Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

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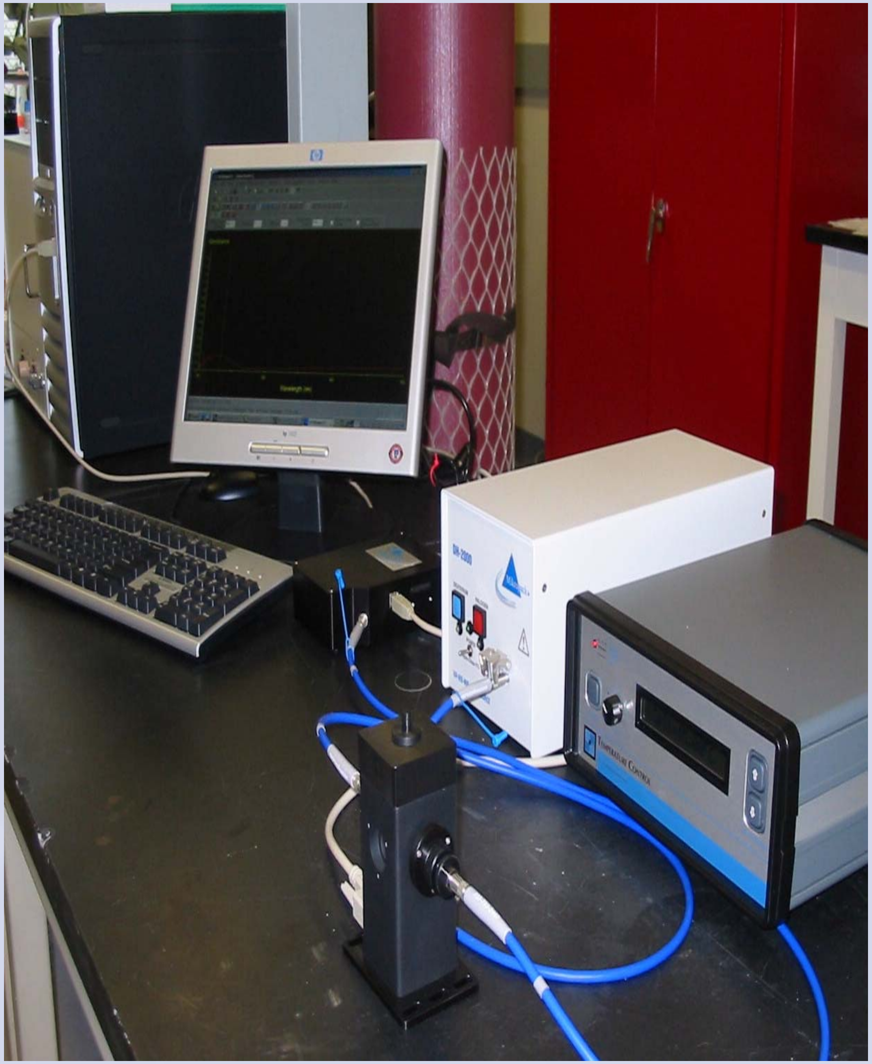
Introduction

- **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
- **Expected Benefits** – the ability to predict FGD re-emissions, and optimize FGD conditions to minimize or eliminate

Technical Approach

- Conduct kinetics experiments
  - Spectroscopic monitoring of the Hg-Sulfite complex reactants
  - Production / stripping of Hg^o
- Construct a kinetics model which describes the results
- Test the model using the URS bench-scale wet FGD system



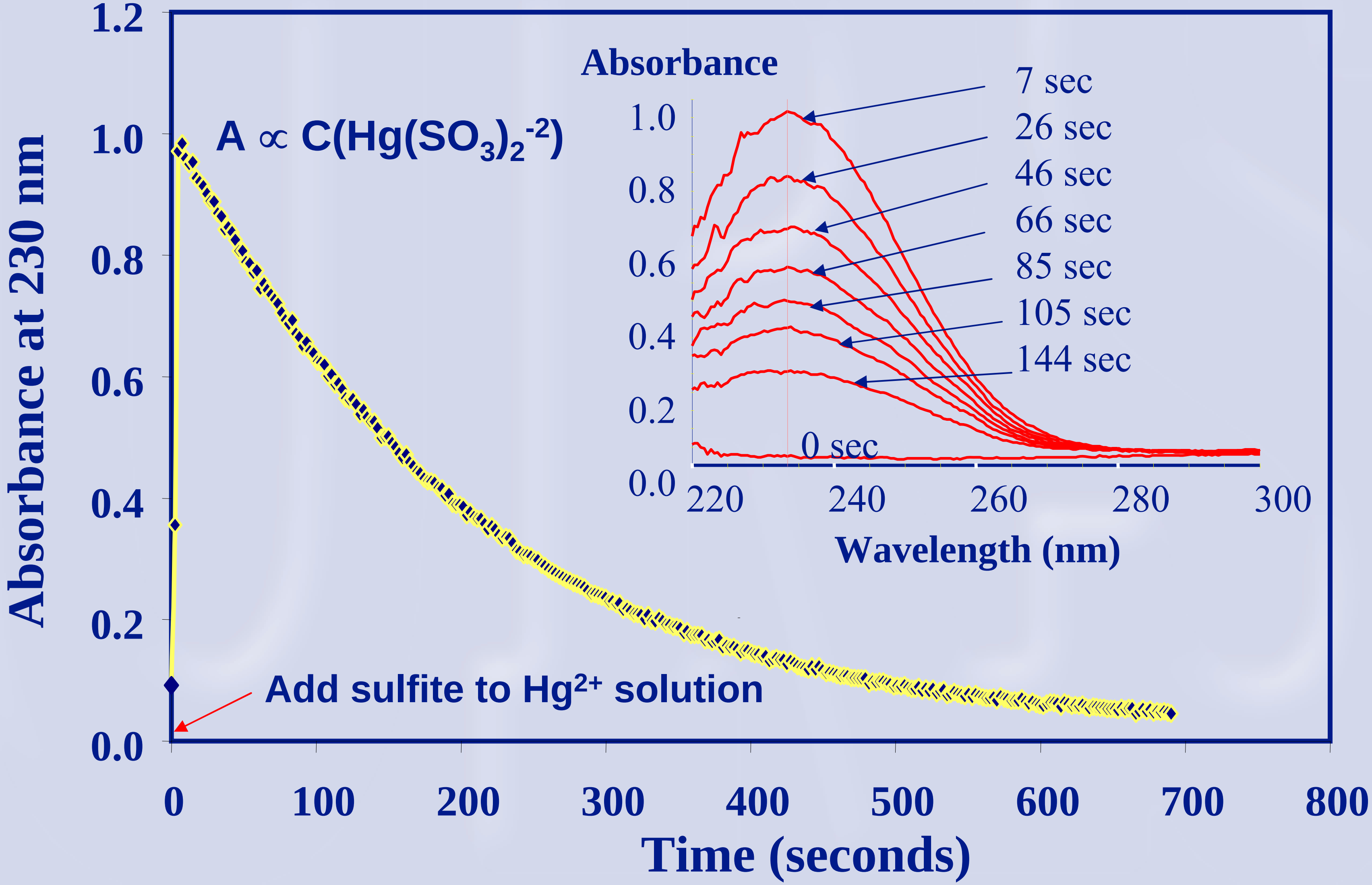
Main Chemical Reactions for Hg Emission without Chloride

