# Mercury Speciation in Coal-Fired Power Plant Flue Gas - Experimental Studies and Model Development

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# Outline

- Background
- Methods
  - Fly ash characterization
  - Hg uptake test
  - TPD studies
  - Modeling
- Results and Discussion
  - Effects of fly ash and its components
  - Interaction between flue gas and carbon surface
  - Theoretical calculations
- Conclusions

# Background: Hg Speciation in CFPP

- $Hg^0$, $Hg^{2+}$, $Hg_p$
- Oxidation
  - Gas-phase
  - **Fly ash mediated**
    - Flue gas components
    - Fly ash characteristics
  - $NO_x$ Control

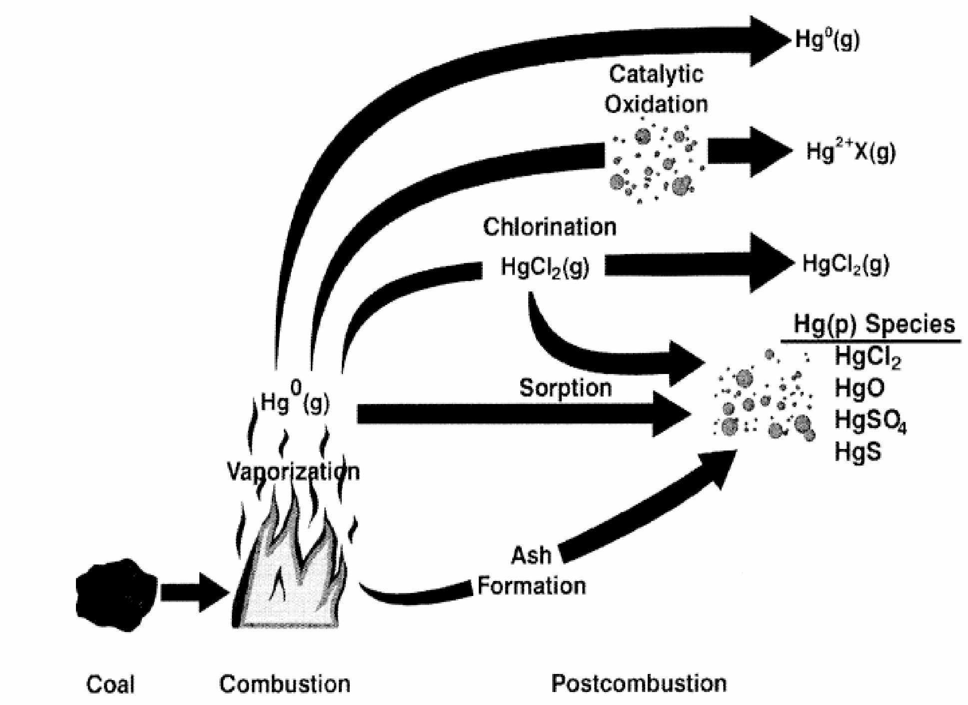



Fig. 1. Potential mercury transformations during coal combustion and subsequently in the resulting flue gas.

Galbreath, K. C.; Zygarlicke, C. J. *Fuel Processing Technology* **2000,** 65, 289-310

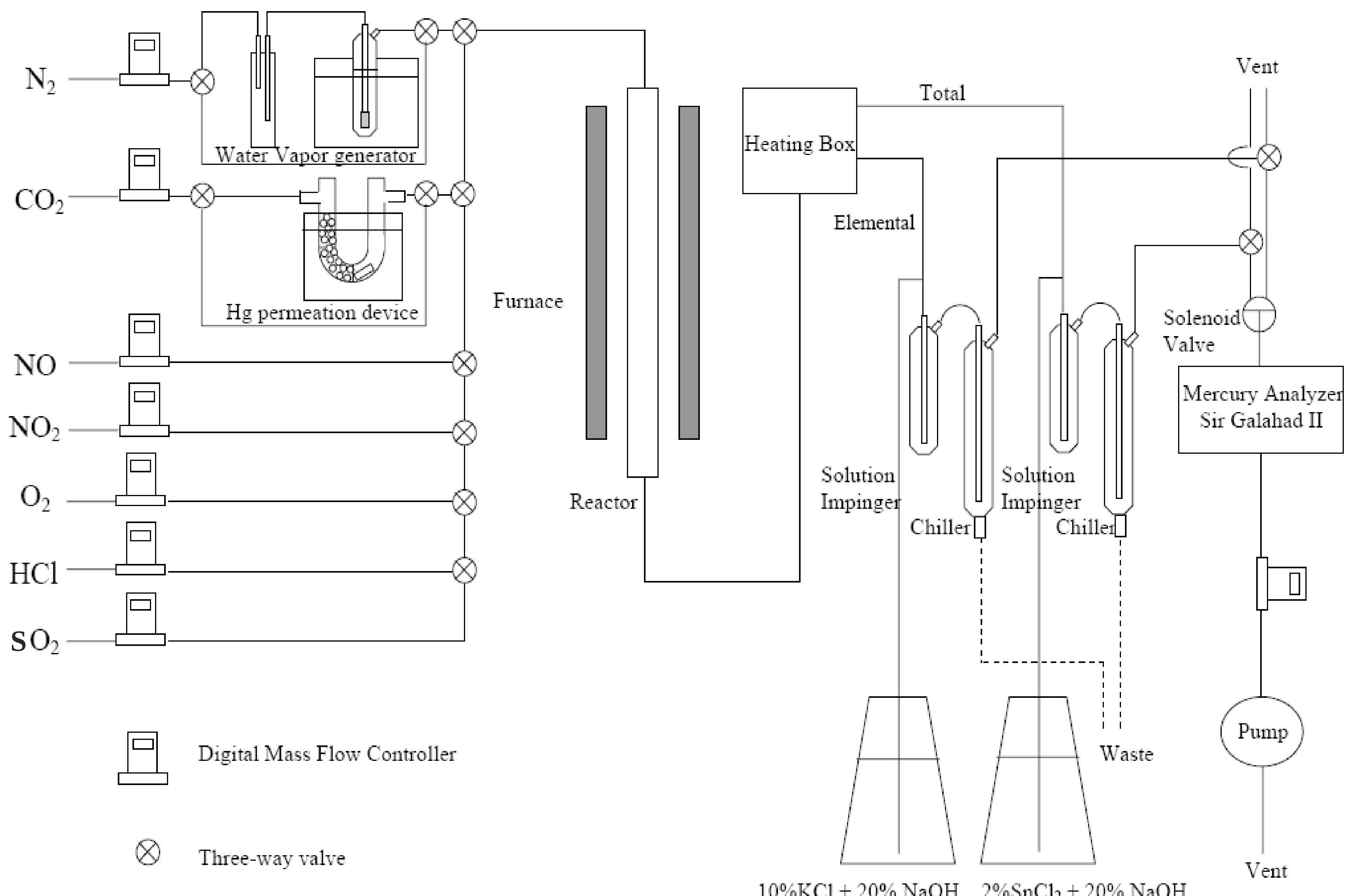
# Fly Ash Properties

- Constituents ($SiO_2$, $Al_2O_3$, $Fe_2O_3$…)
  - Crystalline minerals
  - Non-crystalline aluminosilicate glass
  - Unburned carbon
    - The lighter the color, the lower the carbon content
- Size 0.5μm-100μm

# Samples Characterization

- Six ESP hopper fly ash samples:
  - Salem Harbor (SH), Brayton Point (BP), Gaston, Pleasant Prairie (PP), CE1 and CE2
- One carbon black sample:
  - Cabot Black Pearls 460
- Methods: SEM-EDAX, XPS, LOI, BET, Particle Size Distribution, TPD

# Mercury Uptake Testing



# Flue Gas Composition

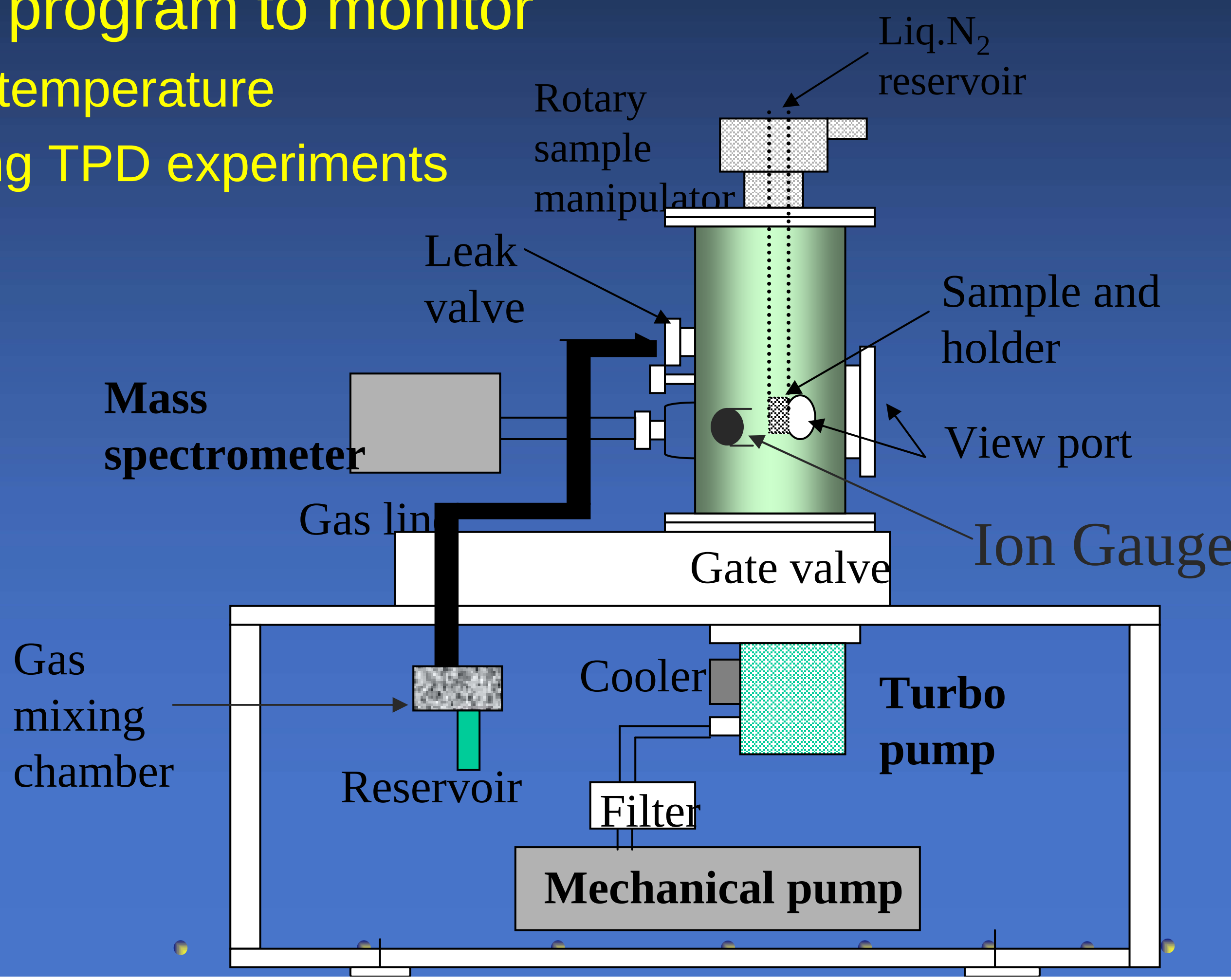
| Gases | $CO_2$ | $O_2$ | NO | $NO_2$ | HCl | $SO_2$ | $N_2$ |
|---|---|---|---|---|---|---|---|
| [Feed Tanks] | 99.99% | 99.99% | 3027ppm | 488ppm | 1022.2ppm | 1.01% | 99.99% |
| [Desired] | 13.5% | 6% | 300ppm | 20ppm | 50ppm | 0.15% | Balance |
| Flow rate (ml/min) | 135 | 60 | 99.1 | 41.0 | 48.9 | 148.5 | 467.5 |

Hg concentration: ~ 18$\mu$g/m$^3$

Sample: 50mg sample mixed with 4 g glass beads

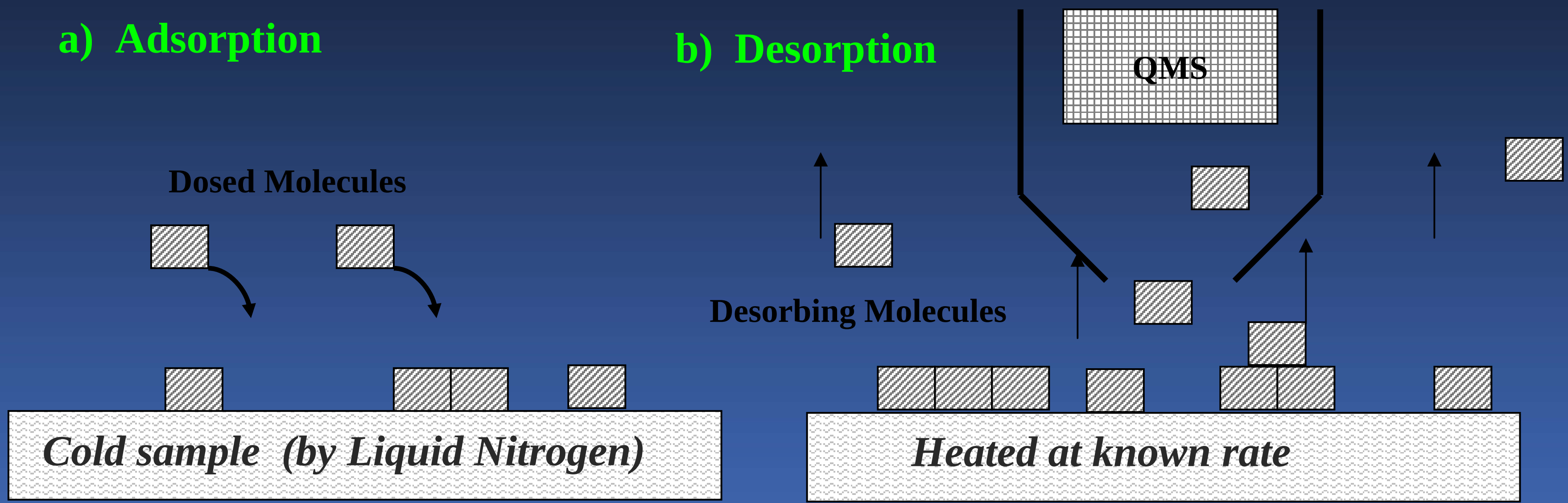
# TPD Analysis

- Ultra-high vacuum (UHV) chamber
- Residual gas analyzer (mass-spec)
- A custom Labview program to monitor
  - total pressure and temperature
  - mass spectra during TPD experiments



# TPD Analysis

- Sequence of Experiments




- Data analysis

$$-\frac{d\theta}{dt} = k_d \theta^n = \nu \theta^n \exp\left(-\frac{E_d}{RT}\right)$$

$d\theta/dt$ = rate of desorption, $k_d$ = desorption rate constant

$\theta$ = surface coverage, T = temperature (K), t = time (s)

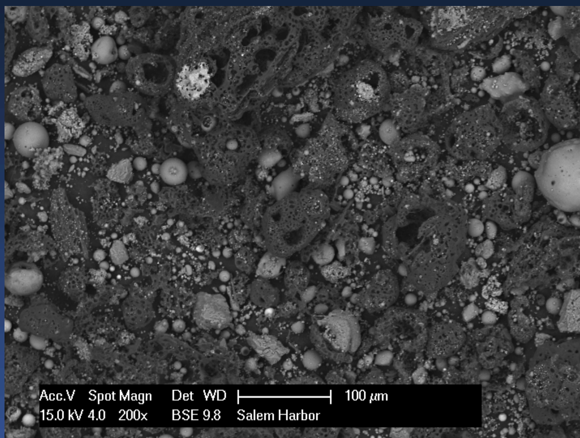
$\nu$ = pre-exponential factor of desorption ($s^{-1}$), n =reaction order.

