

Computational Modeling of Mercury Capture by Activated Carbon Injection

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Mercury Emissions from Coal-Fired Utilities

The Need for Emission Control

The New York Times
nytimes.com

February 10, 2004

E.P.A. Raises Estimate of Babies Affected by Mercury Exposure

WASHINGTON, Feb. 9 — *More than one child in six born in the United States could be at risk for developmental disorders because of mercury exposure in the mother's womb, according to revised estimates released last week by Environmental Protection Agency scientists.*

- **Coal-fired utilities ...**
 - contribute **one-third** of the man-made mercury emissions in the U.S (Source: EPA)
 - are the **single-largest** source of man-made emissions (~50 tons Hg annually)
 - Man-made mercury emissions outweigh natural ones by 2:1 (Source: UNEP)
 - **Impending regulations by the EPA**
 - MACT or market-based regulatory approach?
 - Fast or slow track?



Mercury Capture by Sorbent Injection

Computational Modeling – potential benefits

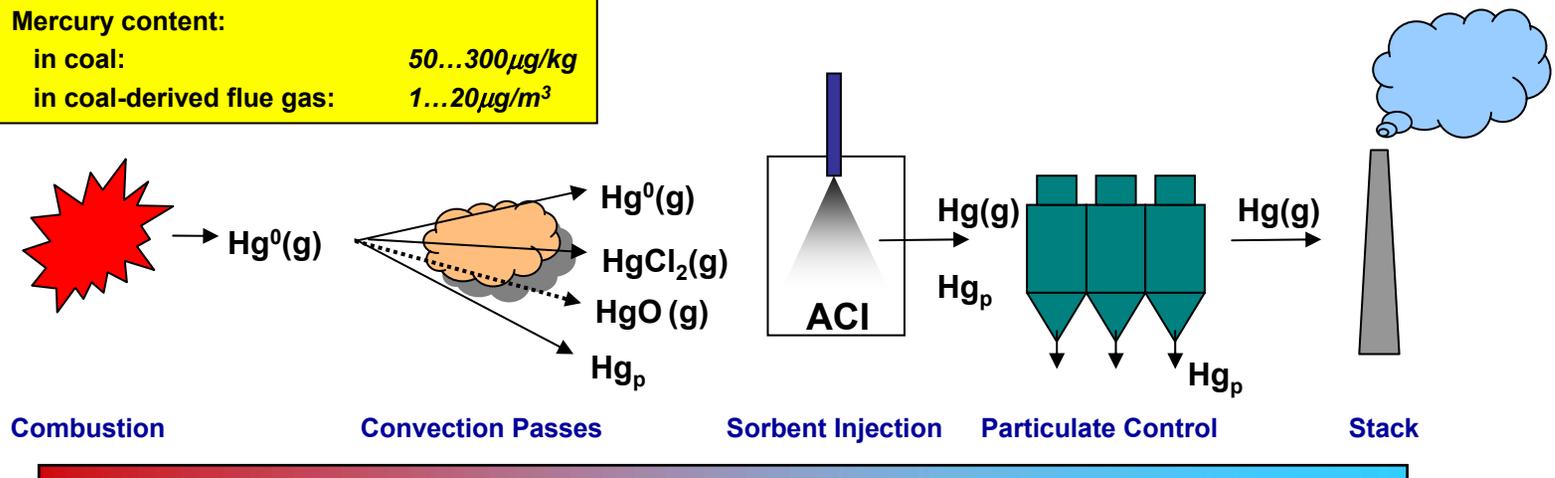
Develop a CFD-based tool that can be used to simulate and improve the understanding of sorbent-based mercury control processes

Computational Modeling ...

- provide **detailed information** on
 - Flue gas flow (local conditions)
 - Sorbent dispersion in the flue gas duct
 - Where the capture takes place
- answer **practical questions** on
 - Improved understanding of mass transfer limitations (at duct- and particle-scale)
 - Prediction of necessary sorbent feed rates
 - Optimize injection methods

Mercury content:

in coal: 50...300 $\mu\text{g}/\text{kg}$
in coal-derived flue gas: 1...20 $\mu\text{g}/\text{m}^3$

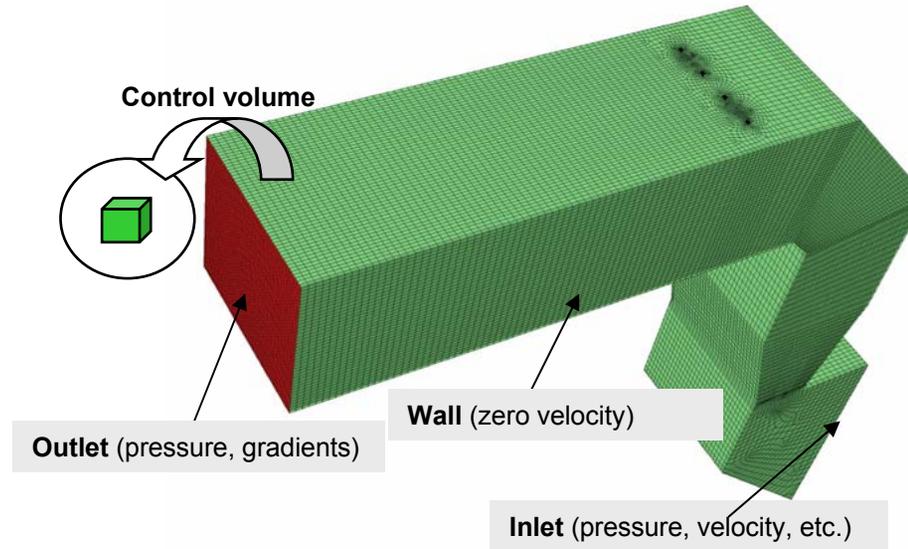


Computational Fluid Dynamics (CFD)

How does it work?

