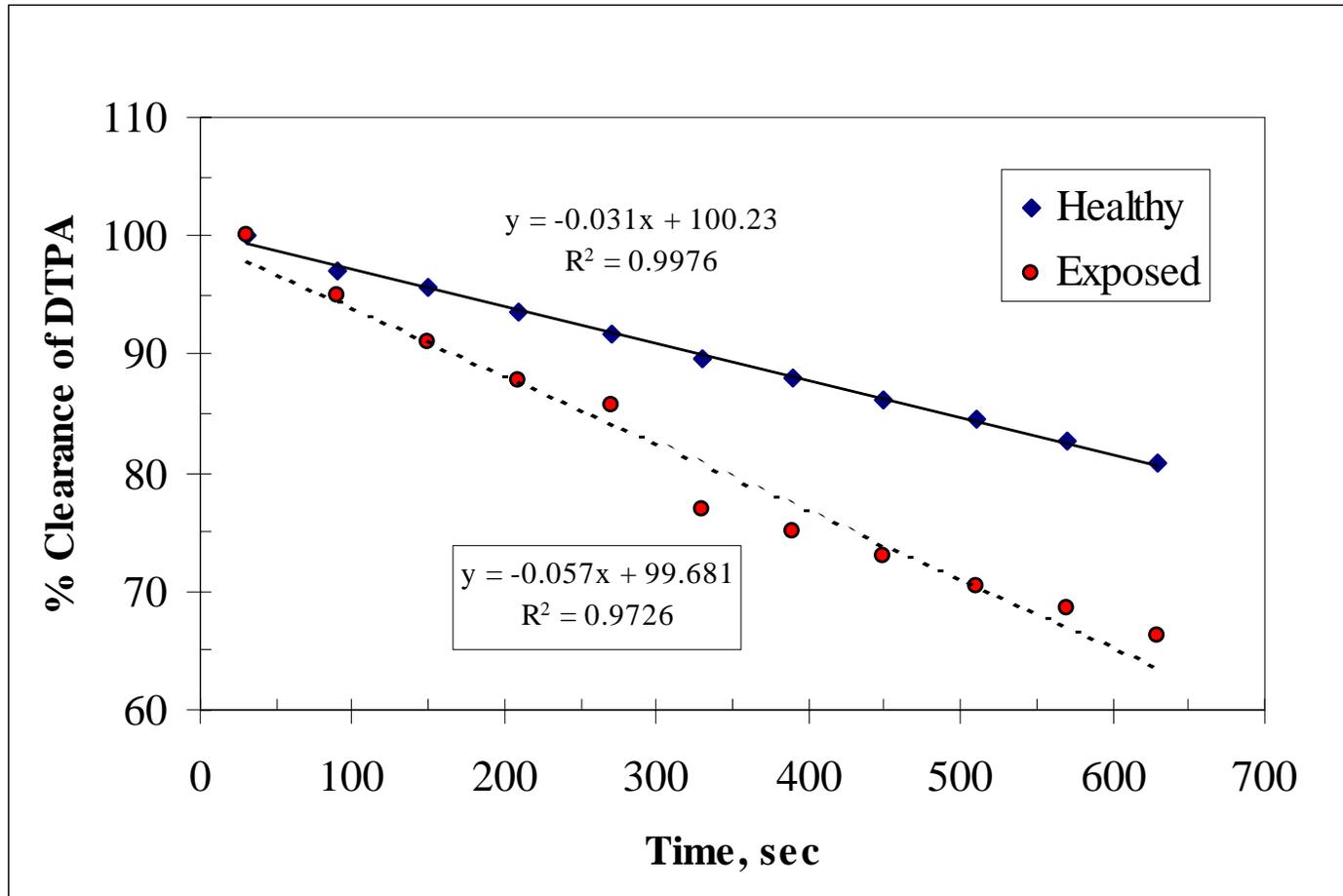


Lung permeability

- Quantified through *in-vivo* measurements of the rate at which a radioactive tracer is expelled from the lungs.
- Increased permeability is an established quantitative measure for incipient lung damage.
- Also a marker that is related to ease of passage of particles and/or other impurities into the blood stream and thus into the cardio-vascular system.
- However, although *increased* permeability is bad, *decreased* permeability may not be totally benign – due to inflammation for example.