- Overall reaction:
  - $Hg^{+2} + HSO_3^{-} + H_2O \rightarrow Hg^{o}\uparrow + SO_4^{-2} + 3\ H^{+}$
- Main pathway is through mercuric-sulfite complexes:
  - $Hg^{+2} + SO_3^{-2} \leftrightarrow HgSO_3$
  - $HgSO_3 + SO_3^{-2} \leftrightarrow Hg(SO_3)_2^{-2}$
- Equilibrium favors $Hg(SO_3)_2^{-2}$ in presence of excess sulfite
- But only $HgSO_3$ decomposes to give reduction of Hg^{+2}:
  - $HgSO_3 + H_2O \rightarrow Hg^{o}\uparrow + SO_4^{-2} + 2\ H^{+}$

Main Initial Variables

Approach	SO_3^{-2} (mM)	pH	Temperature (^oC)	Cl^- (mM)
Spectrophotometric	0.2-10	3-5	45-55	0-1000
Stripping	1-20	3-7	50-55	0-250
Bench-scale	1-20	4-7	50-55	0-250

Example Spectra and Rate Curve



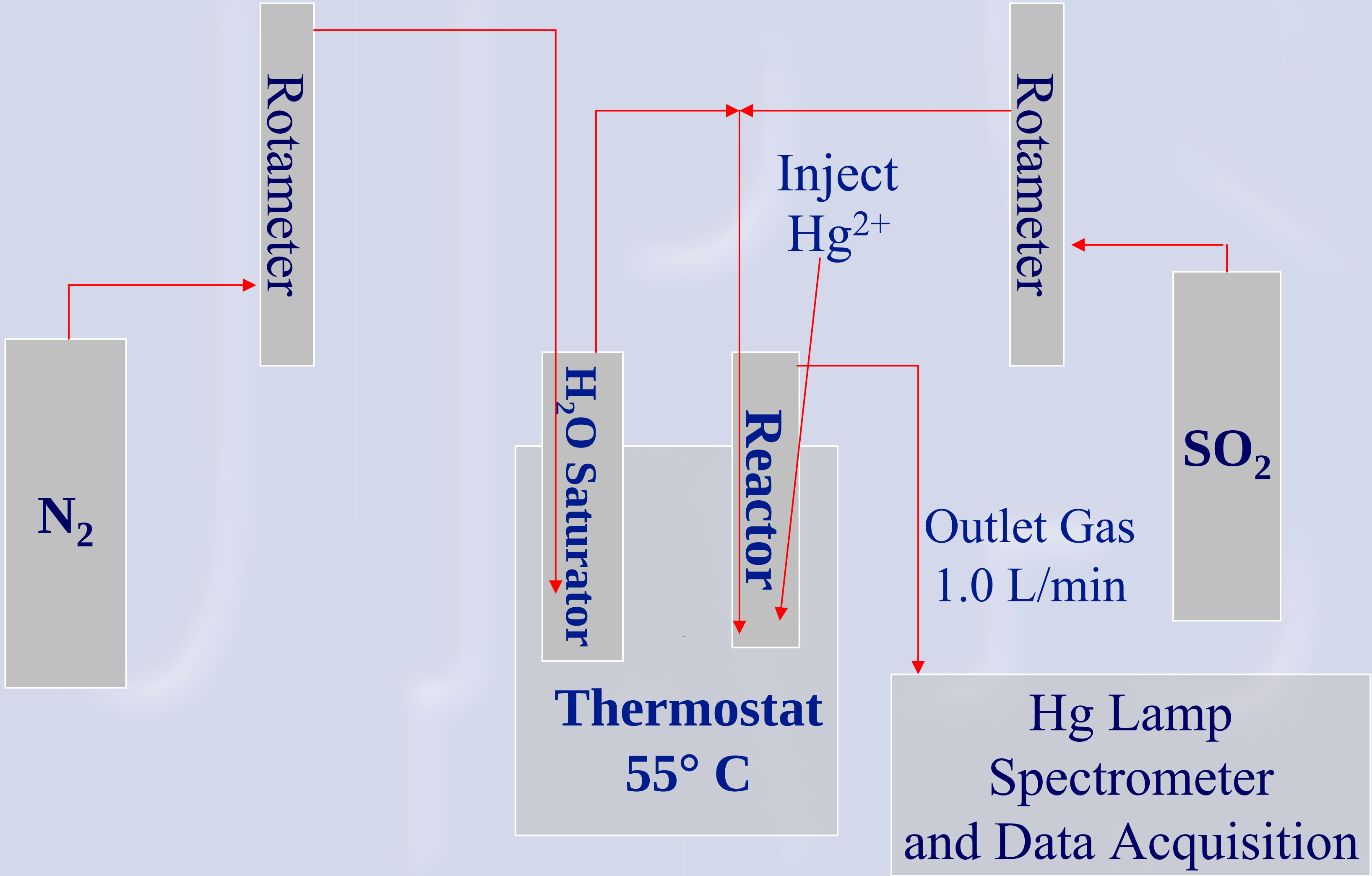
Initial Project Results – Spectrophotometric Tests

