Effects of SO_2 and NOx on Mercury Homogeneous Gas-Phase Chemistry

R.O. Sterling, J. Qiu, and J.J. Helble

Department of Chemical Engineering

University of Connecticut

18th Annual ACERC Technical Conference

Provo, UT

February 12, 2004

Mercury - in the Environment, in the News

USA Today, 11-05-02

Close… but not quite correct

Mercury ***vapor*** is important – an important distinction

Mercury Emission Inventory, U.S. Sources

Mercury Emissions from US Sources*, kg/y, rounded to nearest 500

Source Type	Total Mercury
Medical Waste Incineration	12,000 (8%)
Municipal Waste Combustion and Sewage Sludge Incineration	32,500 (22%)
Electric Utility Boilers	45,500 (31%)
Non-Utility Fossil Fuel Boilers	25,500 (17%)
Non-Ferrous Metal Smelting	8,500 (6%)
Chlor-Alkali Sources	6,000 (4%)
Other Point Sources	12,000 (8%)
Area Sources	6,000 (4%)
Total	148,000

coal

*EPA, 1998

The Issue with Mercury…

Mercury:

is present in coal and waste fuels at 0.02 – 0.2 ppm levels

vaporizes during combustion

oxidizes only partially (important)

more escapes air pollution controls if not oxidized

elemental mercury stays in the air for ~ one year

elemental mercury generally deposits far from its source

is transformed into methylmercury in the environment

bioaccumulates

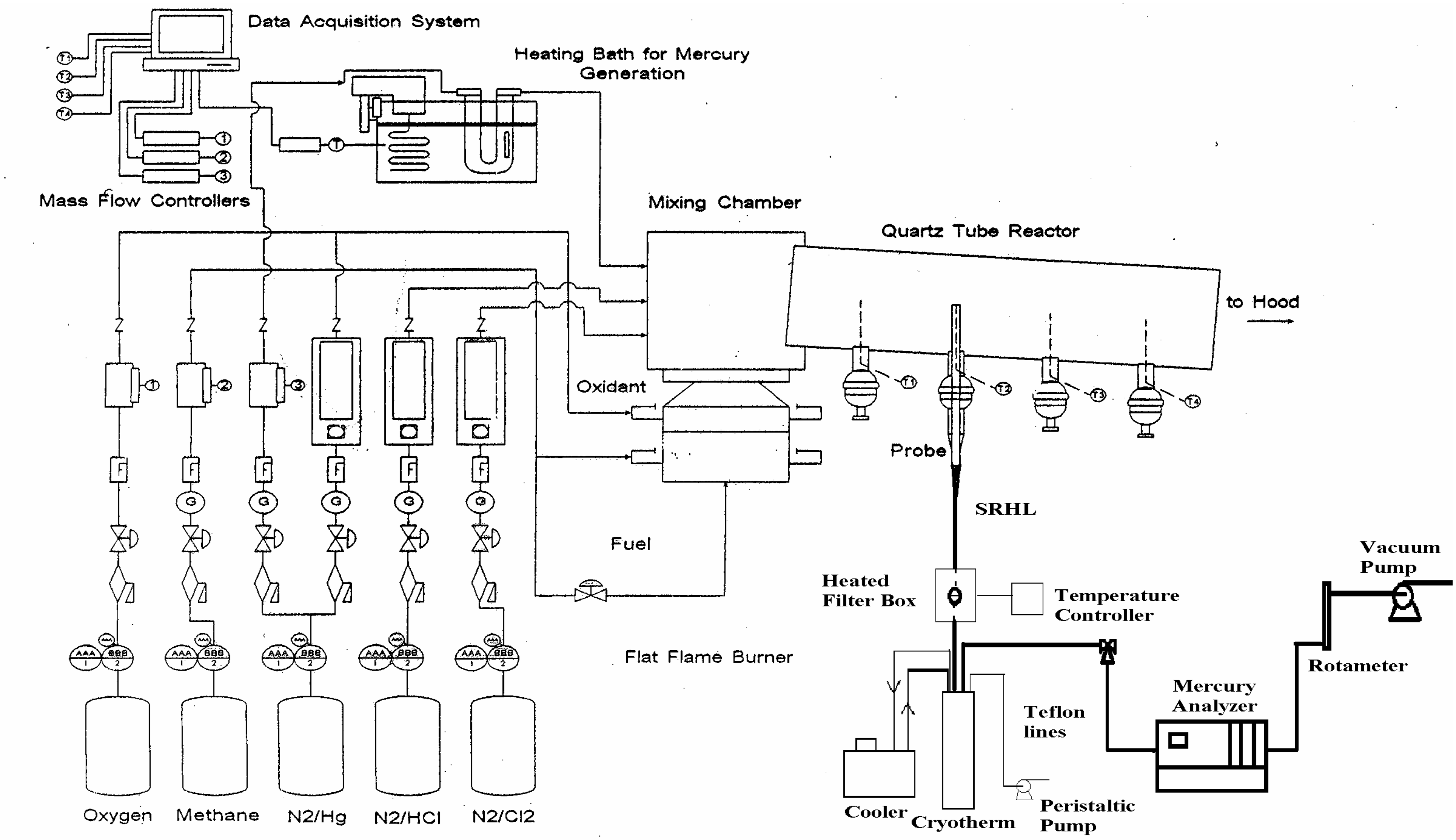
To reduce hazard, must reduce emissions

promote oxidation and capture by existing pollution controls

Background and Objectives

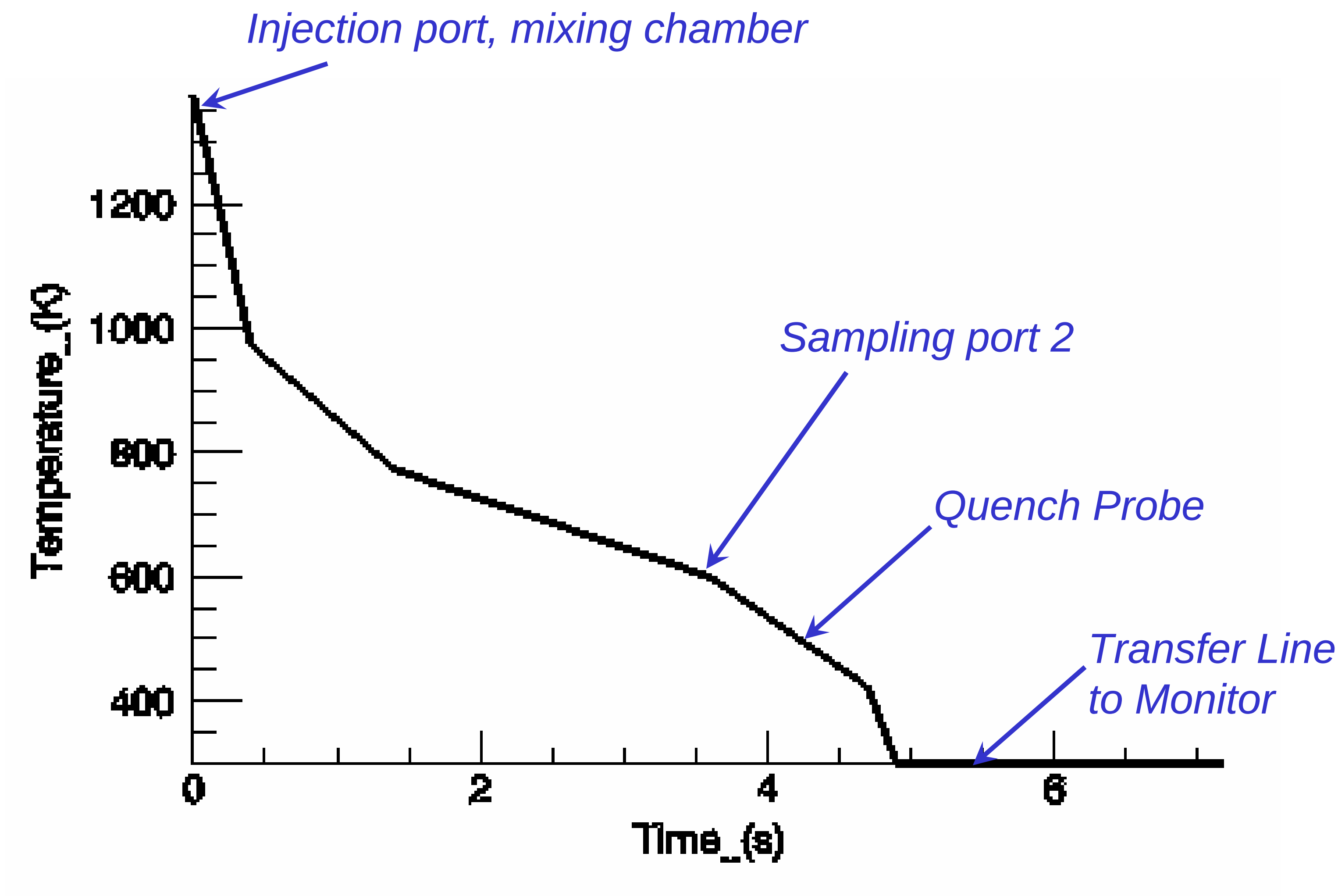
- ***Recent studies of Hg oxidation have indicated that homogeneous pathways can contribute***
- ***Oxidation kinetically limited***
- ***Cl_2 important oxidant; HCl does not promote extensive oxidation***
- ***Questions remain regarding fundamental chemistry, roles of flame stoichiometry, NOx, SO_2***
- ***Goal: expt'l and modeling study of homogeneous Hg oxidation - examine effects of NOx, SO_2, O_2, Cl***

