Solid Fuel Combustion Research in the Energy and Environmental Technology Laboratory at Brown University

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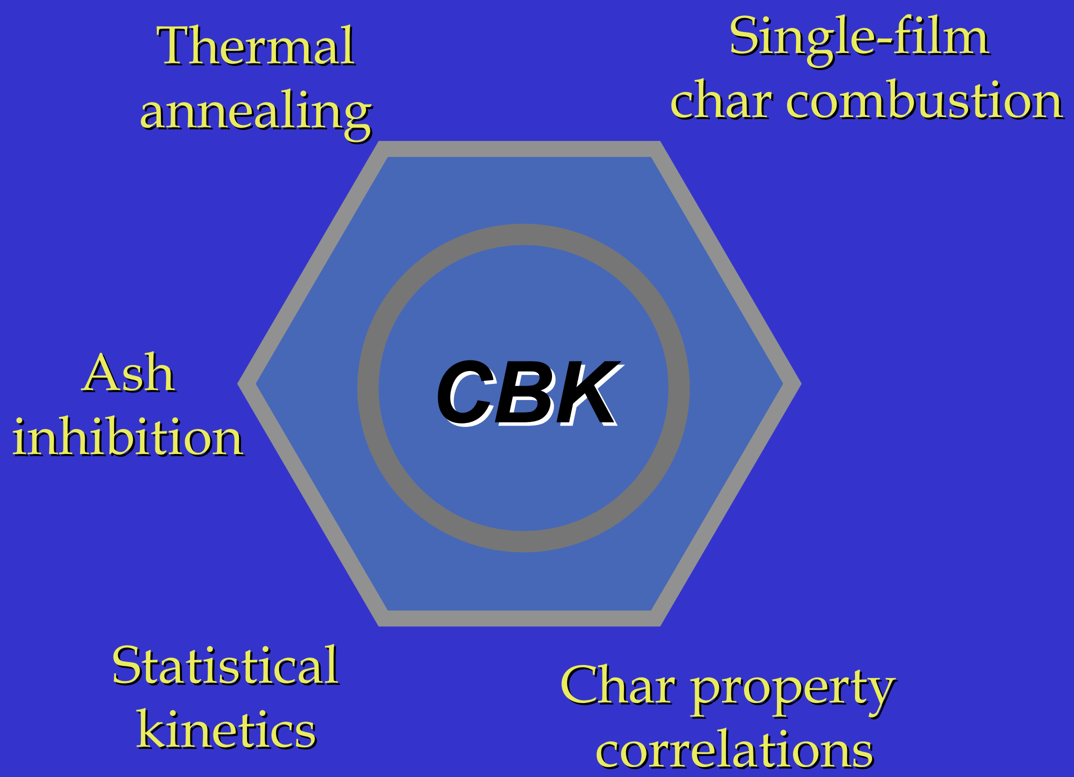
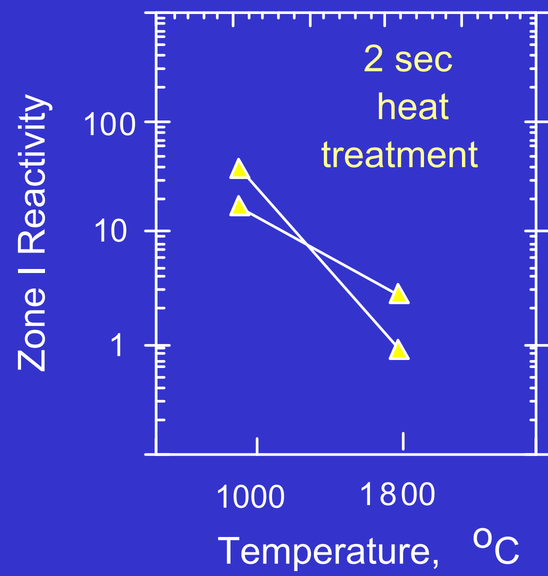
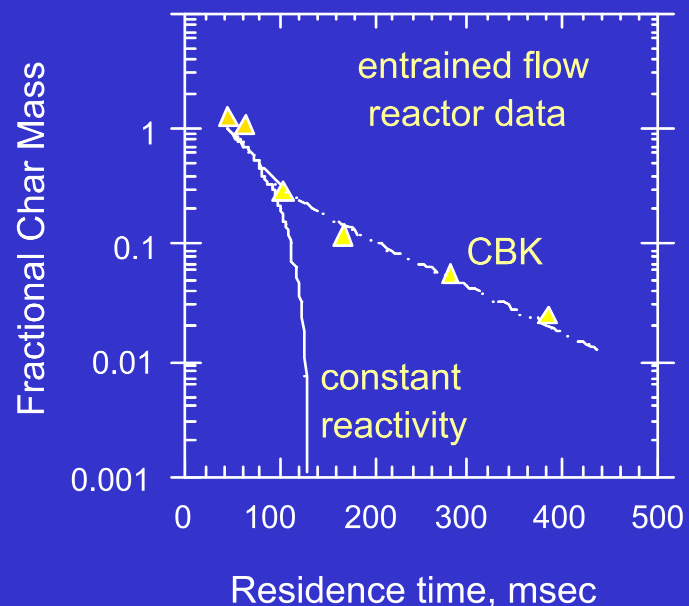
Work at Brown led to the CBK model now integrated in *Fluent* and *Glacier* CFD codes

Carbon Burnout Kinetics







New work to extend CBK to high pressure char combustion

Characteristic Burnout Rate, (1/burnout time) $R_{BO} = \dfrac{dm / dt}{m_o}$

In Zone III
(diffusion-limited reaction)

$$R_{BO} = \frac{k_m X_{ox} P\, d_p^{\,2}}{\rho\, d_p^{\,3}} = X_{ox} / \rho\, d_p^{\,2}$$

$$R_{BO} = \frac{X_{ox}}{(\rho\, d_p^{\,2})_{coal}\, (1\text{-}\mathbf{VM})\, \boldsymbol{\omega}}$$

In Zone I
(kinetically-limited reaction)

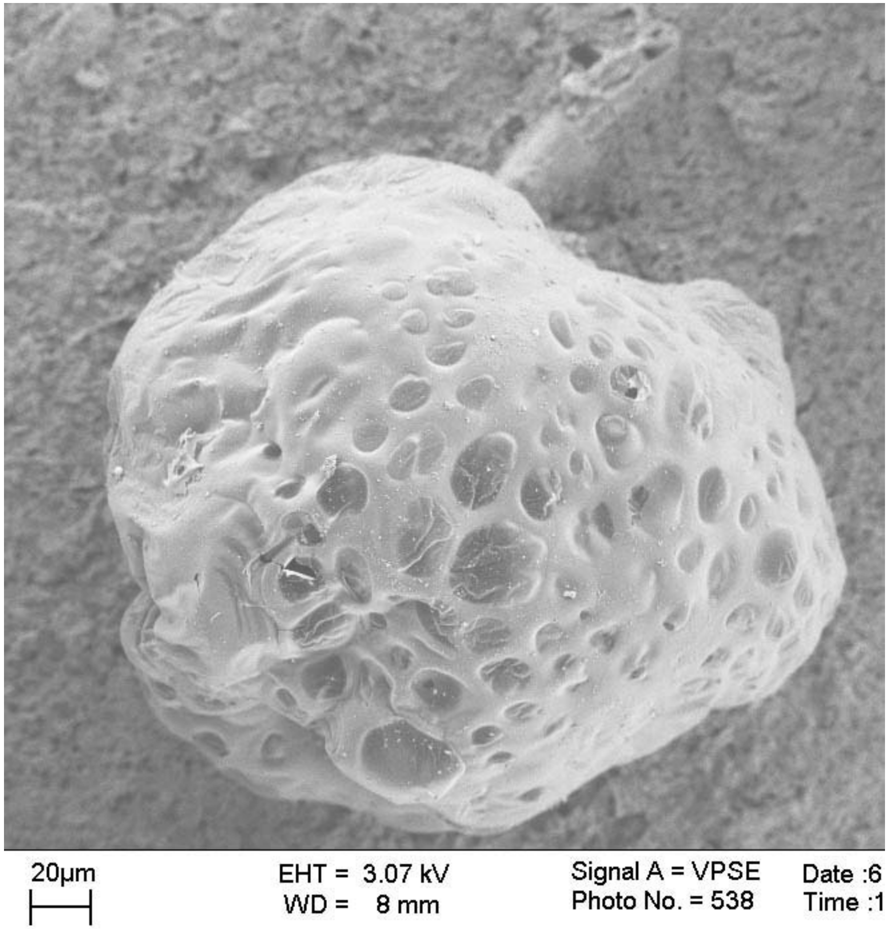
$$R_{BO} = \mathbf{k_{int}}\, P^{\mathbf{n}}$$

CFD-based models need: **VM***, **ω***, $\mathbf{k_{in}}$,*, **n***, $\underbrace{\text{porosity (some models), } \rho_{char}}_{\textit{derivable from other properties}}$