- CFD process entails

- Discretization** of fluid region into a finite set of control volumes (mesh)
- Solution of general **transport equations**
 - Conservation of mass, momentum, energy, species, etc.
- Conservation obtained via **integration** of transport equations over control volumes
- Application of proper **boundary conditions**



$$\underbrace{\frac{\partial}{\partial t} \int_V \rho \phi dV}_{\text{Unsteady}} + \underbrace{\oint_A \rho \phi \mathbf{V} \cdot d\mathbf{A}}_{\text{Convection}} = \underbrace{\oint_A \Gamma \nabla \phi \cdot d\mathbf{A}}_{\text{Diffusion}} + \underbrace{\int_V S_\phi dV}_{\text{Generation}}$$

Equation	ϕ
continuity	1
x-mom.	u
y-mom.	v
z-mom.	w
energy	h

Mercury Capture Modeling Overview

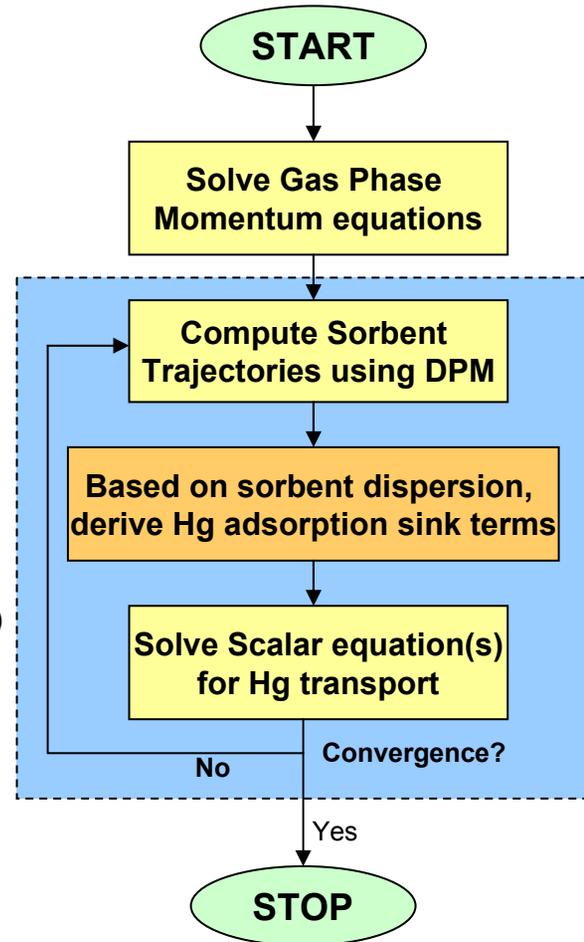
- Simulation of mercury capture as a **post-processing** step (trace amounts)

- Mercury transport** equation(s) solved in ductwork
 - Convection-diffusion type equation(s) (scalar PDE)
 - Determines distribution of gas-phase mercury in duct
 - Flue gas flow distribution known (velocity, pressure, temp.)

$$\frac{\partial}{\partial x_i} \left[\rho u_i c_g - \frac{\mu_t}{Sc_t} \frac{\partial c_g}{\partial x_i} \right] = S_{Hg}$$

sink term

- Lagrangian tracking** of sorbent particles
 - Trajectories found by integrating particle **force balances**
 - Mercury sink terms updated during tracking
 - Particle sub-model → internal mercury concentration profile $C_p(r)$
 - Also keeps track of sorbent usage $(\omega/\omega_{max})(r)$
- Iterative procedure** (tracking / Hg transport)
 - Intraparticle transport and adsorption driven by concentration gradients
 - Trajectories do not change due to mass addition
 - It takes approx. 1/2 lb carbon to remove 1 gram of mercury !



Modeling Approach

Mass Transport and Adsorption inside Particle

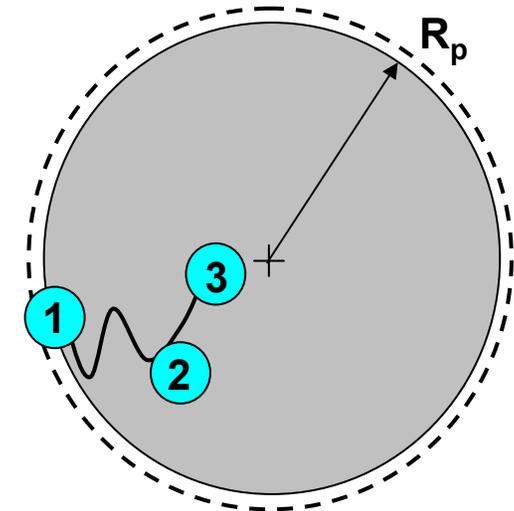
- Assume all sorbent particles are shaped as perfect spheres (One spatial coordinate: the radius r)
- Mercury adsorption takes place in **three steps**:

1. Mass transfer from gas phase to external sorbent surface (**film resistance**)

- Mass transfer coefficient k_f based on empirical relation for *Sherwood* number

$$Sh = \frac{2 k_f R_p}{D_{Hg}} = 2.0 + 0.6 \left(\frac{2R_p u_0}{\nu} \right)^{1/2} \left(\frac{\nu}{D_{Hg}} \right)^{1/3}$$

Slip velocity



Pulverized activated carbon
 Porous structure (pore radius 5-100 Å)
 Large internal surface area (600–1,200 m²/g)