Experimental System



Adapted from Mamani-Paco 2000

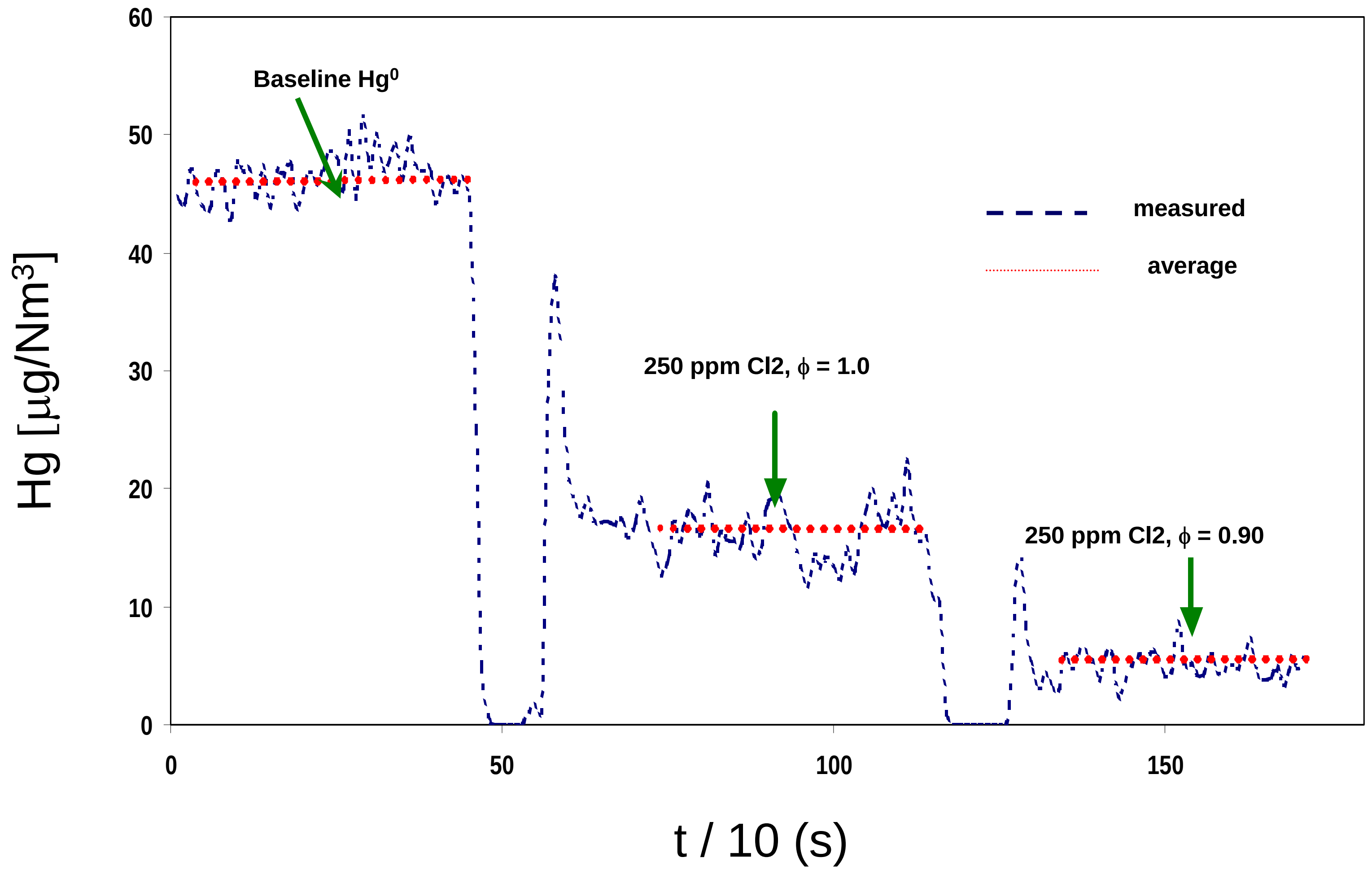
Temperature Profile



Experimental Conditions

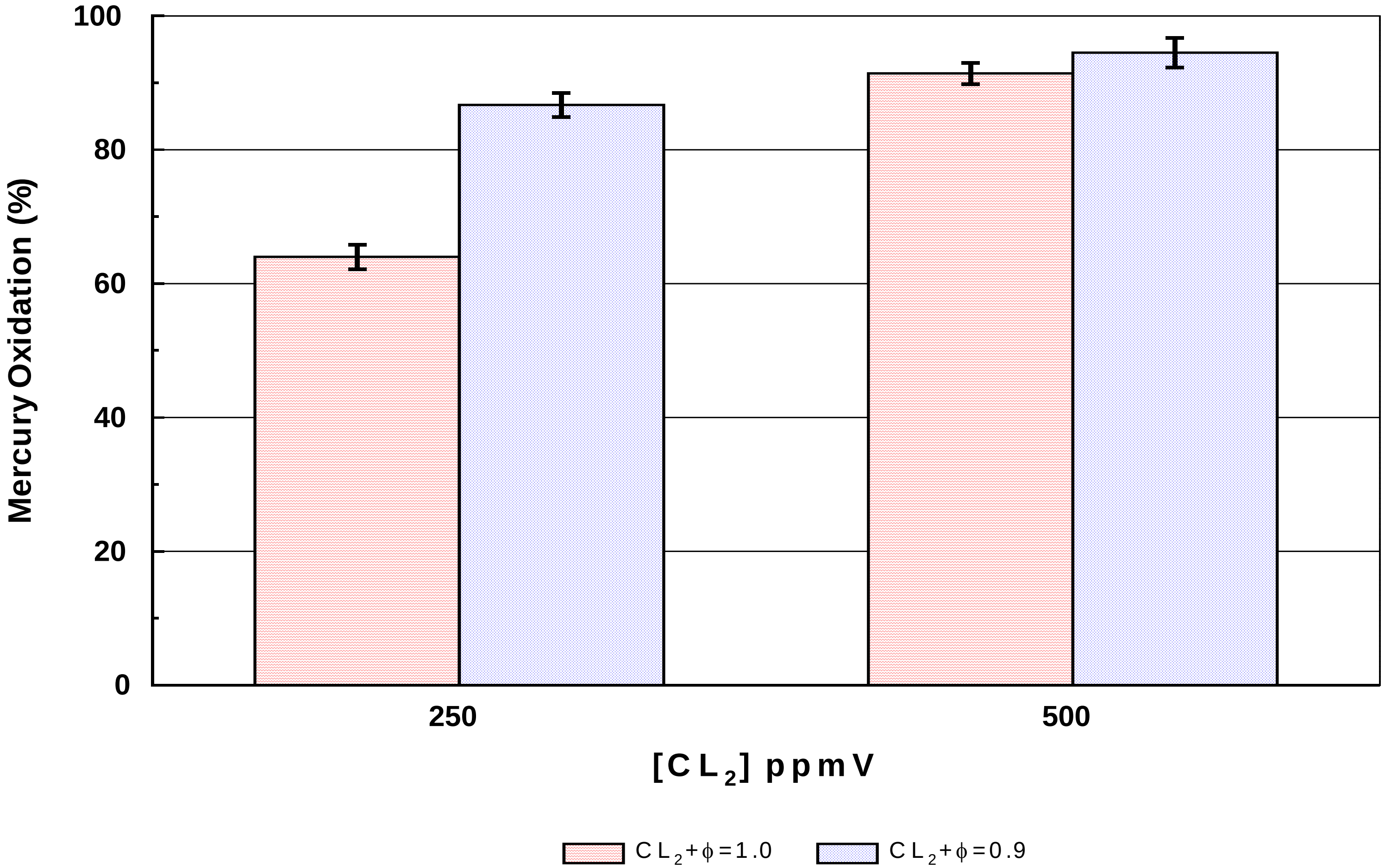
- **$CH_4/O_2/N_2$ flame; 29 slpm total flow**
- **[Hg] 45-50 $\mu g/m^3$**
- **[Cl_2] 150, 250, 500 ppm**
- **[HCl] 100, 300 ppm**
- **[SO2] 100, 400 ppm**
- **[NO] 100, 300 ppm added (baseline = 120-150 ppm NO)**
- ***Flame equivalence ratio 0.9, 0.95, 0.98, 1.0***
- ***Experiments at each condition 3-6***
- ***Mixing chamber 1000 – 1300 K***
- ***Semtech CVAA (elemental Hg)***