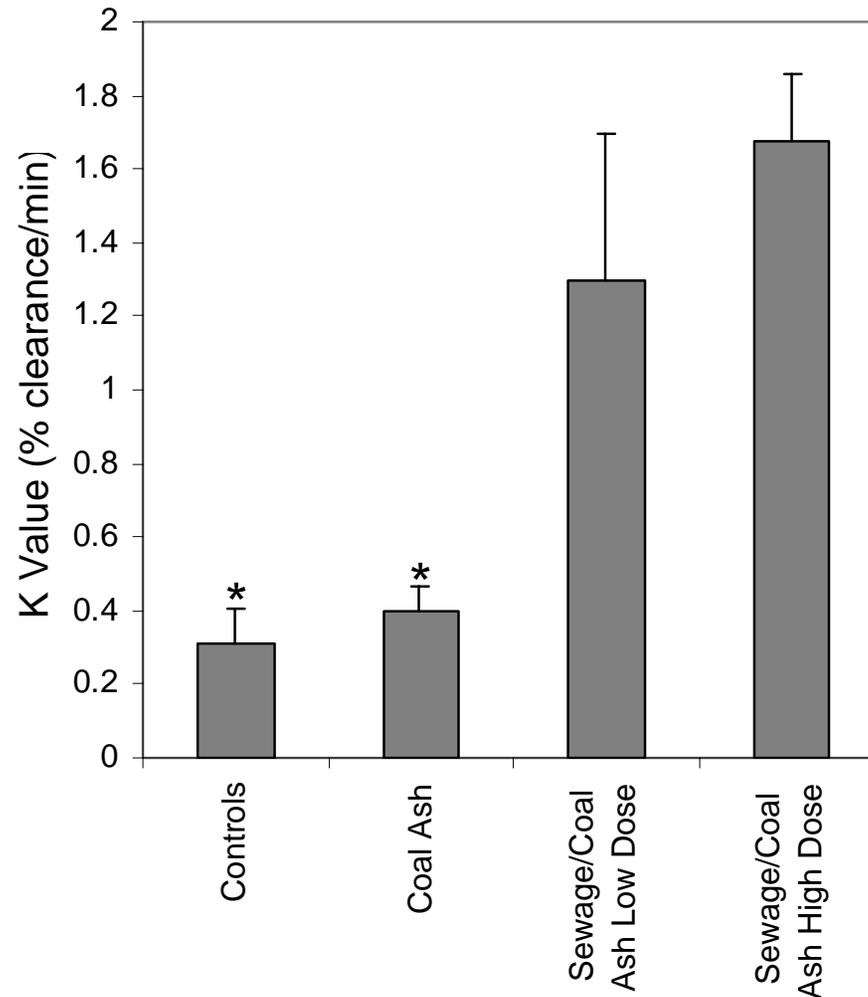
Lung permeability data for single mouse, exposed to re-suspended ash aerosol from RDF/German coal combustion, compared to those for a healthy mouse. Results reported as rate of clearance of DTPA from the lung, %/min (slope)