2. **Diffusion mass transfer** through porous structure to interior of the sorbent particle

3. Surface adsorption on internal surfaces
 - Adsorption equilibrium described by a **Langmuir isotherm**
 - Appears as sink term in the particle sub-model

Modeling Approach

Pore Diffusion Model 2

Mass Diffusion Flux (radial)

$$J^m(r) = -D_p \cdot \left. \frac{\partial c_p}{\partial r} \right|_r \cdot A(r)$$

$$A(r) = 4\pi \cdot r^2$$

Effective Diffusion in Porous Structure (Bosanquet equation)

$$D_p = \frac{\varepsilon_p}{\tau_p} \left(\frac{1}{D_{Hg}} + \frac{1}{D_{Kn}} \right)^{-1}$$



- The less diffusive mode of transport becomes limiting (Knudsen Diffusivity for $d_{\text{pore}} < 100 \text{ nm}$)
- Correction for additional diffusion resistance of porous media (Bruggemann: $\varepsilon/\tau = \varepsilon^{1.5}$)

Molecular Diffusion – intermolecular collisions

- Binary system: air+mercury (Hg^0 or HgCl_2)
- Mean free path of diffused molecules much smaller than pore size
- Chapman-Enskog (molecular) theory

$$D_{\text{Hg}} = 1.86 \cdot 10^{-3} \frac{T^{3/2} \sqrt{1/MW_1 + 1/MW_2}}{p \sigma_{12}^2 \Omega}$$

Knudsen Diffusion – molecule/walls collisions

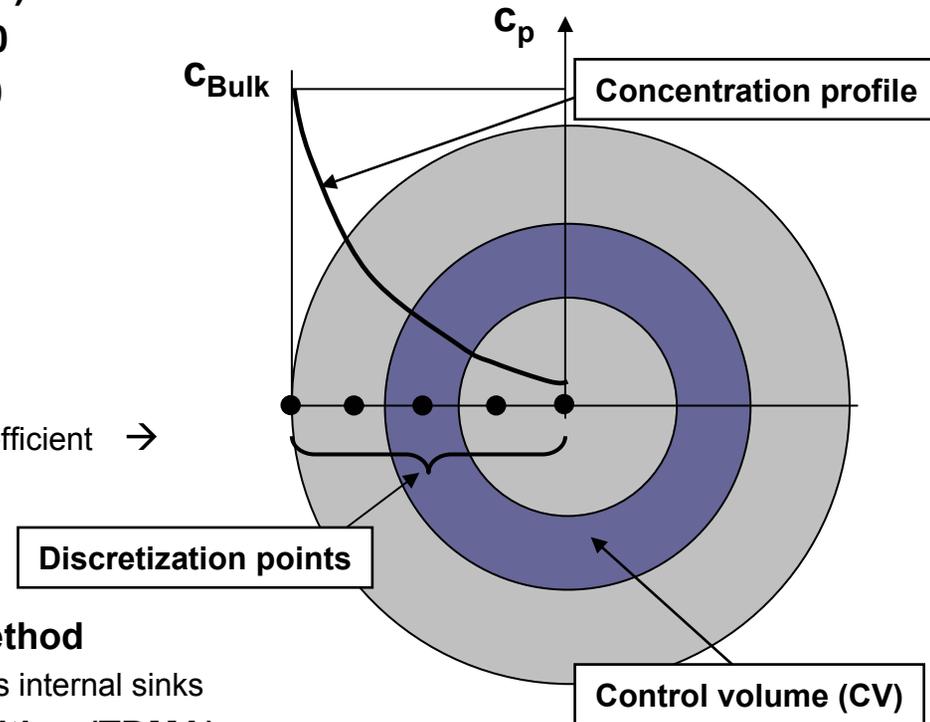
- Narrow pores compared to mean free path
- Does not depend on gas composition or pressure

$$D_{\text{Kn}} = 9700 \frac{d_{\text{pore}}}{2} \sqrt{\frac{T}{MW}}$$

Modeling Approach

Pore Diffusion Model – Boundary Conditions/Numerical Solution

- **Initial conditions (fresh sorbent @ t=0)**
 - No interior mercury vapors $C_p(r) = 0$
 - All available sites unused $\omega(r) = 0$
- **Model boundaries**
 - **Sphere centre (r = 0)**
 - No mass flux $\rightarrow \partial c_p / \partial r = 0$
 - **Sphere surface (r = R_p)**
 - Mass flux determined via film resistance coefficient \rightarrow
 $D_p \partial c_p / \partial r = k_f [C_{Bulk} - c_p(R_p, t)]$
- **Particle Mass Transport equation**
 - **Discretized using the Finite Volume method**
 - Sum of diffusion fluxes over CV-faces equals internal sinks
 - **Solved using Tri-Diagonal Matrix Algorithm (TDMA)**
 - **Use time steps of Discrete Particle Model tracking**



Modeling Approach

Surface Adsorption Model 3

- **Mercury Capture Mechanism: Physical or Chemical Adsorption ?**
 - Desorption studies indicates chemisorption for elemental mercury
 - Recent evidence suggest chemisorption of oxidized mercury (HgCl_2) as well
 - XAFS Spectroscopy studies by Olson et al. (2003)
 - Apparent inability to leach mercuric chloride from activated carbon
- **The adsorption equilibrium is described using a **Langmuir** isotherm**
 - Assumes **mono-layer coverage** of active adsorption sites
 - Well aligned with the supposed chemical adsorption mechanism for mercury