$E_d$ = desorption activation energy (J/mol), R = gas constant (J/mol-K)

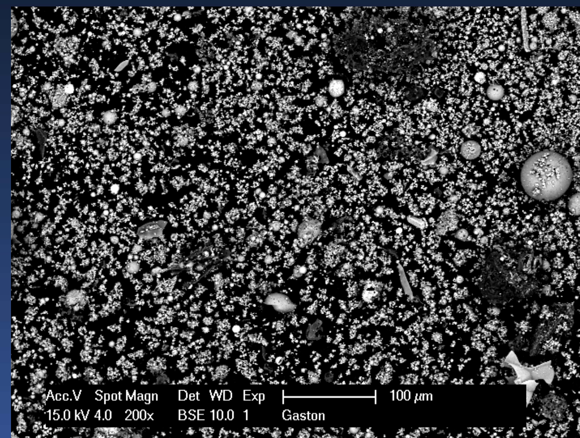
# Results

- Part 1
  - Fly ash characteristics
- Part 2
  - Hg uptake tests with fly ash and its components in flue gas
  - Correlation between Hg uptake and fly ash characteristics
- Part 3
  - Hg uptake tests with carbon black and different flue gas combinations
  - Correlation between Hg uptake and TPD Analyses & XPS Analyses
  - Theoretical calculations

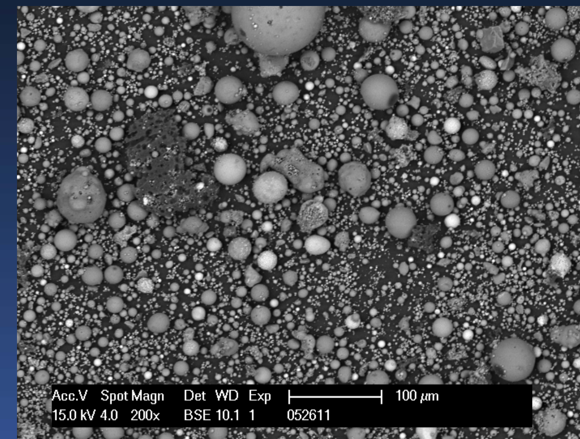
# SEM Images of Fly Ash Samples



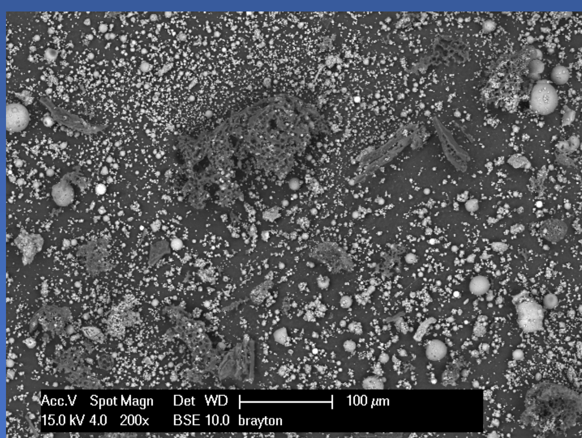

SH



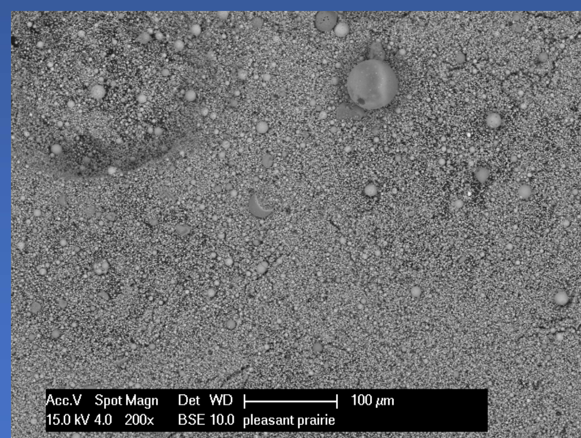

Gaston



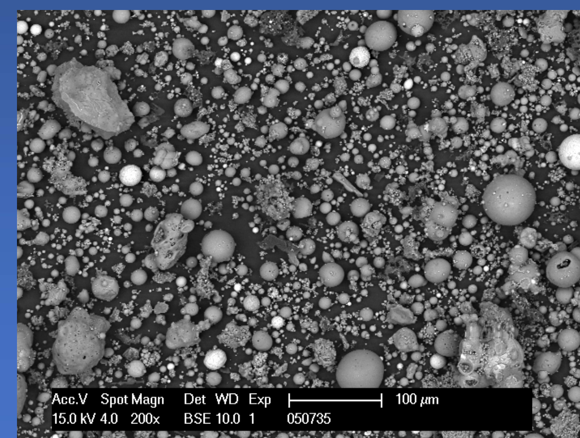

CE1




BP




PP

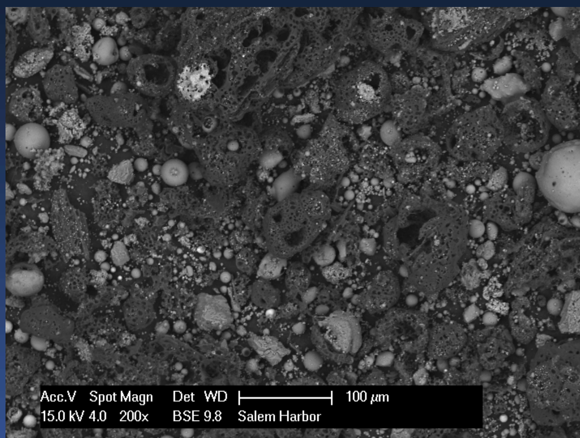



CE2

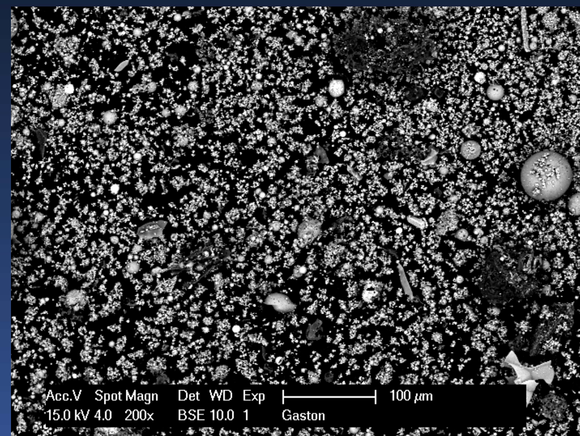
# Fly Ash Characteristics

| Sample | Surface Area ($m^2/g$) | LOI (%) | Moisture (%) | Particle size (μm) |
|---|---|---|---|---|
| **SH** | **17.9** | **37.2** | 0.1 | 92.7 |
| **BP** | 5.8 | 18.1 | 0.1 | 77.6 |
| **Gaston** | 2.1 | 11.9 | 0.2 | 30.3 |
| **PP** | 3.0 | 1.0 | 0.2 | 48.0 |
| **CE1** | 2.5 | 6.0 | 0.1 | 32.7 |
| **CE2** | 1.1 | 3.1 | 0.1 | 23.4 |
| **Carbon black** | 71.4 | - | - | 268 |

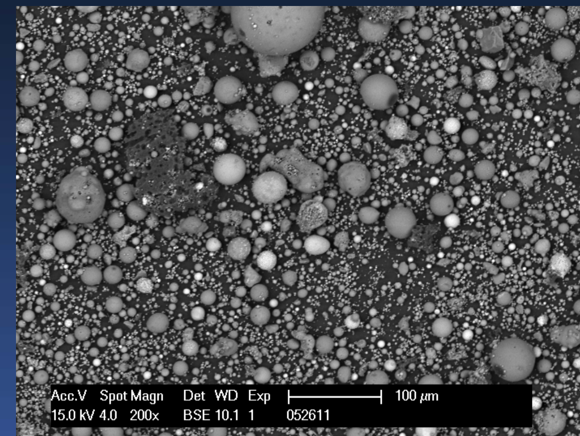
# SEM Images of Fly Ash Samples



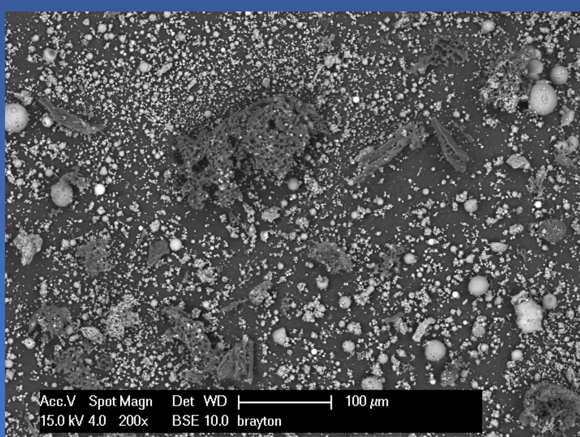

SH



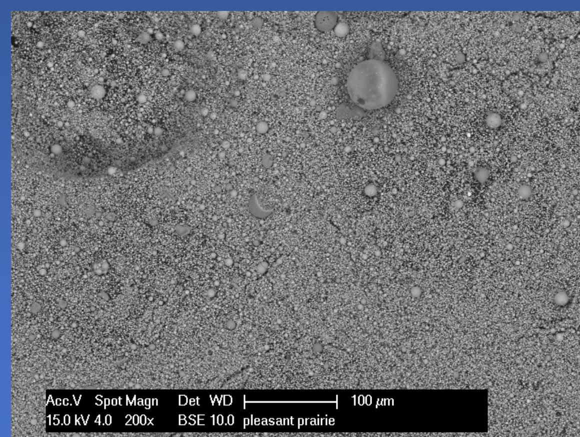

Gaston



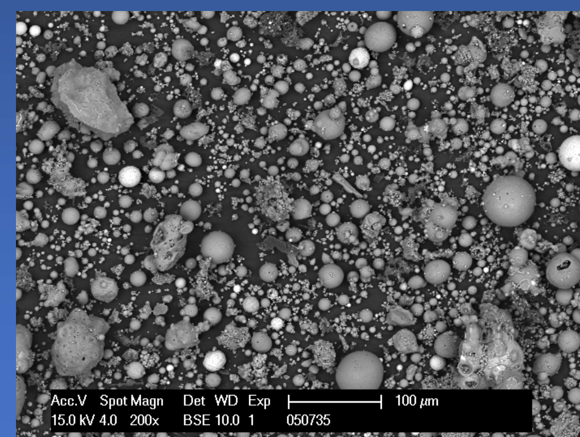

CE1




BP




PP



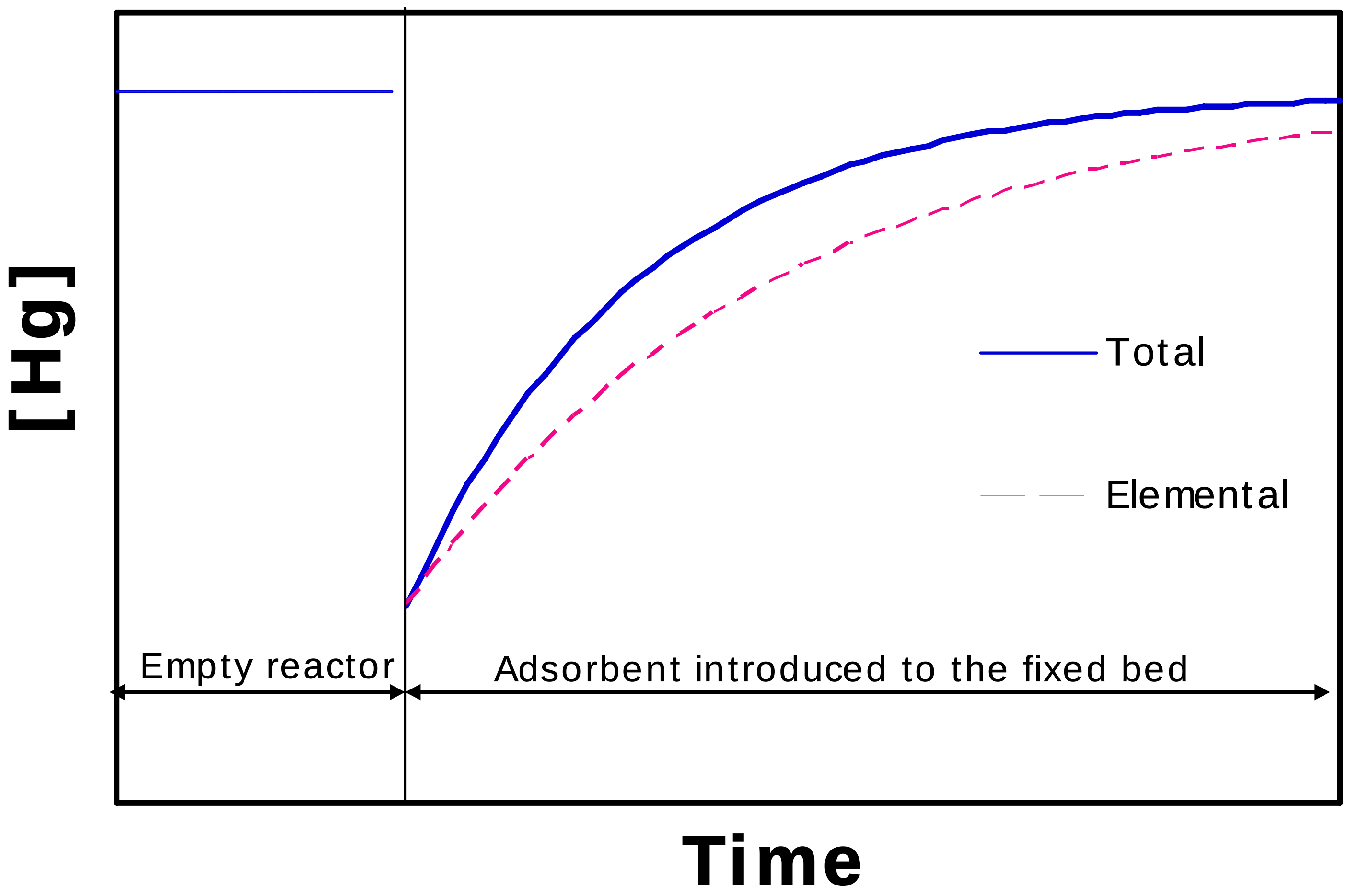

CE2

# XPS (Weight %)

| Fly Ash | C | O | Mg | Al | Si | S | Ca | Ti | Fe |
|---|---|---|---|---|---|---|---|---|---|
| SH | 41.4 | 31.9 | 0.3 | 4.5 | 10.9 | 4.9 | 1.5 | 0.3 | 2.9 |
| BP | 14.9 | 47.1 | 0.4 | 9.0 | 19.8 | 4.2 | 1.1 | 0.5 | 3.1 |
| Gaston | 9.7 | 48.4 | 0.6 | 6.3 | 11.2 | 14.6 | 1.7 | 0.5 | 3.2 |
| PP | 6.0 | 43.3 | 1.6 | 3.5 | 6.5 | 13.9 | 15.7 | 0.5 | 1.6 |
| CE1 | 16.0 | 45.1 | 0.1 | 6.8 | 16.2 | 6.9 | 2.2 | 0.5 | 5.4 |
| CE2 | 15.9 | 44.8 | 0.3 | 8.3 | 18.7 | 4.9 | 1.5 | 0.5 | 4.6 |

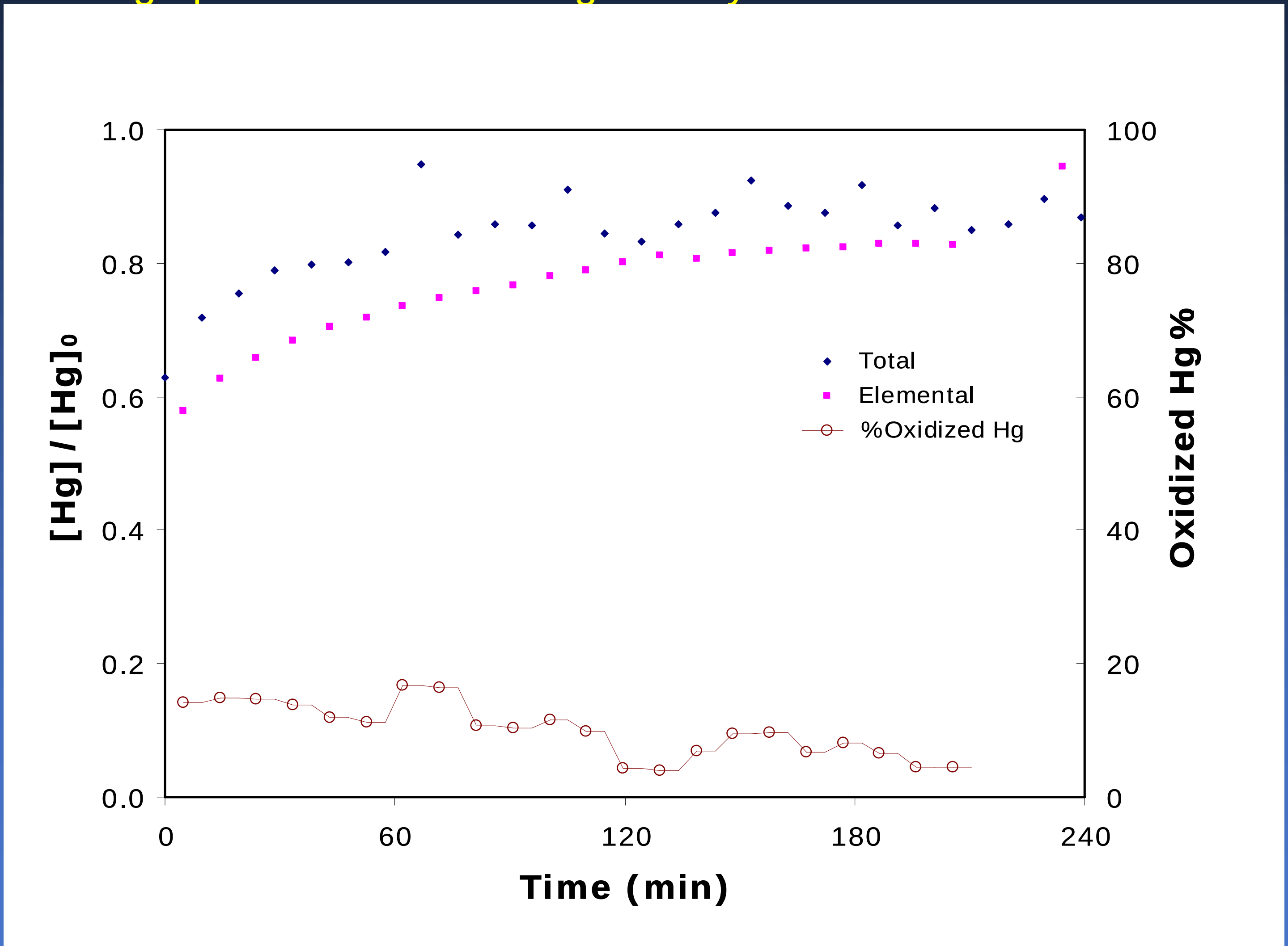
**$MgO$, $Al_2O_3$, $SiO_2$, $CaO$, $TiO_2$, and Unburned Carbon**