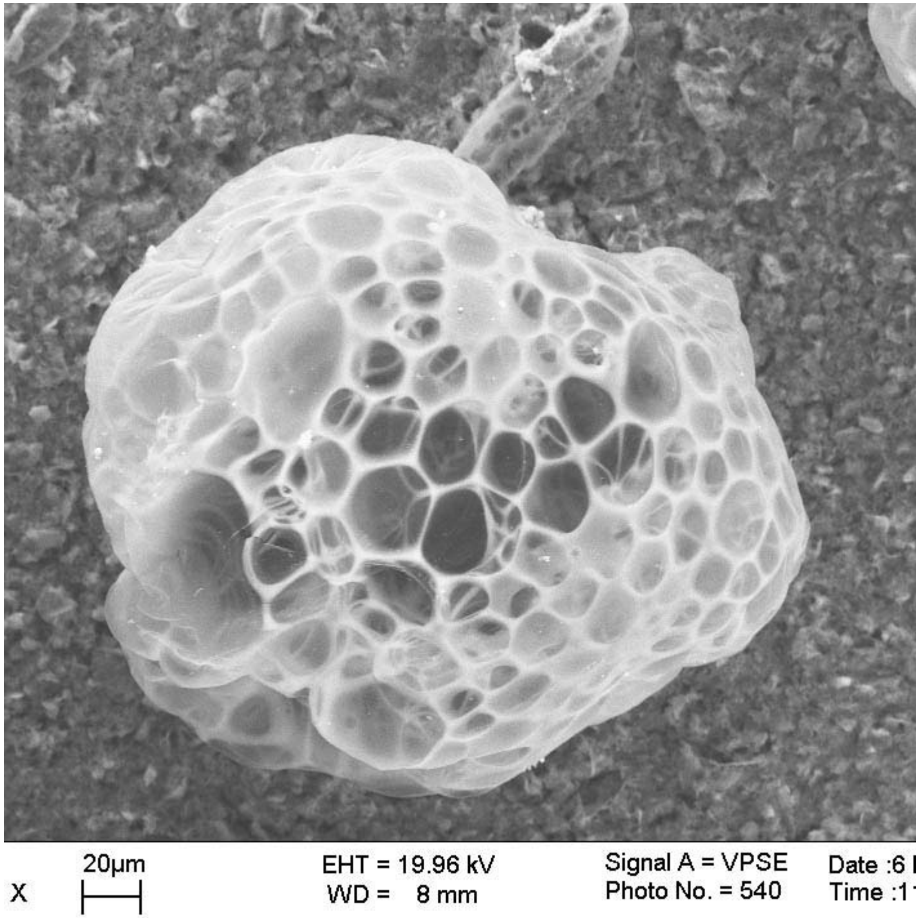
High-Pressure Char Morphology

Illinios#6, 20 atm. O/C: 58%

3 kV e-beam

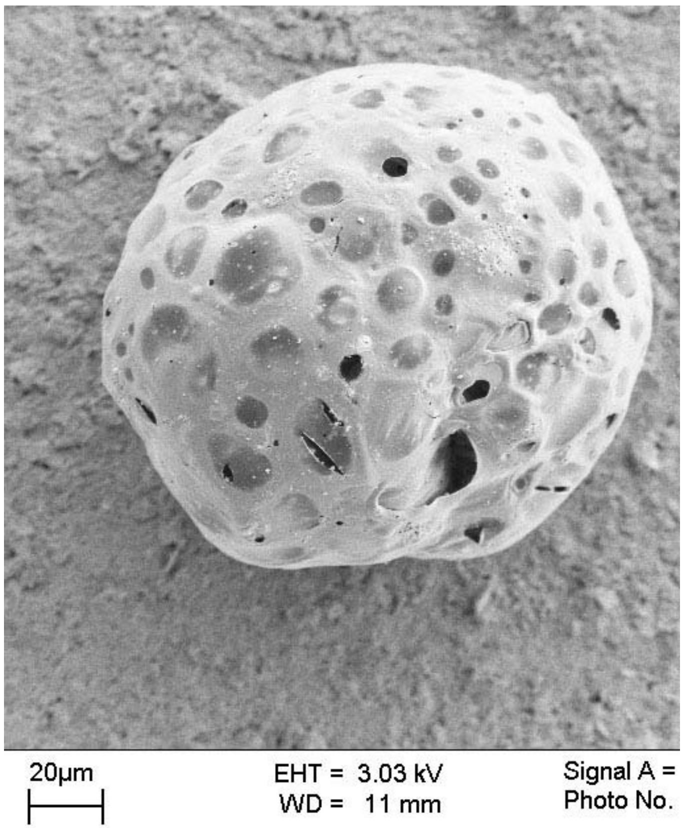


20 kV e-beam

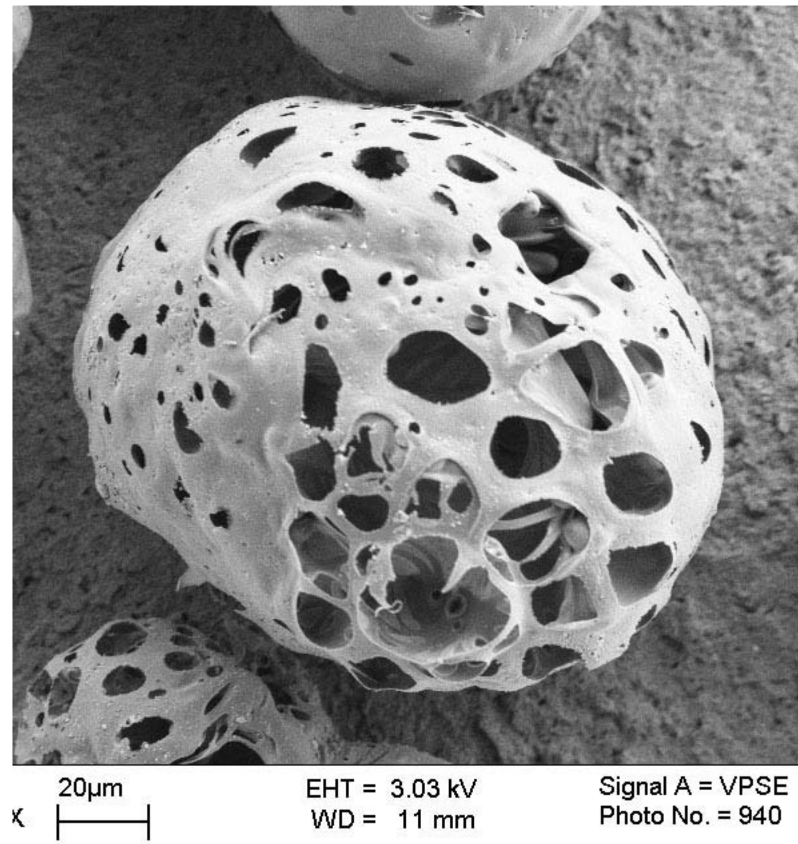


High-Pressure Char Morphology

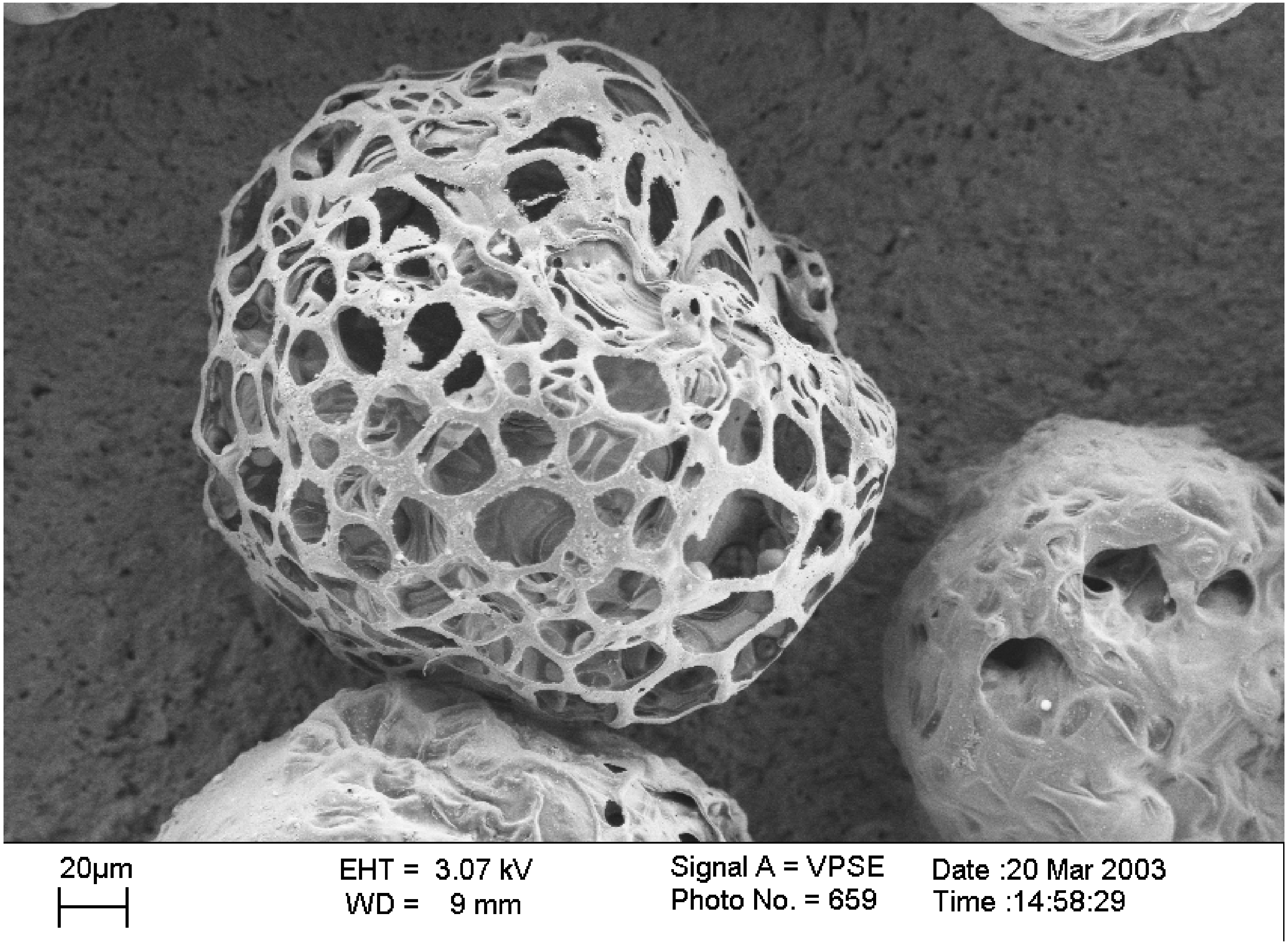
Pitt. #8, 30 bar, O/Coal 48.6%



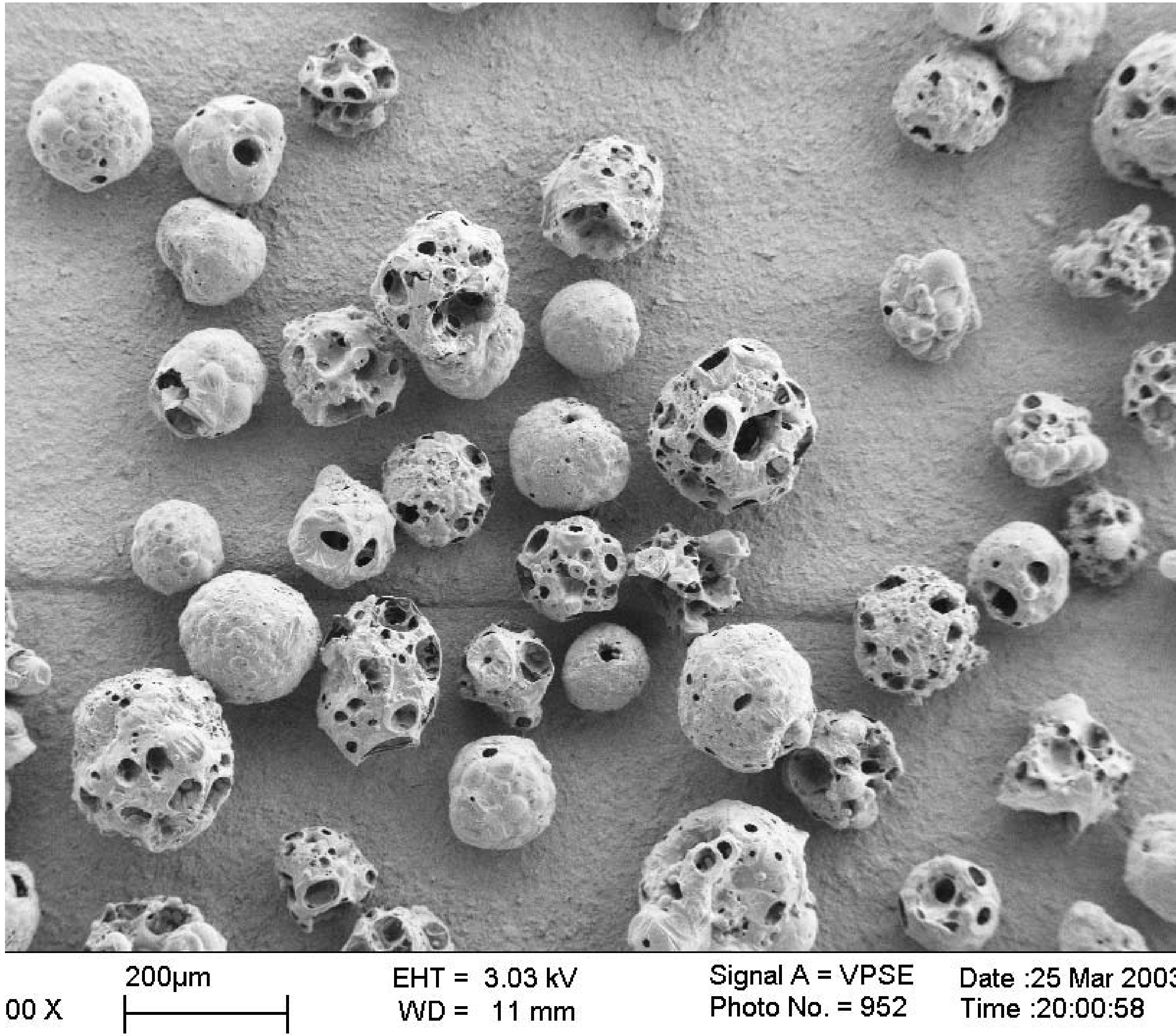
Pitt. #8, 30 bar, O/Coal 103%



Pittsburgh #8, 10 atm. O/C: 29.8%