Langmuir theory 101

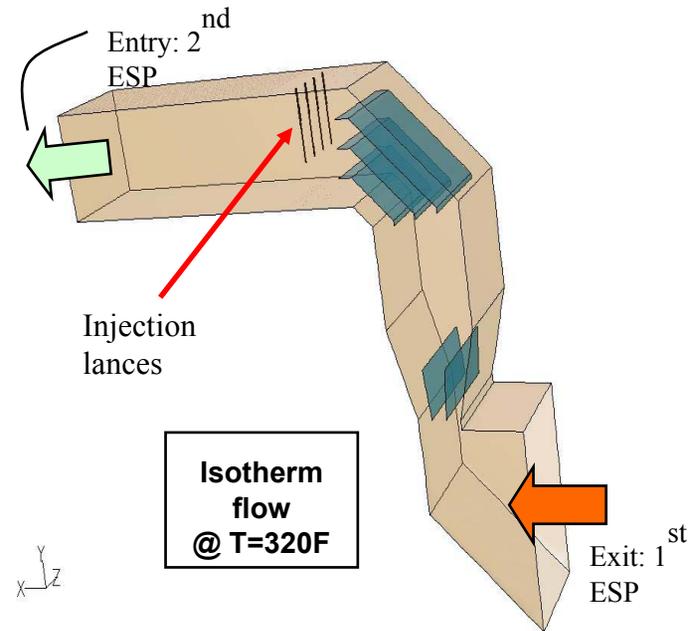
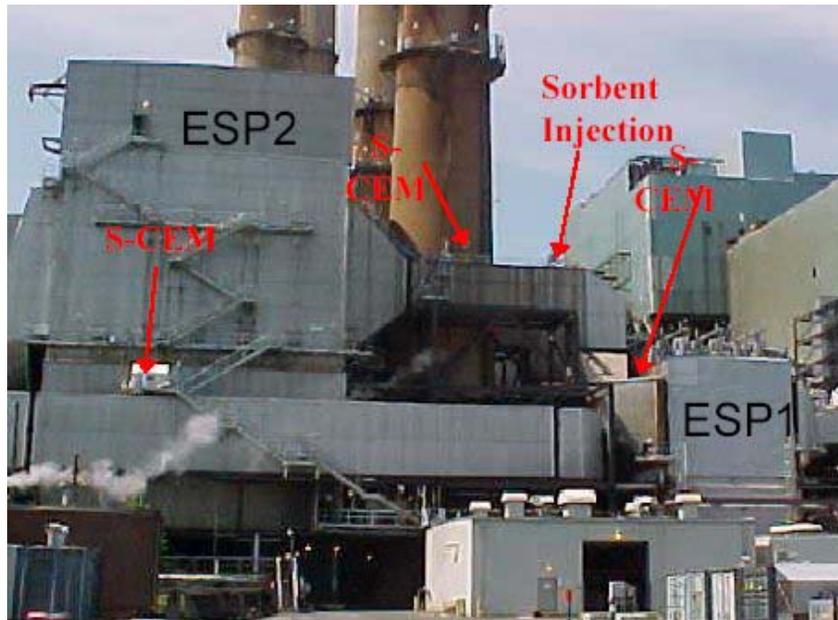
- The net adsorption rate = forward rate (k_1) minus the desorption rate (k_2)

$$\mathfrak{R} = k_1 \omega_{\max} \underbrace{\left[1 - \frac{\omega}{\omega_{\max}} \right]}_{\text{Unused fraction}} c_p - k_2 \omega$$

- ω_{\max} is the max. number of available sites, and ω is the number of occupied ones
- The Langmuir isotherm parameters are calibrated with experimental data

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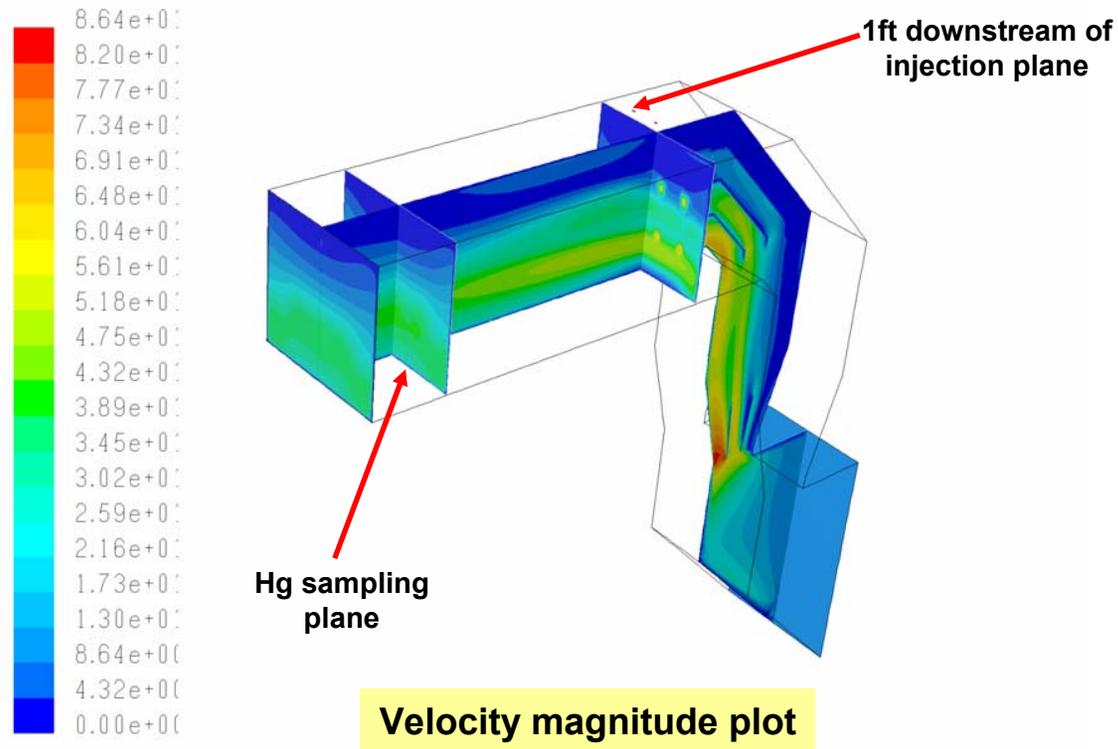
Simulation of Sorbent Injection Field Testing