- No Chloride
  - Shows fastest rate decay
  - Increase in pH and/or sulfite leads to a slower reduction of mercury
- Chloride
  - Slower reaction rate than without chloride
  - Formation of new intermediate, $ClHgSO_3^-$
  - Decomposes at a slower rate then $Hg(SO_3)_2^{-2}$
- Iodide
  - 80 µM iodide leads to similar mercury reduction as 10 mM chloride.
  - Equivalent amount of chloride shows little to no effect.

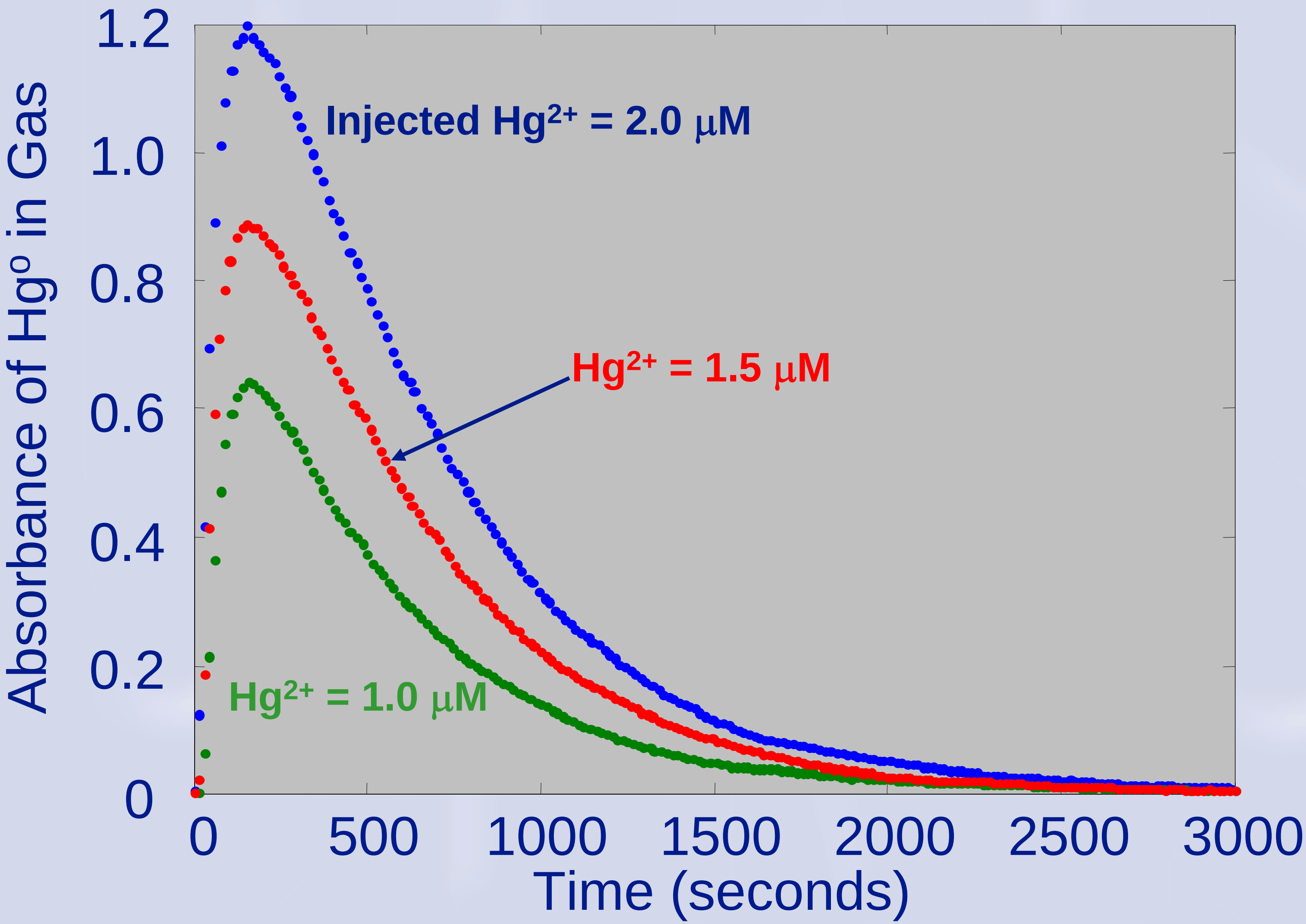
Stripping Method for Measuring Hg^0 Emissions from Test Solutions

- Continuously measures Hg^0 in gas phase as it is emitted following Hg^{2+} injection and stripping from reactor
- Able to use low “FGD levels” of Hg^{2+} in reactor: 0.5 – 2 μM
- Getting close material balances on Hg^{2+} added, Hg^0 measured in gas phase, and Hg left in liquid (which is usually negligible)
- Exponential decay rates of the initial Hg^{2+} concentration are first order, matching spectroscopic results