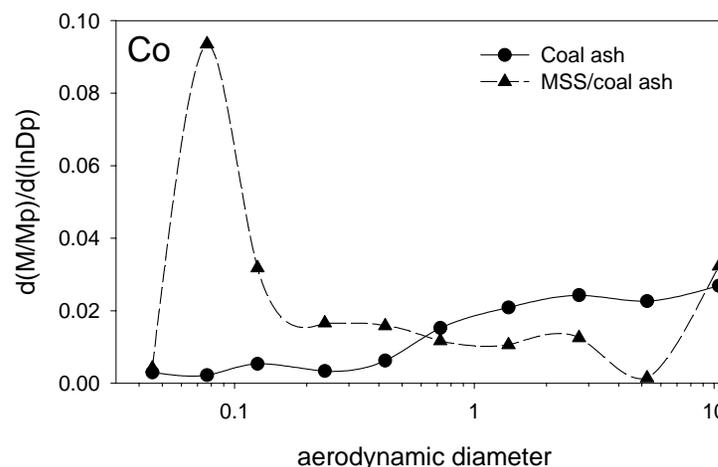
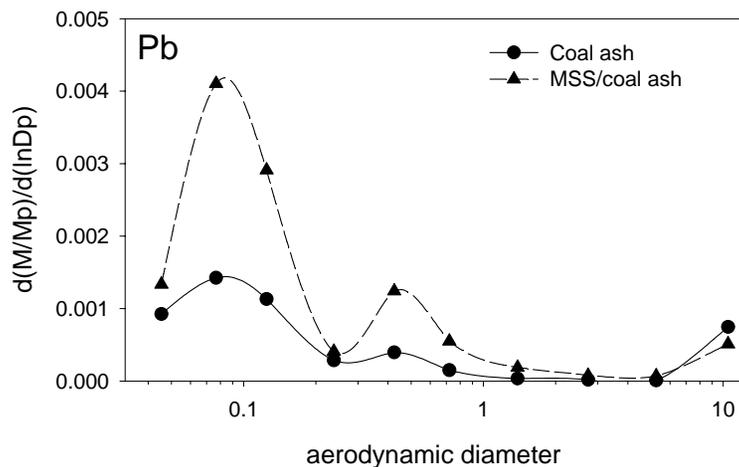
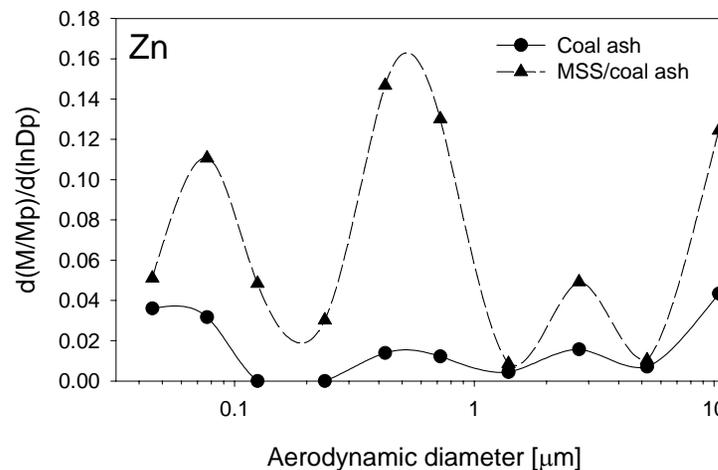
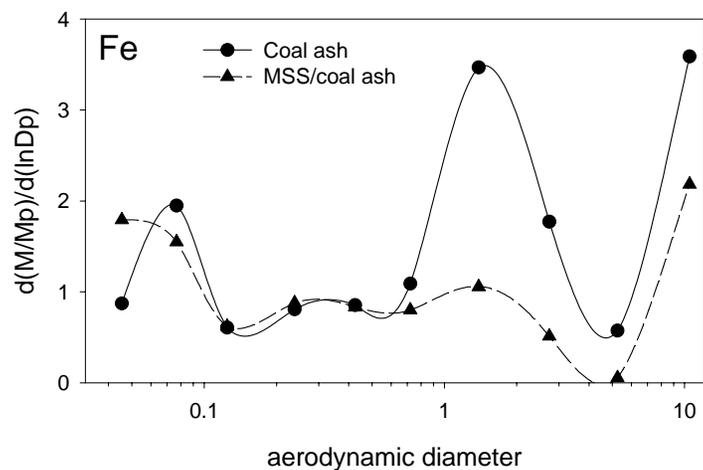
MSS/coal co-combustion: inhaled ash causes lung damage in mice.