- ACI tests 2002 as part of the DOE/NETL Mercury Control field test program
- Power plant equipped with two electrostatic precipitators
 - **Injection** of activated carbon via set of **eight lances** upstream of the 2nd ESP
 - Lances are introduced in pairs via **four ports**
 - No fly-ash in the considered part of ductwork => pure **in-flight** capture !!

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Gas Phase Flow

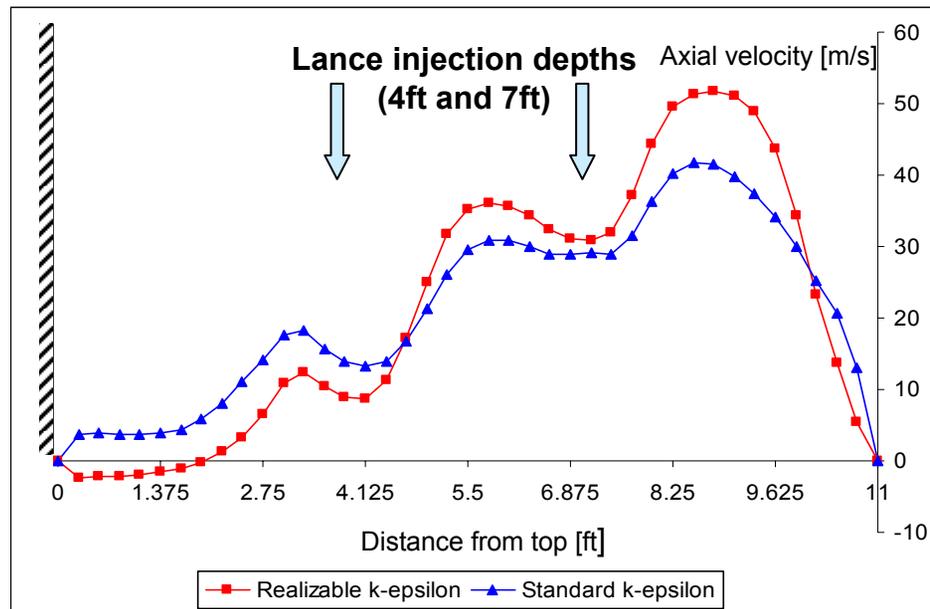


- Flue gas flow is **mal-distributed** at the carbon injection plane
 - Small zone with reverse flow
 - Caused by flow pattern at exit of plenum just downstream of first ESP
 - Injection lances are long enough to penetrate separation zone

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Uneven flow distribution at the injection plane

- **Skewed flow distribution**
 - Flow predominantly travels in **lower half** of duct
 - This could hardly have been anticipated without the use of CFD
 - **Stair-cased** velocity profile is an effect of upstream turning vanes
 - Extent of reverse flow zone is **sensitive** to the choice of turbulence model closure

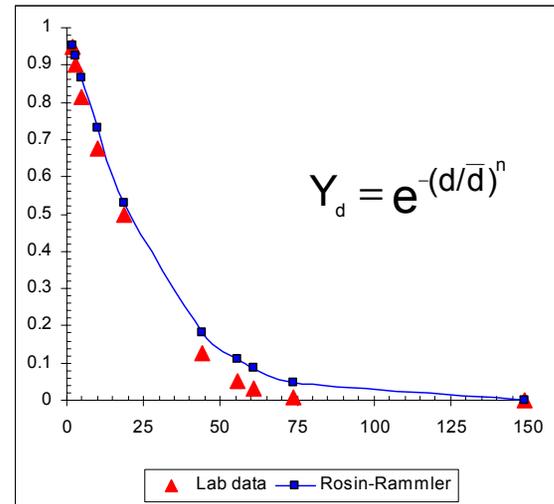
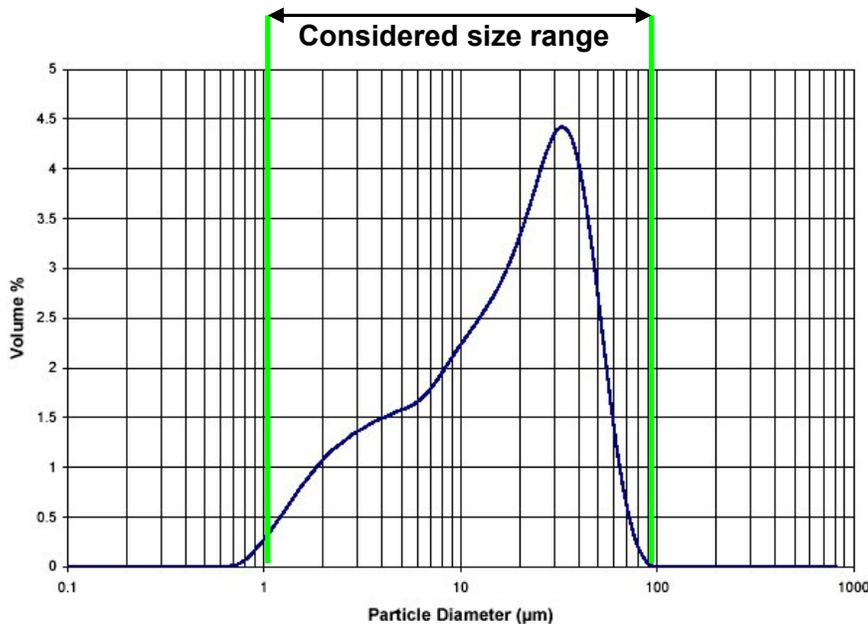