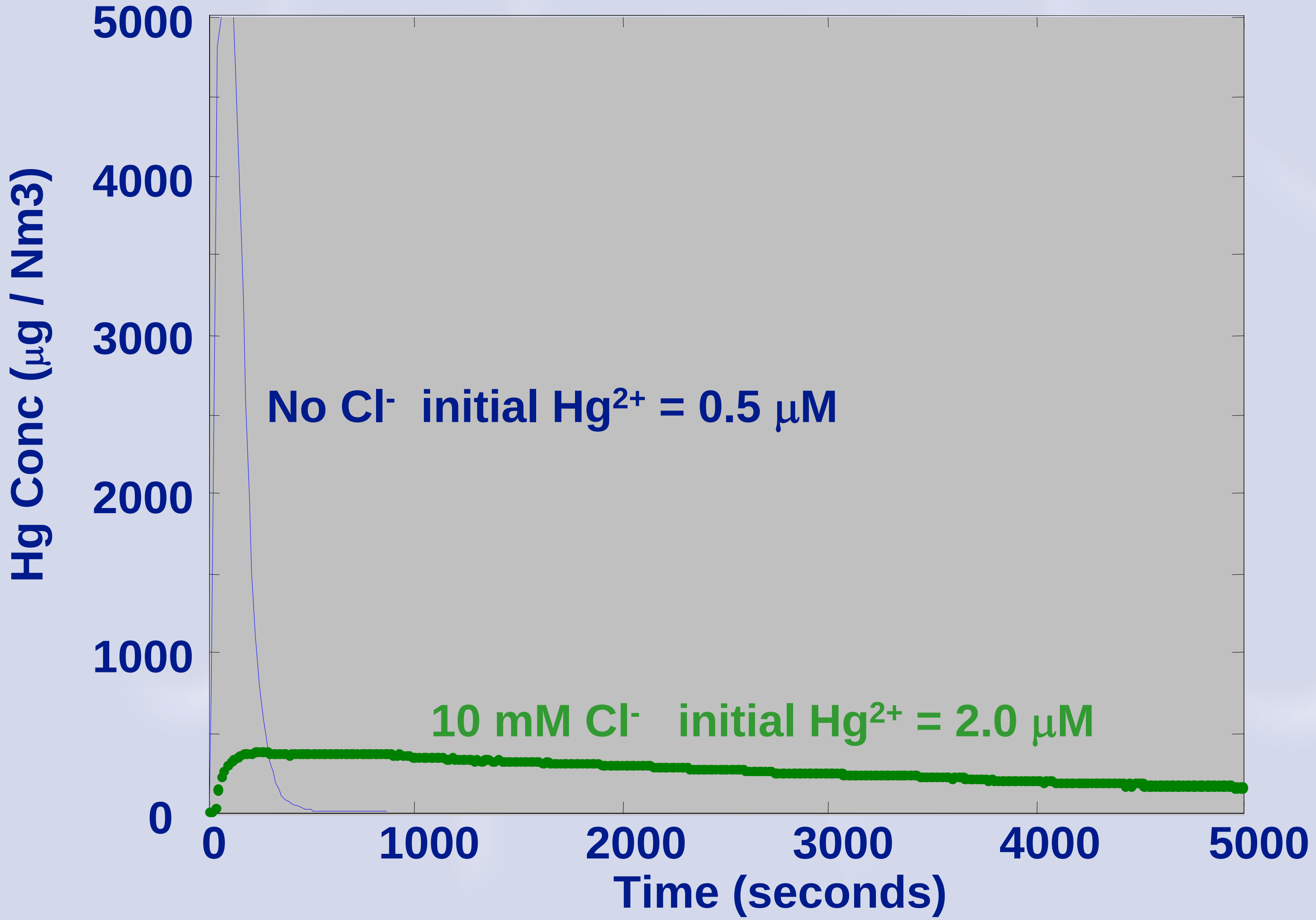
Hg^o Stripping Kinetics Apparatus



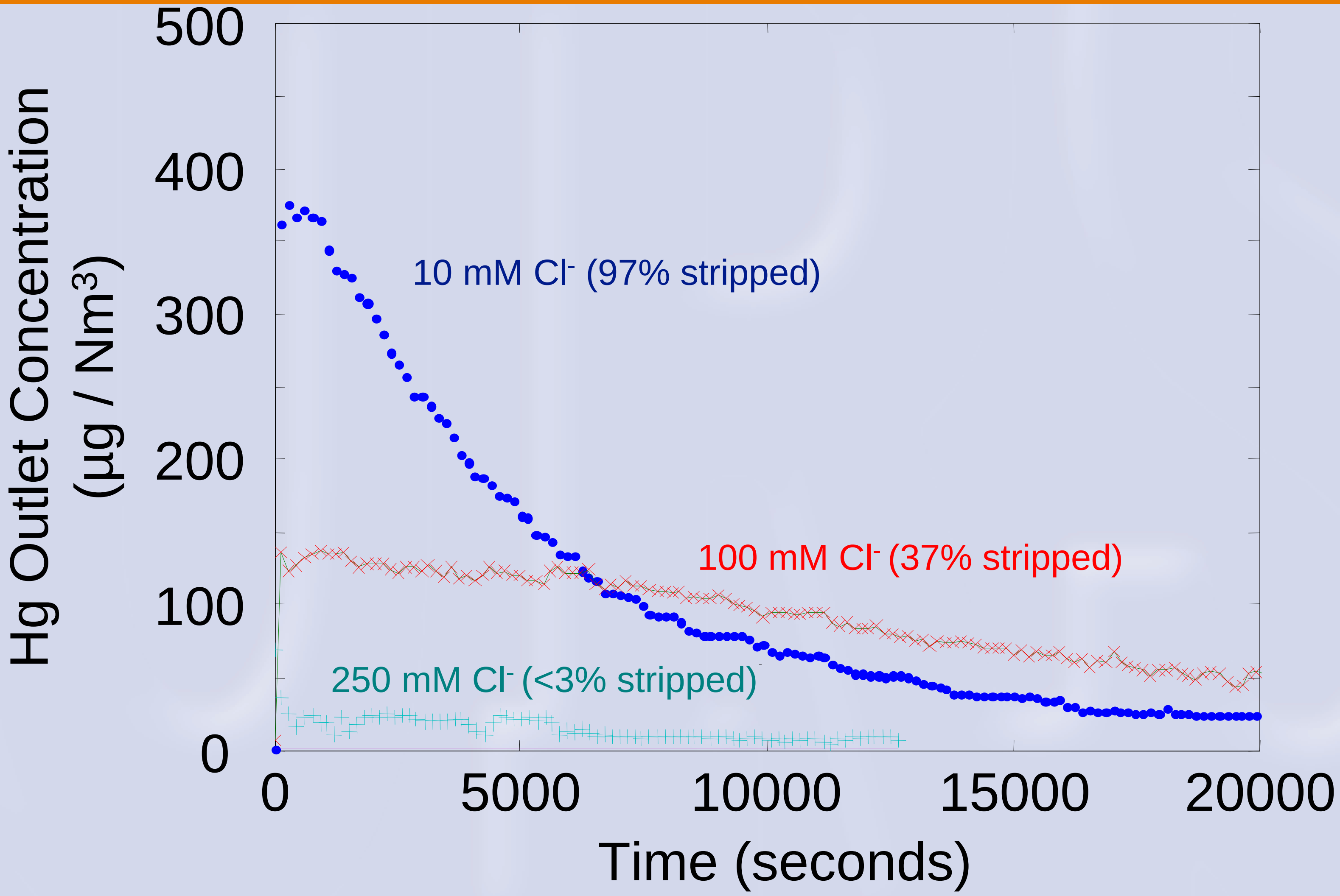
Stripping Runs at Different Initial Hg^{2+} Concentrations



