Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

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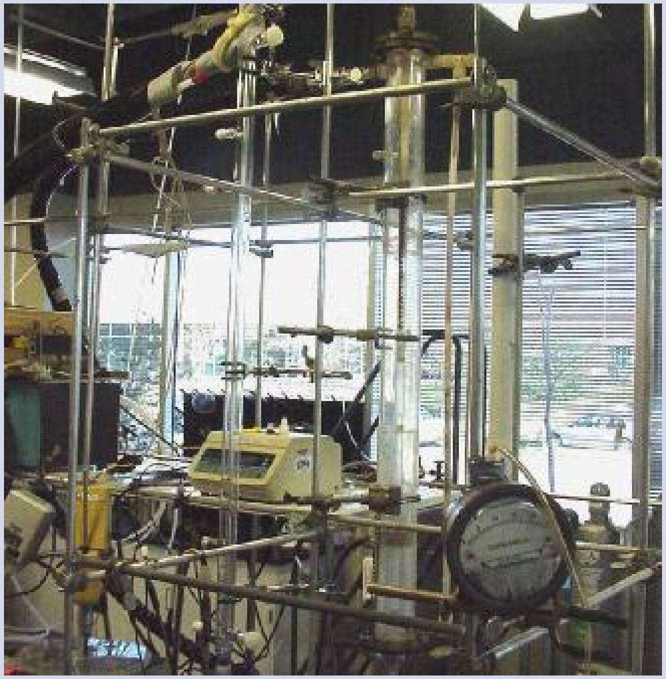


Introduction

- **Project Goal** – develop a fundamental understanding of Hg “re-emissions” from wet FGD systems
  - Seen as FGD outlet Hg^0 concentration > inlet Hg^0
  - Apparent reduction of Hg^{+2} removed in FGD absorber
  - Limits overall Hg removal by FGD system
- **Technical Approach** – conduct kinetics experiments, kinetics modeling, and bench-scale wet FGD model validation tests
- **Expected Benefits** – the ability to predict FGD re-emissions, and optimize FGD conditions to minimize or eliminate

Presentation Outline

- Background on re-emissions
- Re-emissions reaction mechanisms
- Project organization
- Technical approach
  - Fundamental kinetics measurements
  - Modeling
  - Bench-scale testing
- Schedule
- Milestones/Deliverables

Background - Field Observations of Re-emissions

- Observed across wet FGD since early 90's
  - Seen as possible measurement artifact
  - Documented by Gutberlet in 1992
- ICR data showed convincing evidence (measured re-emissions > 1 lb/TBtu)
  - Combined particulate/SO_2 scrubbers (7 of 9)
  - Less evident in SO_2-only scrubbers (3 of 19)
    - Mg-lime, sodium, limestone inhibited oxidation
    - None of 8 LSFO systems

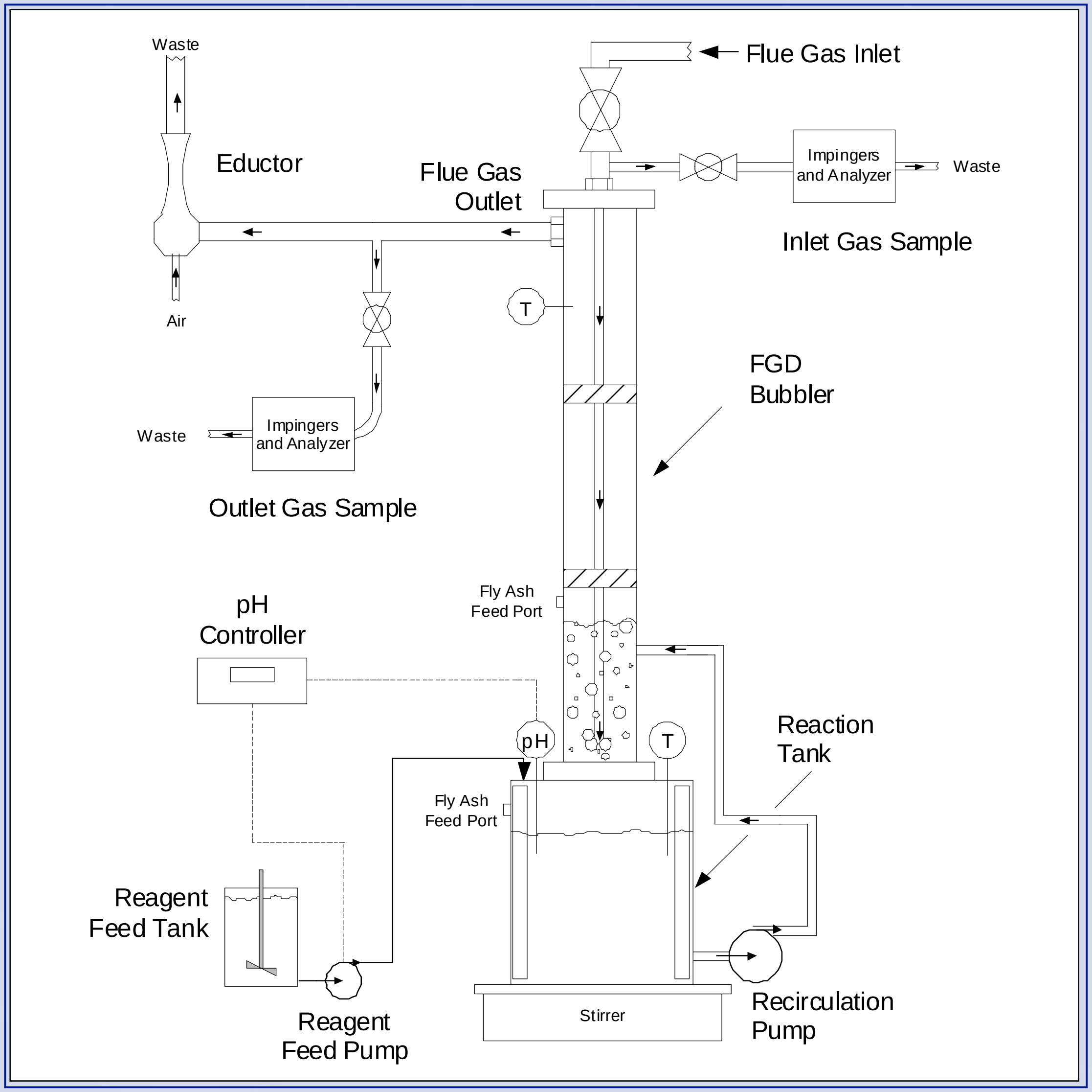
Field Observations - continued

- Further evidence seen in EPRI/DOE co-funded measurements of effects of SCR on Hg speciation
  - Re-emissions seen across two high-S Mg-lime FGD systems
  - Also seen across a combined particulate/SO_2 scrubber
  - SCR operation upstream appeared to reduce re-emissions effect