Vertical velocity profile recorded in 2nd port

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Sorbent Characterization

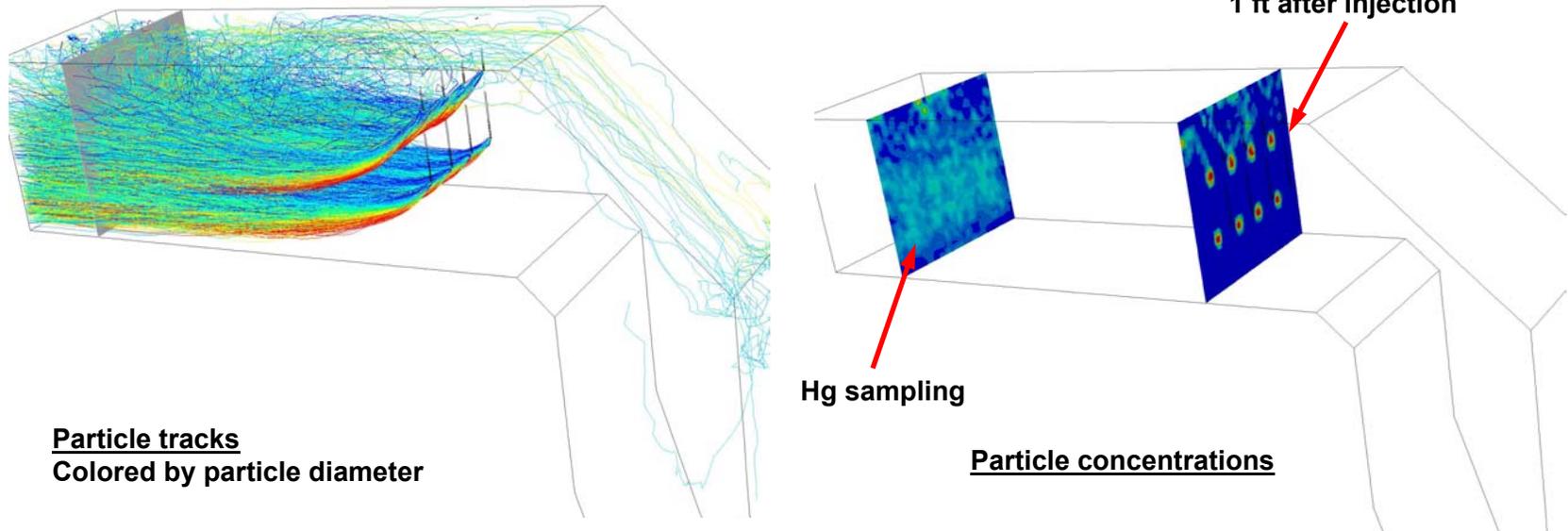
- The Brayton Point field-tests applied *Darco FGD* as the sorbent
 - Industry-standard pulverized activated carbon
 - Mean diameter is approximately **18 μm**
 - Approximated by a **Rosin-Rammler** distribution with 10 size bins
 - Ten representative particles released from each face entity (sized 1...100 μm)
 - Flow rate for tracks representing the individual sizes are weighted
 - Shown simulation considers max. sorbent injection rate of 20lb/Macf