Effect of Chloride on Hg^0 Stripping Kinetics



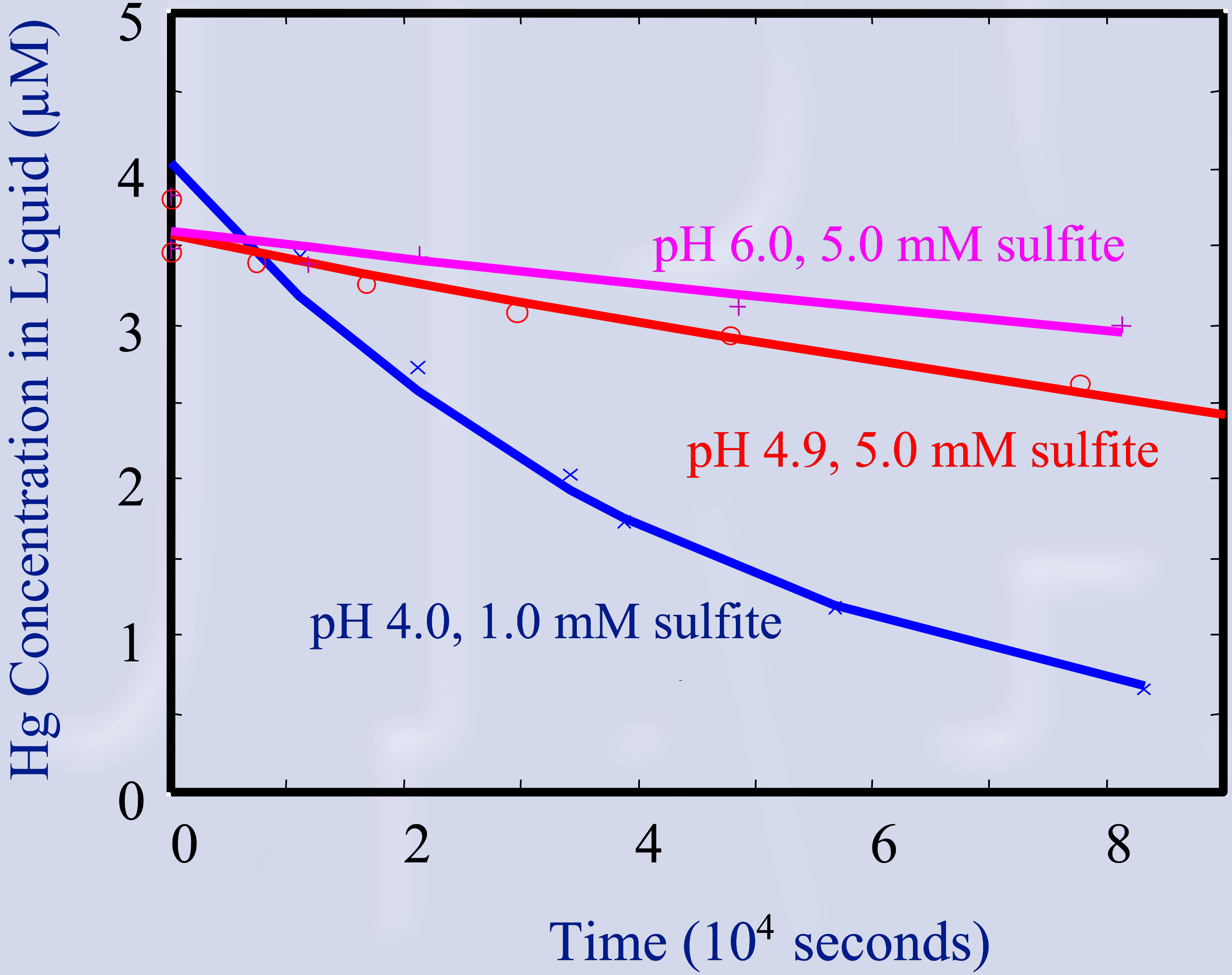
Stripping Kinetics Results with 10 mM, 100 mM and 250 mM Chloride at 55 ºC