Example: Effects of Cl_2 and O_2



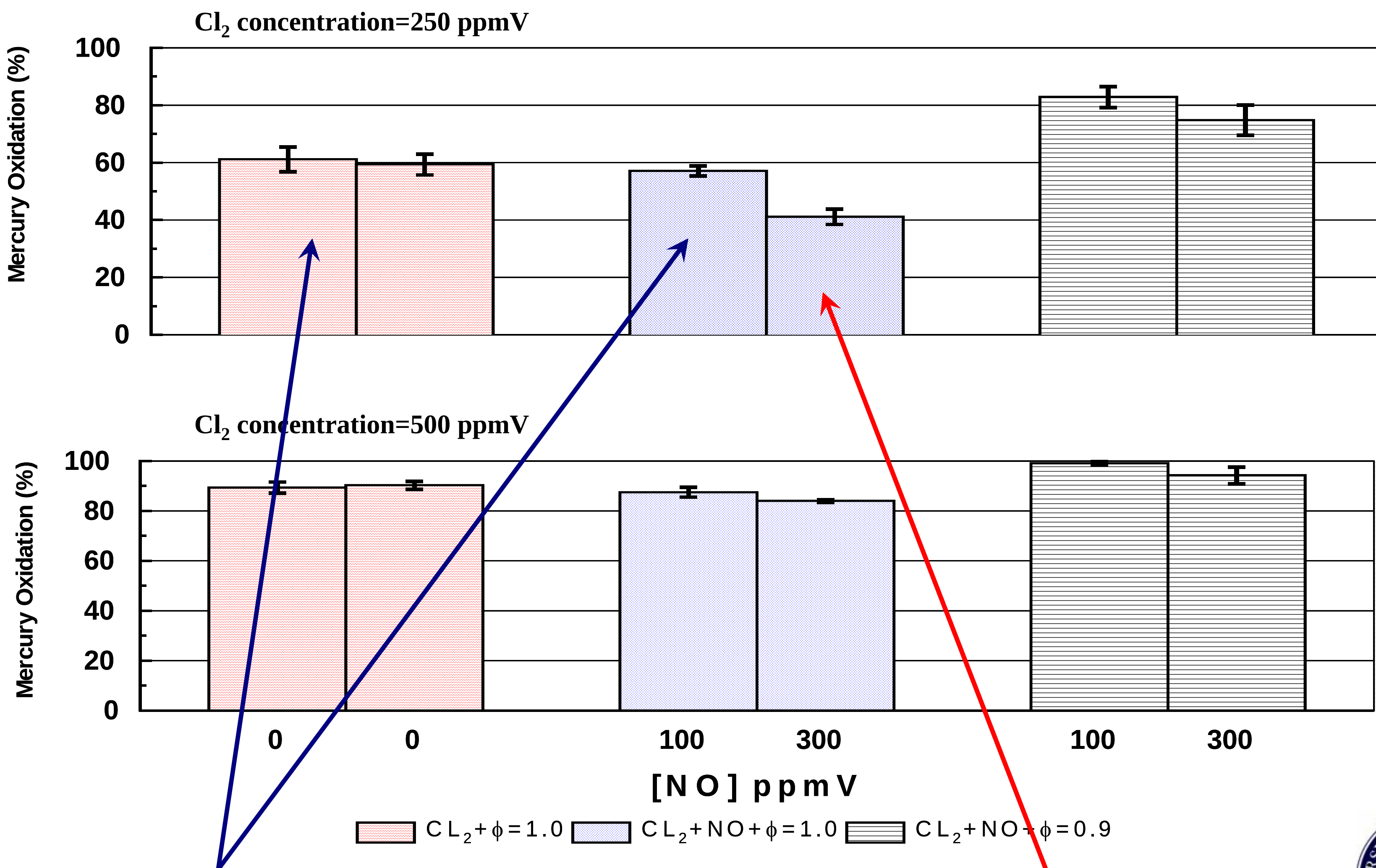
Cl_2 strong oxidant; increasing O_2 increases conversion