# Mercury Uptake Test



# Effects of Fly Ash Samples (CE1)

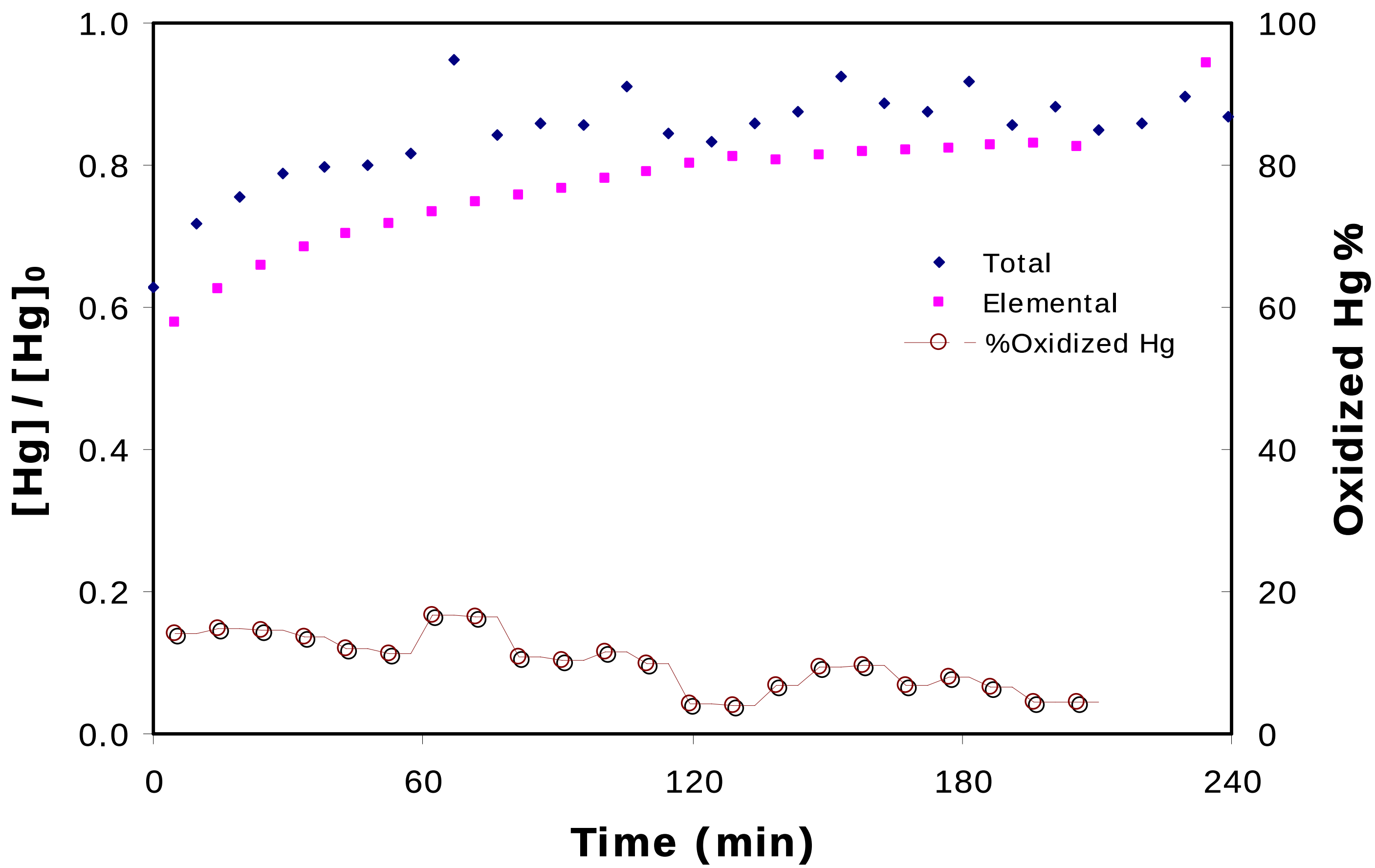
Hg uptake test with 50 mg CE1 fly ash at 140 $^{o}C$




**Oxidized Hg% = $(C_{total} - C_{Elemental})/C_{Total}$ x 100%**

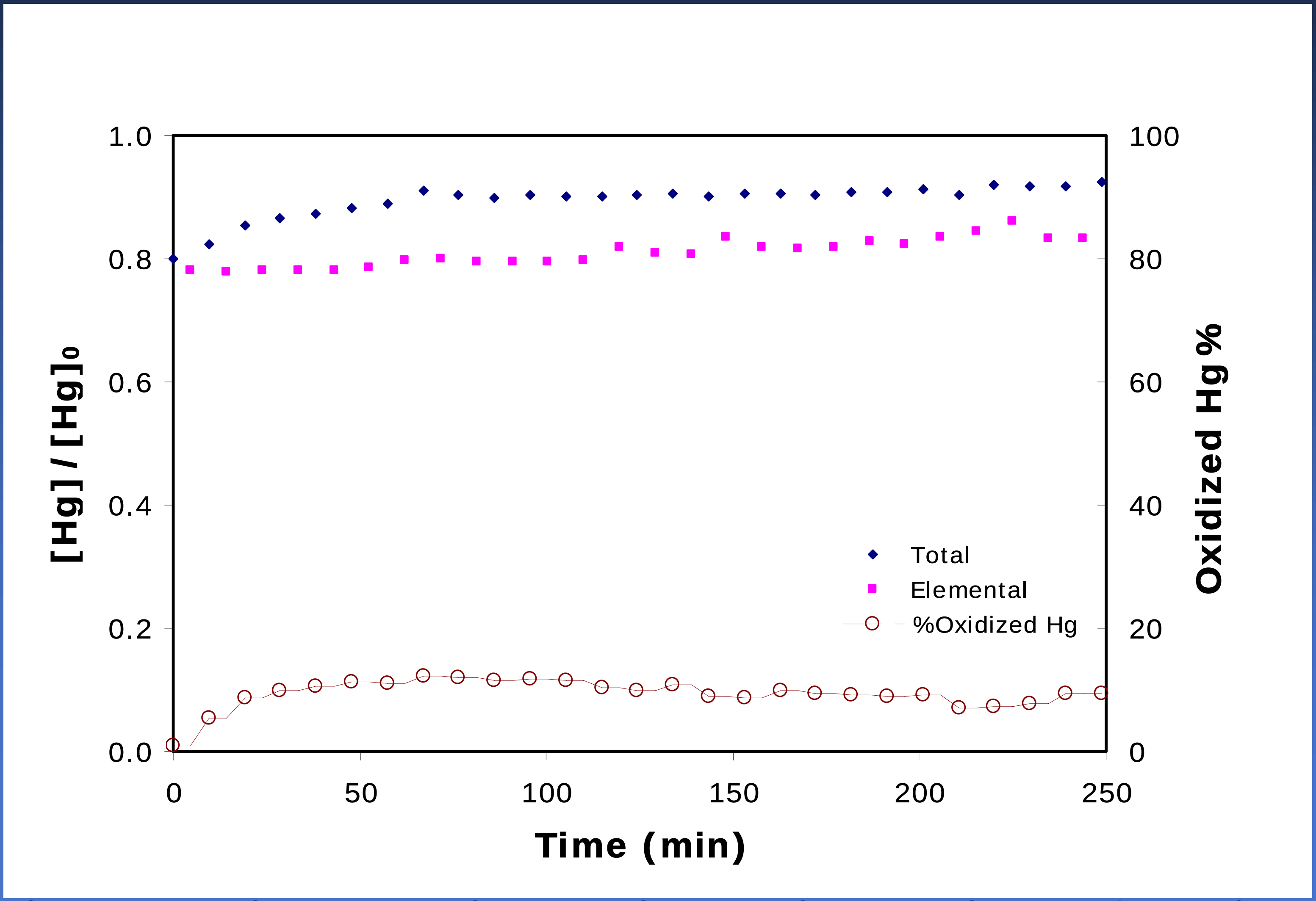
# Effects of Fly Ash Samples (CE2)

Hg uptake test with 50 mg CE2 fly ash at 140 $^oC$



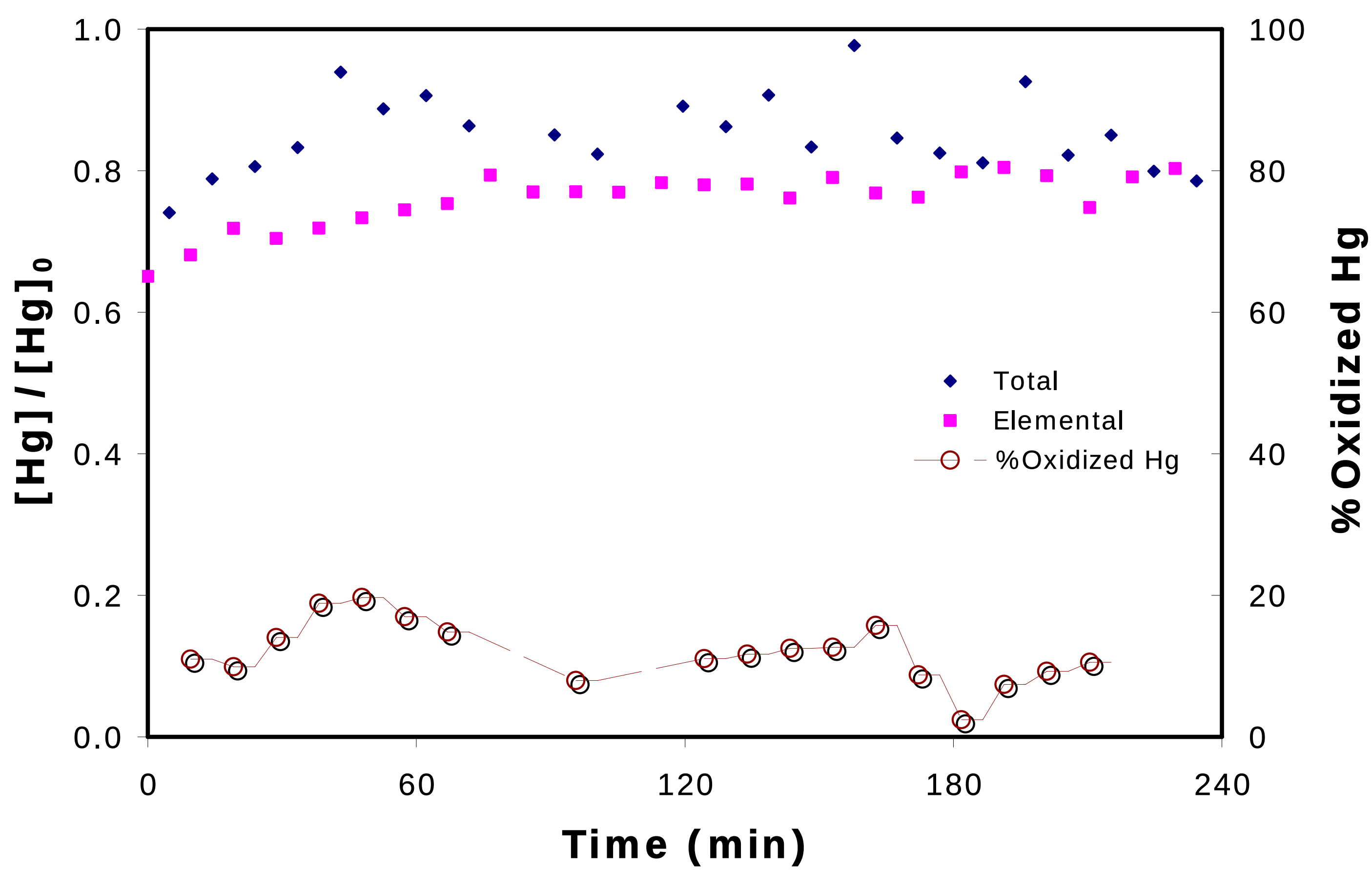
# Effects of Fly Ash Samples (PP)

Hg uptake test with 50 mg PP fly ash at 140 °C



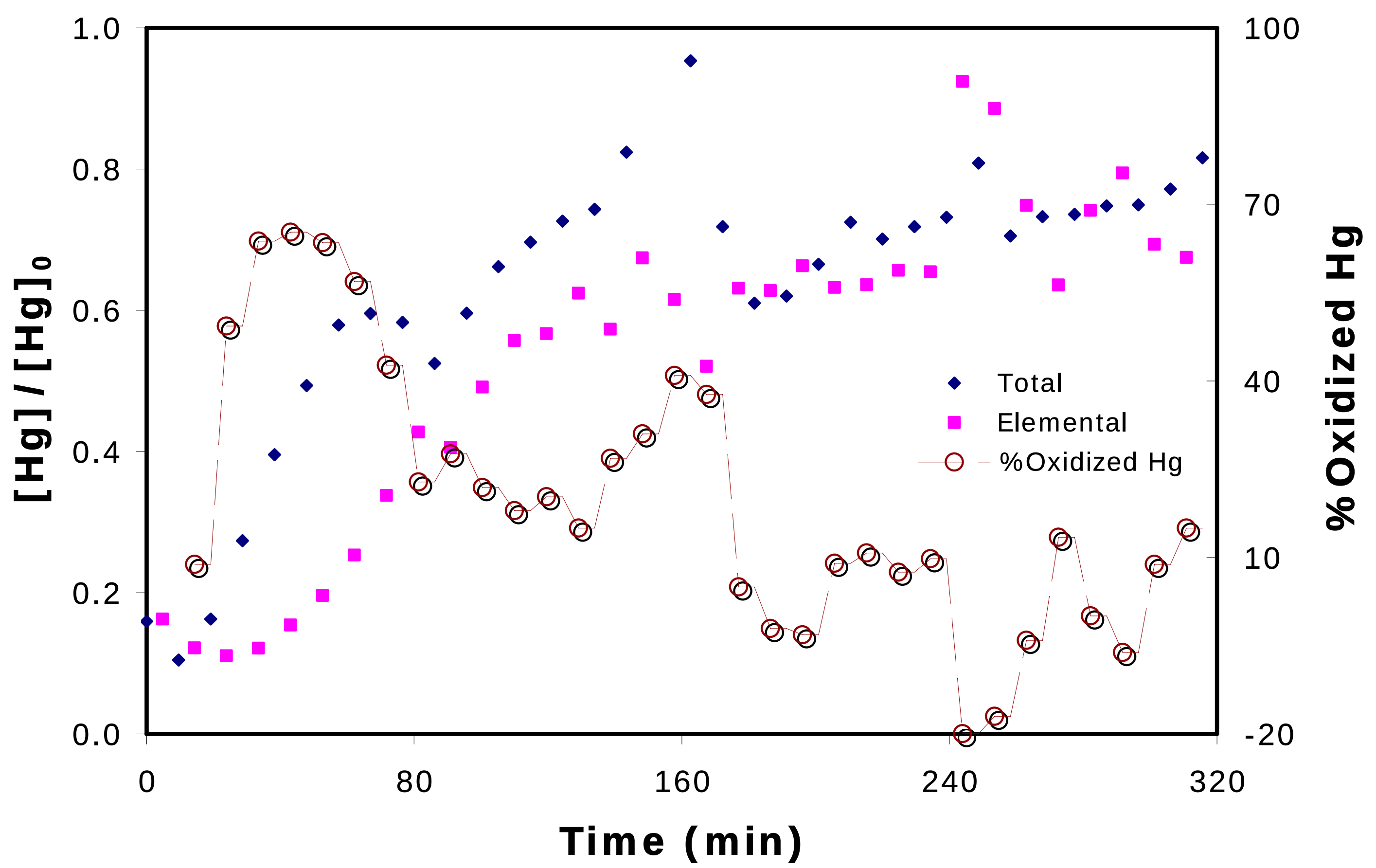
# Effects of Fly Ash Samples (Gaston)