Kinetics from Measurement of Liquid-phase Mercury Loss

- Obtained kinetics results over a range of FGD pH and sulfite conditions at 100 mM chloride
- Hg^{2+} reduction rates are slow at these conditions, so runs are carried out for 24+ hours
- Total Hg liquor concentrations measured by a Perkin Elmer FIMS-100 CVAA

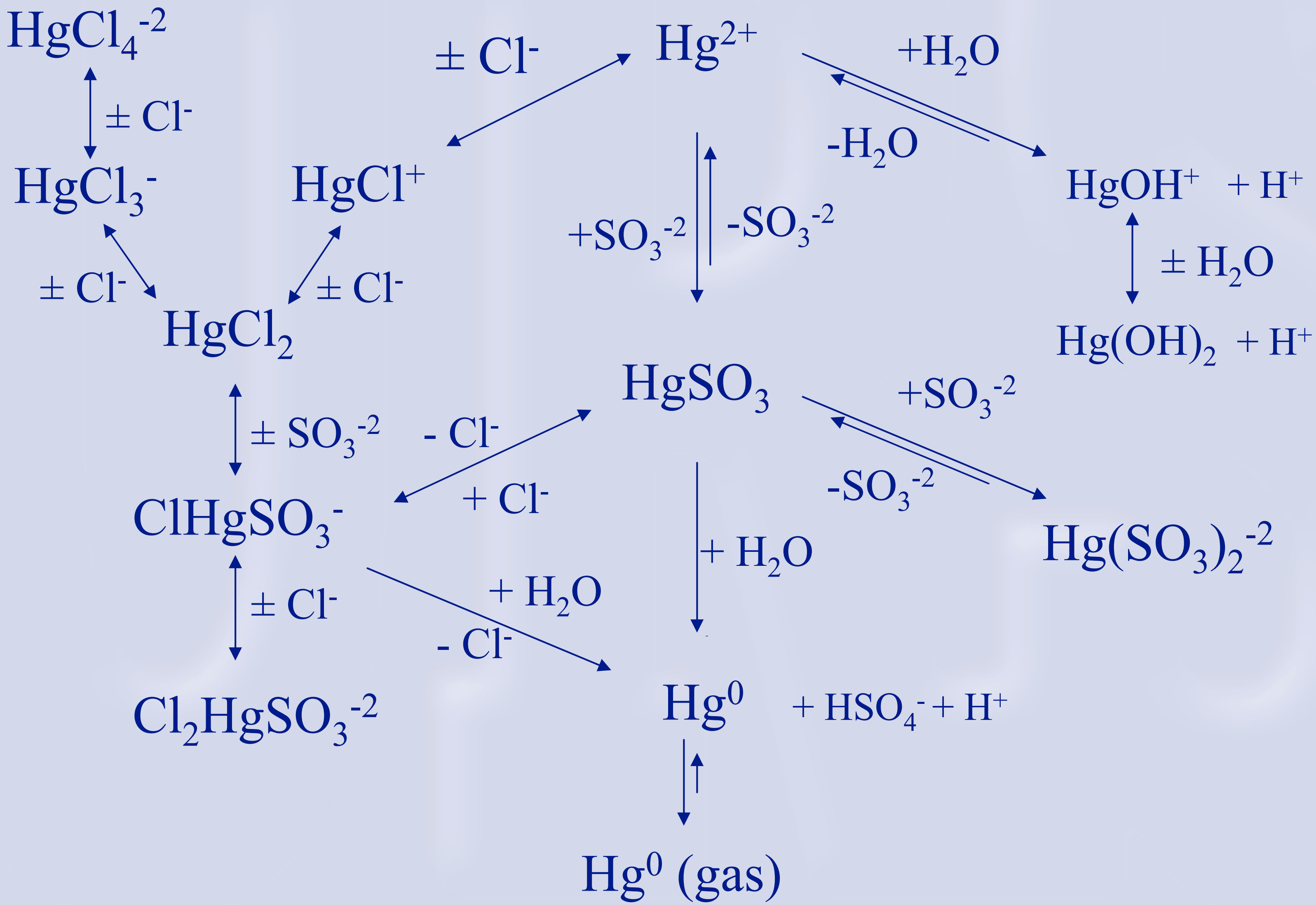
Examples of Loss of Mercury from Reactor Following Initial Injection of Hg^{+2}; 100 mM Chloride, 55 ºC