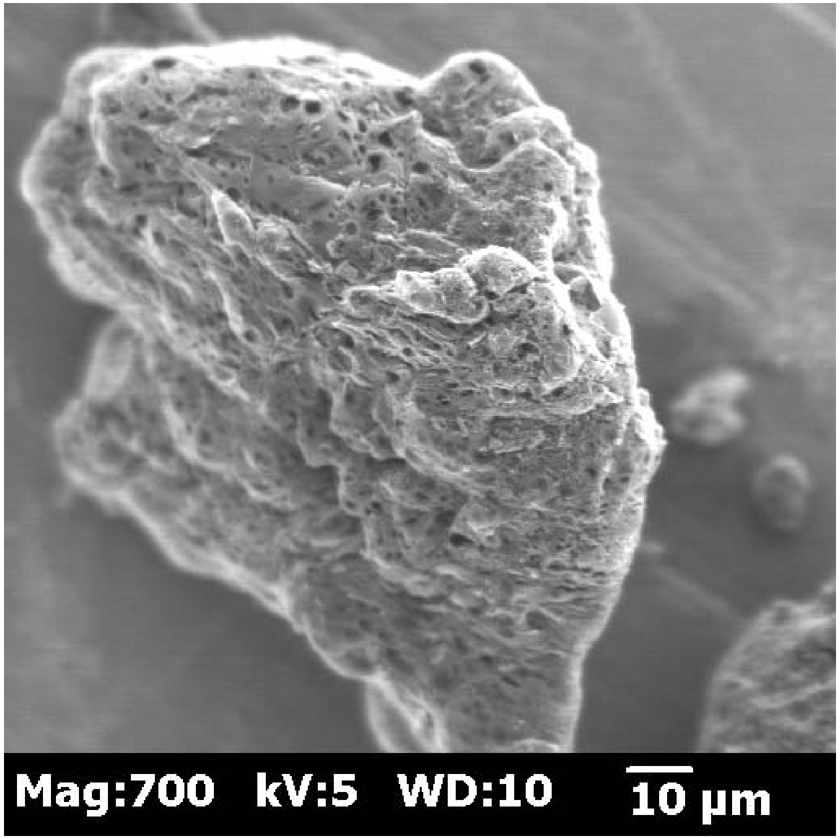


Pittsburgh,
30 atm.
O/C: 9.5%

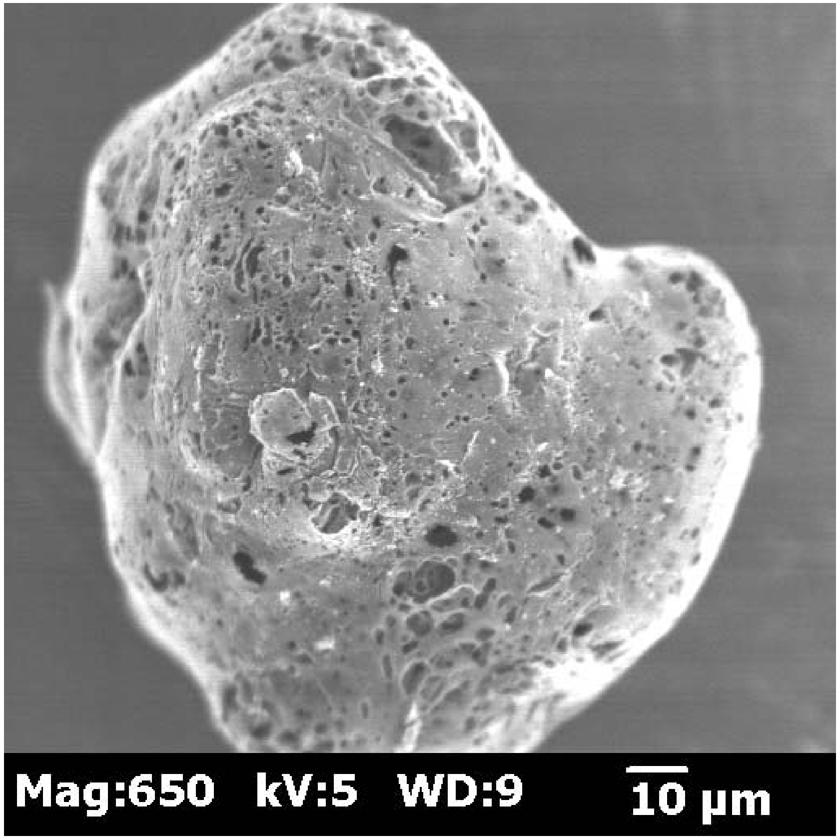


PRB Coal Char

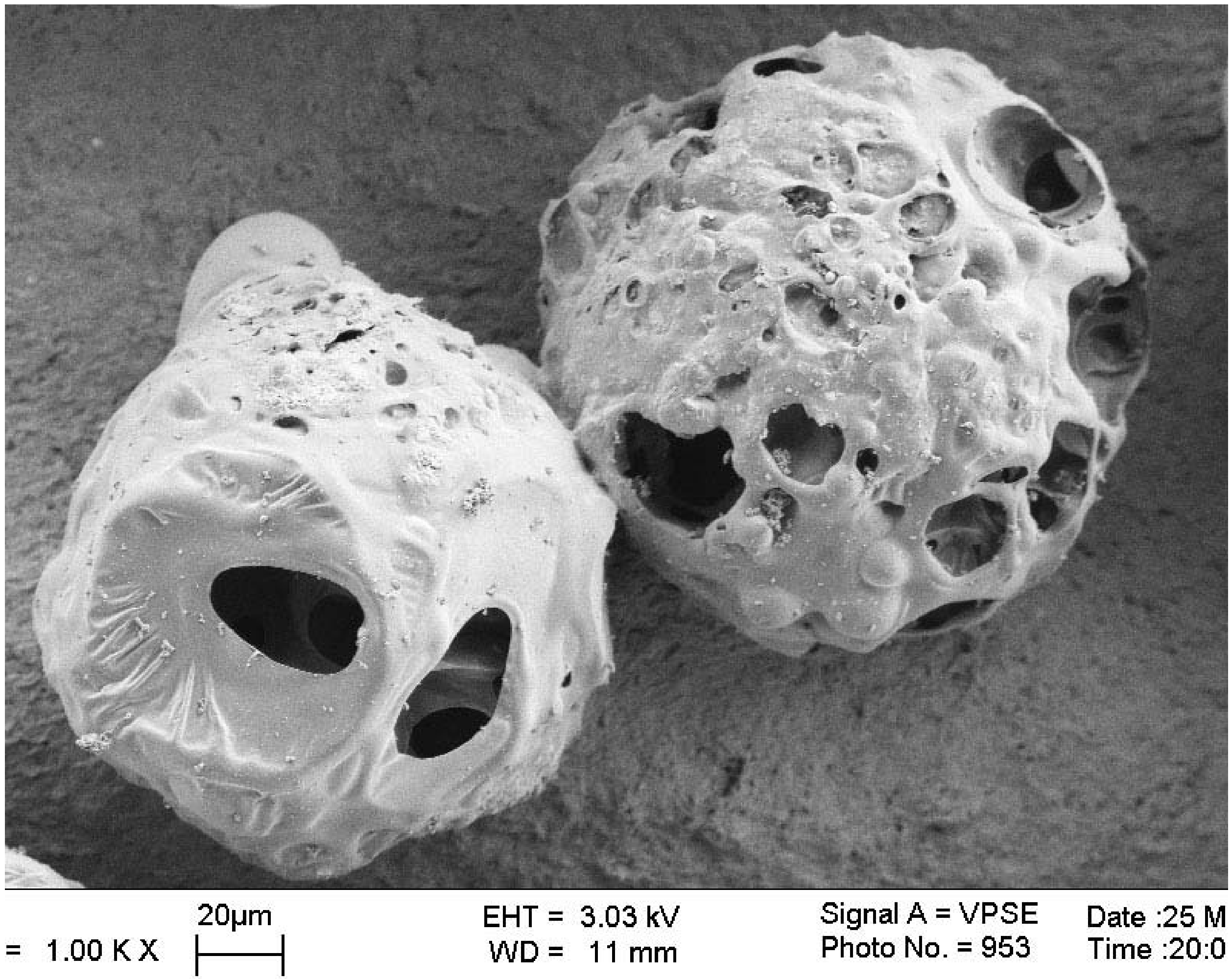
10 bar, O/Coal 200%



30 bar, O/Coal 154%

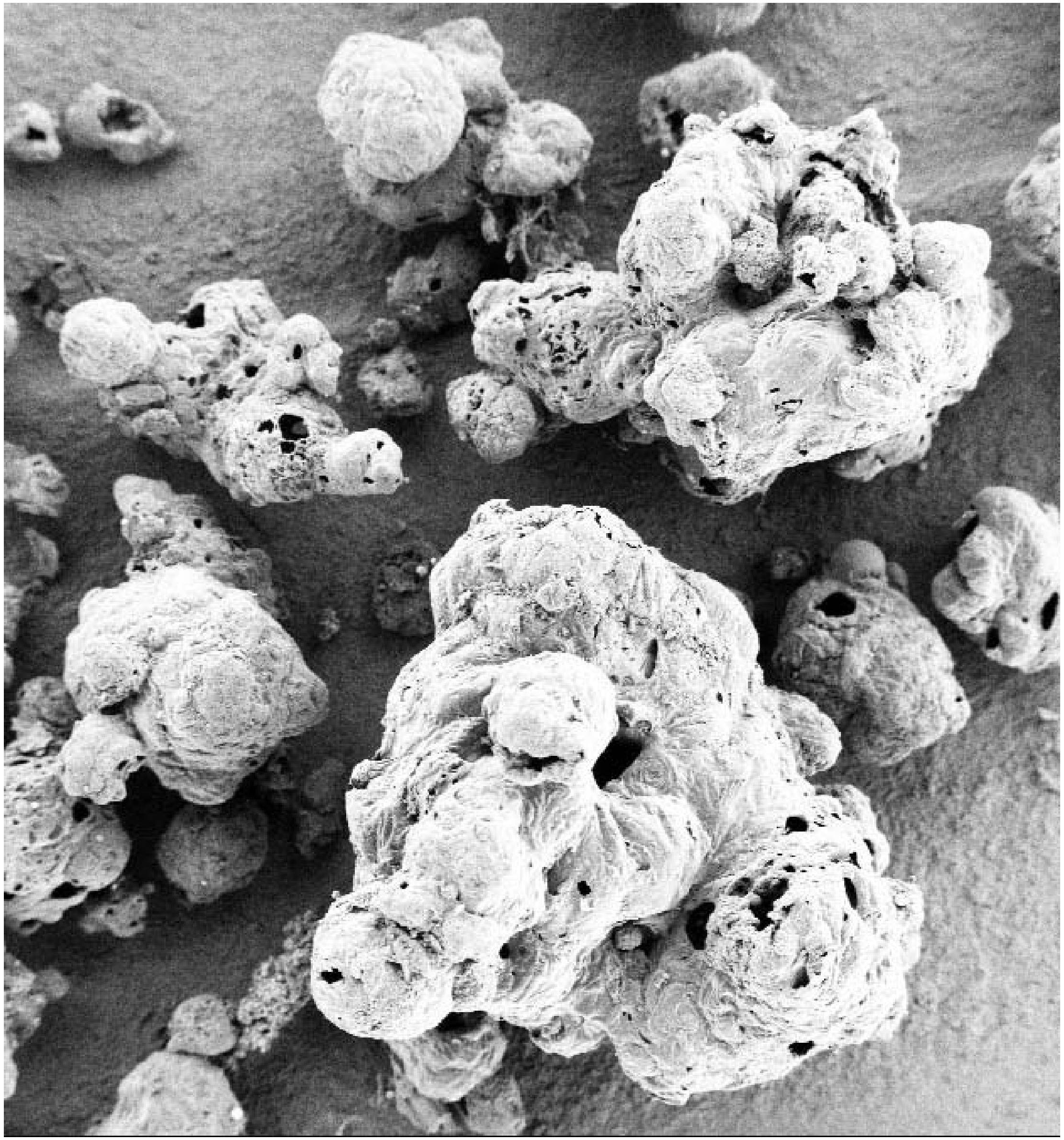


Pittsburgh, 30 atm., O/C: 9.5%



Agglomeration and coalescence

Illinois #6, 2 atm.
O/C: 160%

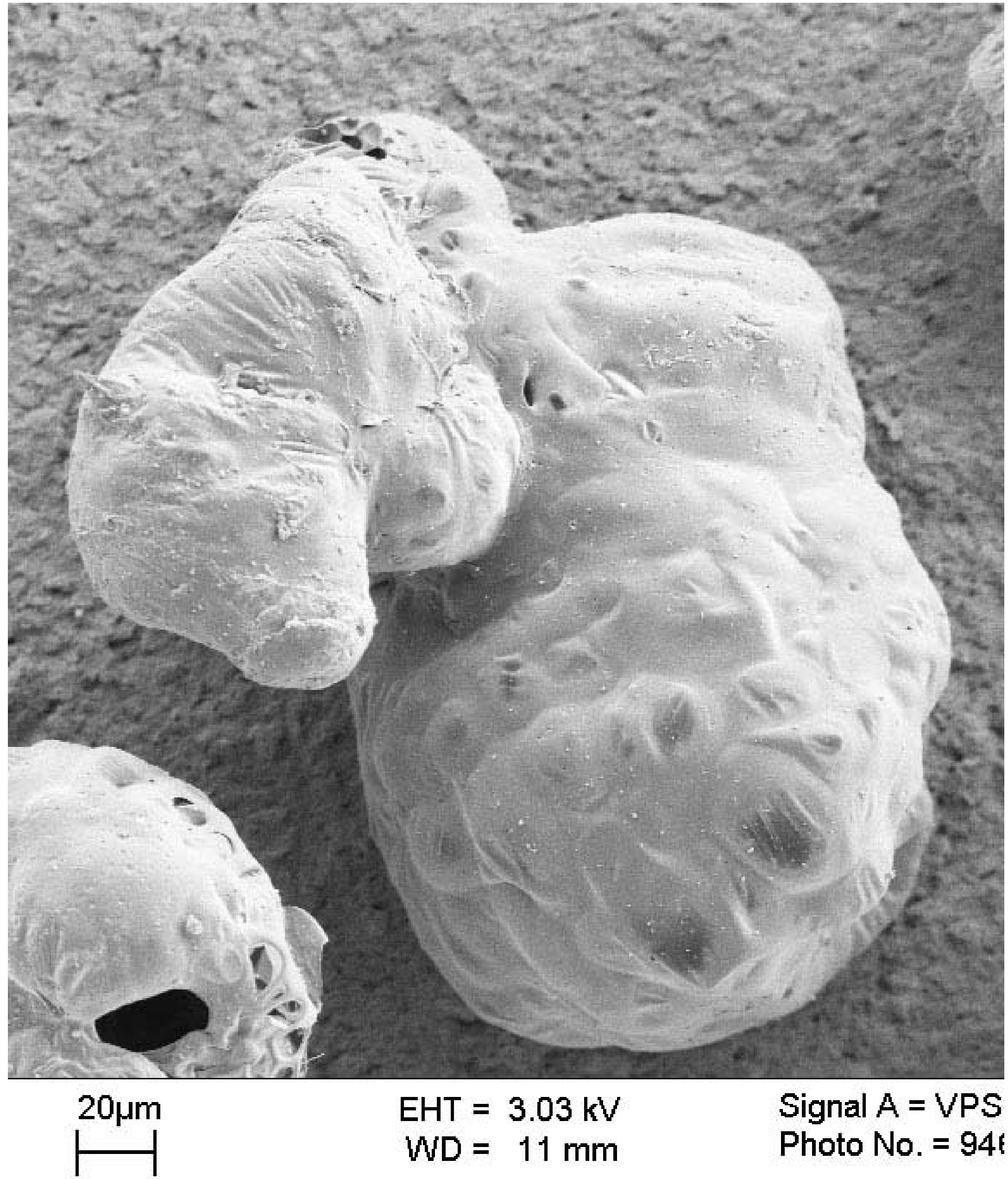


X 200µm

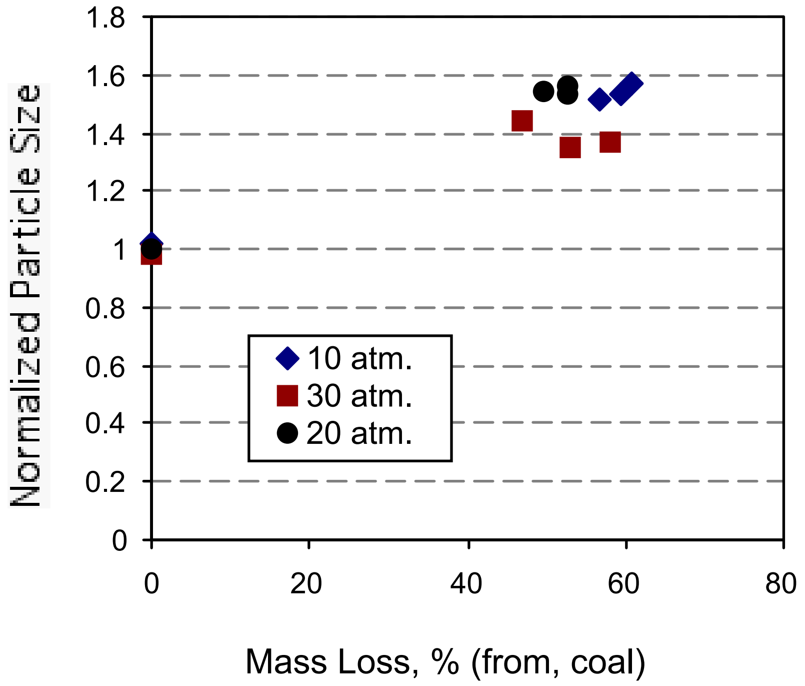