Hg uptake test with 50 mg Gaston fly ash at 140 ºC



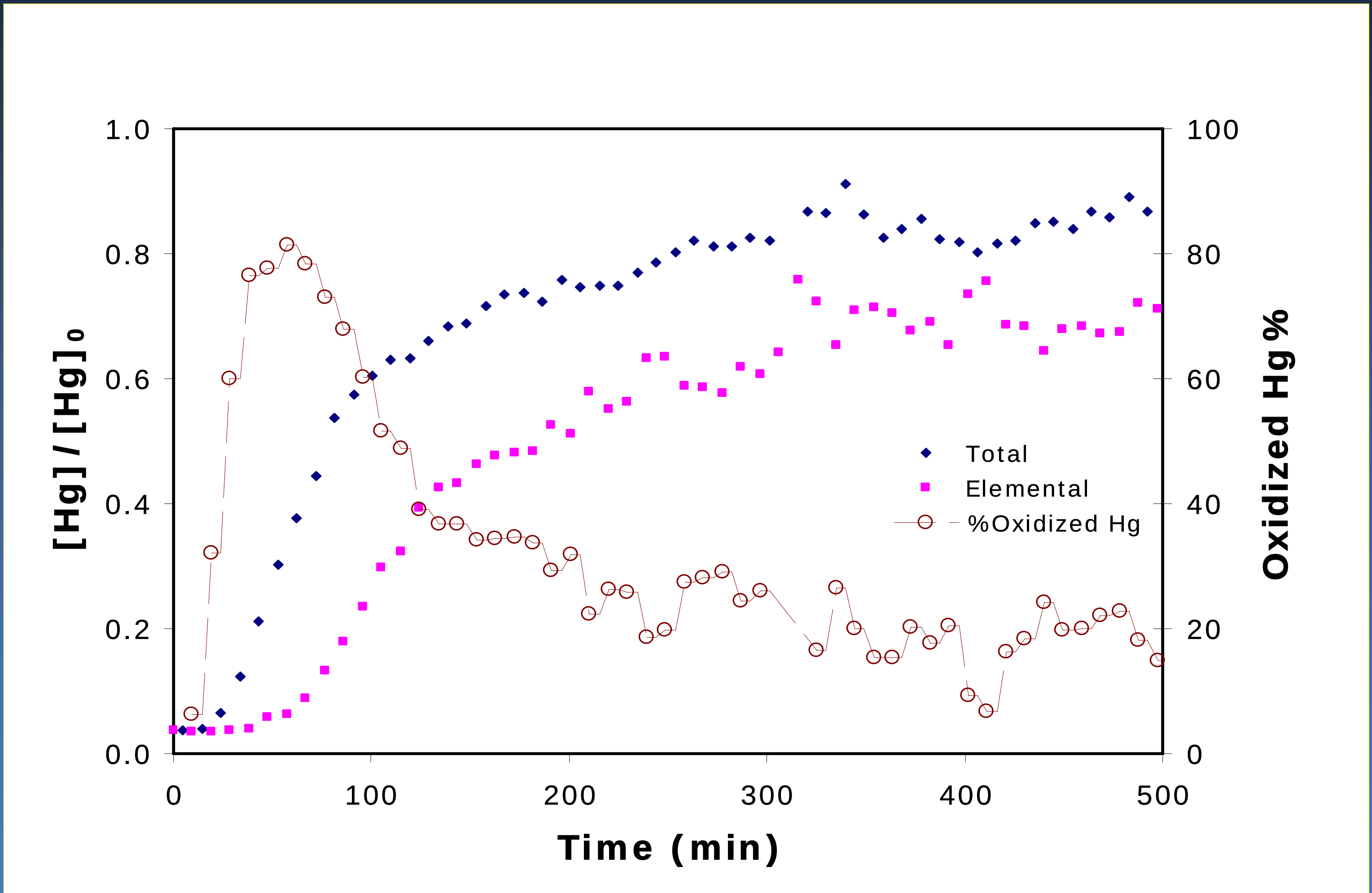
# Effects of Fly Ash Samples (Brayton)

Hg uptake test with 50 mg BP fly ash at 140 $^oC$



# Effects of Fly Ash Samples (SH)

Hg uptake test with 50 mg SH fly ash at 140 $^{o}C$

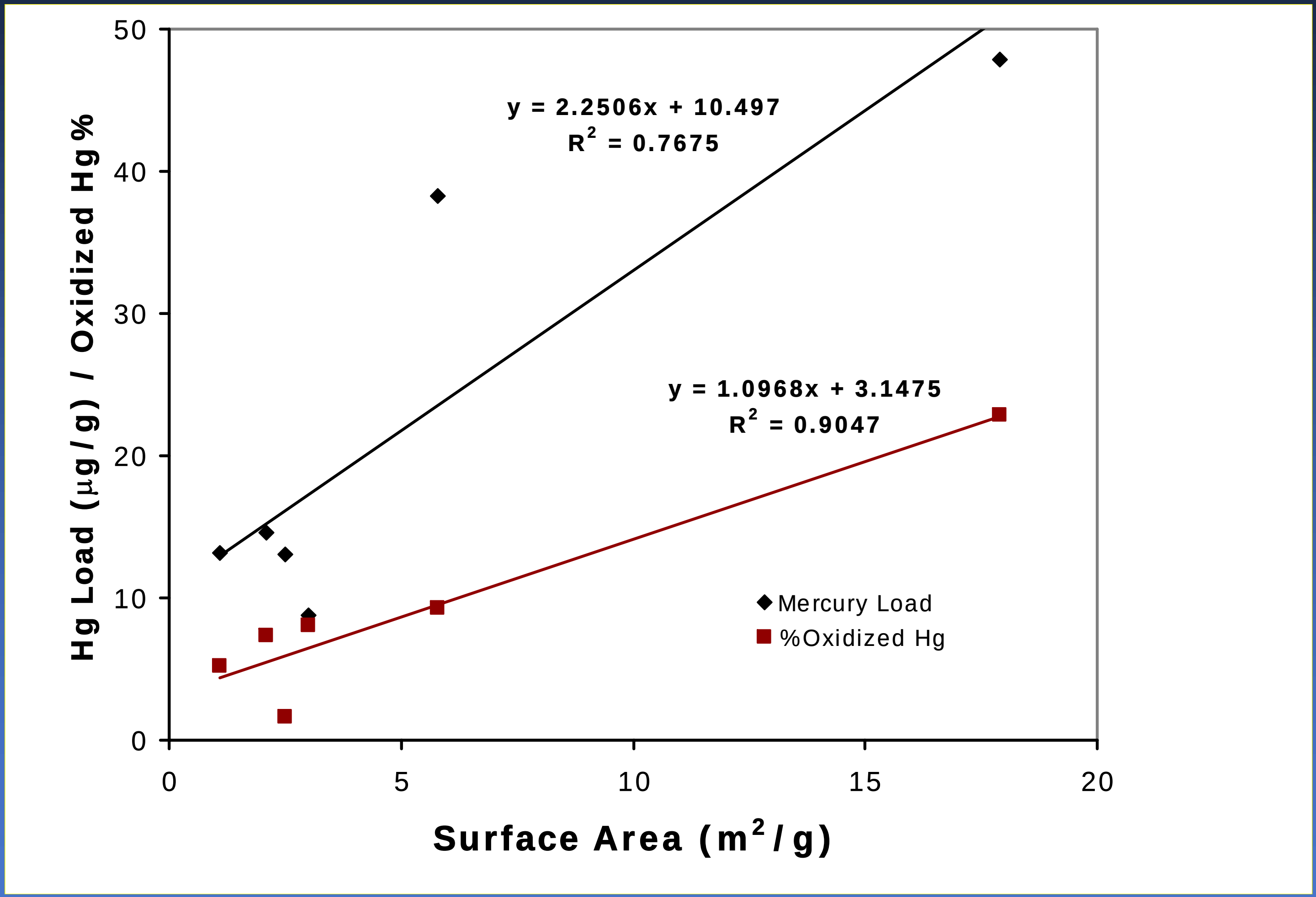


# Effects of Fly Ash Samples

Hg uptake and Oxidation after four-hour exposure

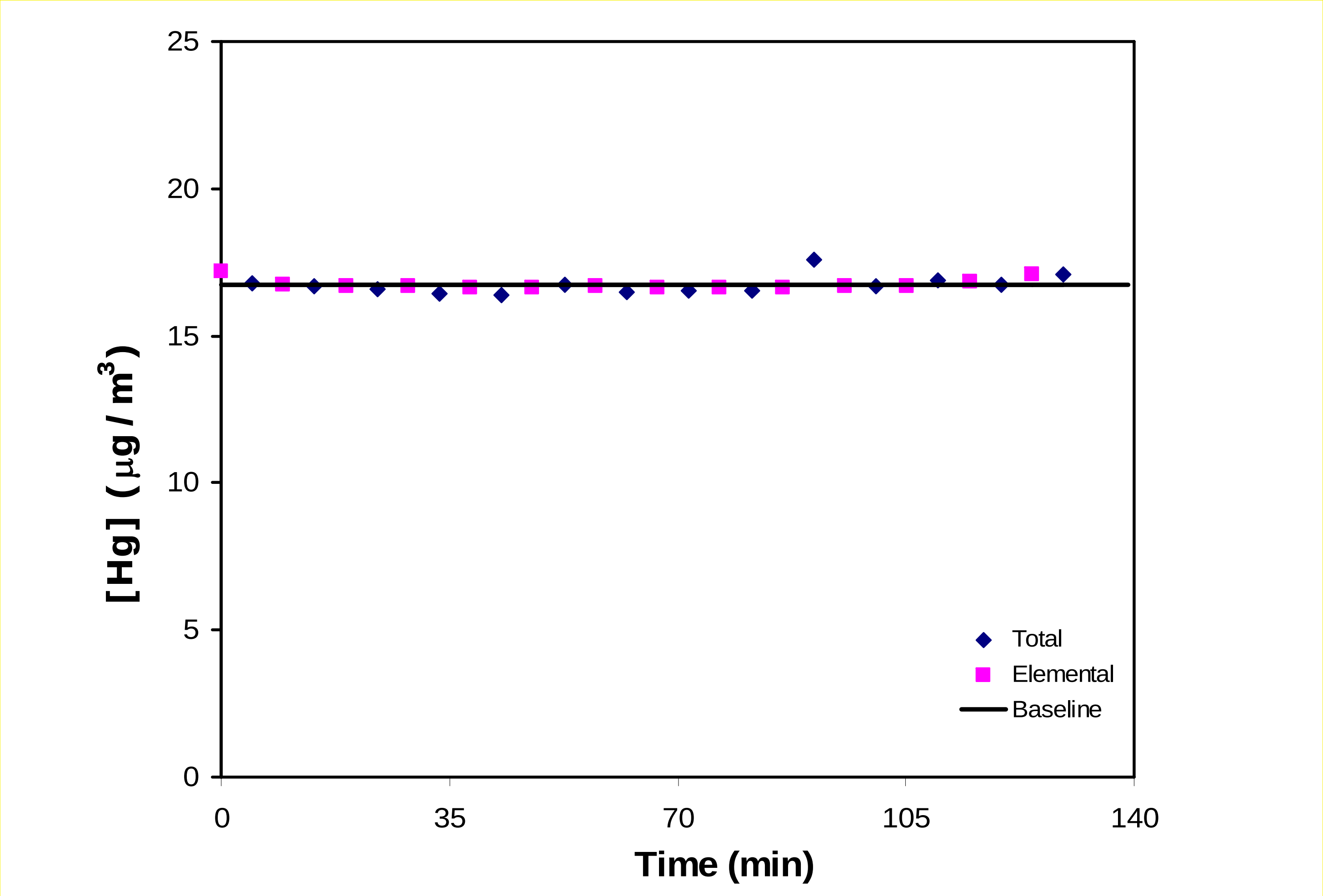
| Sample | Mercury Load (μg/g) | Oxidized Hg % |
|---|---|---|
| SH | 47.9 | 22.89% |
| BP | 38.3 | 9.33% |
| Gaston | 14.6 | 7.32% |
| PP | 8.8 | 8.08% |
| CE1 | 13.1 | 1.60% |
| CE2 | 13.2 | 5.20% |