See: Fernandez,A., Davis,S.B., Wendt,J.O.L., Cenni,R., Young, R.S., and Witten,M.L. "Particulate emission from biomass combustion", *Nature*, 409, 998-999 (2001)

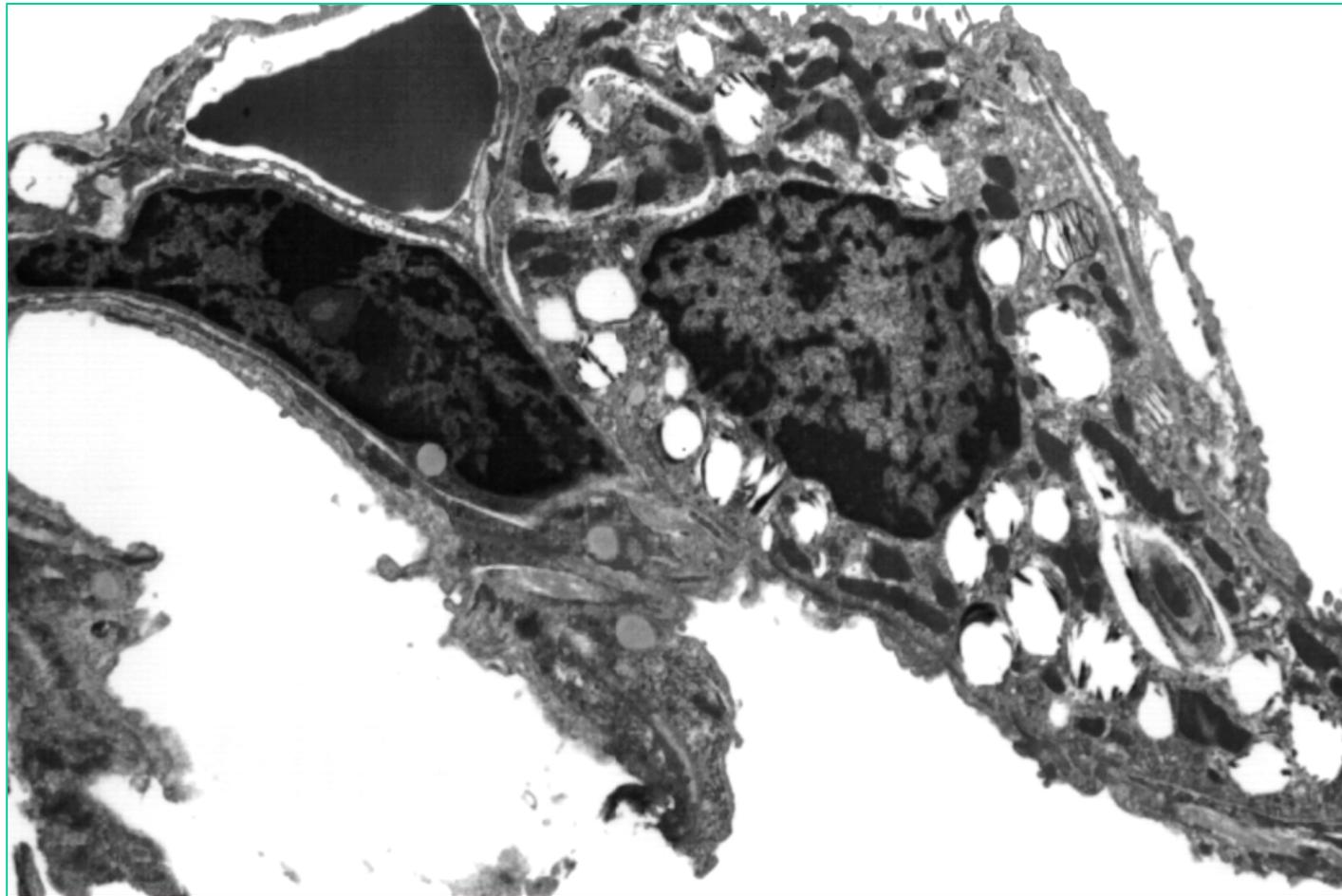
Increased permeability defines "Type 2" behavior.



MSS/coal co-combustion ash vs coal ash elemental psd's



MSS/coal co-combustion: inhaled ash: TEM of mouse lung exposed to ash aerosol, showing damaged cell.