EPRI Bench-scale Investigations

- EPRI has funded URS to conduct bench-scale tests with synthetic flue gas to investigate re-emissions mechanisms
- Testing has been conducted on both SO_2-only and combined particulate/SO_2 scrubbers
- 1 scfm scale
- Project has included literature review and modeling efforts
- EPRI is a co-funder of the current NETL project

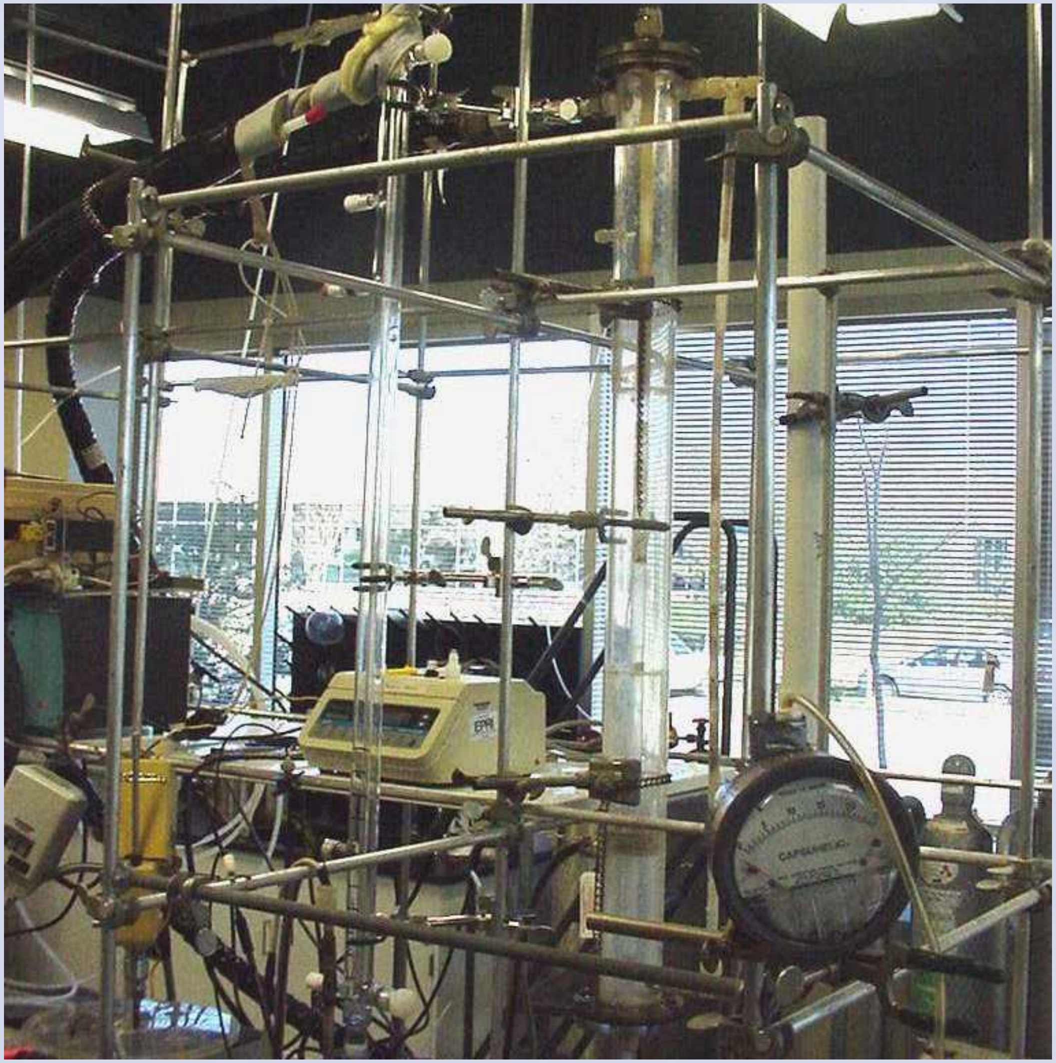
Bench-scale Wet FGD



Simulation gas contains:
SO_2, NO_X, HCl
CO_2, H_2O, O_2, N_2
Hg^{+2}, Hg^0

Inlet and outlet gas simultaneously monitored by SCEM

Bench-scale FGD System



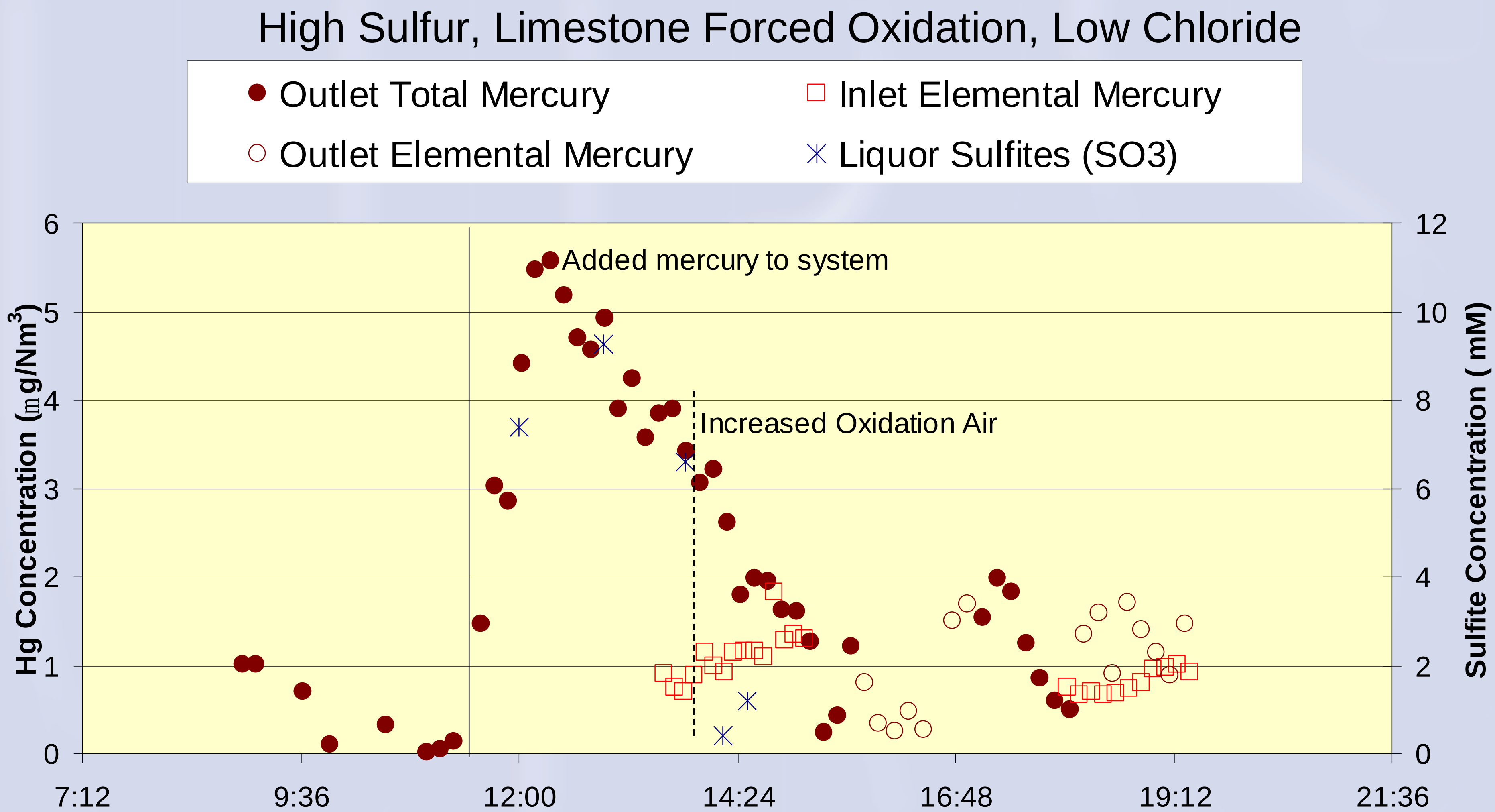
Bench-scale Test Variables (SO_2 removal only tests)

- Primarily simulated full-scale wet FGD systems where Hg removal data were available