Summary of Cl_2 / O_2 Study



O_2 promotion more pronounced at lower Cl_2

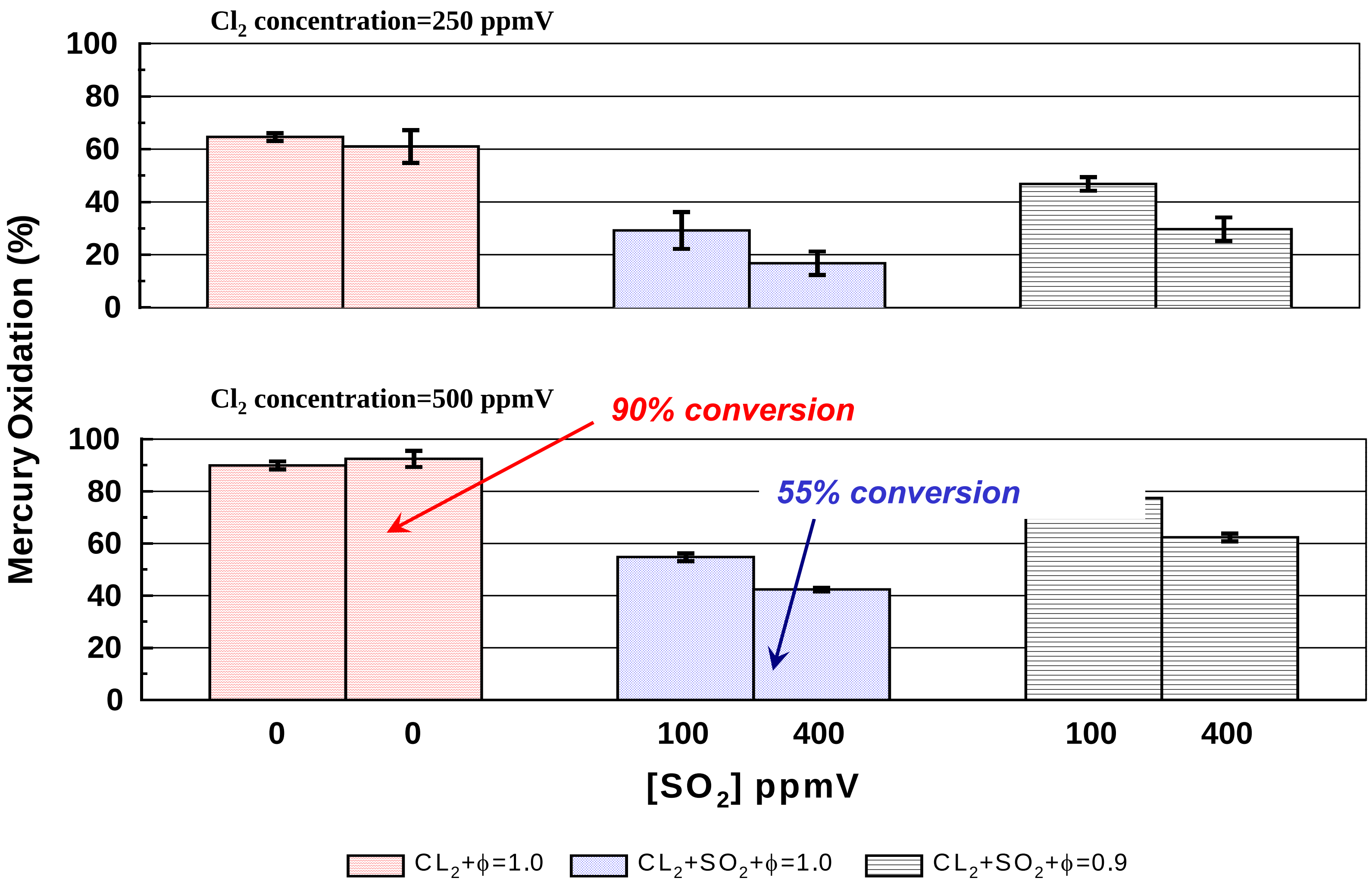
Effects of NO Addition on Oxidation by Cl_2