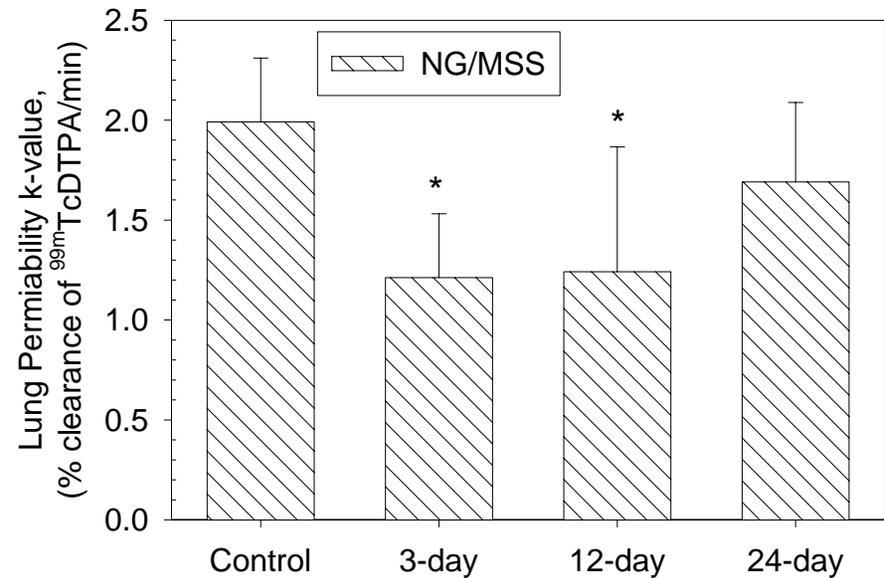
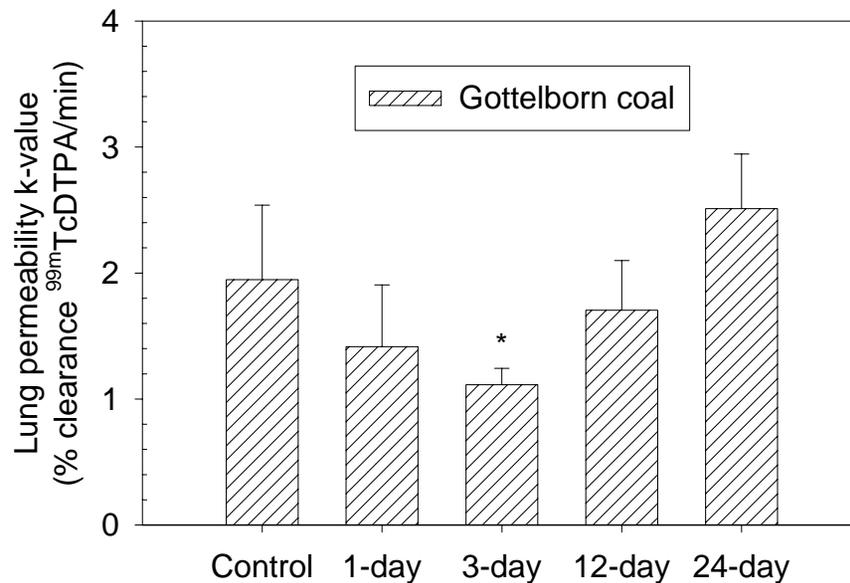