- Variables included sulfur level, FGD reagent, oxidation mode, pH, chloride level, FGD temperature, inlet NO_X concentration

Overview of EPRI Results

- Bench-scale results qualitatively match full-scale results
- Most important variables: sulfite concentration, pH, presence of thiosulfate [$S_2O_3^{=}$] (inhibited oxidation conditions)
- Other variables may be important but were not thoroughly investigated: chloride concentration, inlet NO_X

Example Sulfite Effect



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Proposed Re-emissions Reaction Mechanism

Fast Steps:

$$Hg^{+2} + SO_3^{=} \leftrightarrow HgSO_3$$

$$HgSO_3 + SO_3^{=} \leftrightarrow Hg(SO_3)_2^{-2}$$

Slow Steps:

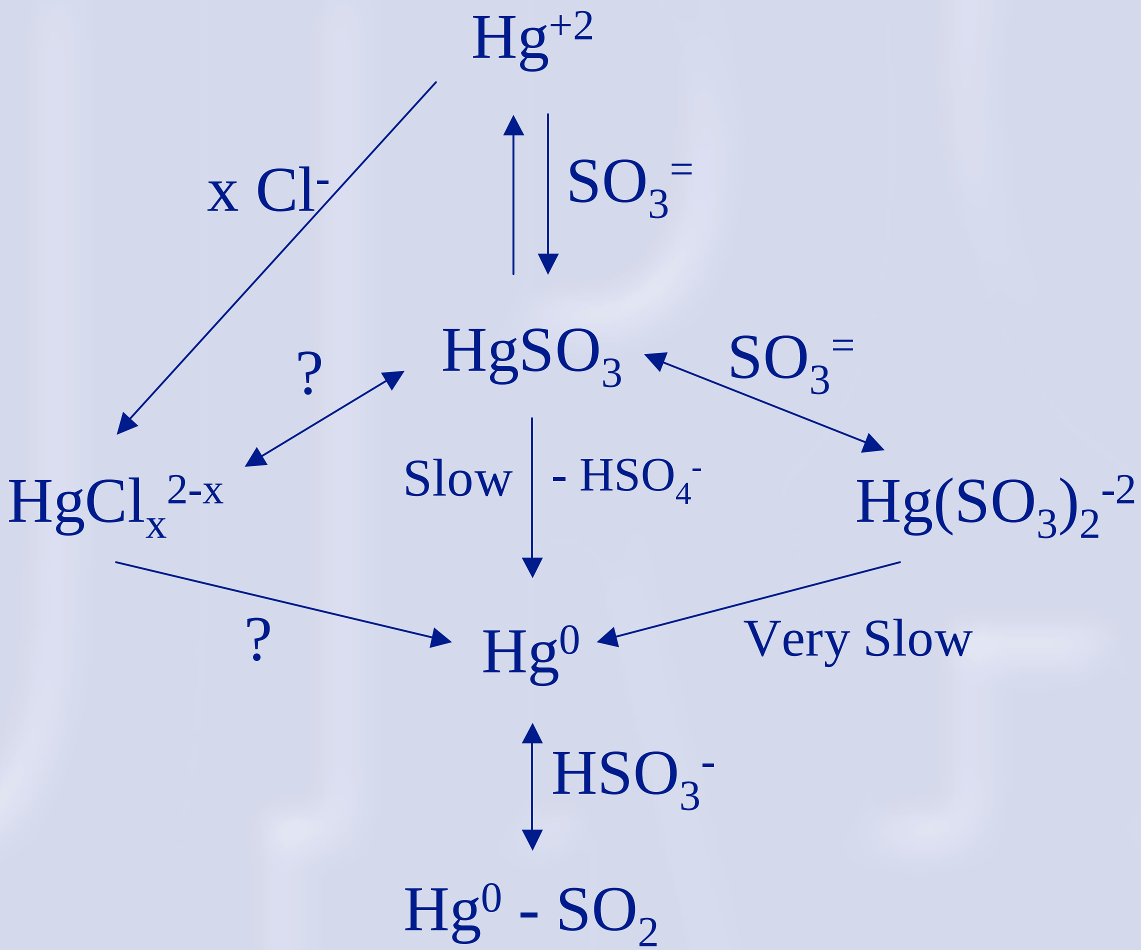
$$HgSO_3 \rightarrow Hg^{+1} + SO_3^{-1}$$