100 ppm – no effect

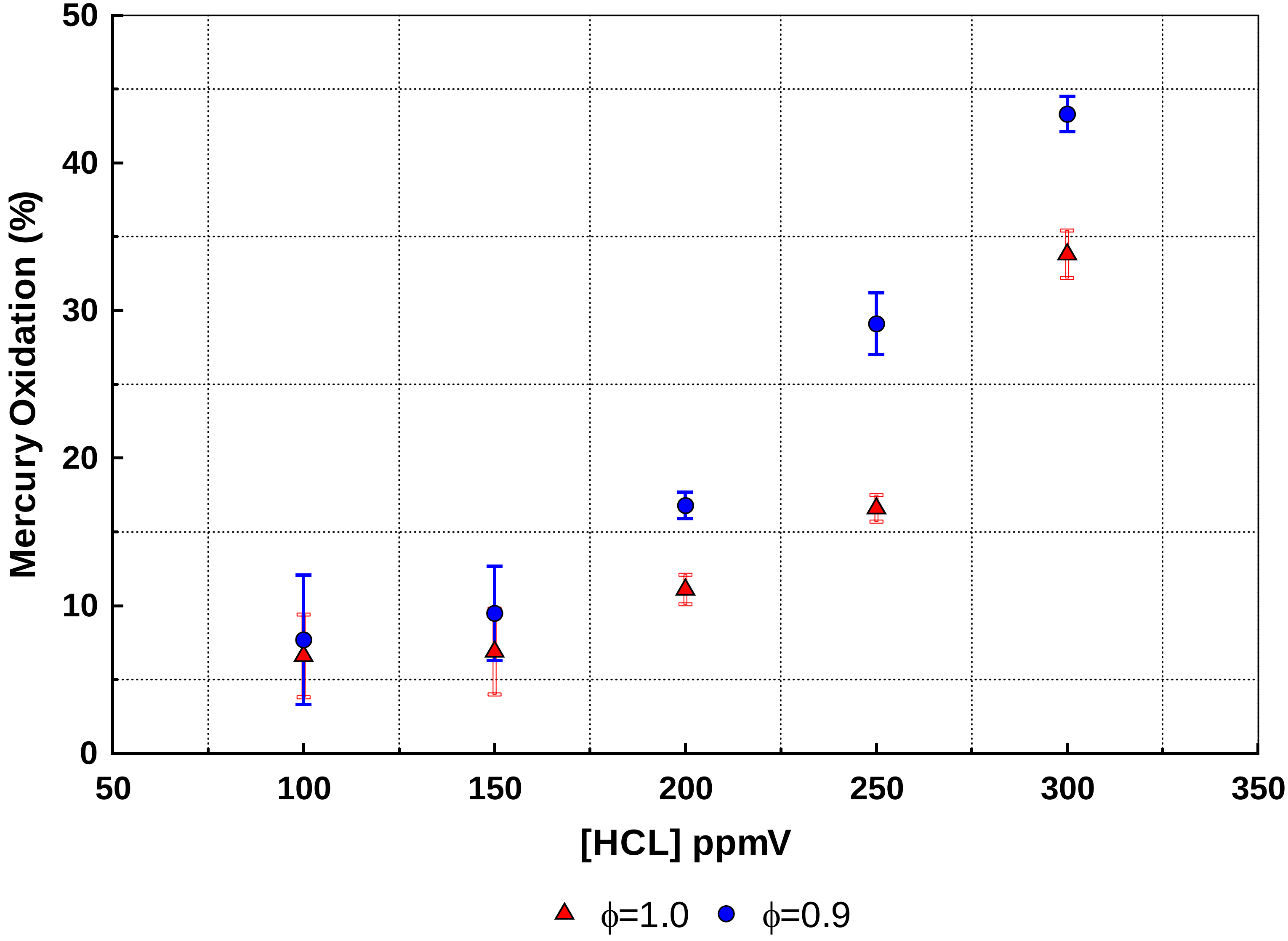
300 ppm NO, 250 ppm Cl_2: ~ 30% ↓

Effects of SO_2 Addition on Oxidation by Cl_2

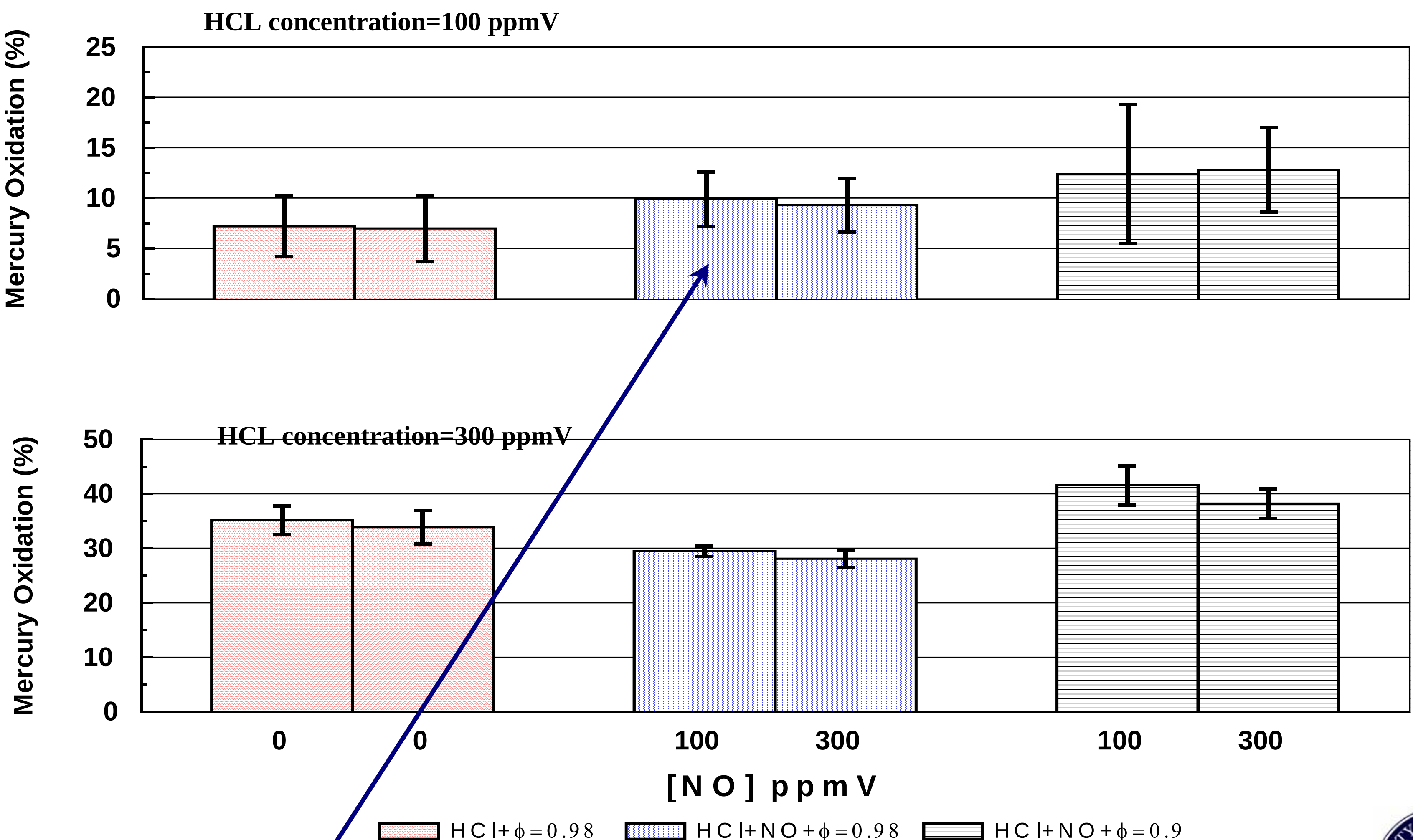