Interim conclusions from *in-vivo* tests on MSS/coal co-combustion ash

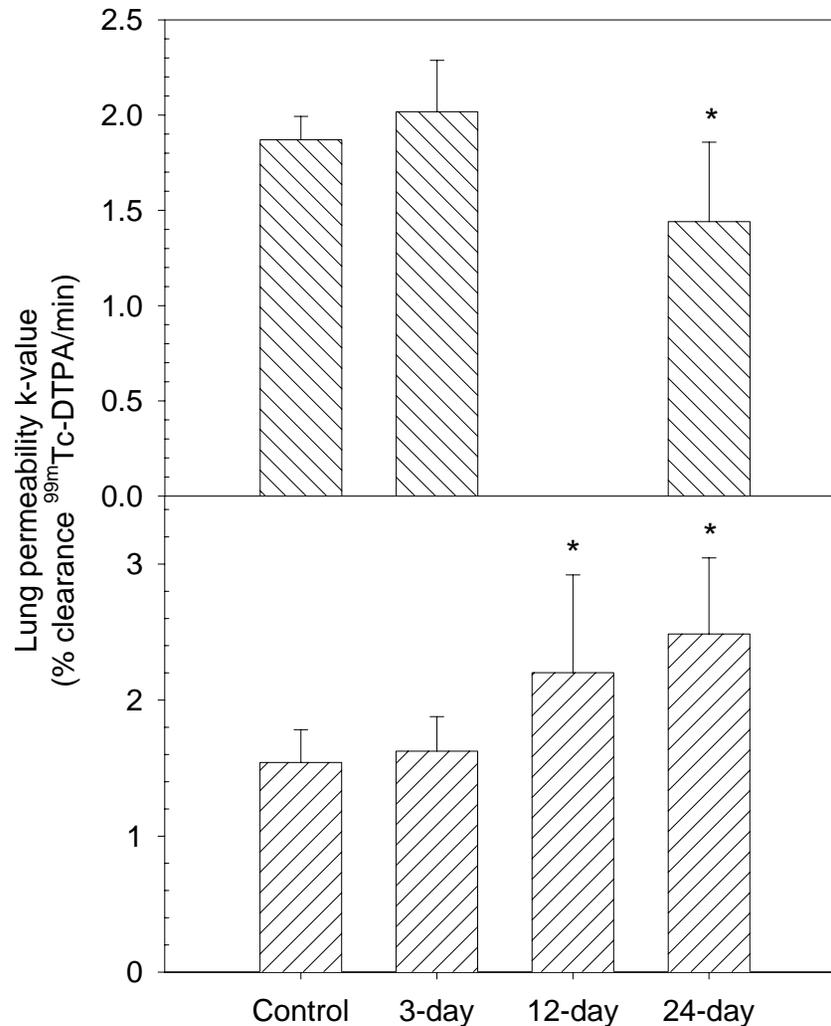
- Collaborative research between engineers and toxicologists has led to useful practical results.
- *In vivo* tests show unique results unobtainable through *in vitro* tests.
- Zinc in combustion generated particles is an important contributor to lung injury, i.e. a “bad actor”, based on size segregated composition data of coal ash, and coal+MSS ash.
- Coal/sewage sludge ash increases lung permeability (and also decreases macrophage cell count- not shown here).
- Coal ash (without MSS) appears to be relatively benign from permeability point of view.
- Switching to some CO₂ neutral bio-fuels might entail additional unforeseen inhalation health risks.



Now consider lung injury from re-suspended ash from coal alone and MSS alone (with gas assist):
Temporal permeability changes thru cell inflammation and repair. “Type 1 with recovery” behavior for both fuels.



Doped distillate oil ash: lung permeabilities for ZnO aerosol (upper) and ZnSO₄ aerosol (lower) for various exposure periods (1 hour per day, ~ 1000μg/m³).