$$Hg^{+1} + HSO_3^{-} \rightarrow + Hg^{0} + SO_3^{-} + H^{+}$$

or

$$HgSO_3 + H_2O \leftrightarrow Hg^{0} + HSO_4^{-} + H^{+}$$

Schematic of Hg^{2+} - SO_3^{2-} Reaction Pathways



Possible thiosulfate ($S_2O_3^=$) interactions are not shown

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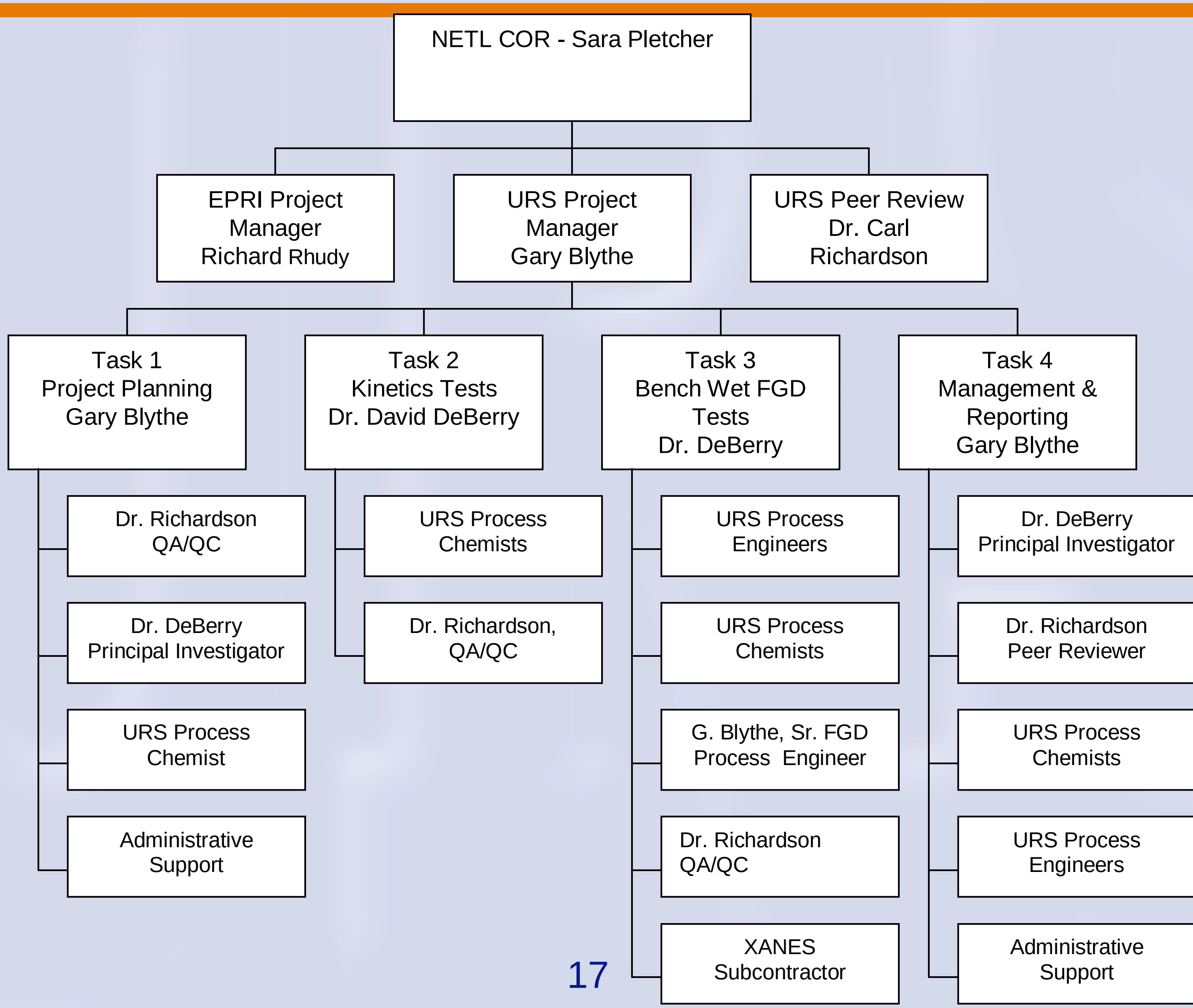
Project Task Structure

- Task 1 – Project Planning
- Task 2 – Kinetic Data Gathering and Initial Model Development
- Task 3 – Model Refinement, Bench-scale Validation and Additive Testing
- Task 4 – Reporting and Project Management