# Effects of Surface Area on Hg Uptake and Oxidation



# Mercury Uptake by Fly Ash Components

Hg uptake test with 50 mg $Al_2O_3$ at 140 °C




**No promotion:**

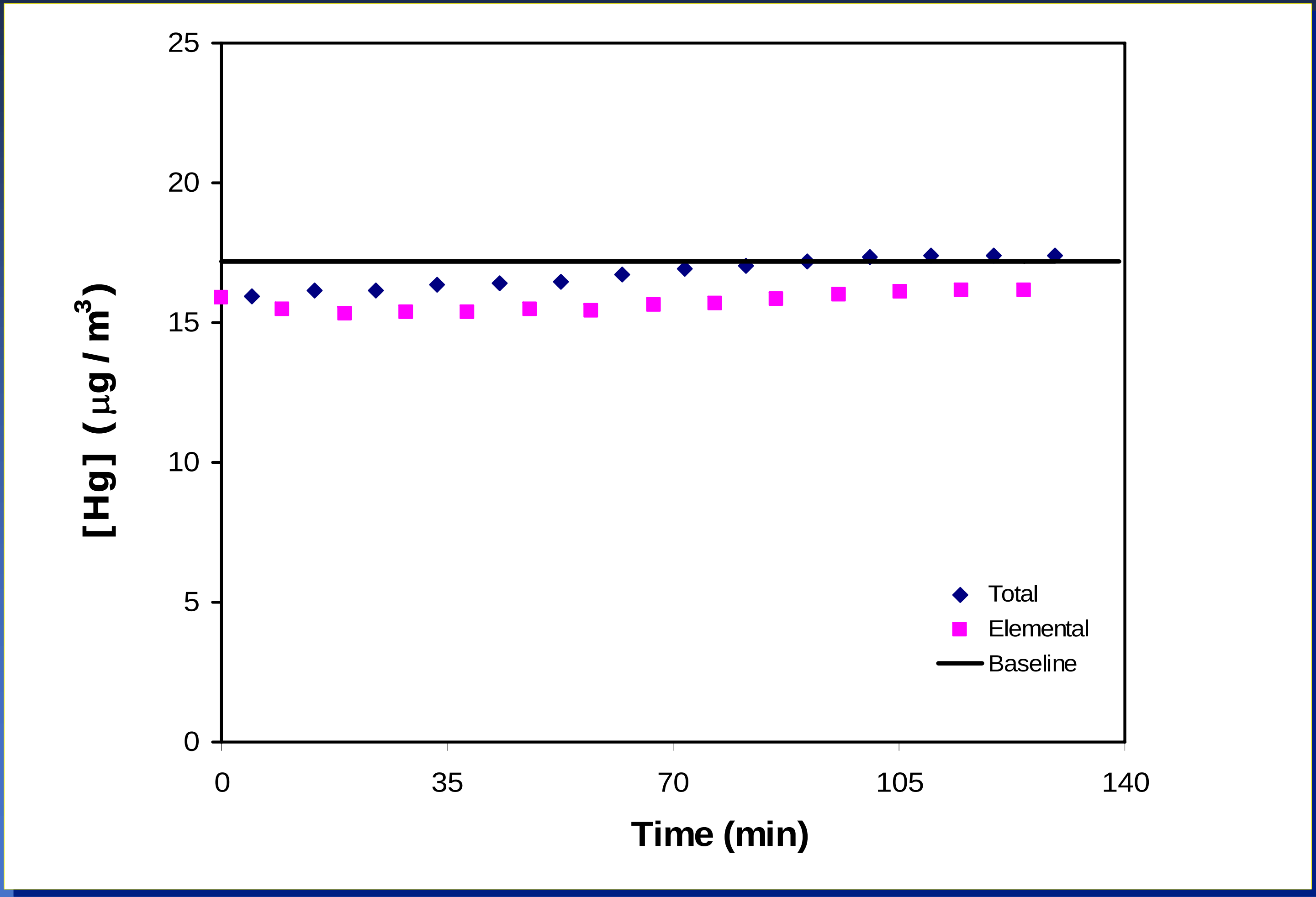
**MgO,**

**CaO,**

**$TiO_2$ (anatase)**

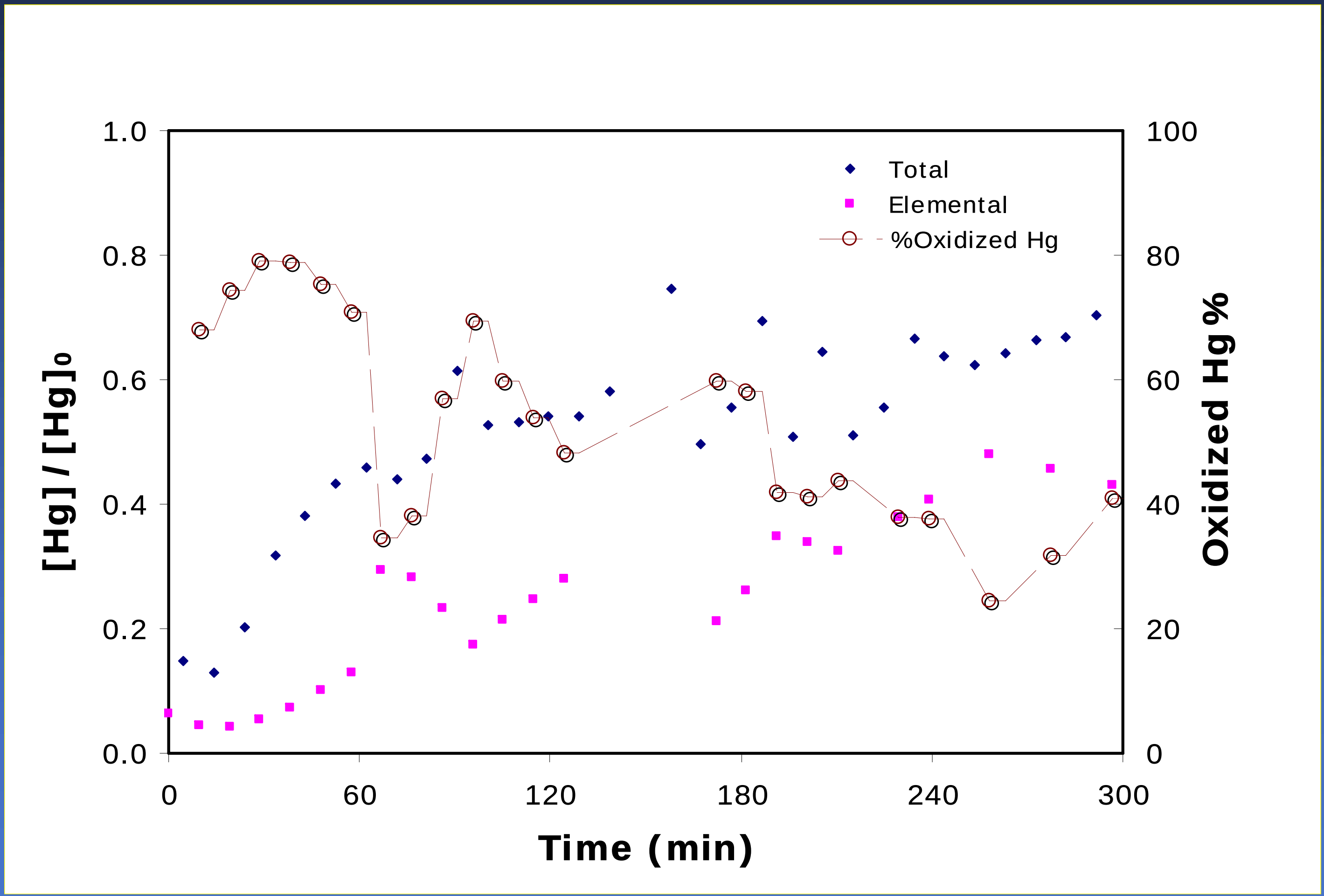
# Effects of Fly Ash Components

Hg uptake test with 50 mg $SiO_2$ (Pretreated with Aqua Regia) at 140 °C



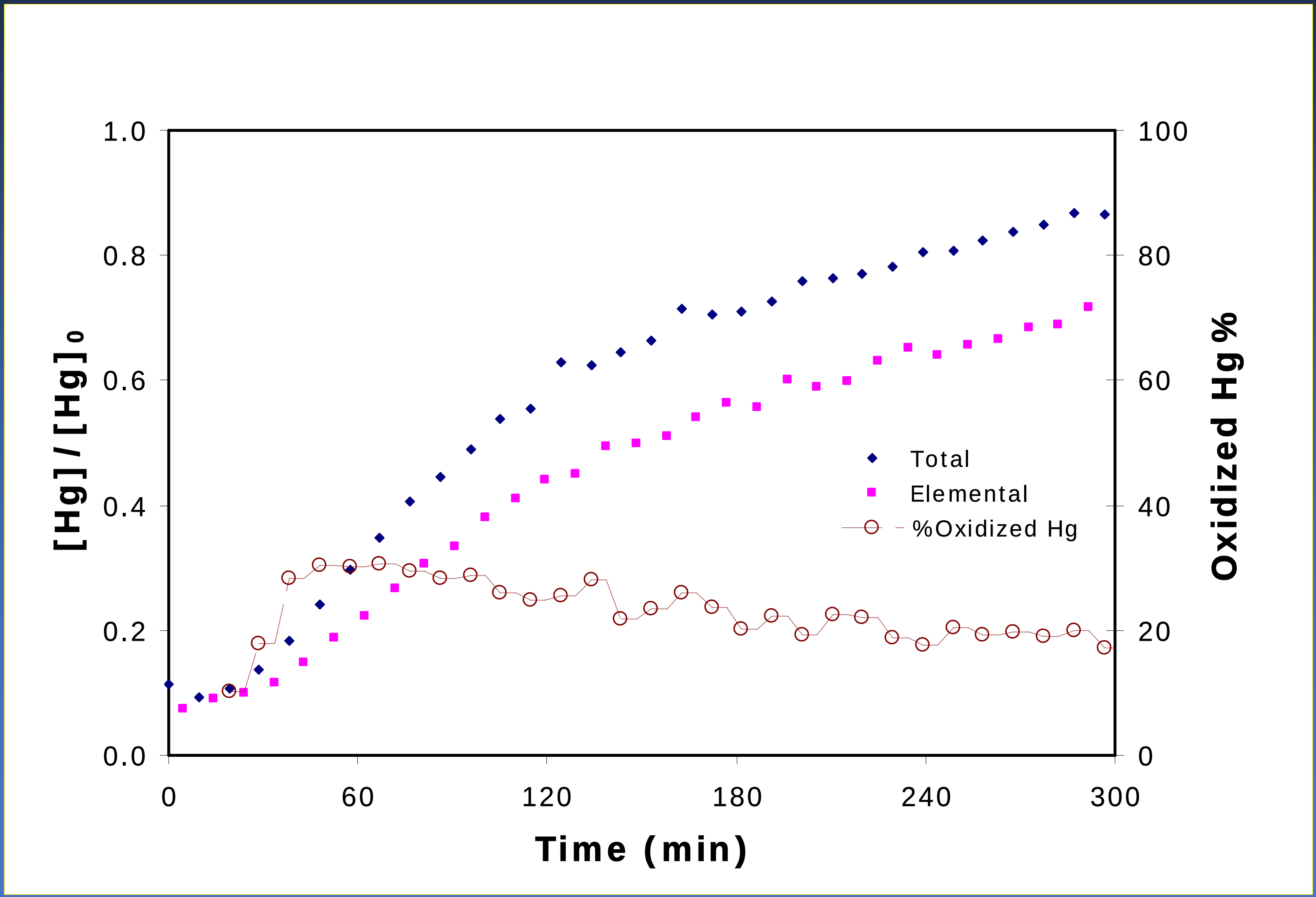
# Effects of Fly Ash Components

Hg uptake test with 50 mg $Fe_2O_3$ at 140 °C

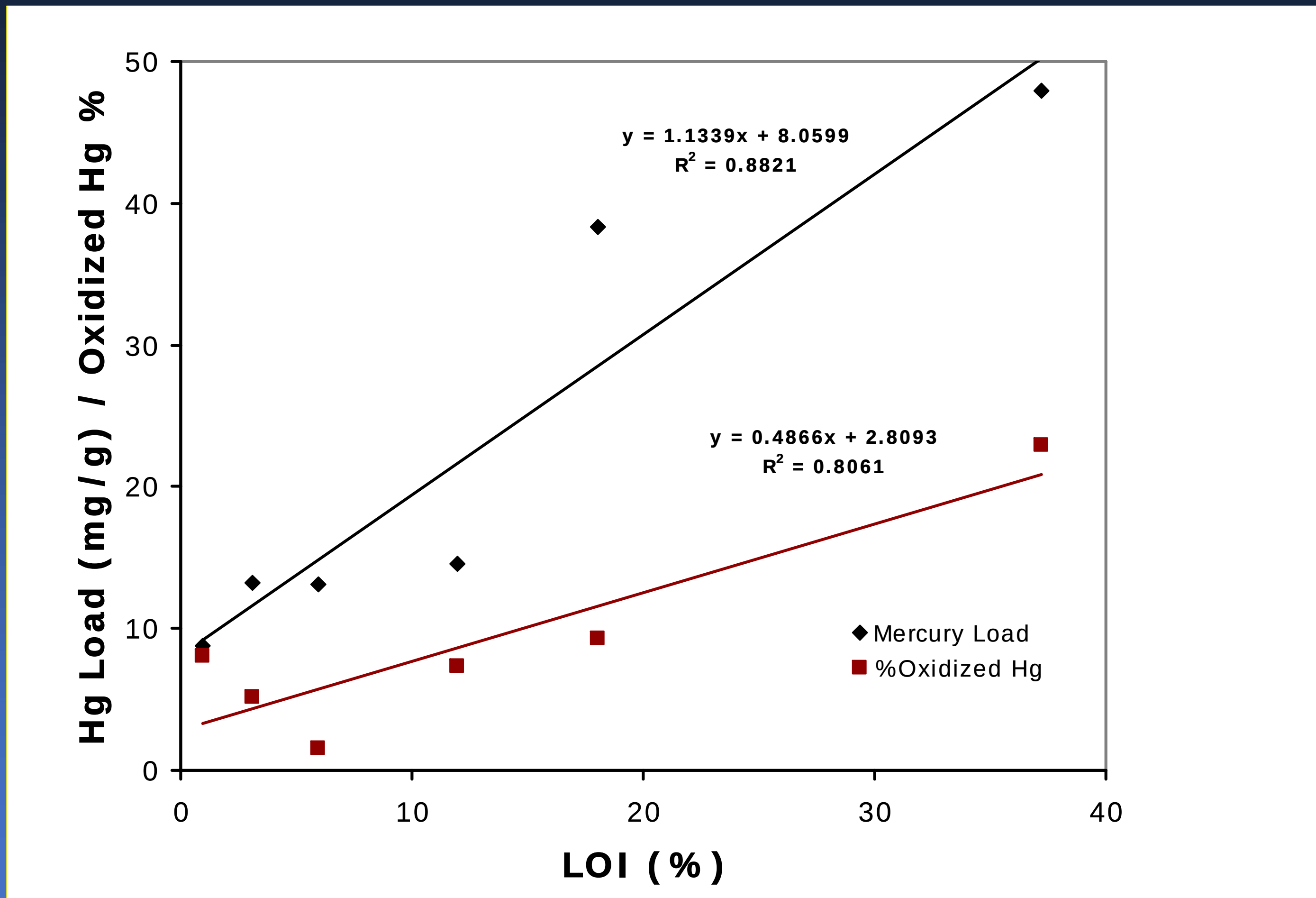


# Effects of Fly Ash Components

Hg uptake test with 50 mg Carbon Black at 140 °C



# Effects of LOI on Hg uptake and Oxidation




**Mercury uptake and oxidation are both proportional to LOI; carbonaceous component actively participates in both processes**

# Summary of Experiments with Fly Ash

- Both adsorption and oxidation increased with surface area and LOI.
- Carbon, and $Fe_2O_3$ promoted Hg adsorption and oxidation , $SiO_2$ had little effect, while $Al_2O_3$, MgO, CaO, or $TiO_2$ didn't promote Hg adsorption or oxidation.
- Carbon is present at 6 - 41 wt.% while $Fe_2O_3$ is present at 1.6 – 5.5 wt. %

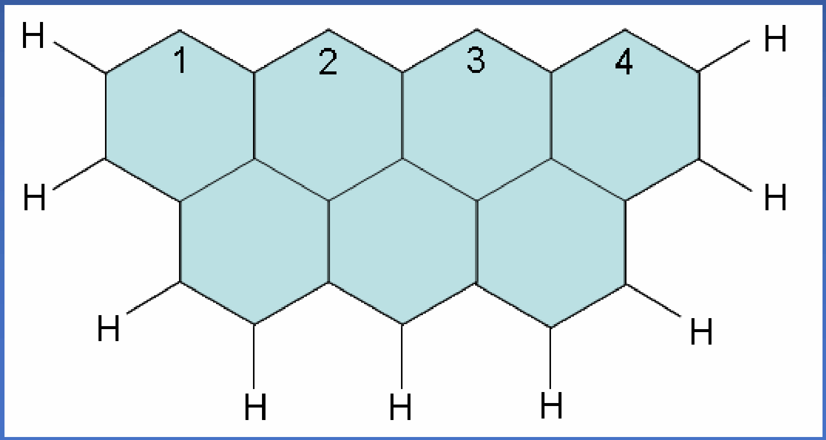
- **Focus on carbon component of fly ash**

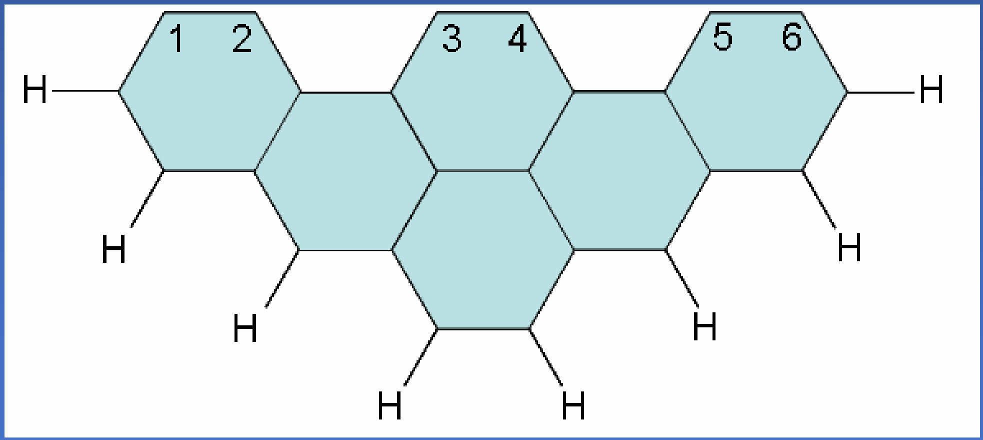
# Interaction of Flue Gas Components with Carbon Black

- General procedure:
  1. Baseline of $Hg^0$ with $N_2$ / $N_2+CO_2+O_2$
  2. Introduce 50mg carbon black
  3. After the "breakthrough", $SO_2$, NO, $H_2O$, $NO_2$, HCl or a combination of different gases will be introduced into the gas flow ( A flow rate 1L/min is kept)
  4. Monitor changes in Hg speciation in the effluent

# Modeling

- Quantum Modeling
  - Gaussian 03W package for preliminary calculations
  - PC GAMESS package for production runs on 8-32 node computer cluster
  - DFT/B3LYP for geometry optimization and energy calculations
  - Basis Sets – 6-31G(d) for elements other than Hg
  - Effective Core Potential for Hg – SBKJC