ZnO
No sulfur present
Type 1 behavior

ZnSO₄
With sulfur
Type 2 behavior



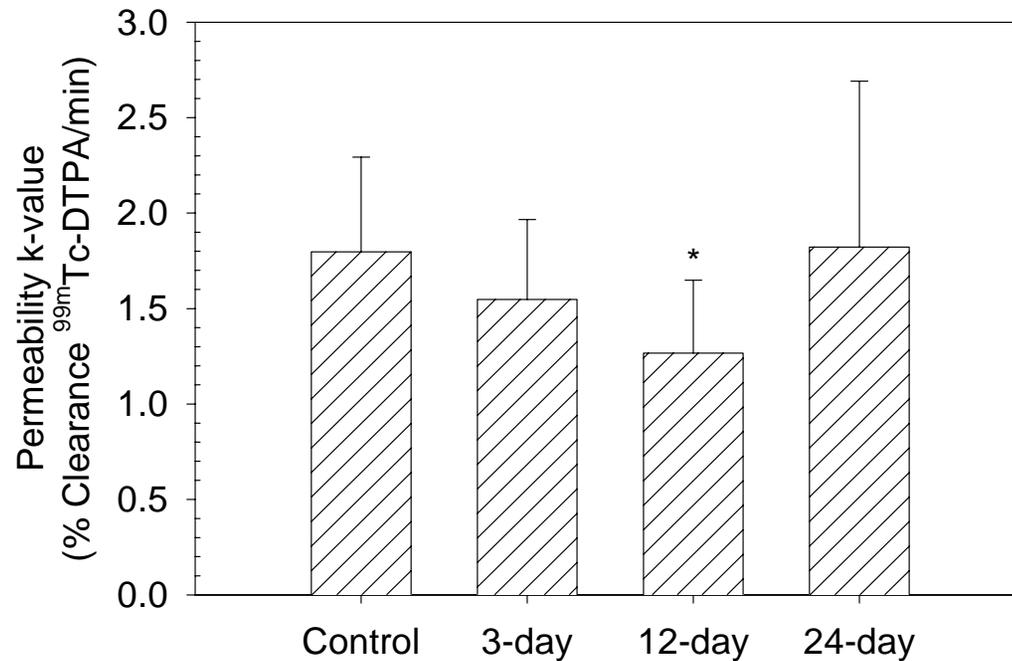
Health effects engineering: the effects of fuel composition.

MSS and coal combustion conclusions

- Co-combustion of MSS and coal leads to greatest lung injury from inhaled particles, namely a permanent increase in lung permeability (Type 2 behavior).
- Coal ash alone, and MSS ash alone have similar effects on lung permeability, namely an initial decrease followed by a recovery (Type 1 behavior).
- ZnO particles exhibit Type 1 behavior.
- Sulfated Zn particles exhibit Type 2 behavior, like coal+MSS
- Therefore co-combustion of MSS with coal is bad because MSS supplies the Zn while coal supplies the S, and the combination results in the most toxic fly ash.



Health effects engineering using kaolinite sorbent powder addition: Lung permeabilities from particles containing sequestered Zn (Type 1, benign, behavior, decrease in permeability followed by recovery)



Organic particles: Another potential application of Health Effects Engineering

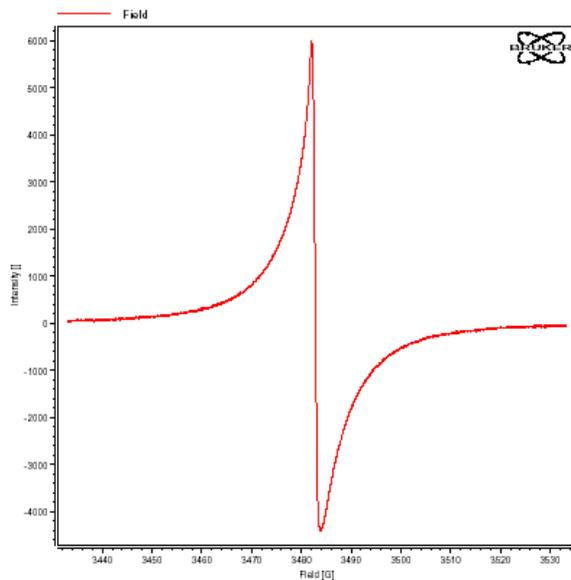
-Stable free radicals on soot and other particle surfaces

- Stable free radicals have been discovered on atmospheric particles sampled in Singapore (Private communication from Professor Liya Yu, National University of Singapore, with permission)
- Free radicals in general have been identified as promoters of cell mutations
- Can particles function as carriers of free radicals into the blood stream, and hence cause distress?
- Free radicals are stable within coal and synthetic fuel molecules (Petrakis and Grandy, 1983).
- Formation conditions should affect the stability of free radicals on soot aerosol particles.
- Issue: Can combustion treatment of diesel exhaust particles diminish their adverse health effects?