Project Organization Chart



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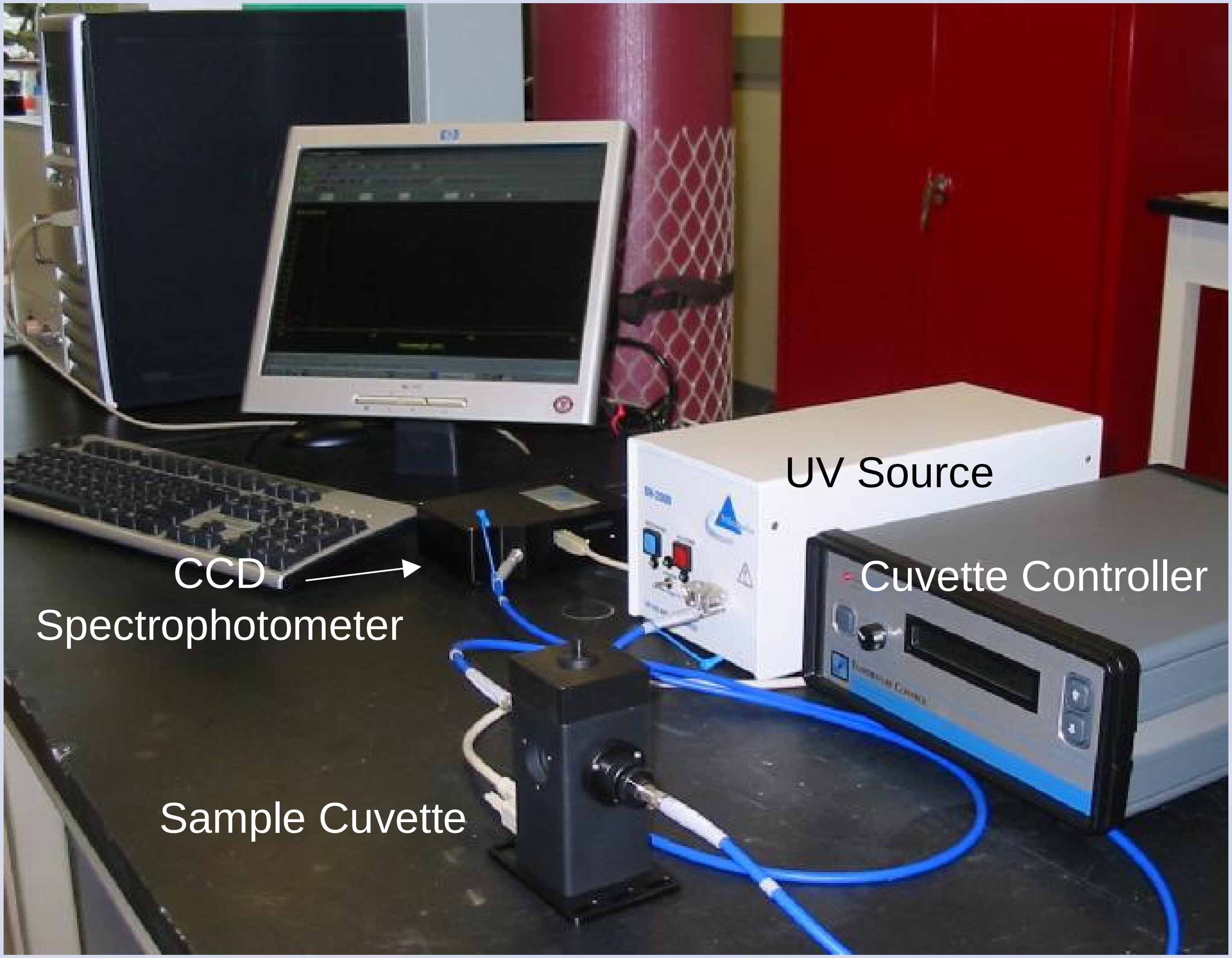
Project Technical Approach

- Collect reaction kinetics data (Task 2)
  - $HgSO_3$ complexes are formed rapidly, then decompose
  - They have UV absorption so can monitor rates with UV spectra
  - High resolution UV analyzer with a CCD spectrophotometer will be used to track byproduct concentrations vs. time
- Monitor rate of emission of elemental mercury (Hg^0) from similar solutions by CVAA (Task 2)
- Incorporate results into a chemical kinetics model (Tasks 2 and 3)
- Confirm model with FGD bench-scale tests (Task 3)

Task 2 – Fundamental Investigation of Hg^0 Re-emissions

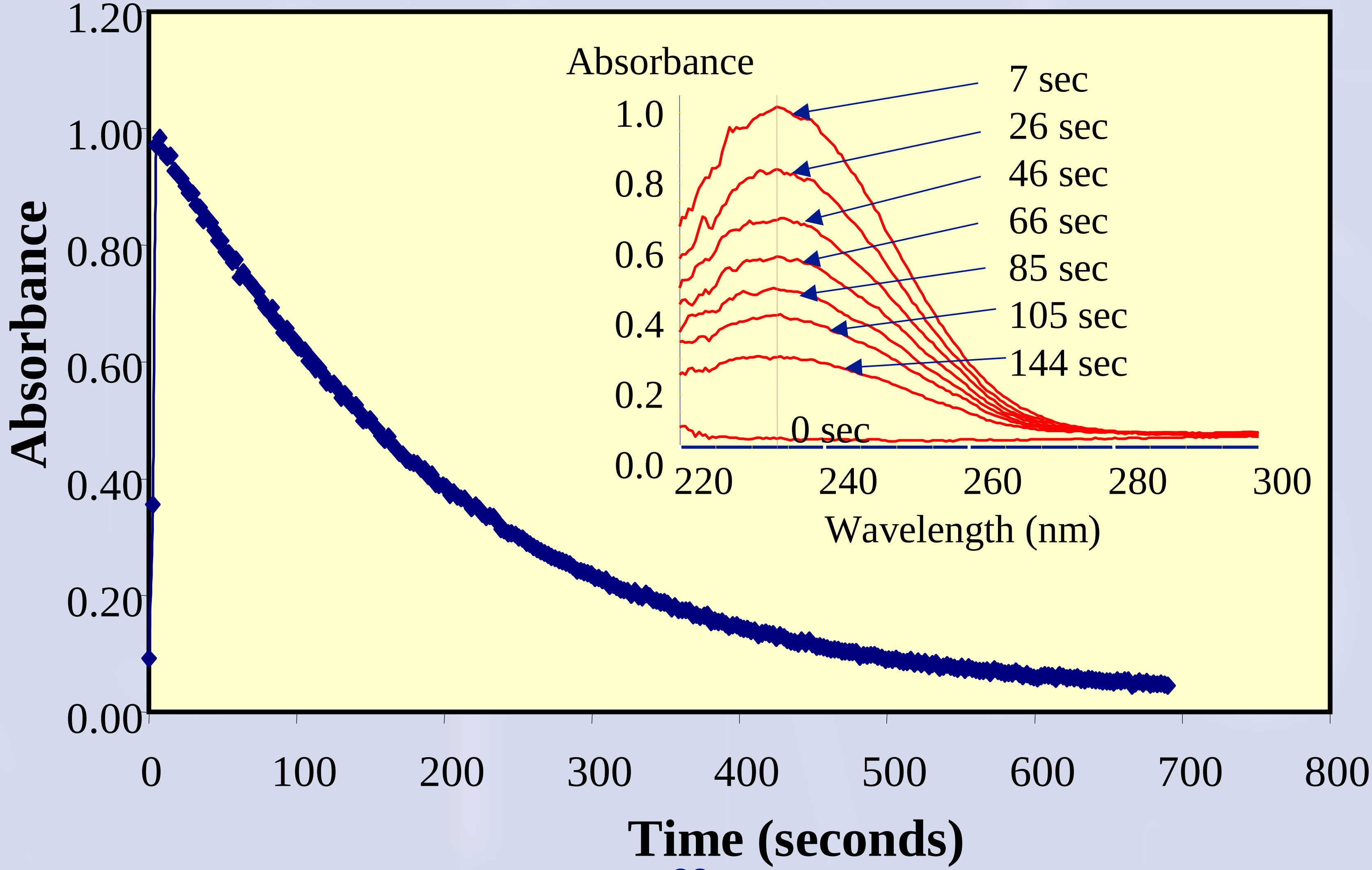
- Hg^{+2} – sulfite reaction rates appear to be a key factor
- Some kinetic data are available in the literature for simple liquid compositions
- But, species in FGD liquor are expected to affect kinetics
  - Chloride ion
  - Thiosulfate ion
  - Additives (affect Hg residence time in the FGD liquor)