EHT = 3.07 kV
WD = 10 mm

Signal A = VPSE
Photo No. = 568

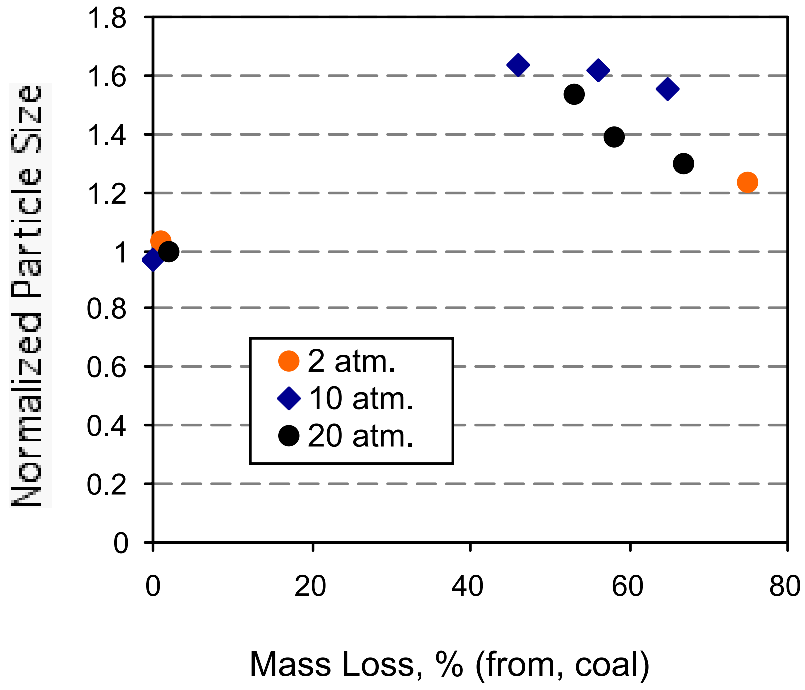
Pittsburgh,
30 atm.
O/C: 48.6%



Quantitive Swelling Data from For High Pressure Chars



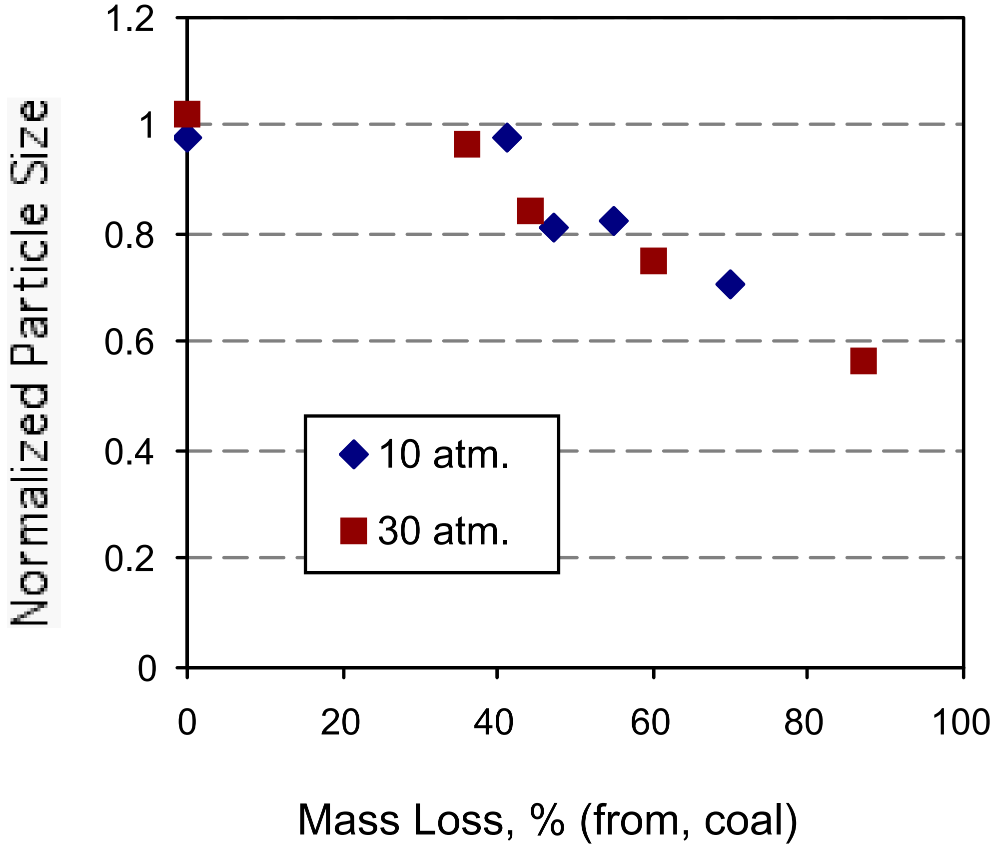
Pittsburgh #8



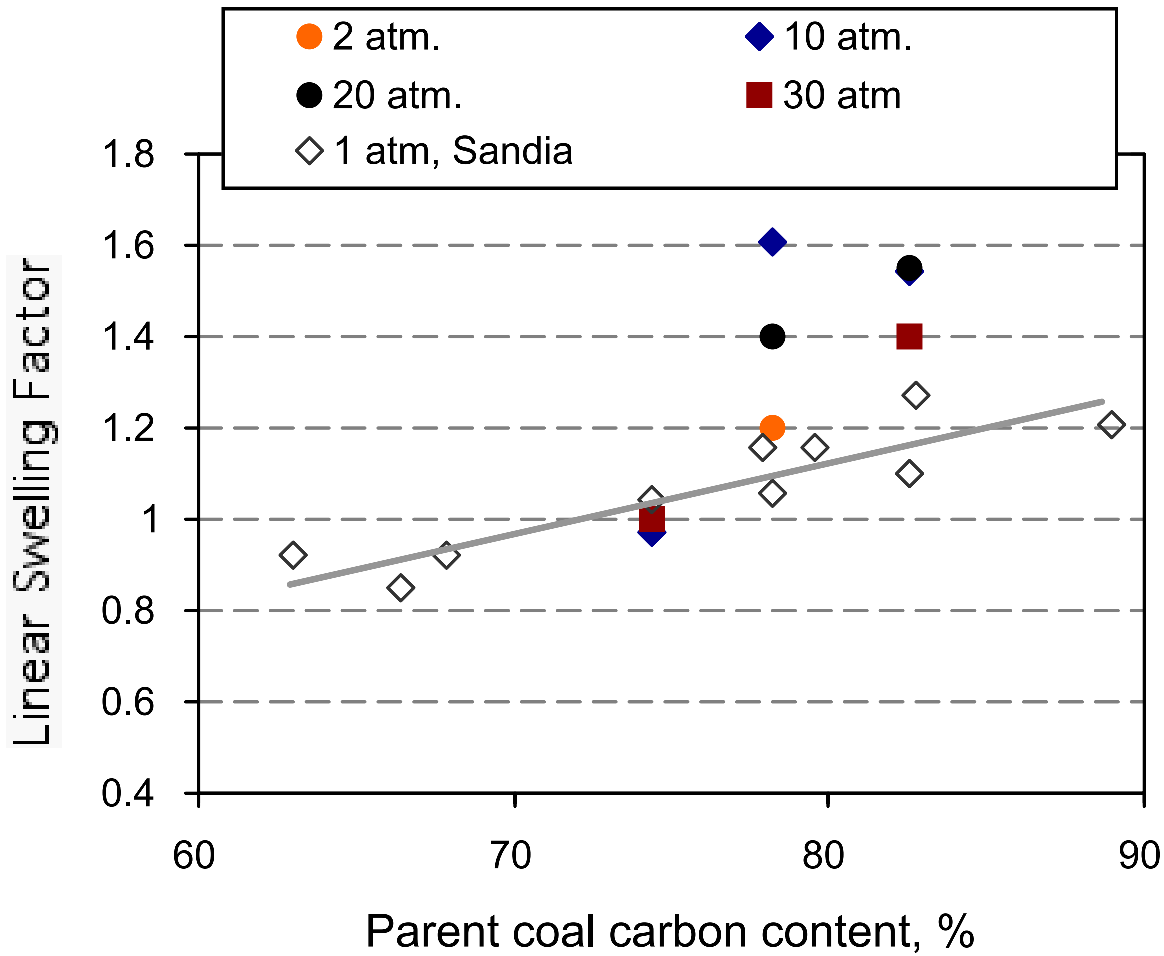
Illinois #6

Quantitive Swelling Data for High Pressure Chars

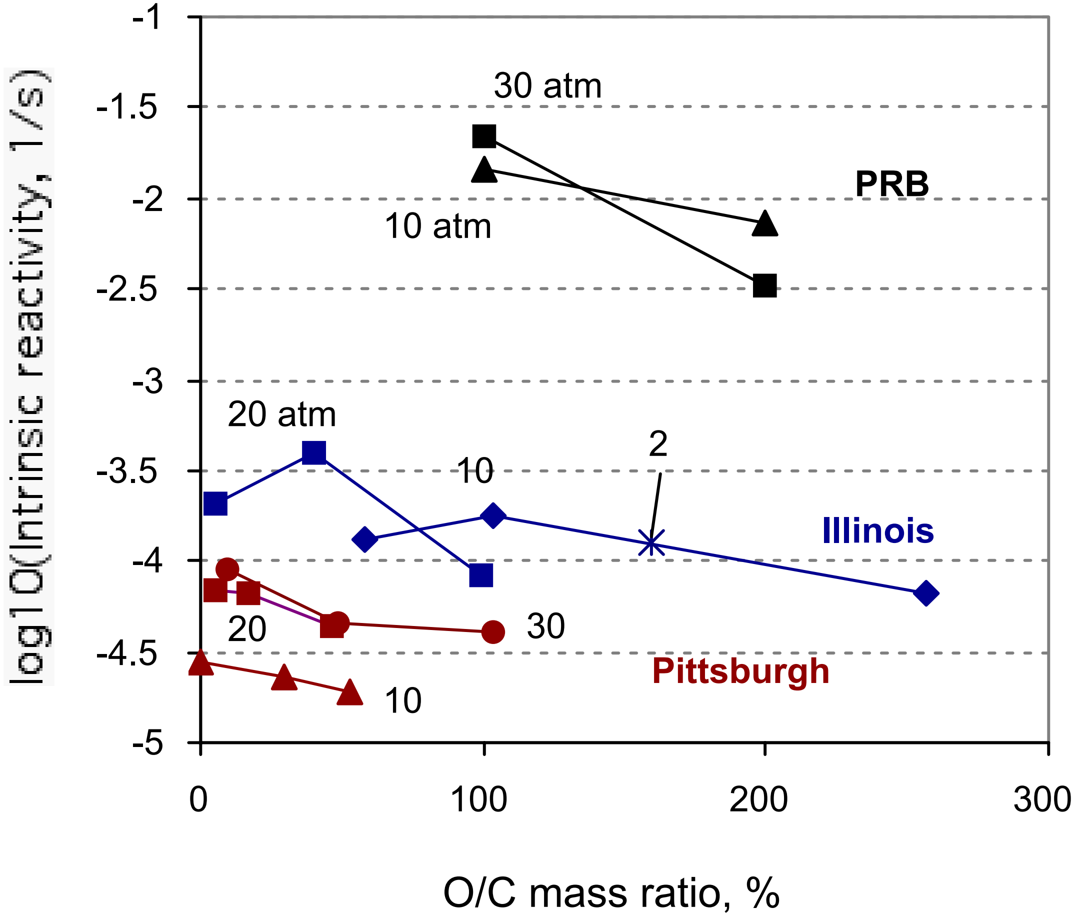
PRB coal



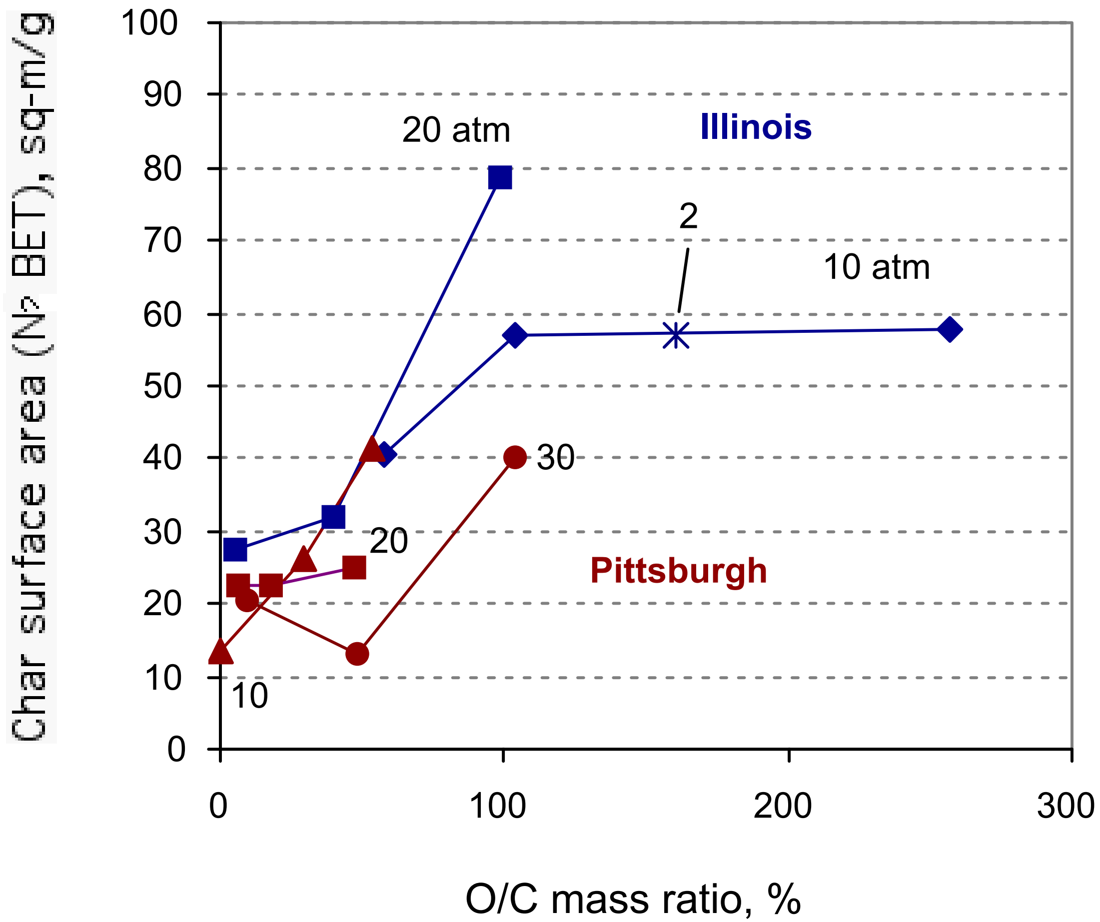