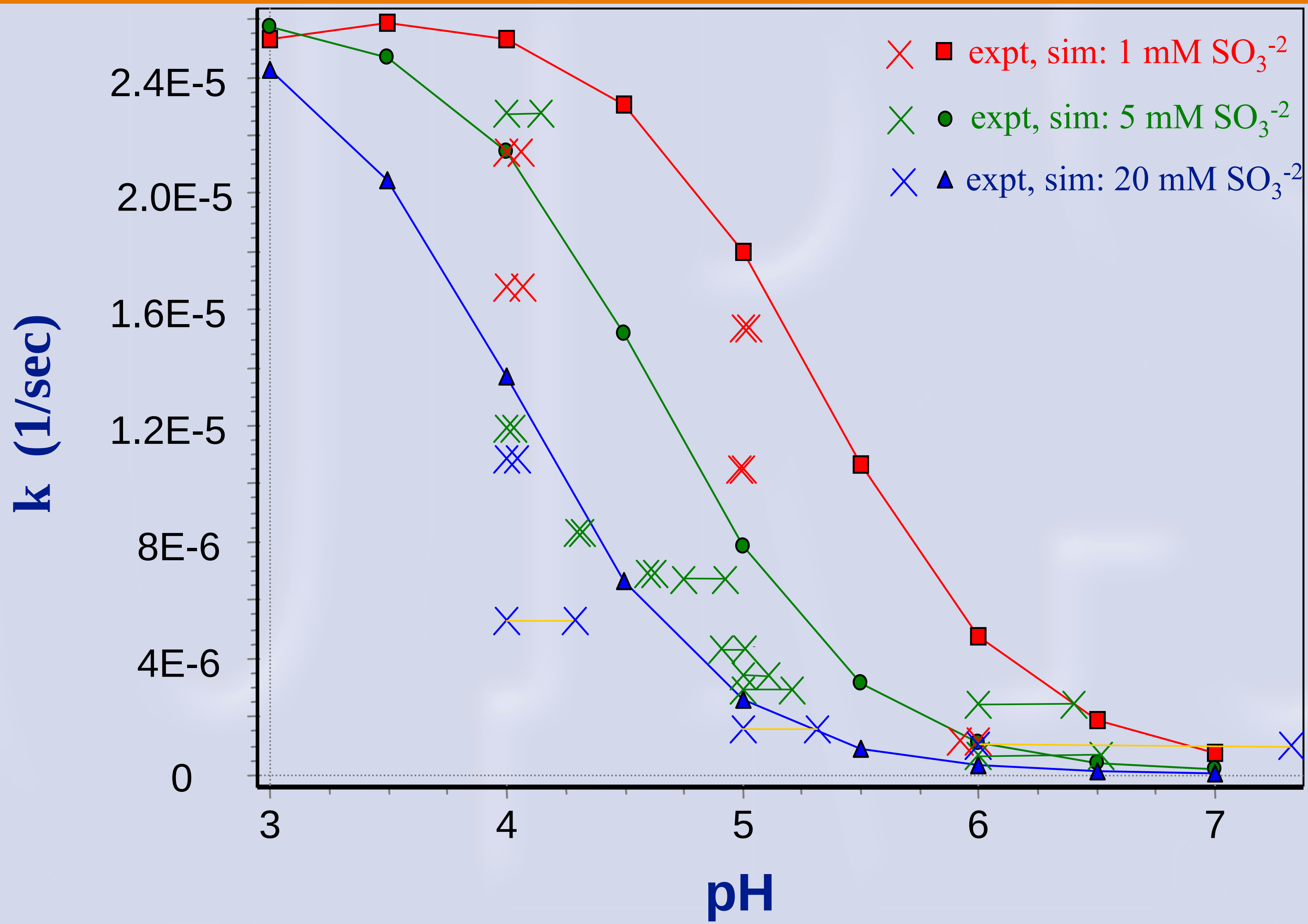
Kinetics Model Development

- Kinetics model generally reproduces observed trends of mercury reduction rates with varying pH and sulfite
- Preliminary interpretation of modeling results is that re-emissions rate is controlled by mercuric chloro-sulfite complexes at low pH (near pH 4) but increasingly by mercuric sulfite complexes alone at higher pH
- Model indicates that the concentration of the aqueous species "sulfite" (SO_3^{-2}) is of major importance - higher sulfite slows down reduction of Hg^{2+}

Schematic Diagram of Main Reaction Pathways in Current Kinetics Model



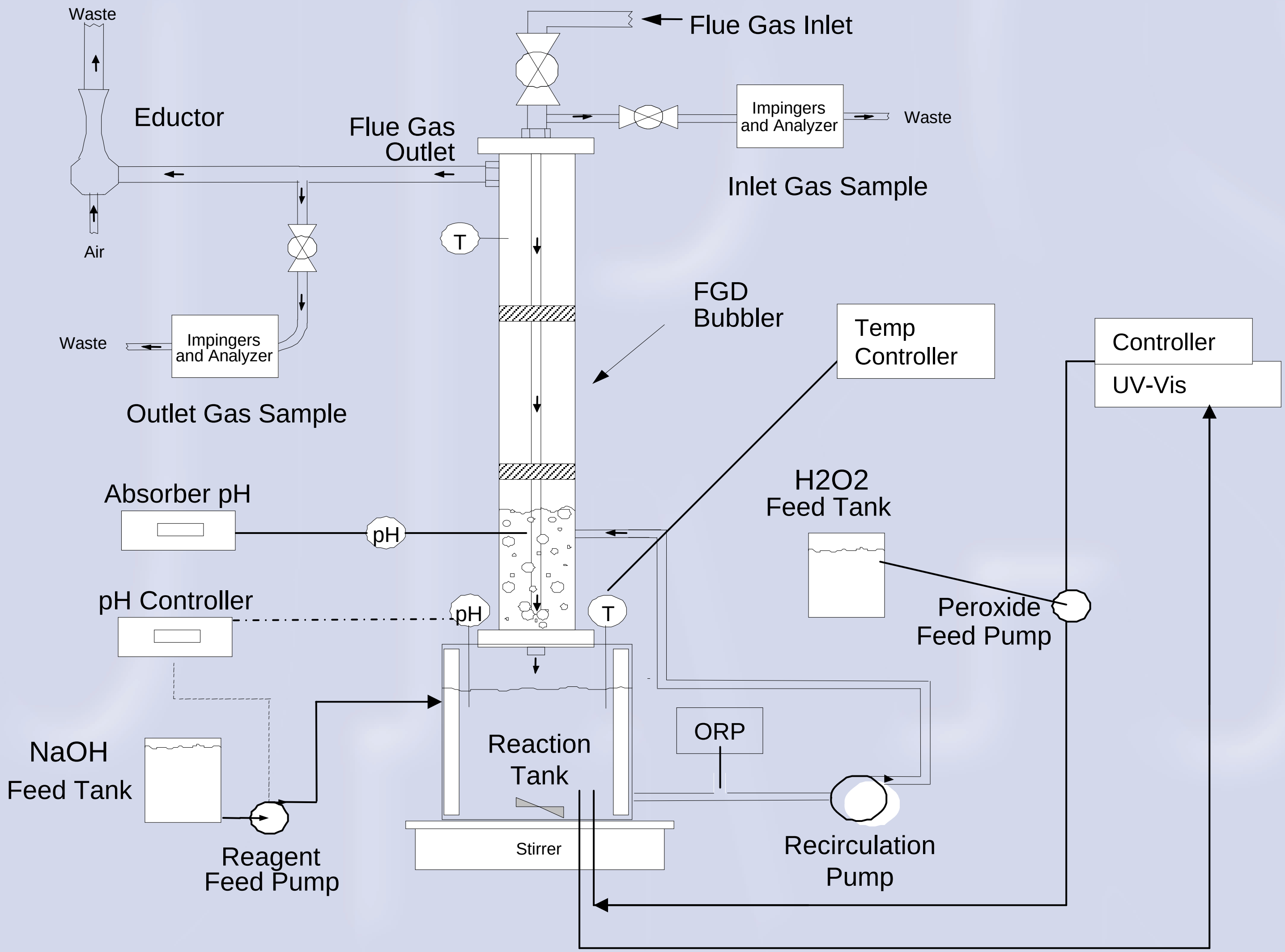
Observed and Model-simulated Rate Constants for Reduction of Mercury in 1.0, 5.0, and 20 mM Sodium Sulfite Solutions (100 mM NaCl and 100 mM sodium acetate at 55 °C)