SO_2 suppresses oxidation by Cl_2 under all conditions

Oxidation by HCl: Importance of O_2

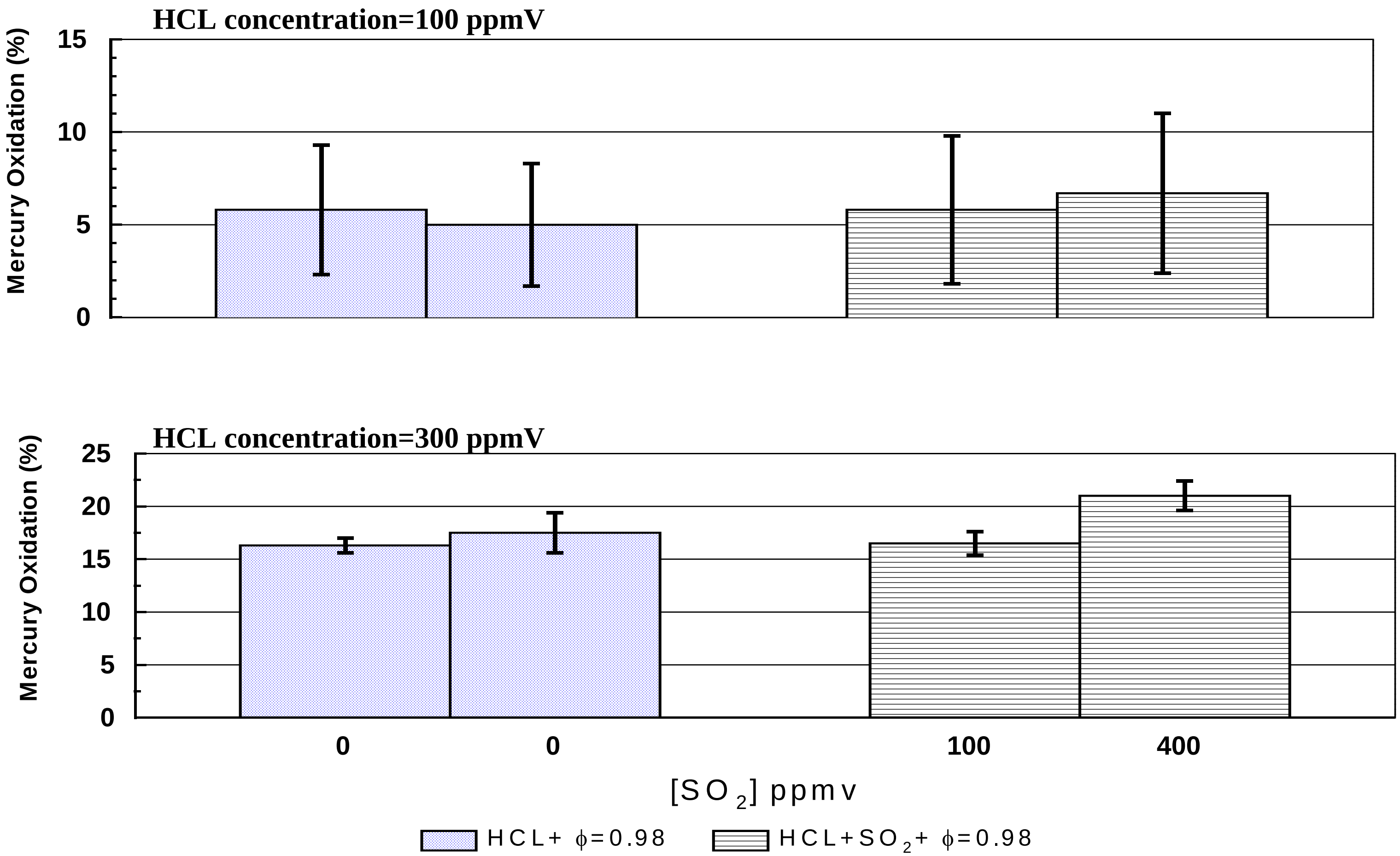