Summary of High Pressure Swelling Data and Comparison to 1 atm Flow Reactor Data (Sandia)



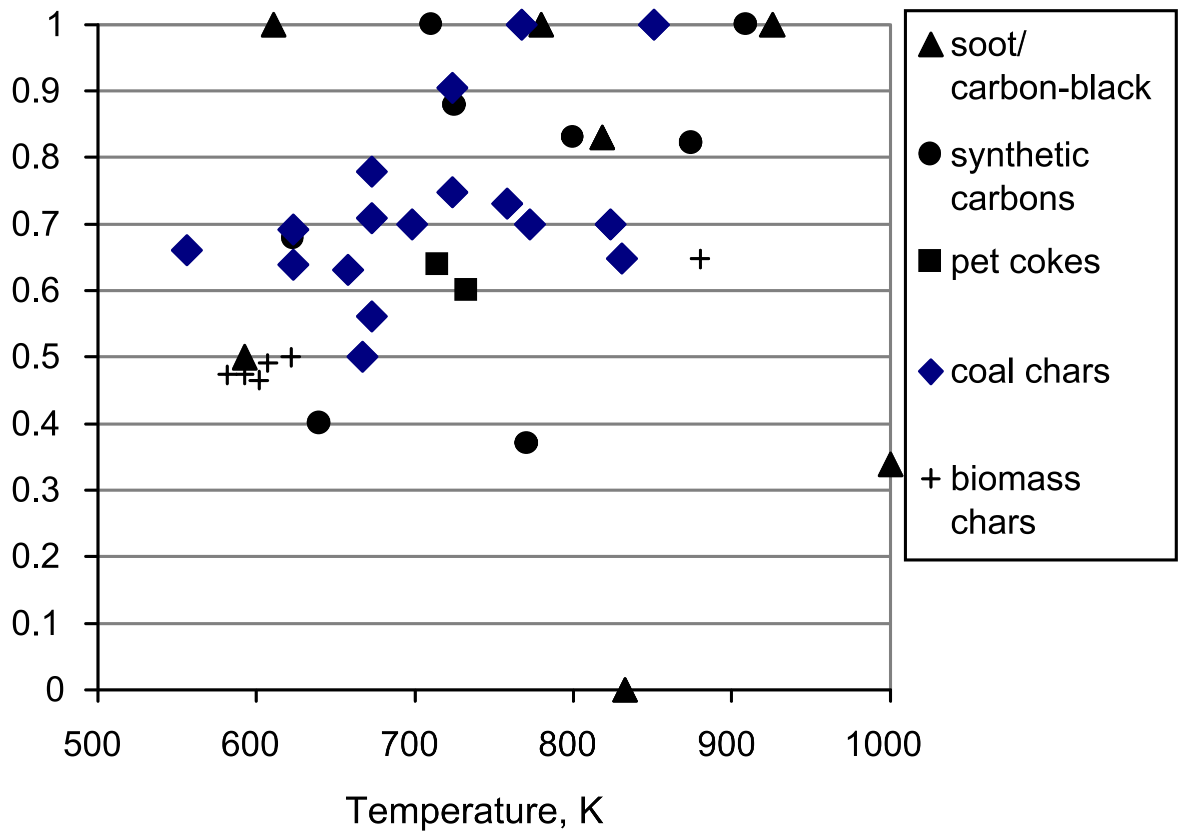
Intrinsic Reactivities of High Pressure Chars



Total Surface Areas of High Pressure Chars



Carbon/Oxygen Reaction: Review of Measured Reaction Orders in Intrinsic Regime



The observed high, fractional reaction orders are not consistent with the simple 2-step mechanistic kinetic models in current use