URS UV/Visible Spectrophotometer

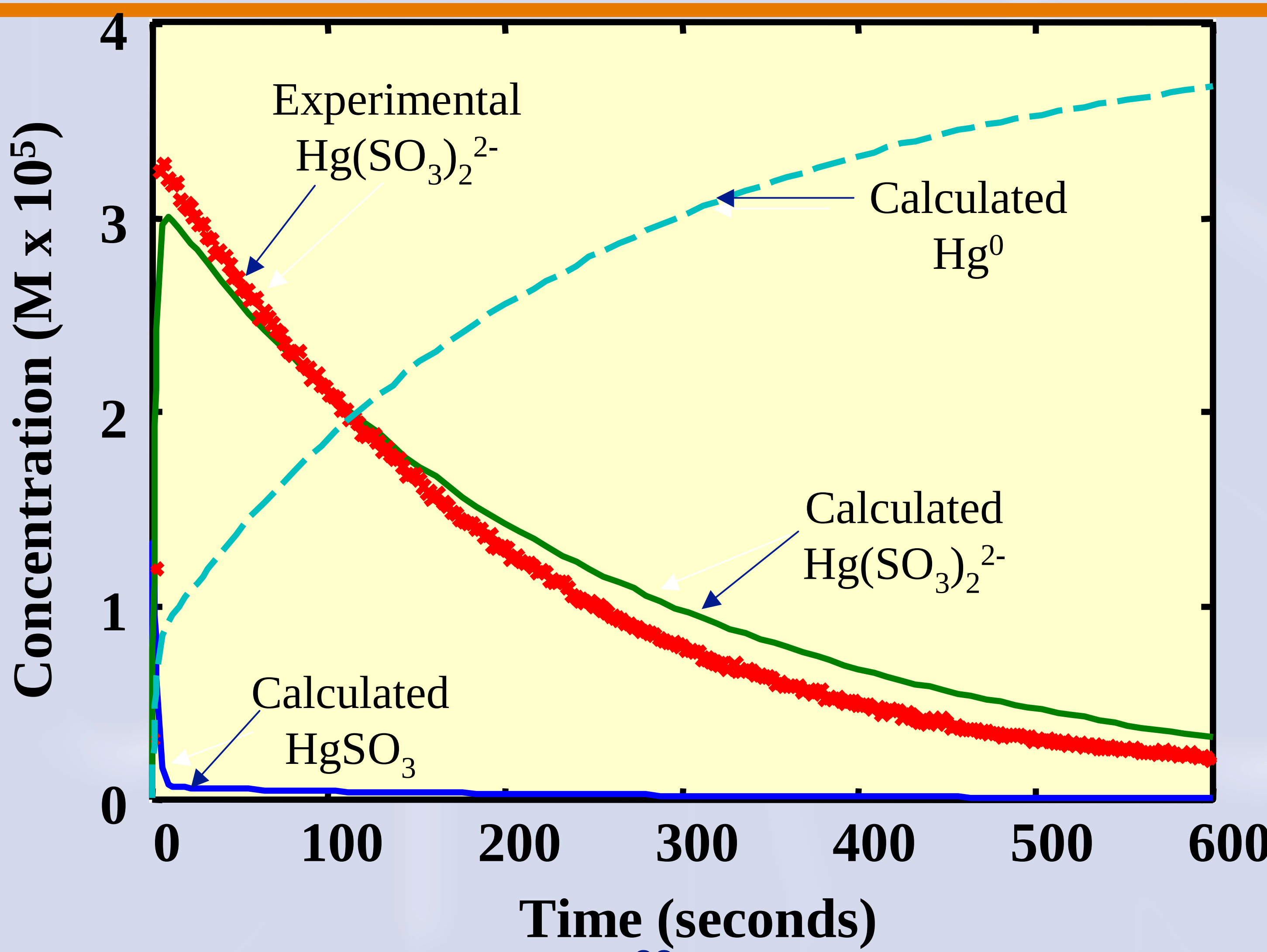


Experimental Results - Hg Disulfite Absorbance

0.040 mM Hg^{+2} + 0.23 mM sulfite, pH 3.0, 45°C



Experimental and Model Results - for 0.040 mM Hg^{+2} reacting with 0.23 mM sulfite at pH 3.0, 45^{o}C