Hg Oxidation - HCl, NO, O_2



NO has no effect at low [HCl]

Hg Oxidation - HCl, SO_2



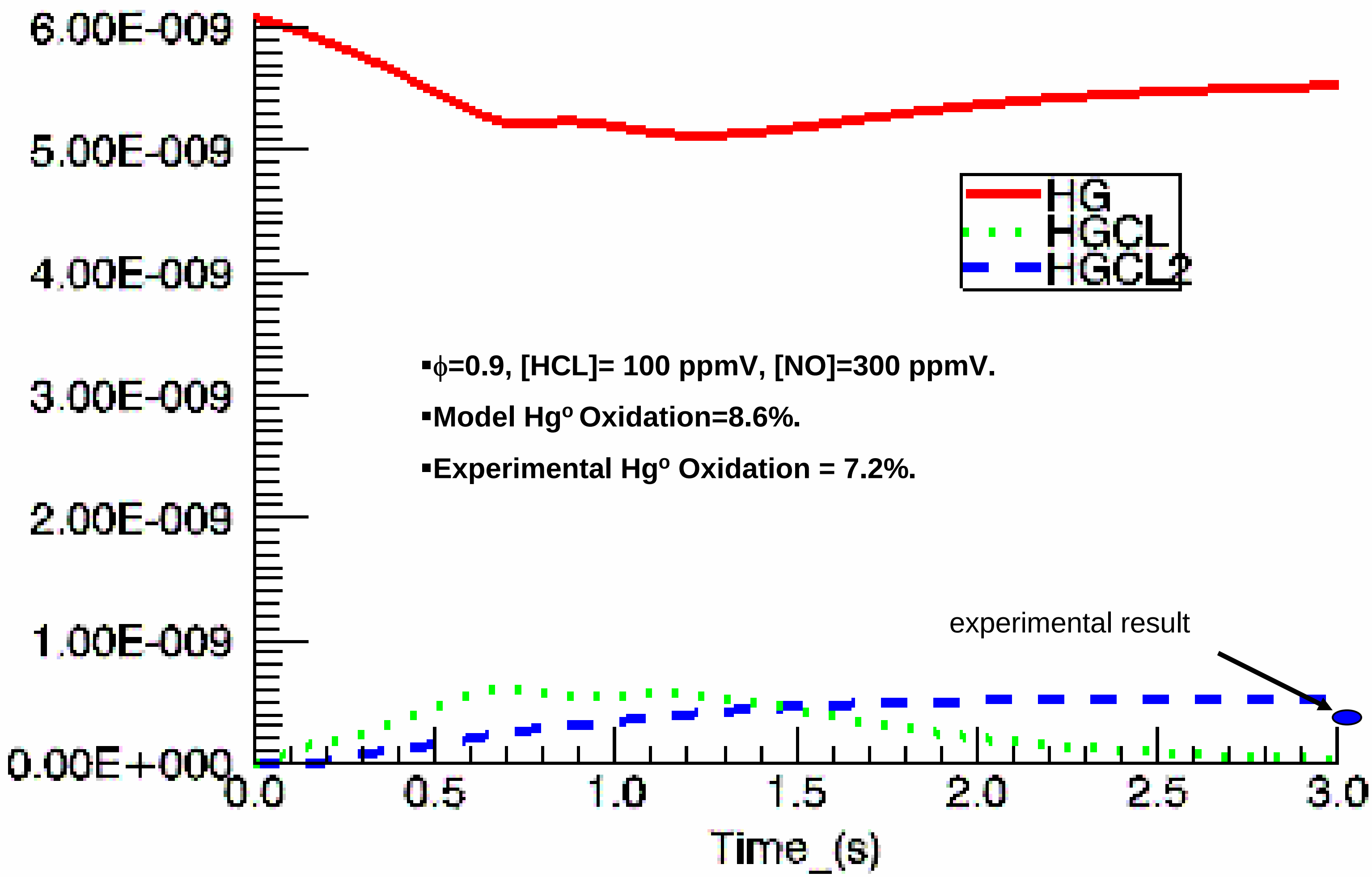
SO_2 has little effect on oxidation by HCl