High Pressure Combustion Kinetics

Proposed 3-step semi-global mechanism

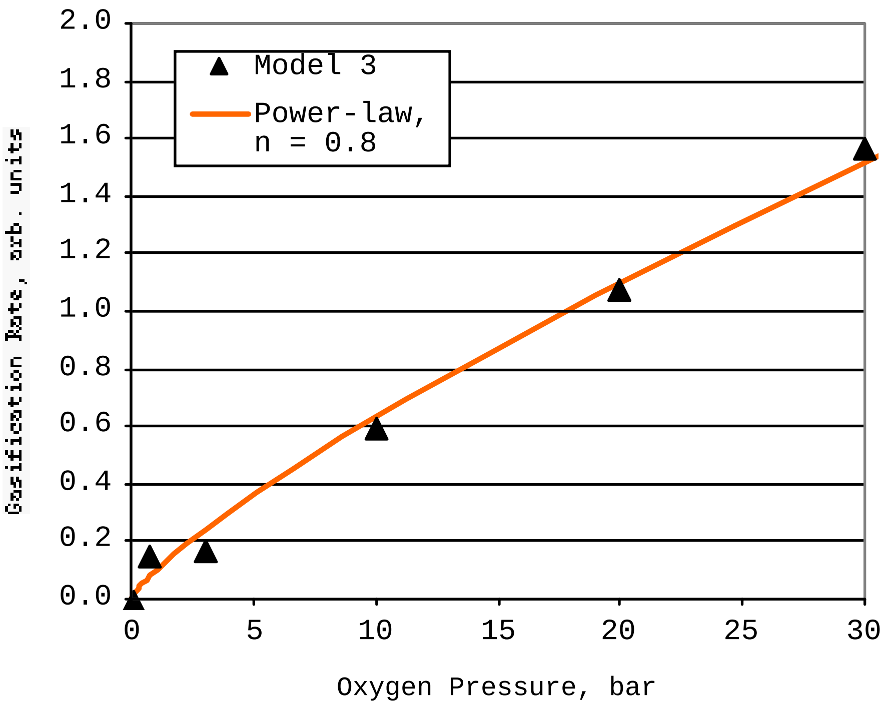
1. $C + O_2$ ---> $2C(O)$

2. $C(O) + O_2$ ---> $CO_2 + C(O)$

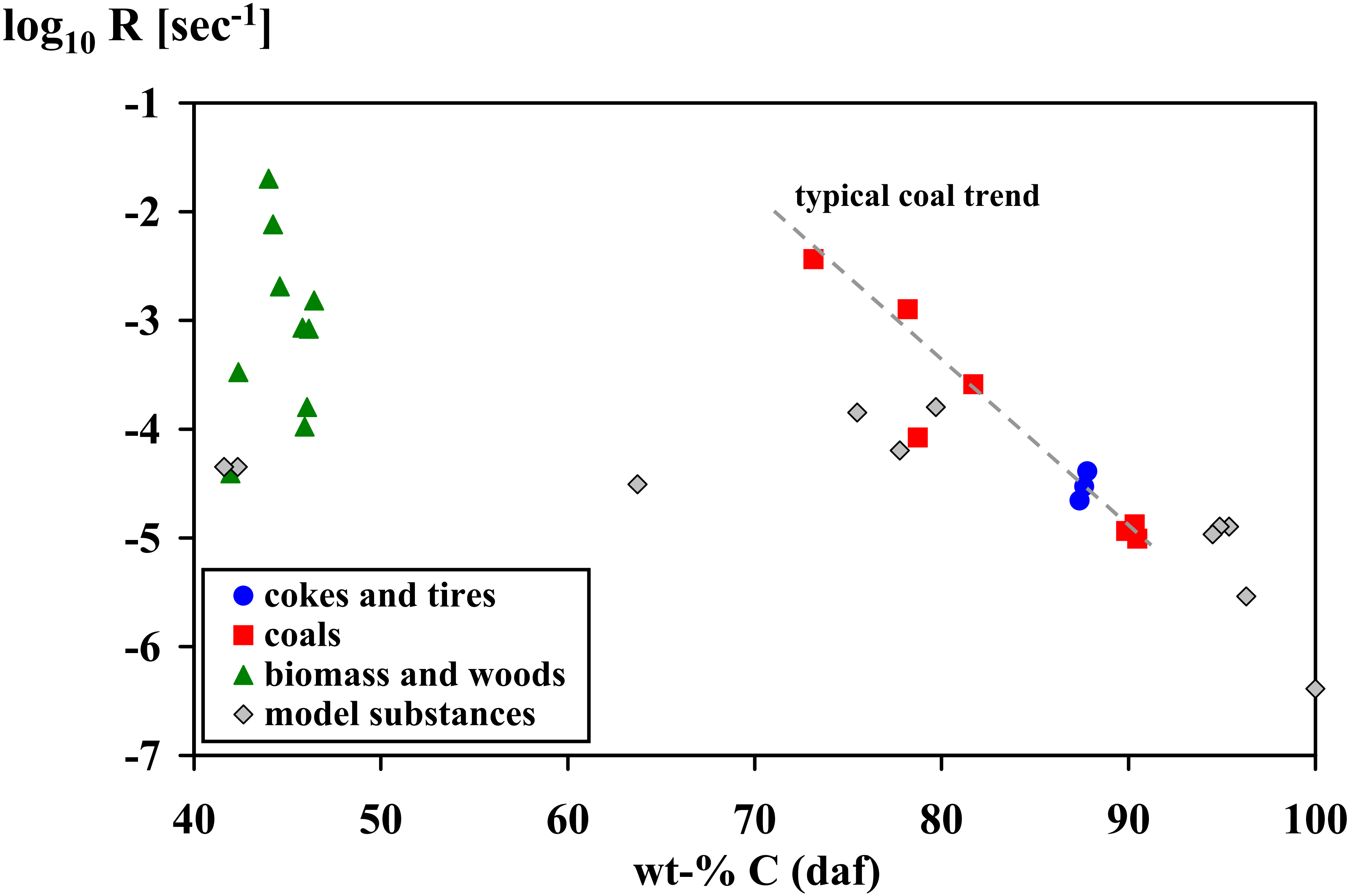
3. $C(O)$ ---> CO

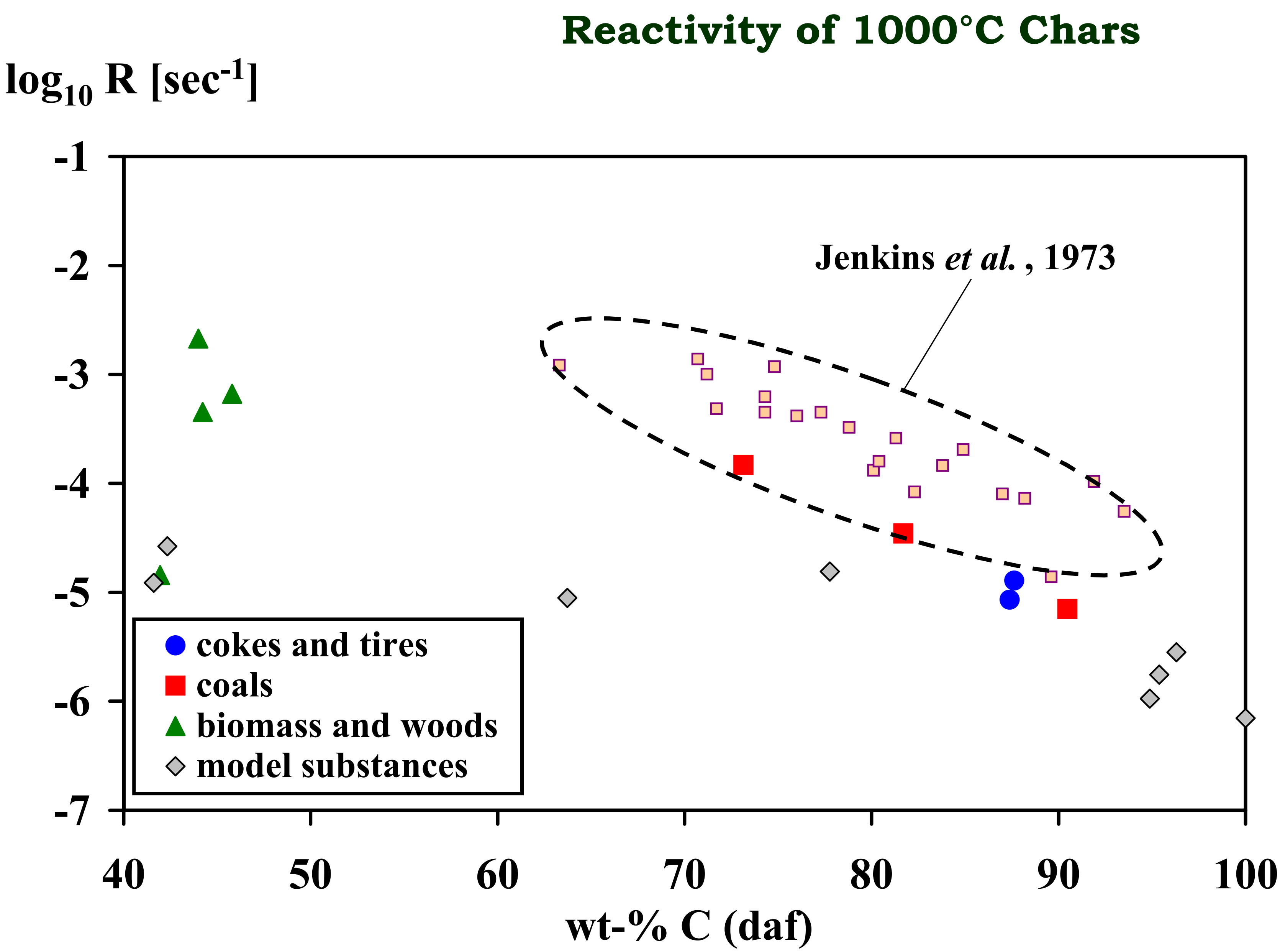
$$r_{gas} = \frac{k_1 k_2 P_{O2}^2 + k_1 k_3 P_{O2}}{k_1 P_{O2} + k_3/2}$$

$$CO/CO_2 = \frac{k_3}{k_2 P_{O2}}$$

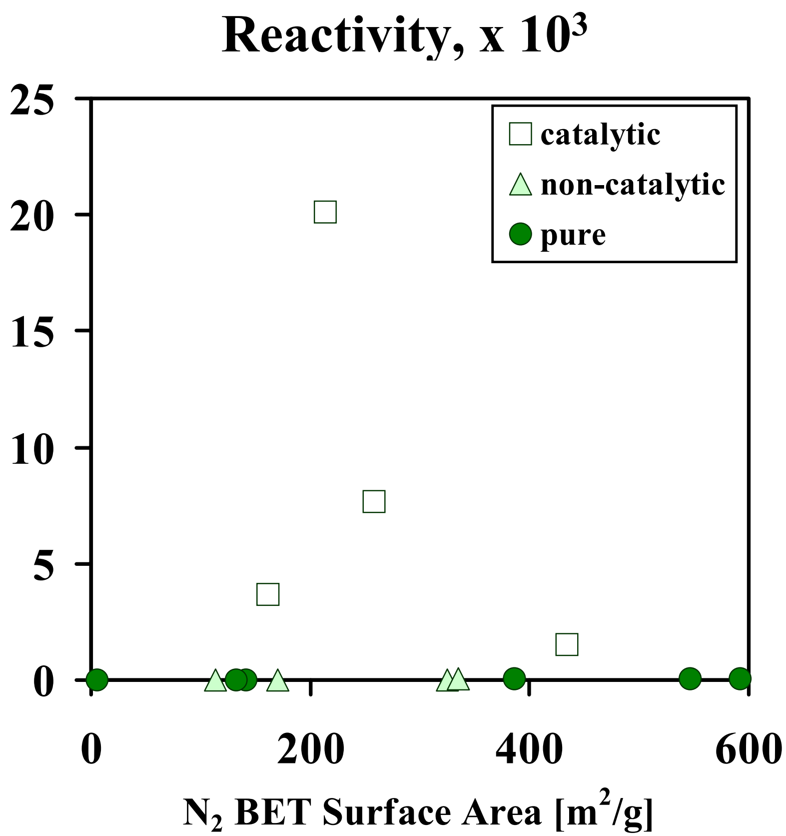


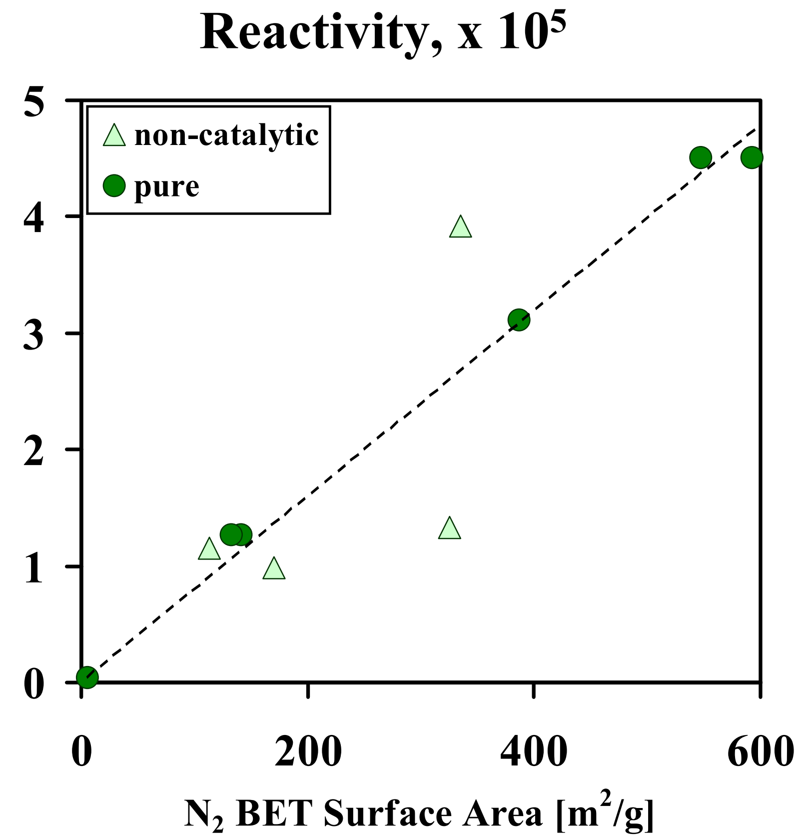
Project on Predicting Reactivities of Diverse Solid Fuel Chars




Reactivity of 1000°C Chars
log10 R [sec-1]
-1
-2
-3
-4
-5
-6
-7
40
50
60
70
80
90
100
wt-% C (daf)
Jenkins et al. , 1973
cokes and tires
coals
biomass and woods
model substances

Total Char Surface Area





POOR correlation:
entire sample bank

STRONG correlation:
non-catalytic mat'ls

Hybrid chemical/statistical approach

Two independent, parallel, non-catalytic and catalytic components are assumed:

$$R_{700°C} = R_{carb} + R_{cat}$$

R_{carb} = function of:

%C (parent fuel)

or

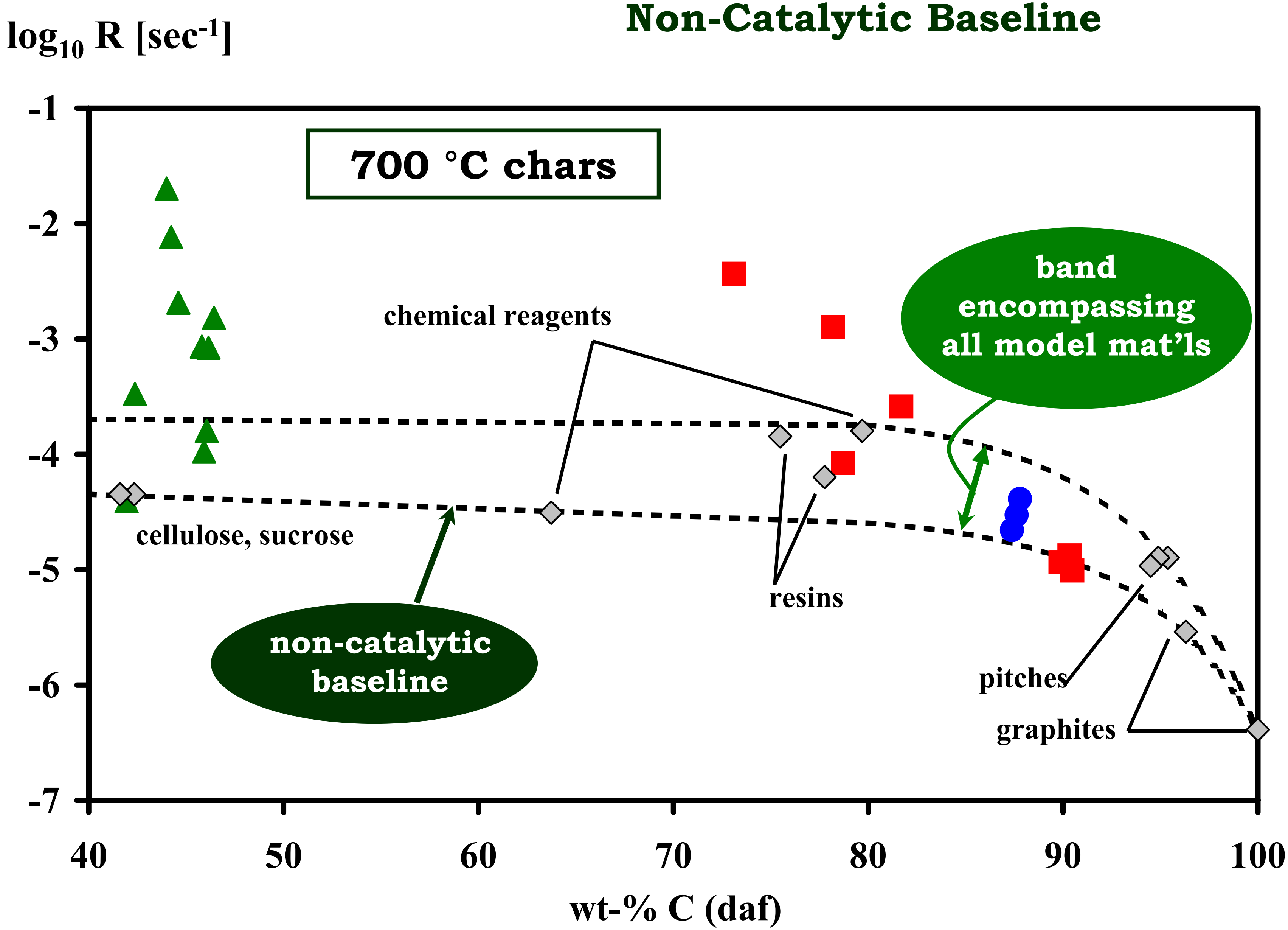
char surface area

R_{cat} = function of:

concentration
and
dispersion
of
Group I, II, and
transition metals*

*in this data set: K, Ca+Mg, V

Non-Catalytic Baseline



Catalyst Dispersion

Catalyst activity depends strongly on grain size [Radovic *et al.*, 1983; Cope *et al.*, 1994; numerous heterogeneous catalysis studies]

Bulk granular mineral matter in coals has low catalytic activity [Tomita *et al.*, 1977]

in parent materials

- exchanged cations
- soluble salts
- organometalics w/ essential biofunction

- mineral grains
- granular additives
- soil

carbonization

in chars

nanophase particles (highly active)

bulk inorganic matter, d>1μm (low activity)

"nanophase dispersion"