Cumulative Size Distribution Chart

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Sorbent Dispersion



Particle tracks
Colored by particle diameter

Hg sampling

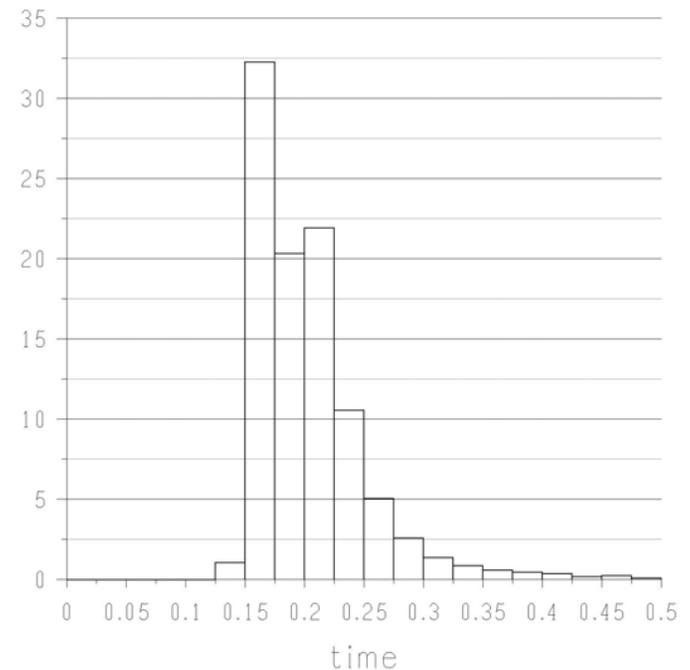
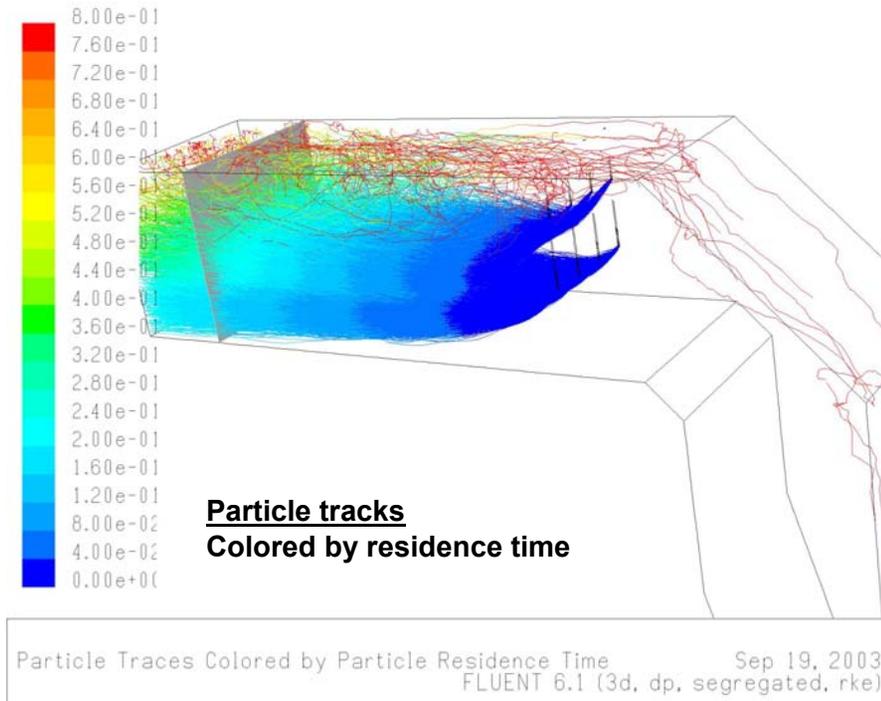
Particle concentrations

- A reasonable **distribution** of sorbent across the duct was predicted
 - Larger particles (red) : travel in bands in lower part of duct (high inertia)
 - Smaller particles (blue) : diffuse motion with some tracks caught in reverse flow
- **Stochastic tracking** accounts for local turbulent fluctuations
 - There are 9,600 trajectories computed (3 x No.Size bins x Injection faces)

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Sorbent Trajectories and Residence Times

- Short injection duct → residence time has been a concern
 - From simple average consideration t_{res} was estimated as ~ 0.45 sec.
 - Uneven flow distribution → locally higher velocities → lower residence times
 - An amazing mercury capture efficiency of up to 90% was observed



NETL 500lb/hr Pilot-Scale Facility

Motivation for CFD Modeling



- This test rig stands at NETL in Pittsburgh
- Designed to enable parametric studies:
 - Sorbent injection rate
 - Temperature
 - Residence time