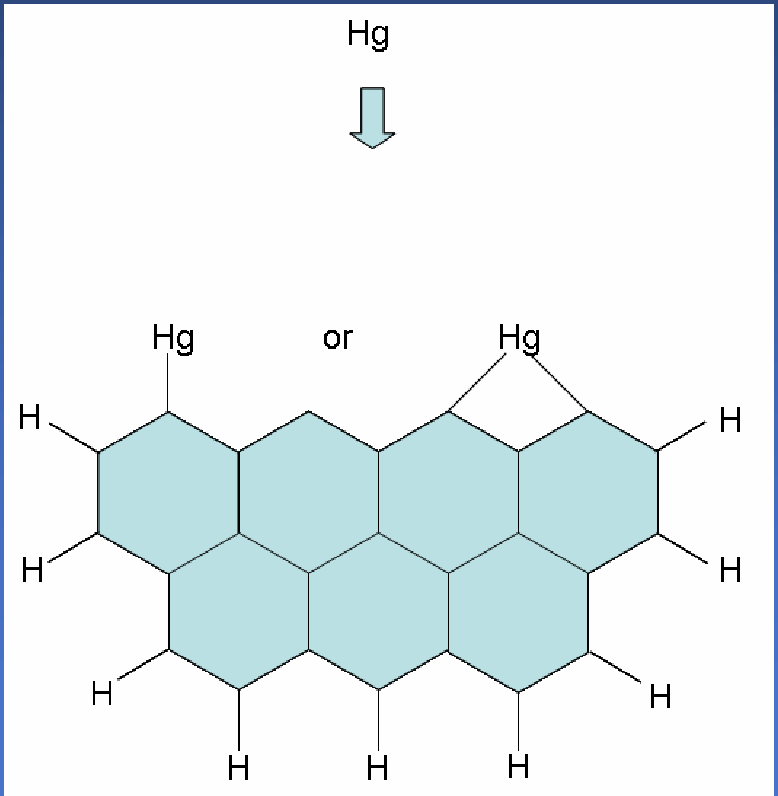



**Carbon Model Structures**

# Theoretical Calculations

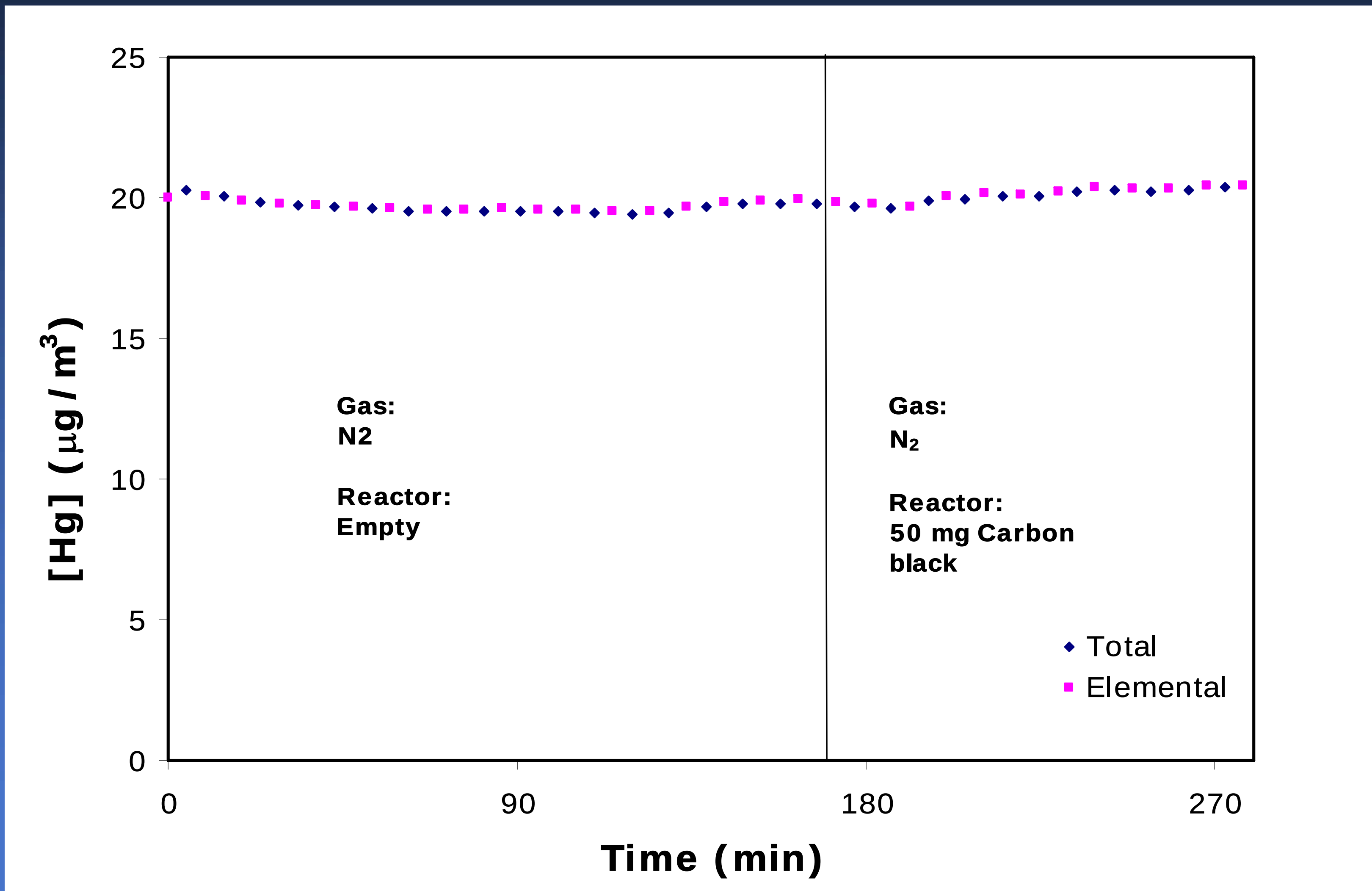
**Binding Energy = E(CS–Hg) – E(CS) – E(Hg)**



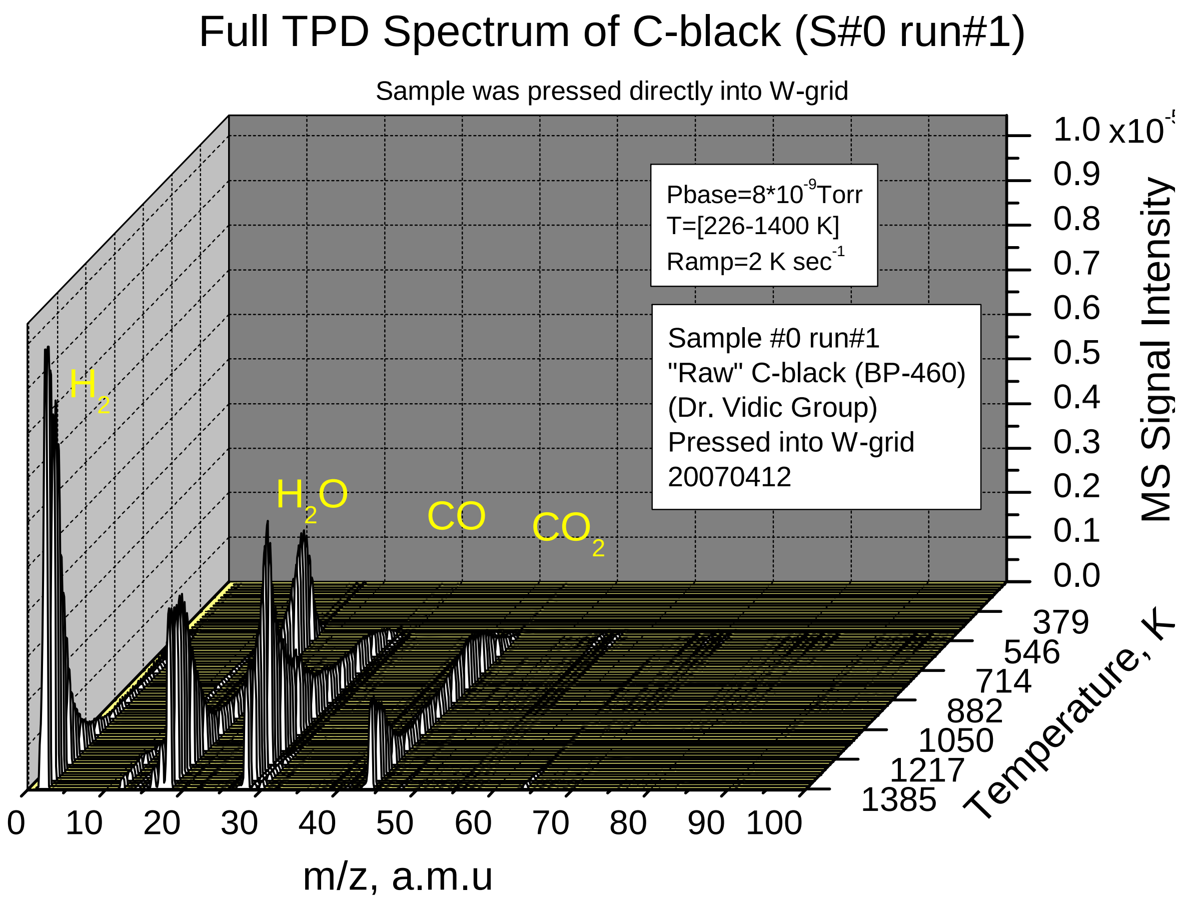

**$Hg^0$ Binding Energy: -5.0 to -9.1 kcal/mole depending on position**

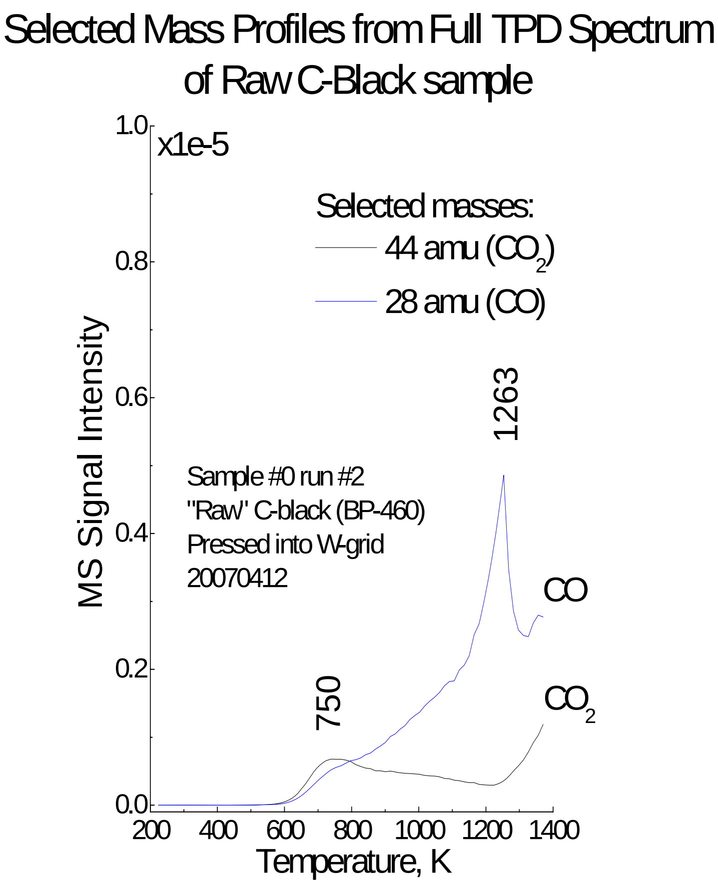
# Mercury Uptake Test with Carbon black in $N_2$

Mercury uptake by carbon black in $N_2$ at 140 °C



# TPD analysis of Carbon Black

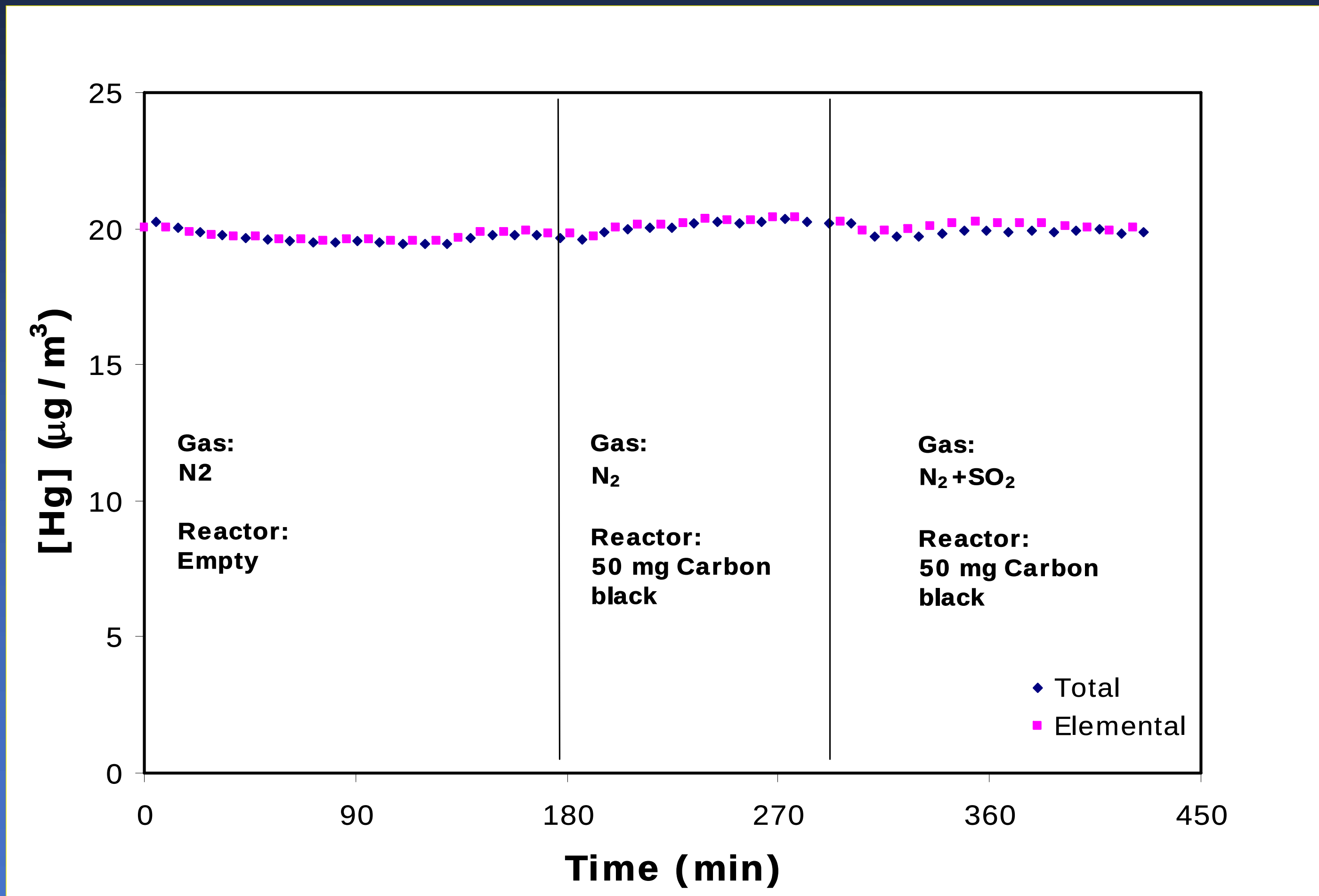



**Species desorbing from C-black are mainly oxygen functionalities**

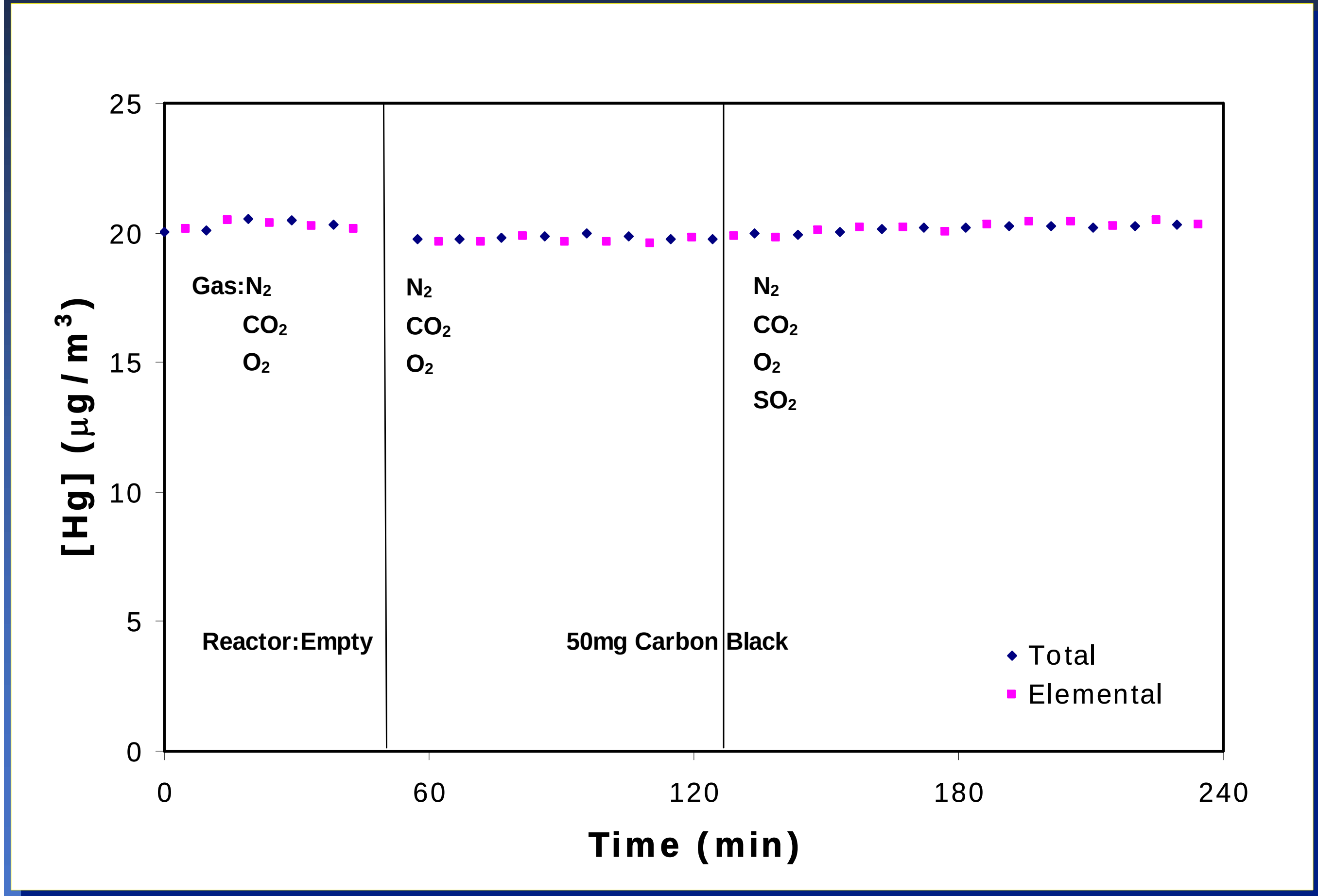
# Mercury Uptake Test with Carbon Black in $SO_2$