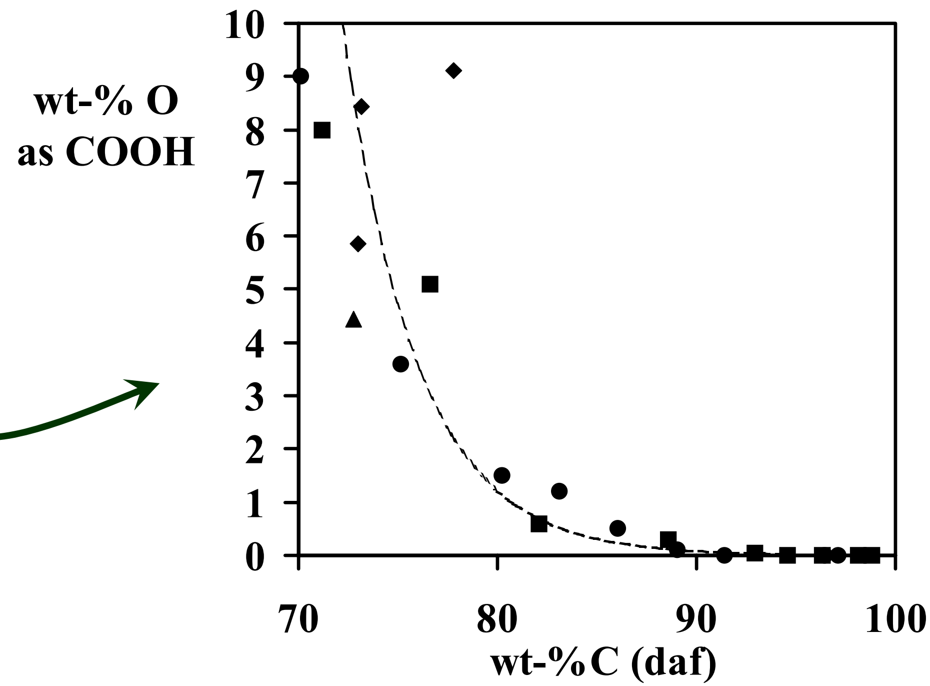
"granular dispersion"

Fuel-Specific Dispersion Rules

coals

mixed nano- and granular dispersion

nanodispersed fraction determined by comparing concentration of ion-exchange (carboxylic) sites to catalyst loading



biomass

mixed nano- and granular dispersion

K (dominant) and Ca: primarily in soluble or ion-exchangeable forms [Jenkins *et al.*, 1998], except bagasse, which has been washed during processing.

tires

granular inorganic impurities

cokes

V is nano-dispersed in porphyrins

Hybrid Approach Result

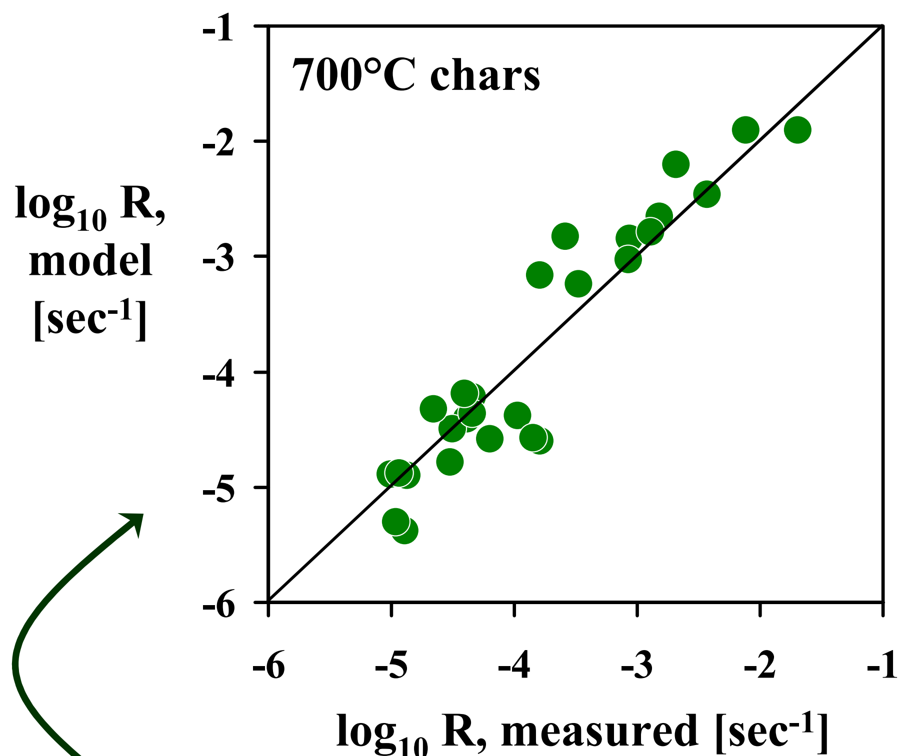
Reactivity, R

=

R_{carb} = fxn (wt-% C of precursor)

+

$$R_{cat} = 7.9 \cdot 10^{-7}\,(K_{nano}) + 1.3 \cdot 10^{-7}\,(Ca_{nano} + Mg_{nano}) + 3.1 \cdot 10^{-8}\,(V_{nano})$$



Most reactivity variation explained through 4 precursor properties:

K_{nano}, $(Ca+Mg)_{nano}$, wt-% C, V_{nano}

(*in order of decreasing importance*)

Reactivities of Diverse Solid Fuels: Conclusions

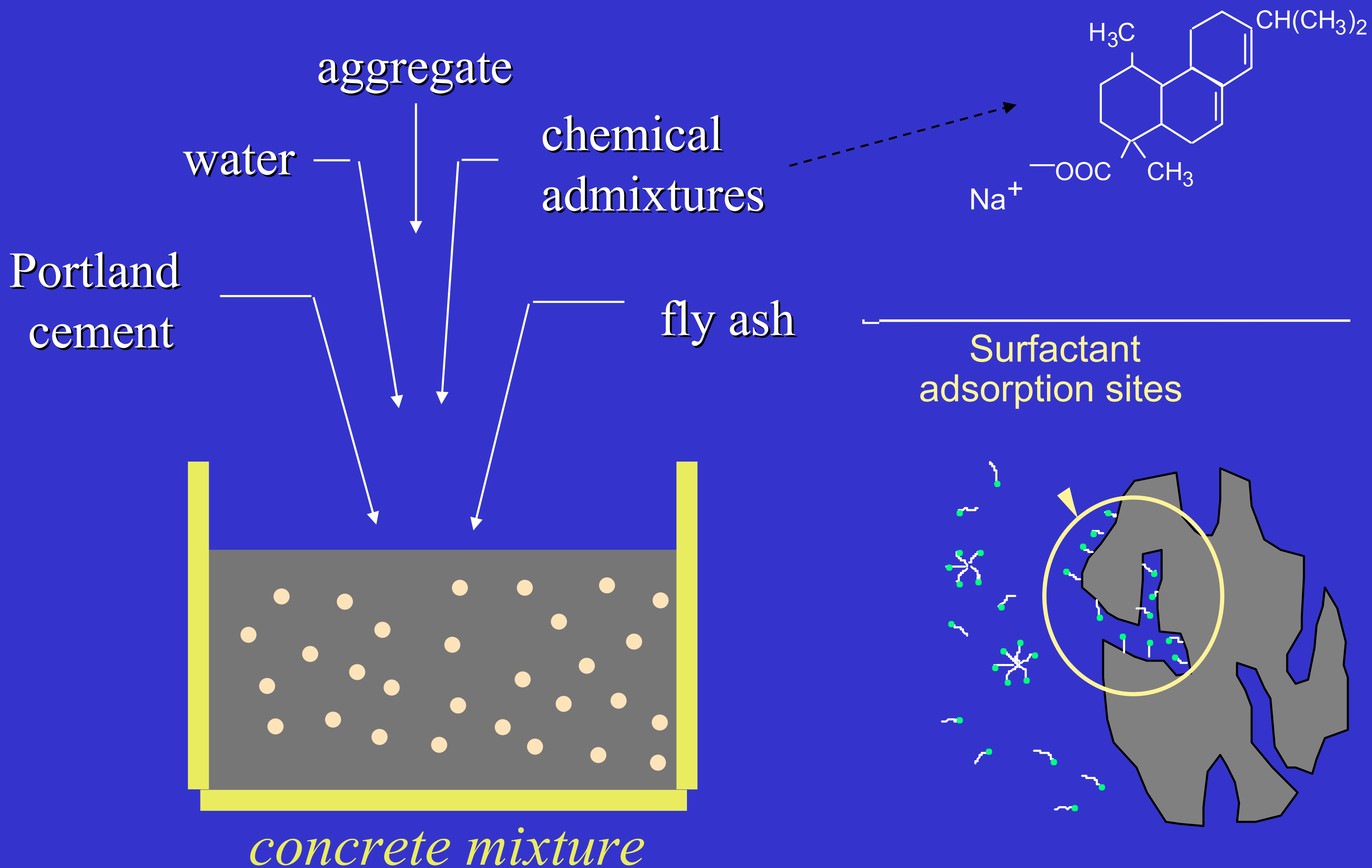
For coals, reactivity correlates well with organic composition (C,H,O,N,S), but the trend is NOT evident for solid fuels of < 80% C, daf (most practical fuels).

For 700°C chars, catalysis is the dominant factor determining reactivity trends (in agreement with most demineralization studies).

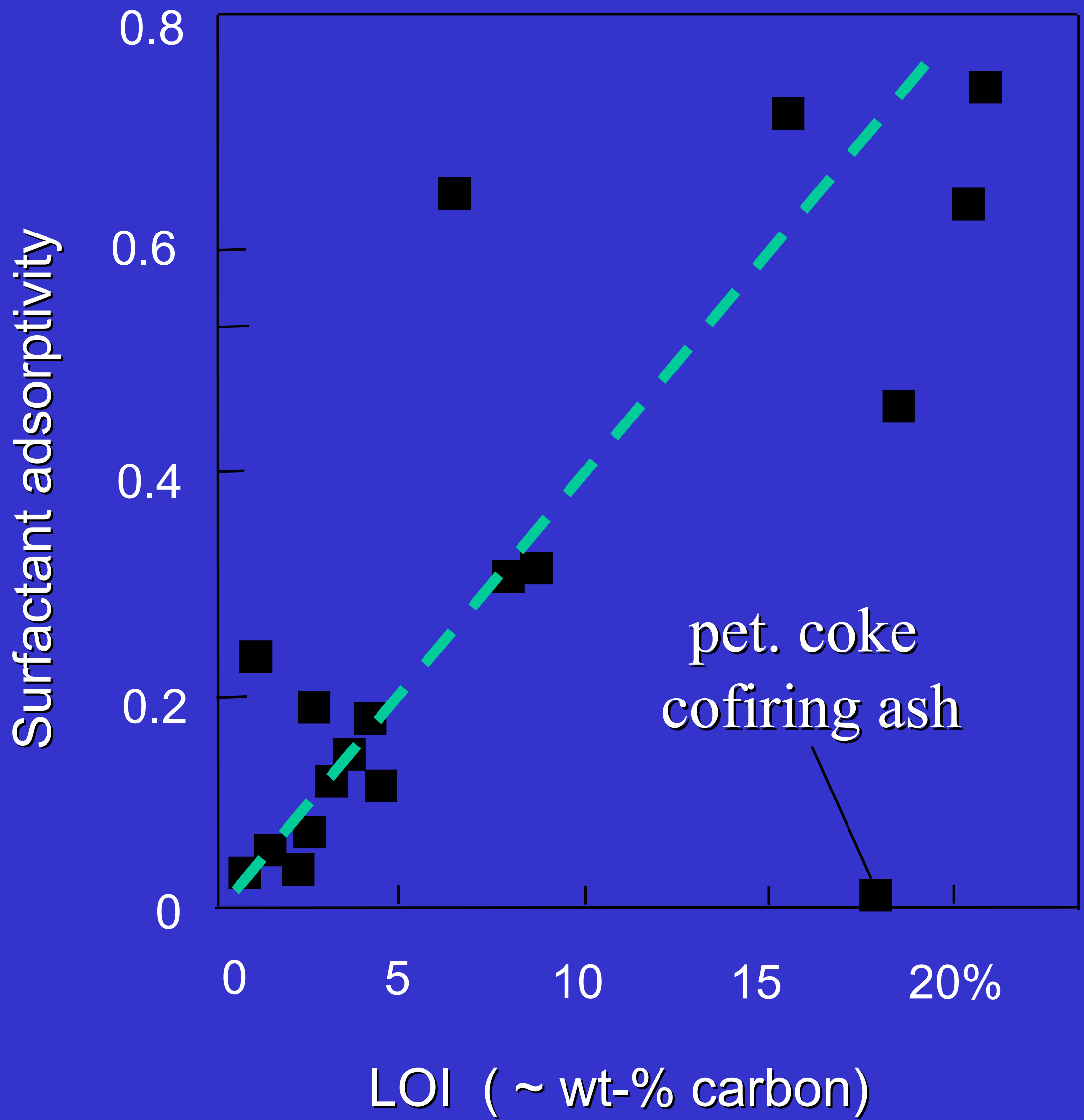
Sensitivity studies (according to model coefficients) suggest that virtually no natural materials can be safely assumed to be non-catalytic. [K_{nano} must be < 44 ppm; $(Ca+Mg)_{nano}$ < 270 ppm]

Crude estimation of reactivity is possible based on parent fuel characterization alone, *if* the model incorporates literature information on the form and dispersion of inorganic matter.