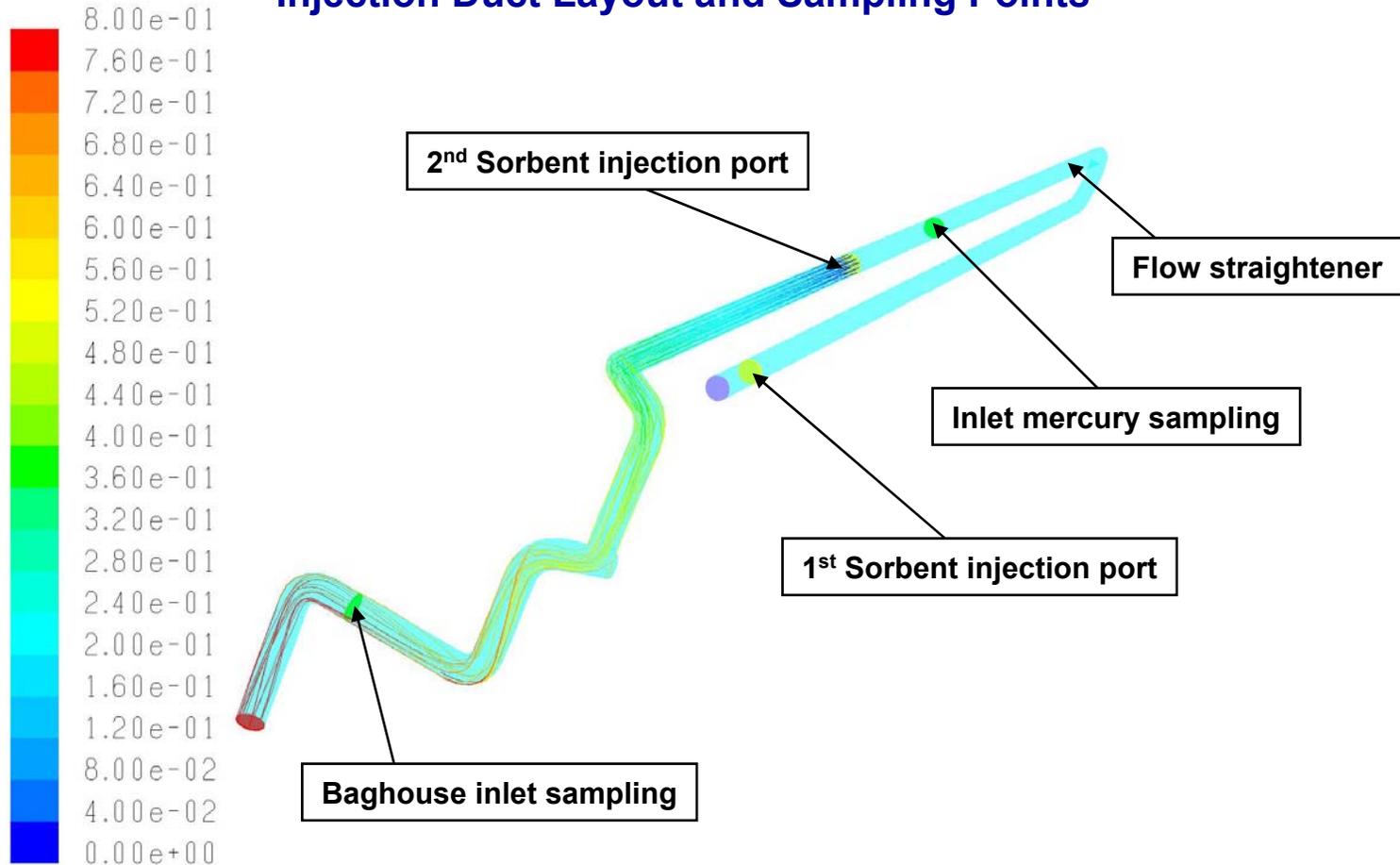


- Use CFD modeling results to
 - Verify sorbent residence times
 - Calibrate adsorption isotherms in capture model



NETL 500lb/hr Pilot-Scale Facility

Injection Duct Layout and Sampling Points



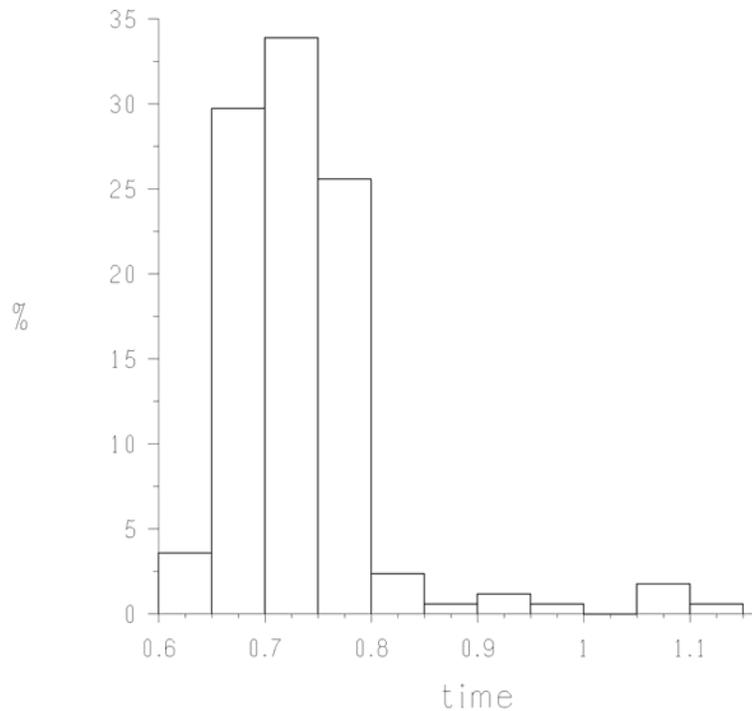
Path Lines Colored by Time (s)

Jul 13, 2004
FLUENT 6.1 (3d, segregated, rke)

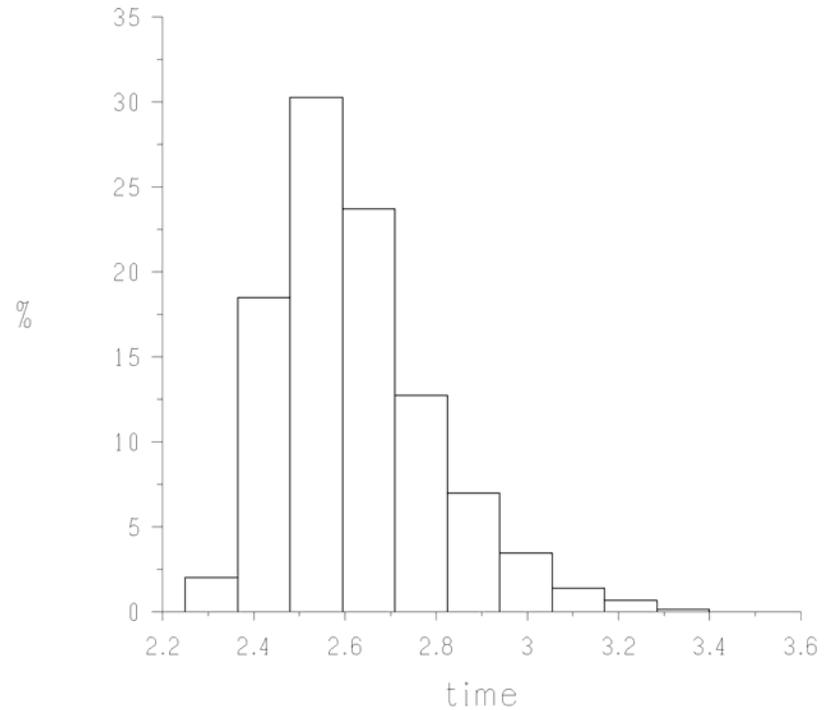


NETL 500lb/hr Pilot-Scale Facility

Verification of Residence Times – reality check



Duct length: ~32ft (w/o bends)
Gas velocity: ~52ft/s
Estimated res.time = 0.62s
CFD prediction = 0.73s



Duct length: ~125ft (w/o bends)
Gas velocity: ~52ft/s
Estimated res.time = 2.40s
CFD prediction = 2.62s