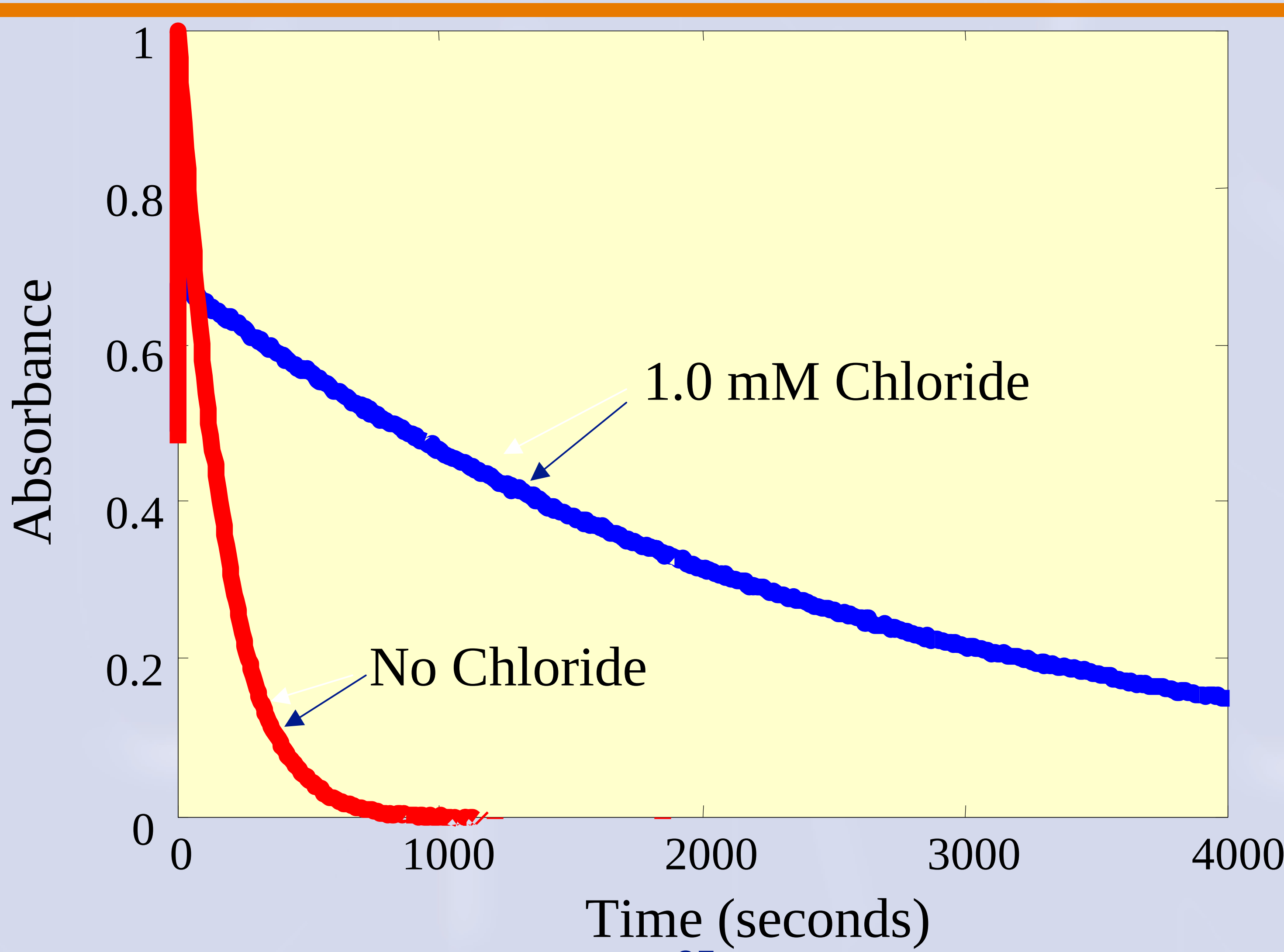


Probable Effects of Chloride, Thiosulfate

- Form a complex with Hg^{+2}, competing with sulfite
- Hg^{+2} - chloride or Hg^{+2} - thiosulfate complexes are probably weaker oxidizing agents, so they are slower to oxidize sulfite
- Thiosulfate may also act as a reductant for Hg^{+2}

Effect of Cl on Decomposition of Hg^{+2}-Sulfite Complex

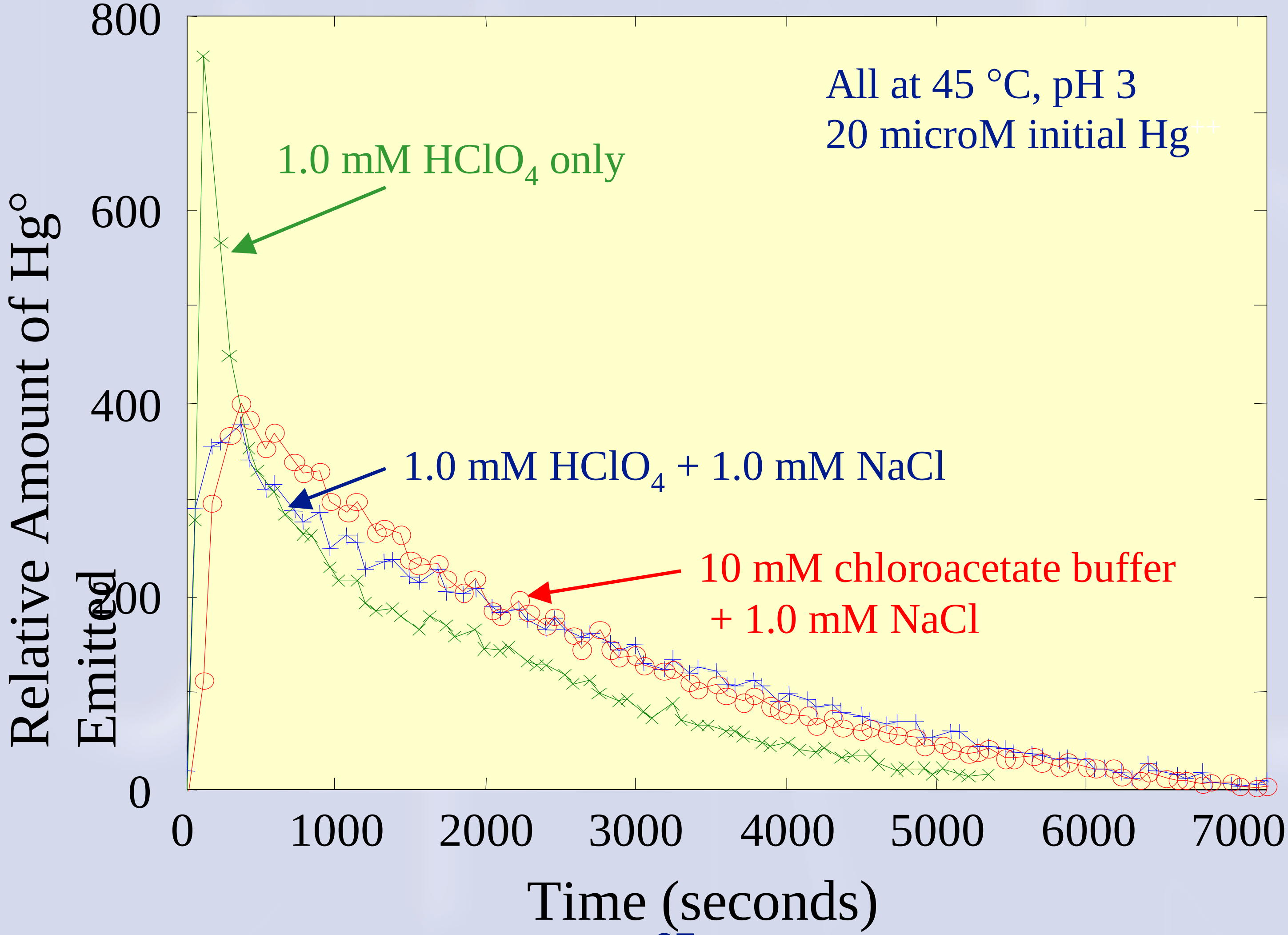
starting with 0.040 mM Hg^{+2} and 0.23 mM sulfite at pH 3.0, 45°C