Interpretation – Kinetic Modeling

Basis: 8-step mechanism from literature (Widmer et al., 2000; Sliger et al., 2000; Niksa et al., 2001)

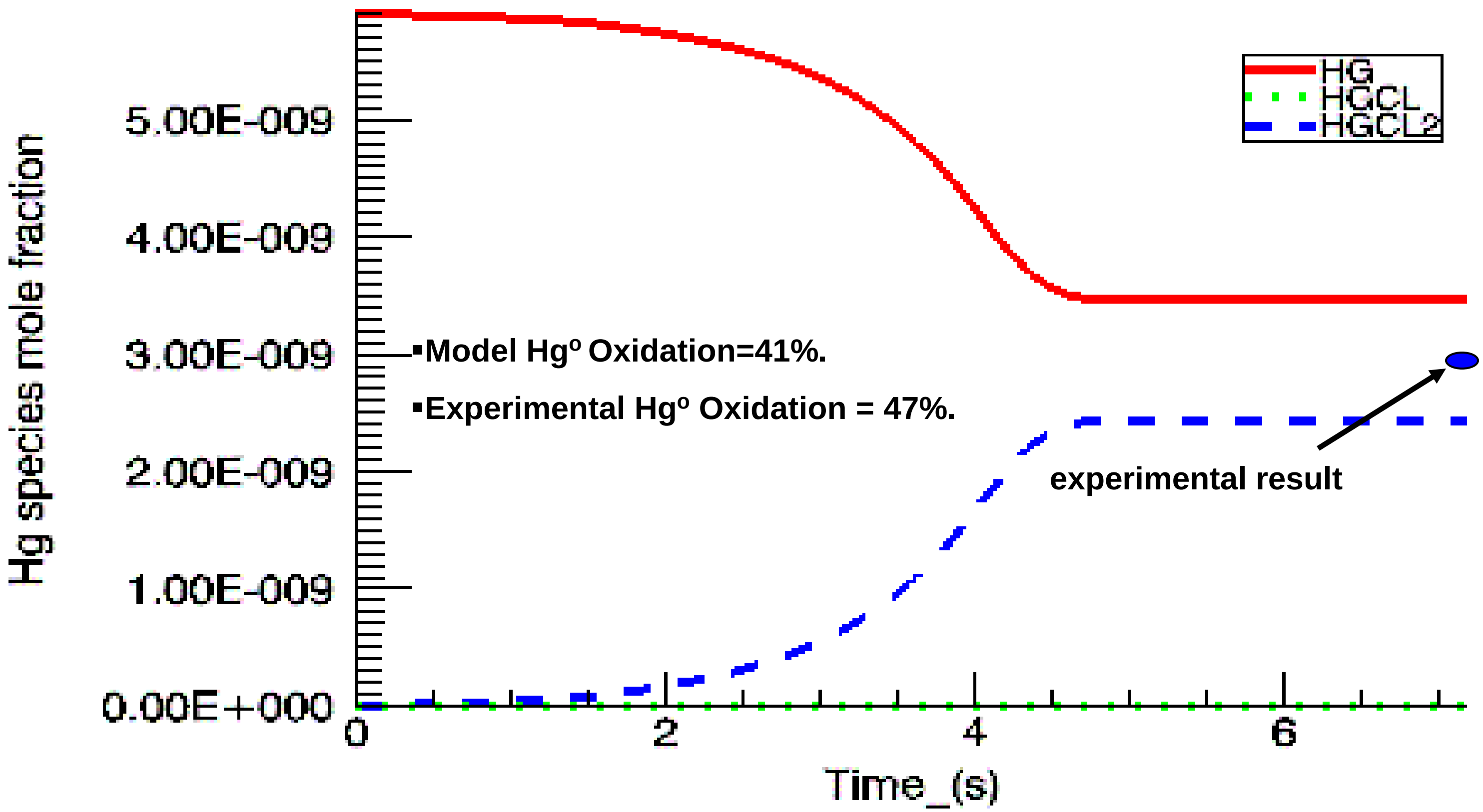
1. Hg + Cl + M = HgCl + M
2. Hg + Cl_2 = HgCl + Cl
3. Hg +HCl = HgCl + H
4. Hg + HOCl = HgCl + OH
5. HgCl + Cl_2 = $HgCl_2$ + Cl
6. HgCl + Cl + M = $HgCl_2$ + M
7. HgCl + HCl = $HgCl_2$ + H
8. HgCl + HOCl = $HgCl_2$ + OH

Experimental vs Model Result for Mercury Oxidation with HCL and NO



Experimental vs Model Result for Mercury Oxidation with CL_2 and SO_2

Φ=0.9, Cl_2=250 ppmV, SO_2=100 ppmV



Interpretation of Effects

Promotion of Cl

OH + HCl = Cl + H2O

Suppression of Cl

$$OH + NO + M = HONO + M$$

$$OH + SO_2 = SO_3 + H$$

$$OH + SO_2 + M = OHSO_2 + M$$

$$O + SO_2 + M = SO_3 + M$$

Summary and Conclusions

- **Fuel-lean conditions (v. stoichiometric combustion) promote Hg oxidation by either HCl or Cl_2**
- **In the presence of Cl2, [SO_2] of 100, 400 ppm, [NO] of 100, 300 ppm suppress Hg oxidation. SO_2 effects greater.**
- **$HCl_{(g):}$ $SO_{2(g)}$ concentrations of 100 and 400 ppm had no effect**
- **HCl: $NO_{(g)}$ concentrations of 100 and 300 ppm had zero to marginal effect**
- **Homogeneous chemistry alone appears insufficient to account for levels of oxidized Hg observed in coal combustion systems, confirming role of surface reactions**

Acknowledgements

EPA STAR Grant R0828170

Alstom Power

Dr. Connie Senior, REI