Effect of $SO_2$ on mercury uptake by Carbon black in $N_2$ at 140 °C



# Mercury Uptake Test with Carbon Black in $SO_2$

Effect of $SO_2$ on mercury uptake by Carbon black in $N_2$+$CO_2$+$O_2$ at 140 ºC

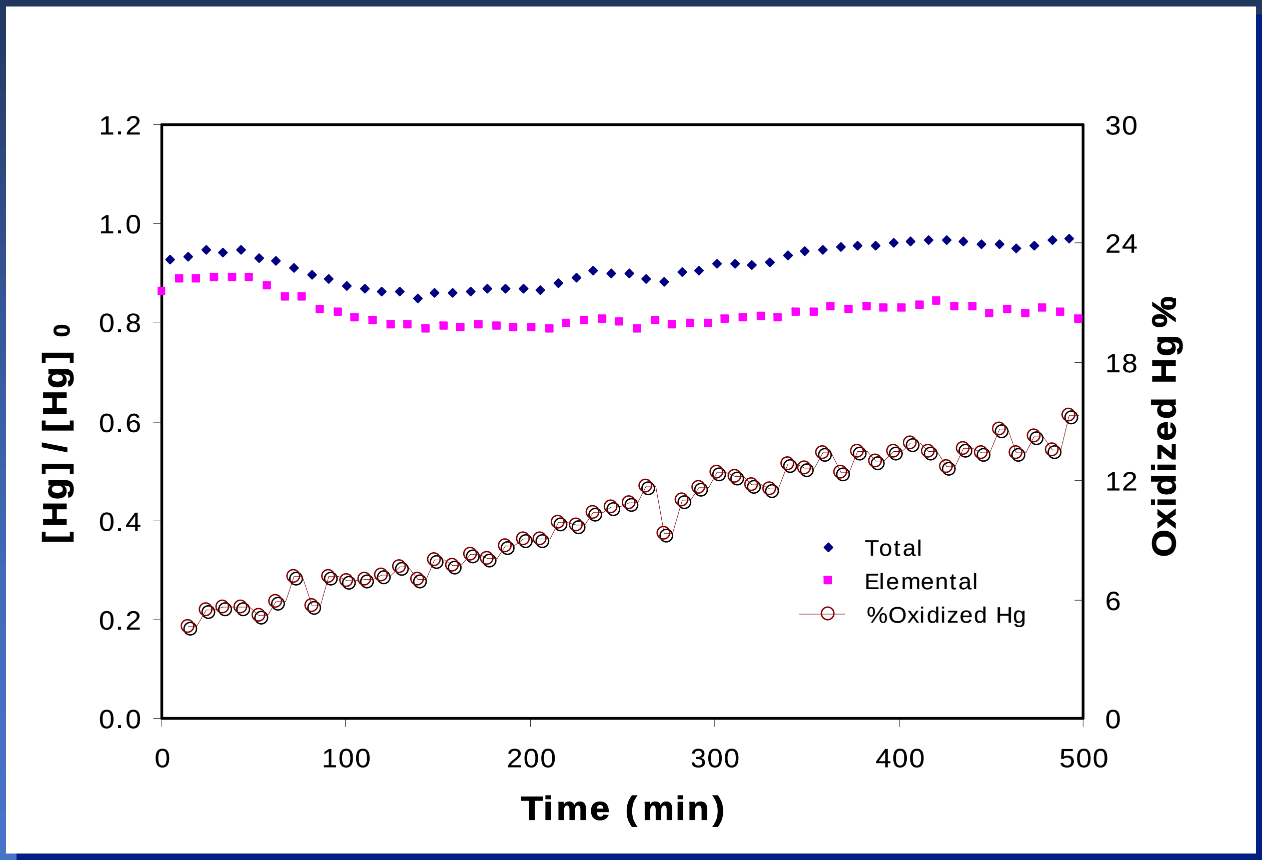



Similar results with NO, and $H_2O$ in

$N_2$/$N_2$+$CO_2$+$O_2$

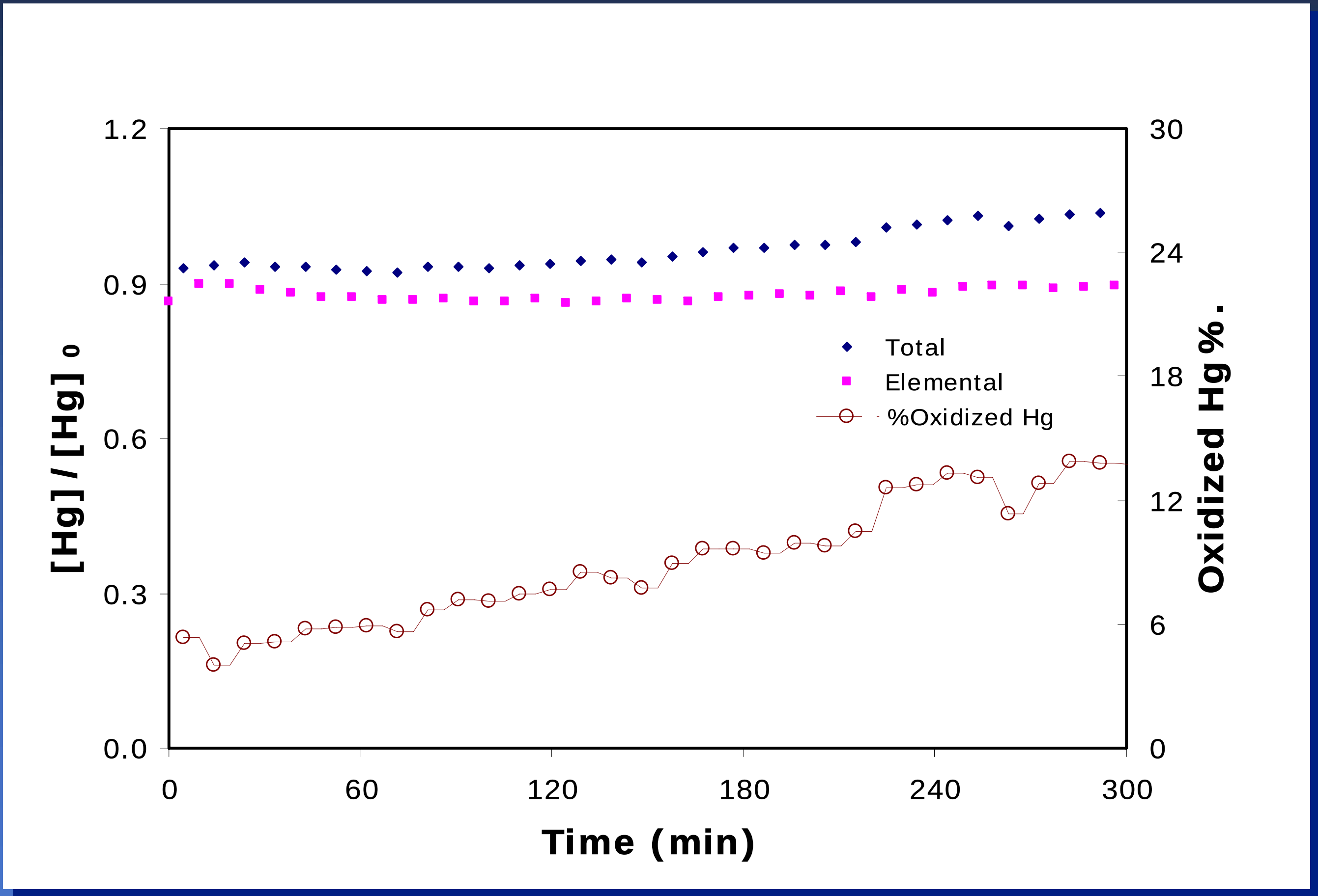
# Mercury Uptake Test with Carbon Black in $NO_2$

Effect of $NO_2$ on mercury uptake by carbon black in $N_2$ at 140 °C



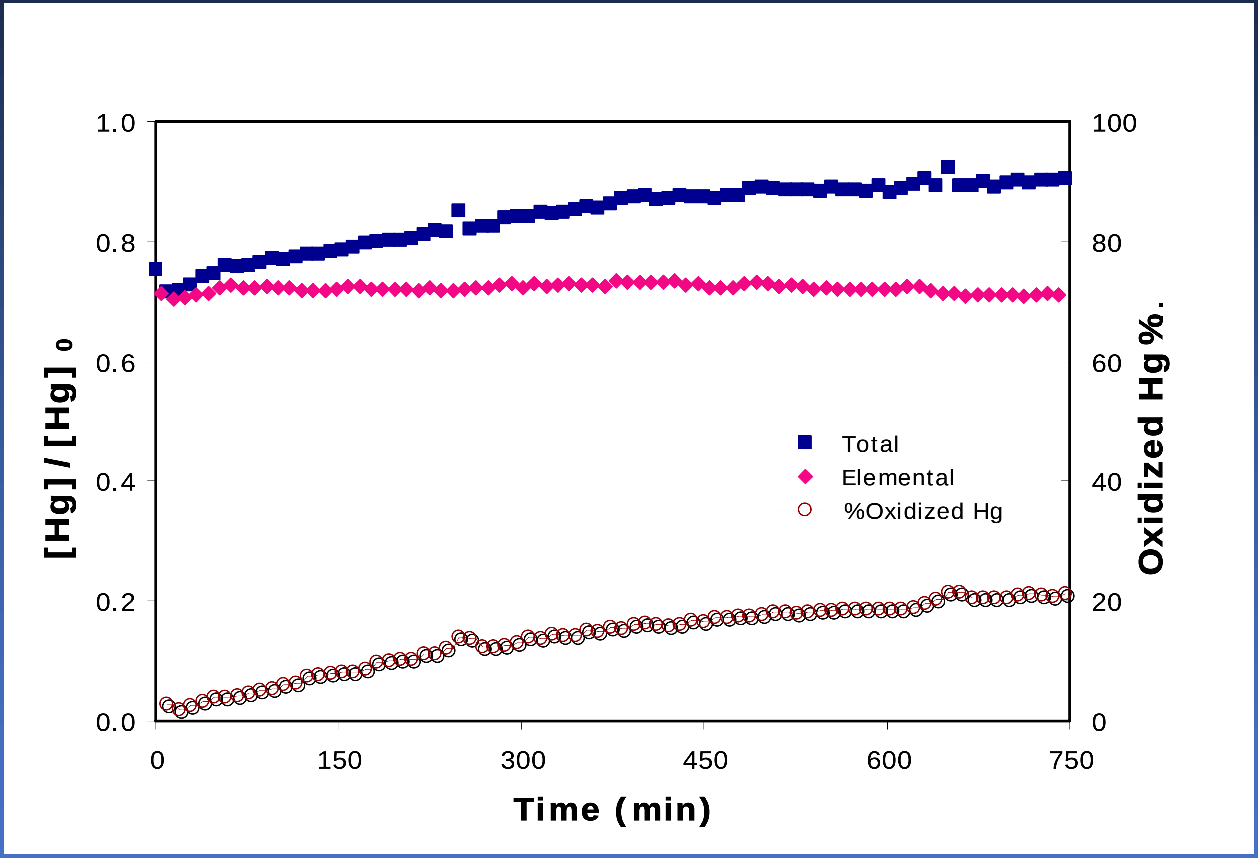
# Mercury Uptake Test with Carbon Black in $NO_2$

Effect of $NO_2$ on mercury uptake by carbon black in $N_2+CO_2+O_2$ at 140 °C



# Mercury Uptake Test with Carbon black in HCl

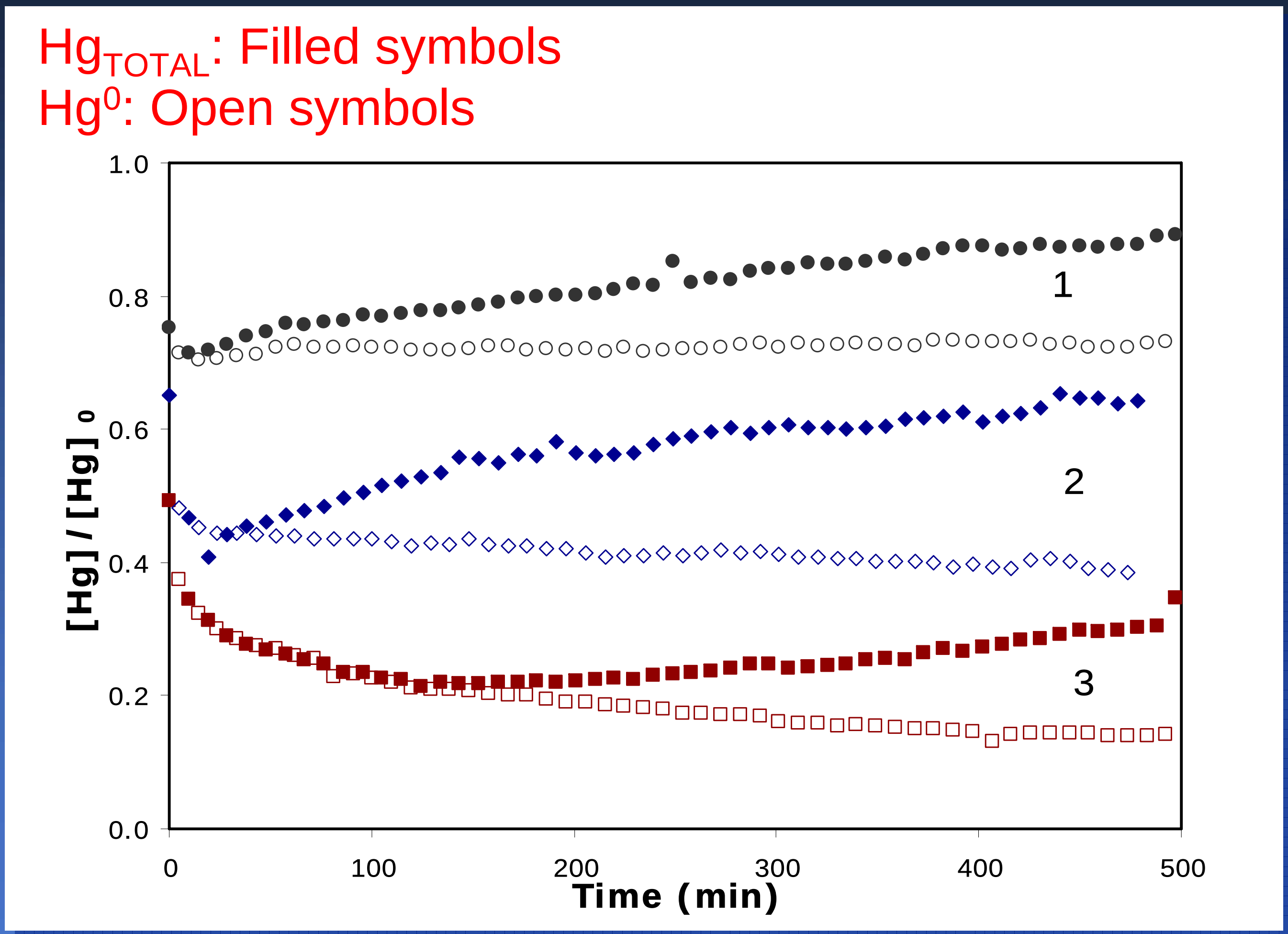
Effect of HCl on mercury uptake by carbon black in $N_2$ at 140 °C