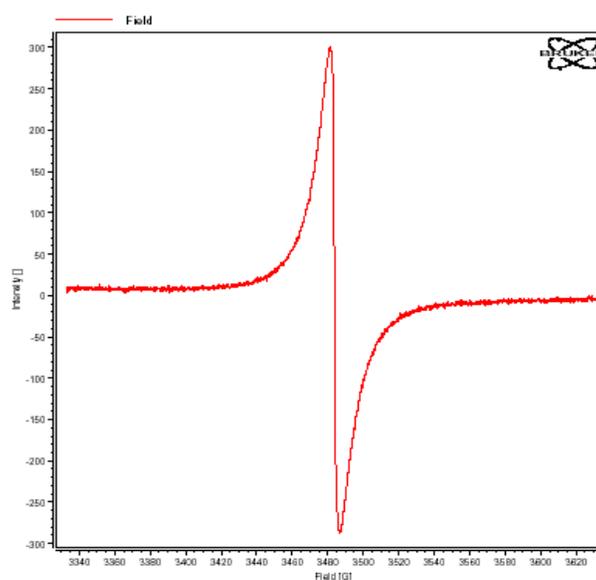


Electron Paramagnetic Resonance data on sampled soot particles: Free radicals are stable on aged soot particles

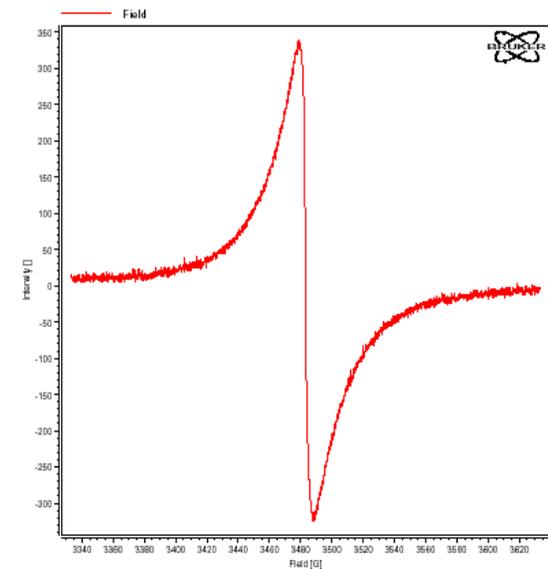
(Preliminary data reported August 31, 2003: by Nikolai Kocherginsky, Iouri Kostetski, and Liya Yu, Division of Bioengineering, and Dept. of Chemical and Environmental Engineering, National University of Singapore)



- Scraped off cold walls after dilution
 - Japanese soot
 - High extractable organics
 - 2.38×10^{19} spins/g
- MARCH 31, 2005



- German soot
- 1.54×10^{20} spins/g



- US (NIST standard) soot
- Hot filtered sample
- Low extractable organics
- 2.25×10^{20} spins/g



Conclusions

- Both elemental composition and speciation of ultra-fine particles are very important in determining their inhalation health effects.
- Relationships between engineering aspects and health effects are complicated and needs collaboration between health effects scientists and physical scientists/engineers.
- Health Effects Engineering results from this observation, and can be used :
 1. to identify effects of reactants and operating conditions on health effects of particles produced.
 2. To devise process modifications to diminish potentially bad health effects.
 1. Sequestration (high temperature) of semi-volatile metals such as Zn, Pb, Cd, Na on metals
 2. Elimination of free radicals stabilized on particles



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- Mark R. Riley, Ph.D., College of Agric. & Life Sciences
- Professor Dr-Ing Klaus H.G. Hein, IVD, Universitat Stuttgart, and his team: Dr Roberta Cenni, Natascha Wolski and Wolfgang Sheurer
- William P. Linak, Ph.D., U.S. EPA, NRMRL, NC
- Sheldon B. Davis, Ph.D., ChEE, UA
- R. Scott Young, Lung Injury Lab, Dept Pediatrics, UA
- Juanita D. Hyde, Lung Injury Lab, Dept. Pediatrics, AHSC
- Steven A. Rowland, Lung Injury Lab, Dept Pediatrics, AHSC
- Tom Gale, Ph.D., ChEE, UA
- Ellen Kitchen, Jamshid Sorooshian, John Logan, Chris Hammond -all undergraduate students at the ChEE Dept., University of Arizona