Air Entrainment in Fly Ash Concrete

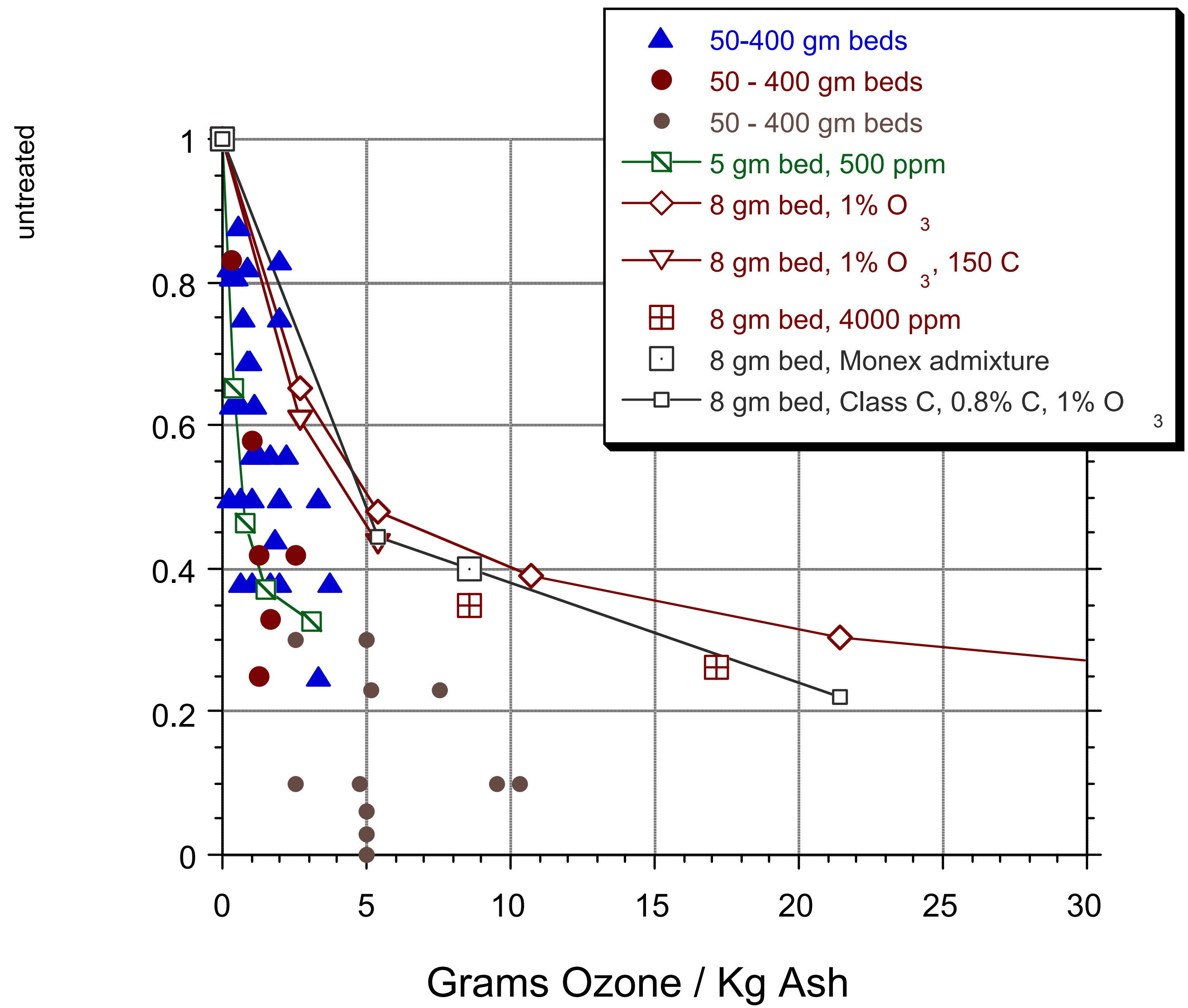


[Freeman, et al., 1996; Smith et al., 1998]

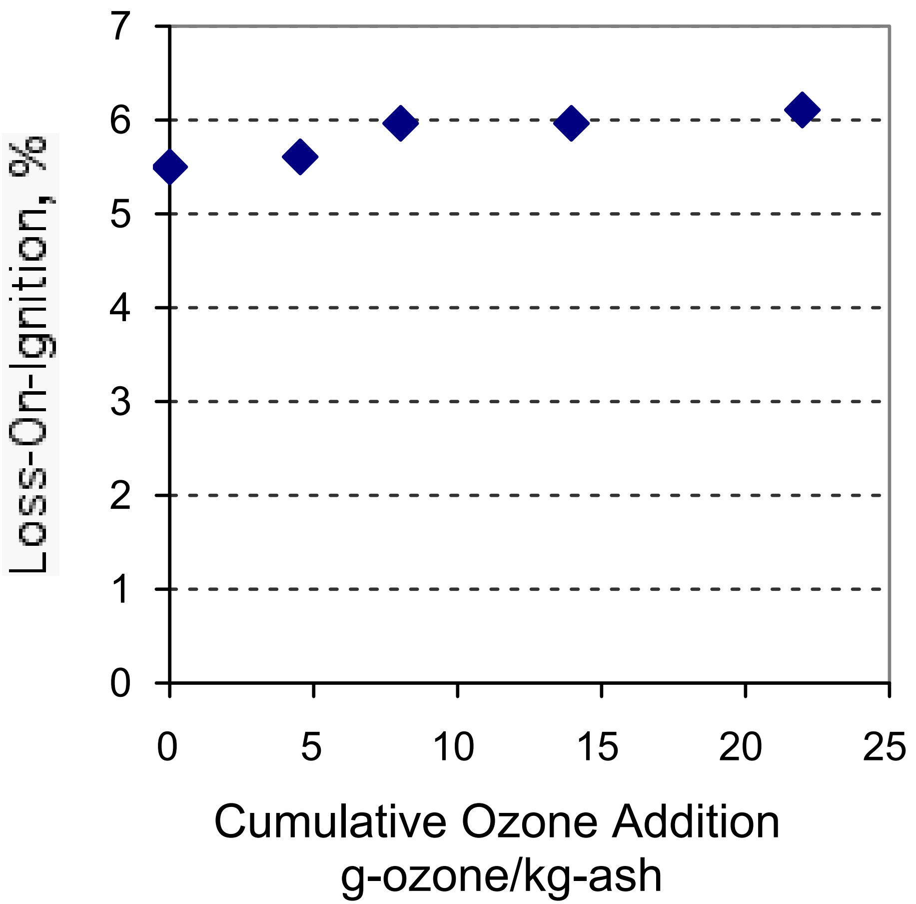


- surfactant adsorptivity varies widely
- variation at constant LOI is <u>significant</u>
- behavior related to carbon *properties*

Ozone Treatment Found to Reduce Surfactant Adsorptivity (Foam Index) And Improve Ash Performance in Concrete

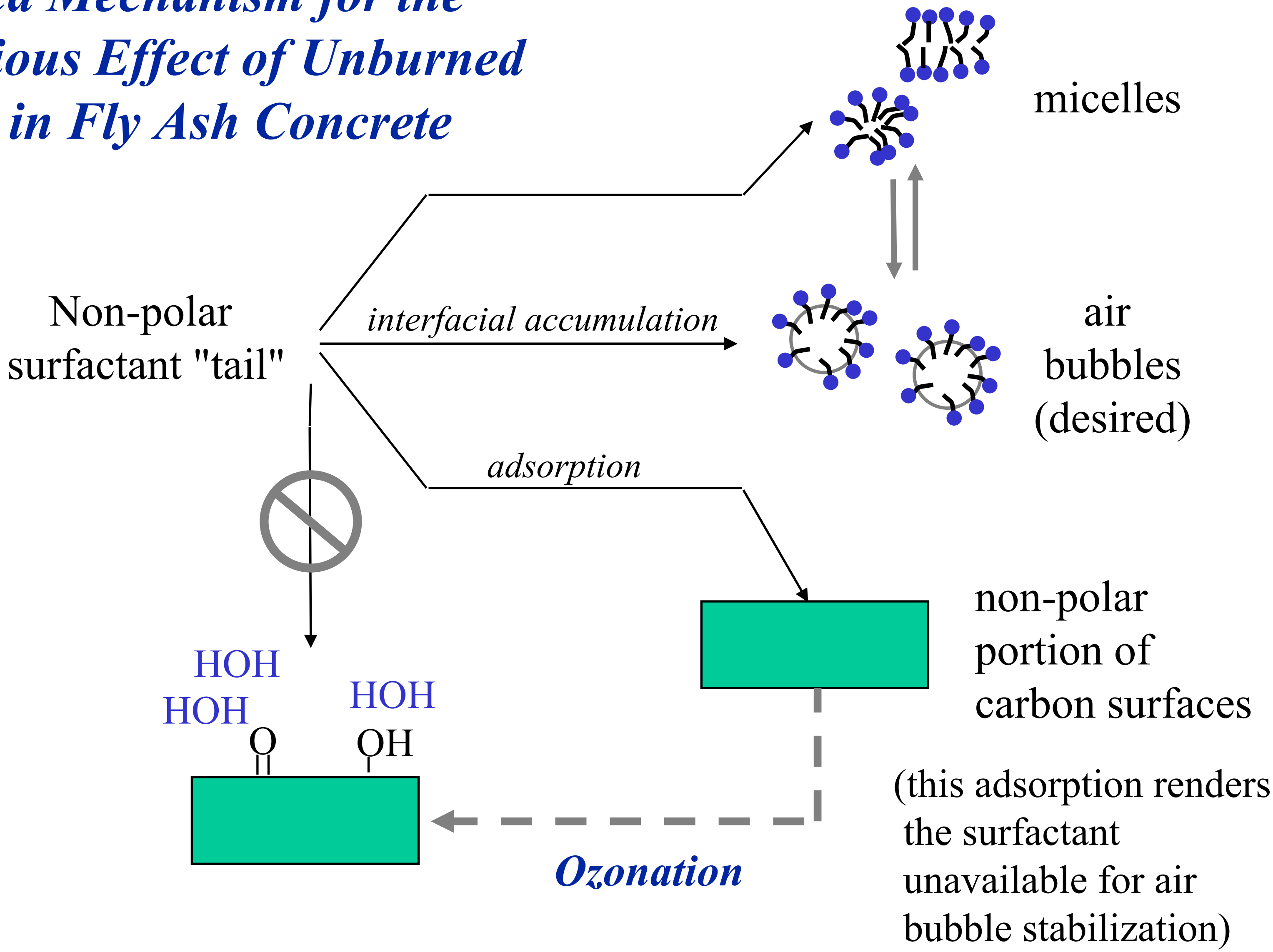


Effect of Ozonation on Carbon Content



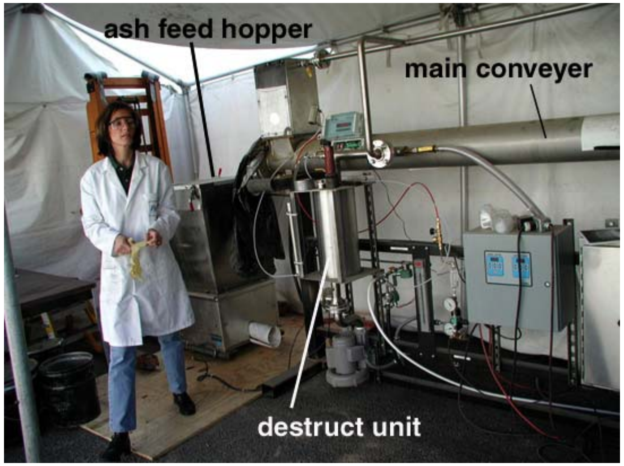
The major effect is *surface* oxidation, not carbon consumption

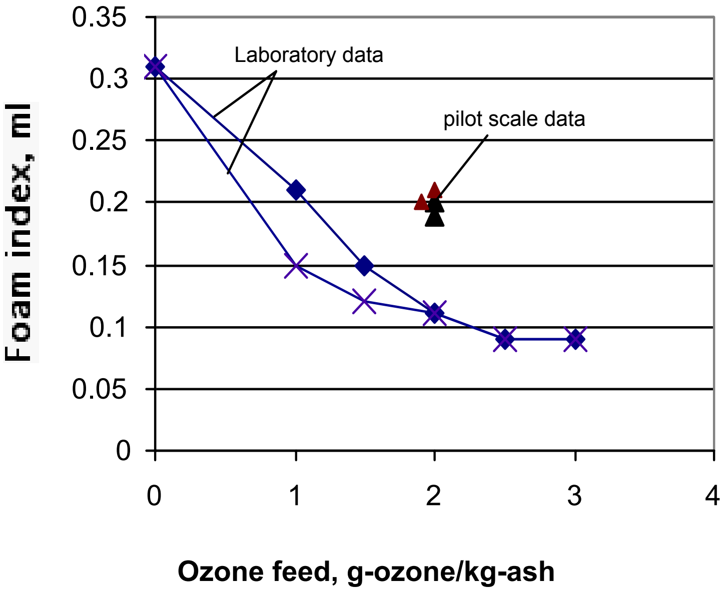
Proposed Mechanism for the Deleterious Effect of Unburned Carbon in Fly Ash Concrete



Development and Scale-up of Ash Ozonation Process

A team of organizations has been assembled to pursue the densign, scale-up and commercialization of Brown's patented fly ash ozonation technology. The team includes: PCI-Wedeco, PP&L (power generating utility), Fuller Bulk Handling, EPRI, Brown, and EES for support and project management. along with funding from the Dept. of Energy, National Energy Technology Laboratory





First generation pilot plant at PCI-Wedeco, West Caldwell N.J., the world's leading manufacturer of ozone generators. **Left:** portion of the pilot plant; **Right:** early results.

ACKNOWLEDGMENTS

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