Monitoring Hg^0 Emission from the Reaction of Sulfite and Hg^{+2}

- Use impinger containing desired liquor composition except without any mercury
- Impinger placed in a thermostatted bath
- Saturate liquid with gas at SO_2 partial pressure calculated to maintain desired pH
- Initiate reaction by injecting aqueous solution of mercuric perchlorate into impinger with a syringe via a septum port
- Monitor the outlet Hg^0 by sampling for CVAA about every two minutes

Hg^0 Emitted at Several Conditions, by CVAA



Initial Hg^0 Emission Results

- Results are qualitative because of difficulty measuring Hg^0 evolution
  - Hg evolved overwhelms CVAA detector
  - Sample times therefore limited to only 1 second
  - Apparatus will be modified to improve ability to quantify Hg losses (e.g., lower Hg concentrations in liquor, higher gas rate through impinger)
- Time response of emitted Hg^0 is qualitatively similar to decay of Hg^{+2} - sulfite complex spectra shown previously
- Chloride slows the reaction, similar to effect observed with UV spectrophotometer
- Chloroacetate buffer has little effect on rate, will help maintain constant pH in future tests

Tasks 2 and 3 – Kinetics Modeling

- Proprietary URS kinetics modeling software will be used
  - Keeps database of reactions, rate constants, reaction conditions
  - Differential equation solver produces time-dependent species concentrations
  - URS will compare experimental data to calculated values
  - Adjust rate constants as needed to improve fit over a range of FGD conditions

Kinetics Modeling Deliverables

- Chemical reaction mechanisms
- Reaction rate constants
- Reaction activation energy values
- Model output over a range of FGD conditions
  - Re-emissions rates
  - Effects of additives
- Optimum FGD conditions to minimize re-emissions

Task 3 – Bench-scale Tests

- To be conducted using apparatus previously described, 1 scfm
- Used to confirm model predictions
  - Hg SCEMs used to quantify Hg^0 re-emissions
  - UV/Vis analyzer integrated for some tests to verify liquor concentrations of re-emission intermediates
  - FGD liquor and solids Hg concentrations measured for mass balance calculations
- Verify FGD additive effects
- Generate samples for XANES [X-ray Absorption Near Edge Spectroscopy] analyses (attempt to determine Hg compound in solid phase)

Task 4 – Final Report

- Background and literature survey results
- Details of experimental apparatus, procedures
- UV/Vis and Hg^0 emission bench-top test results
- Kinetics modeling results as detailed earlier
- Bench-scale results
  - – Comparison with model predictions
  - – Additive effectiveness

Task 4 – Final Report (continued)

- Results of XANES analyses of bench-scale FGD solids (Hg compounds in FGD solids)
- Recommendations for how to optimize FGD conditions to minimize re-emissions

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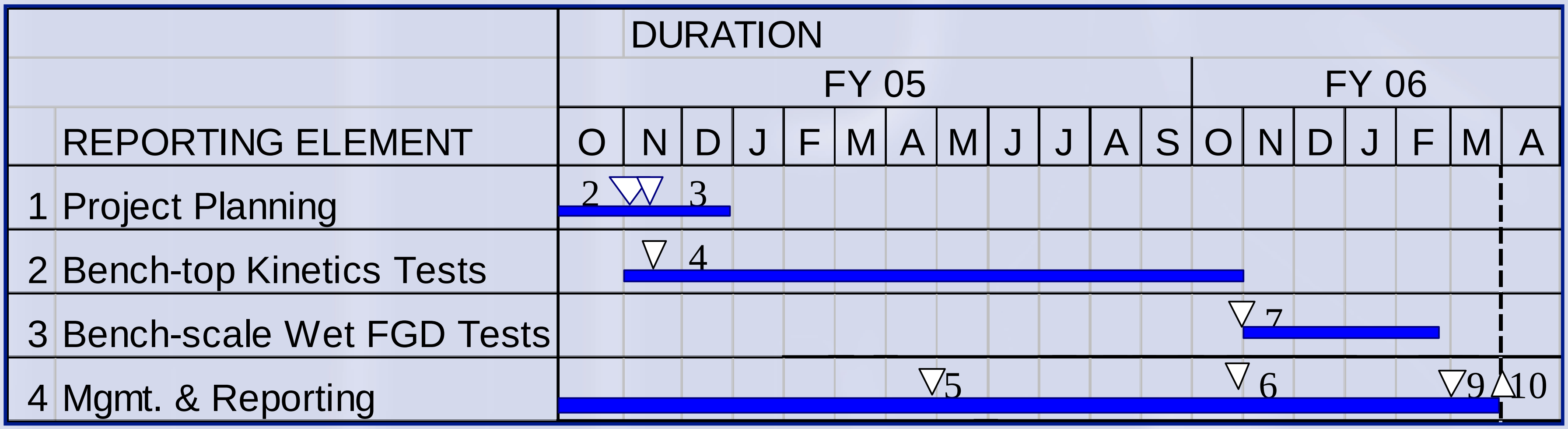

Project Milestones

1	Begin Project	9/30/2004
2	Submit draft Test Plan	11/9/2004
3	Test plan review/Project Kickoff Meeting	11/16/2004
4	Begin bench-top kinetics tests	11/22/2004
5	Submit 1st Semiannual Technical Progress Rpt	4/25/2005
6	Submit 2nd Semiannual Technical Progress Rpt	10/25/2005
7	Begin Bench-scale Wet FGD Tests	11/1/2005
9	Submit Draft Final Report	2/28/2006
10	Submit Final Report, 3rd Semiannual Tech Prog Rpt	3/31/2006