HCl promotes Hg oxidation on the surface of carbon black

**Deacon Reaction:** $4HCl + O_2 \xrightarrow{M} 2Cl_2 + 2H_2O$

# Mercury Uptake Test with Carbon black in HCl



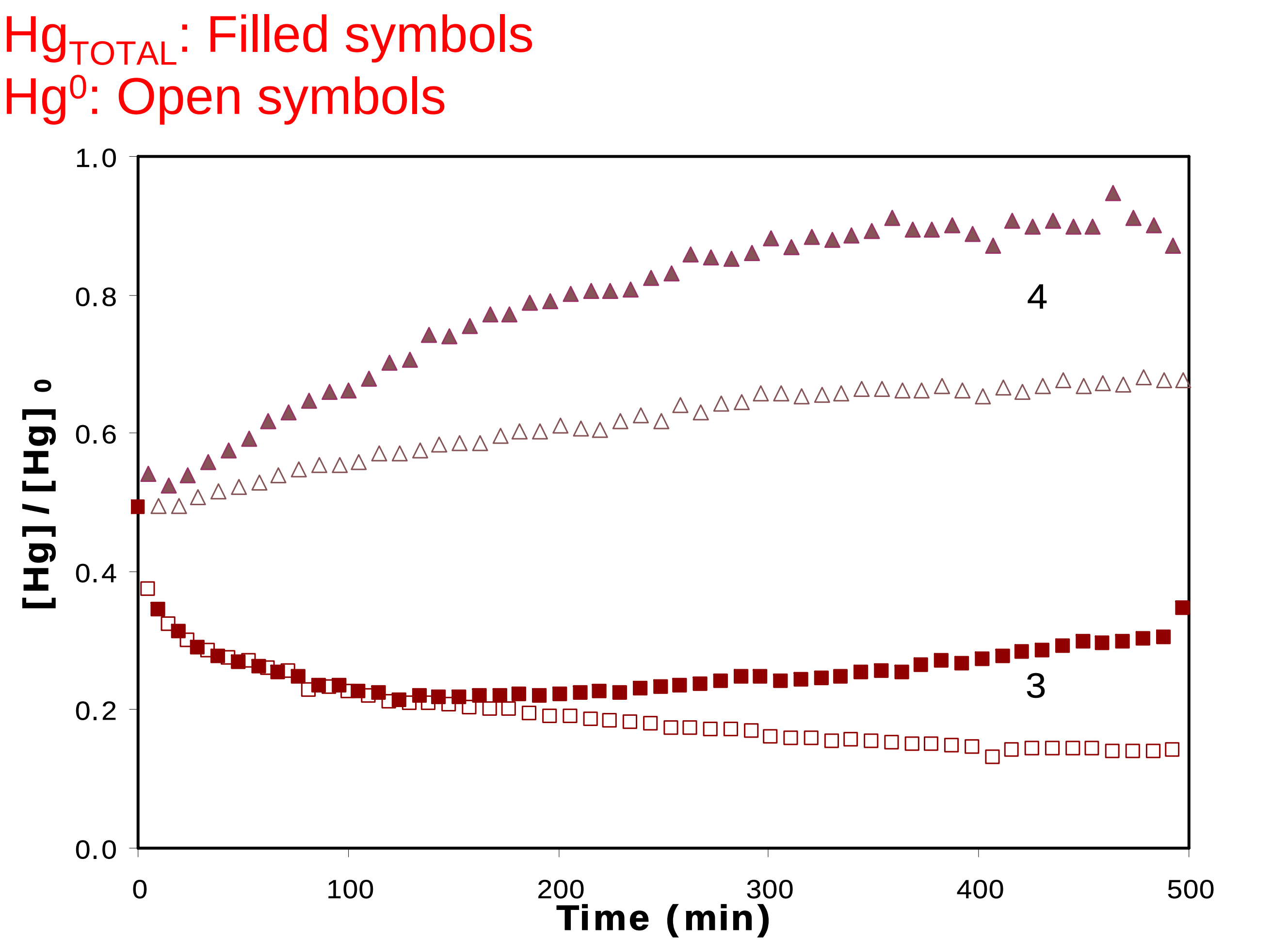

1: $N_2$+HCl

2: $N_2$+HCl

(Sample exposed to $O_2$ for 4 hrs)

3: $N_2$+HCl+$CO_2$+$O_2$

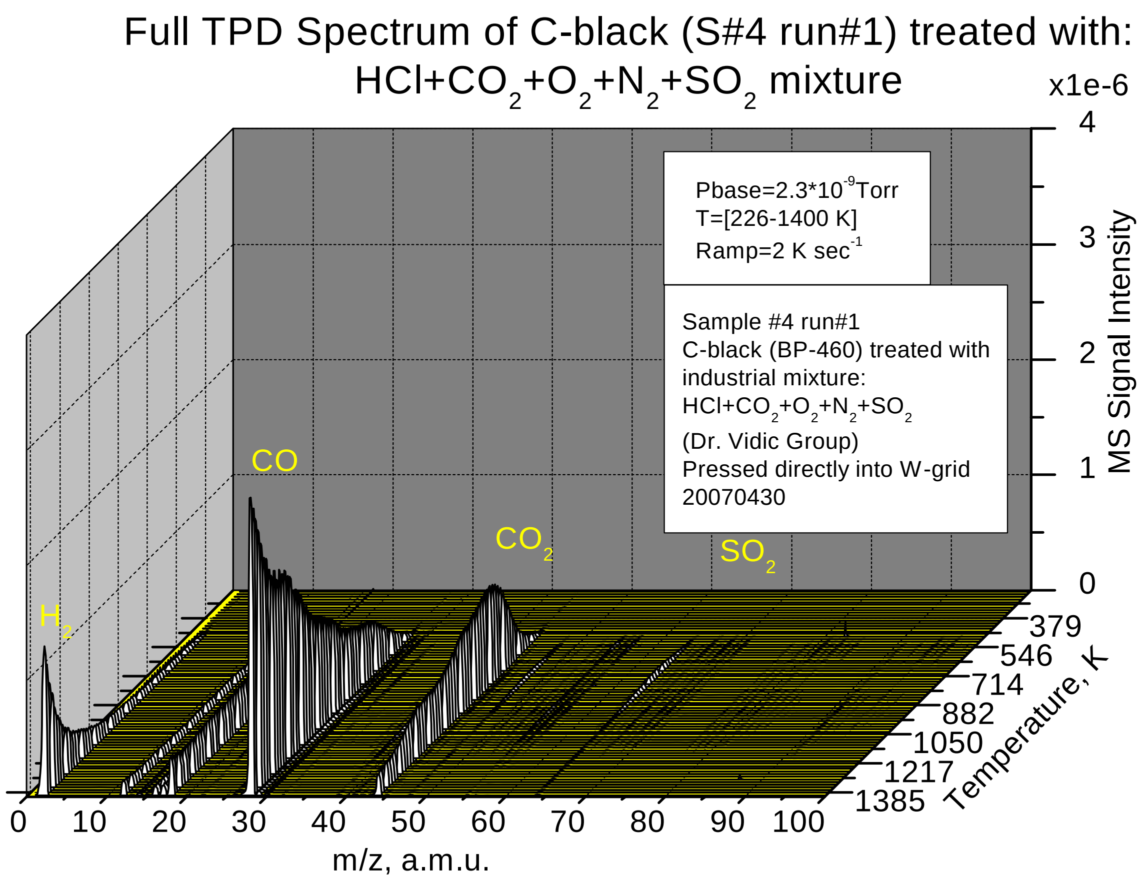
# Mercury Uptake Test with Carbon black

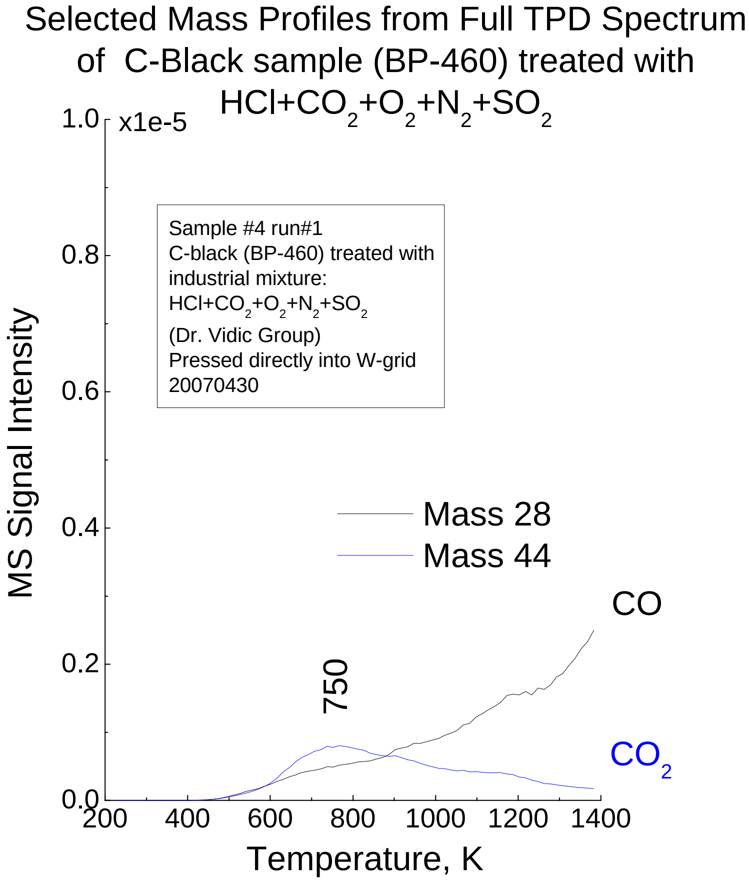



4: $N_2$+HCl+$CO_2$ +$O_2$+$SO_2$

3: $N_2$+HCl+$CO_2$+$O_2$

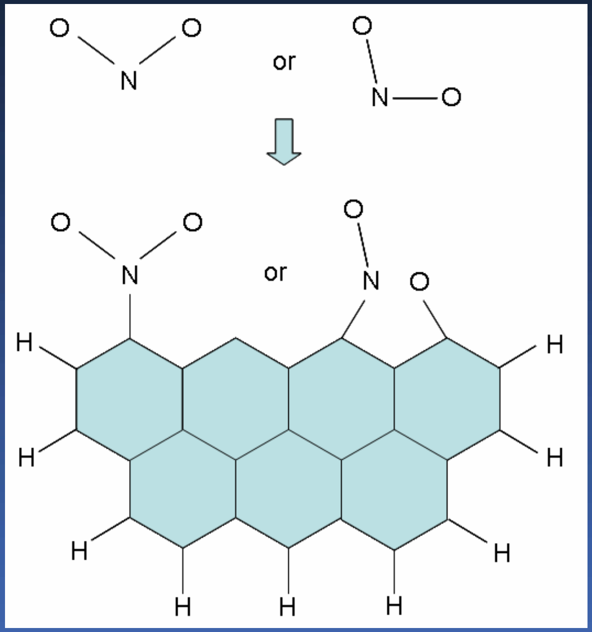
# TPD of Spent Sorbent

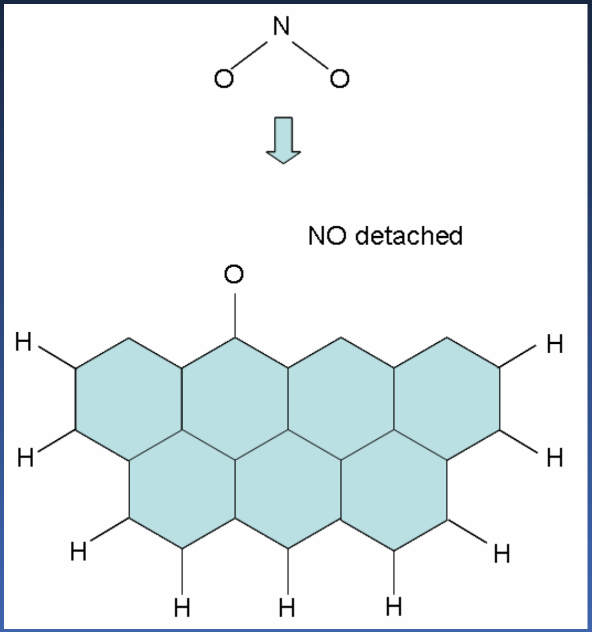



**Species desorbing from C-black are mainly oxygen functionalities**
**Traces of $SO_2$ can be detected (64, 48, and 32 a.m.u.)**
**No Cl-traces detected**

# Different $NO_2$ approaches




**Broken $NO_2$ structure has lower energy (more stable)**

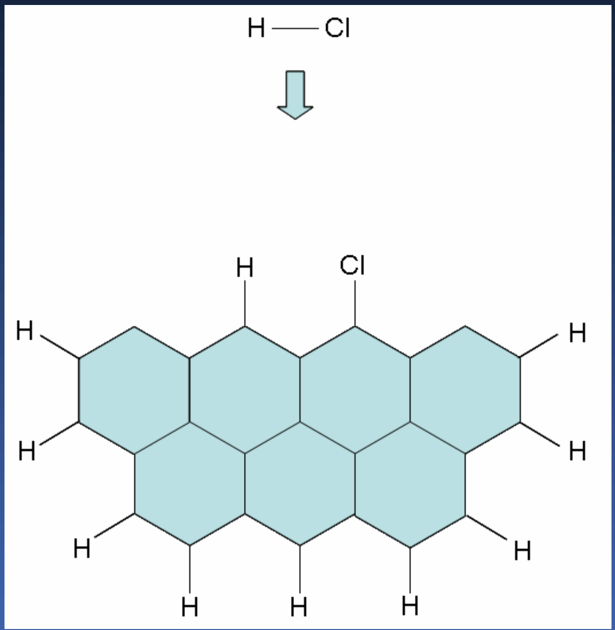
**$Hg^0$ Binding Energy:**

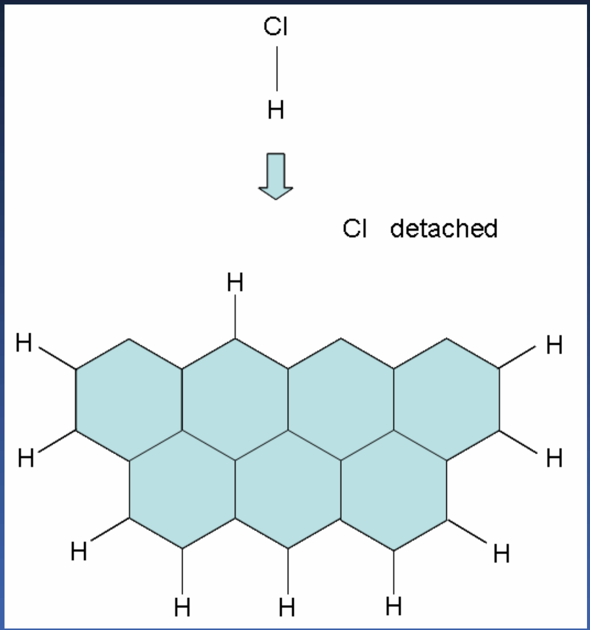
**-2.6 to -8.2 kcal/mole for Y structure**

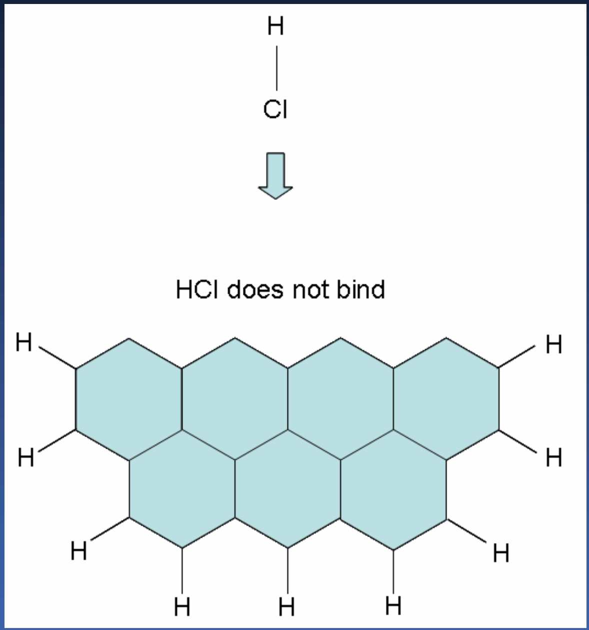
**-32.1 to -38.1 kcal/mole for broken structure**

**Runs ongoing for attached O, expected lower binding energy (favorable $Hg^0$ binding)**

# Different HCl approaches




**$Hg^0$ Binding Energy:**

**-1.9 to -7.7 kcal/mole with 1 H and 1 Cl attached**

**-1.3 to -10.7 kcal/mole for various H attachments**

**Possible bulk $Hg^0$ reactions with detached Cl – preliminary calculations show HgCl binding energy of -66.7 kcal/mole**

# Conclusions

- $Fe_2O_3$ and carbon black promote Hg adsorption and oxidation
- Increase in LOI and surface area resulted in increase Hg adsorption and oxidation
- HCl and $NO_2$ promote Hg adsorption and oxidation on carbon black in $N_2$
- Oxygen plays an important role on Hg adsorption and oxidation when combined with HCl
- $SO_2$ inhibited Hg adsorption by inhibiting mercury oxidation and by competitive adsorption

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