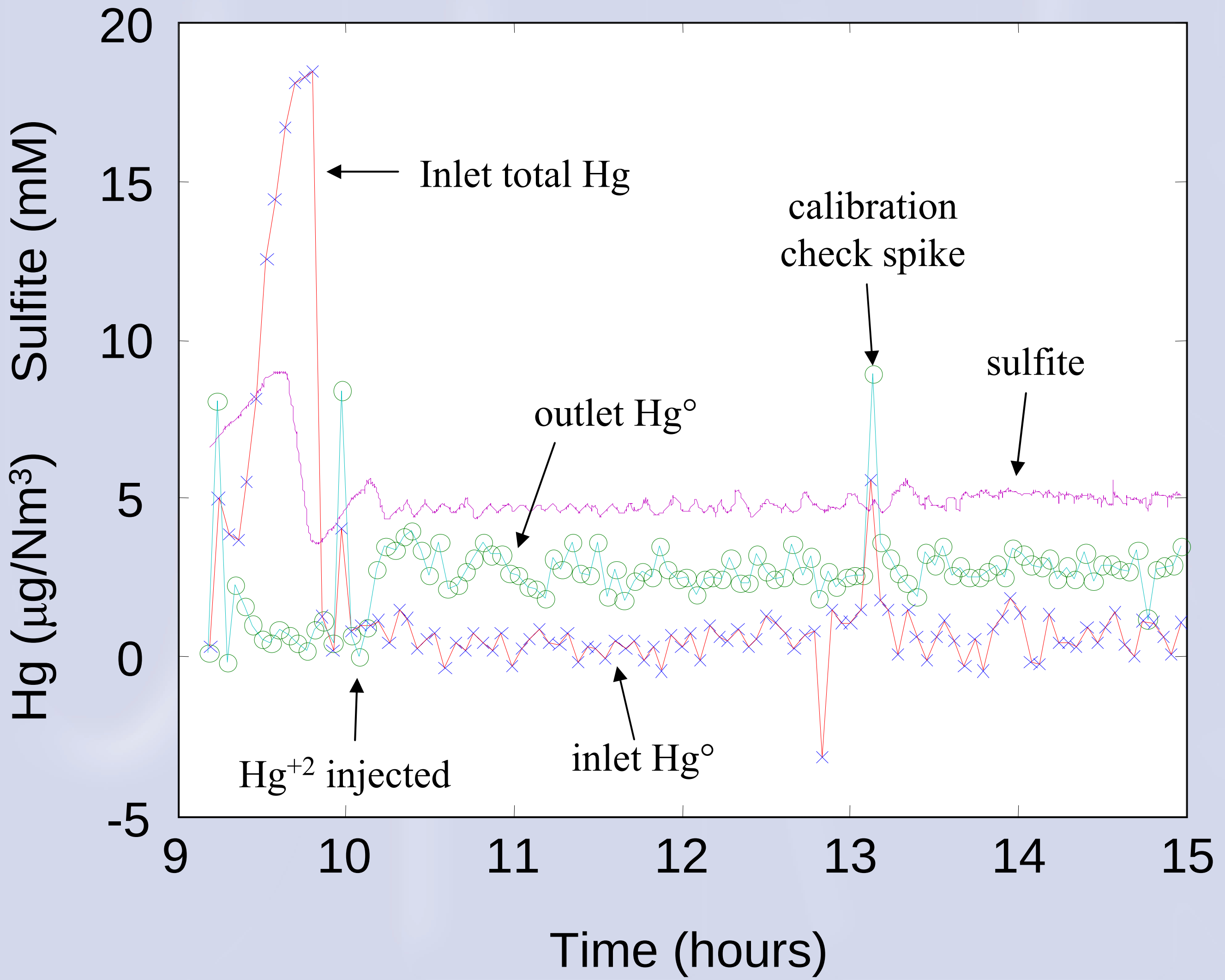
Bench-scale FGD Test Series

- Using simulated flue gas containing SO_2, $HgCl_2$, CO_2, O_2, HCl, N_2
- First test series uses clear liquor (NaOH for pH control), realtime sulfite monitoring and H_2O_2 for sulfite control
- Test matrix for pH/sulfite/chloride effects along with testing of many other chemical and physical variables

Bench-scale FGD System

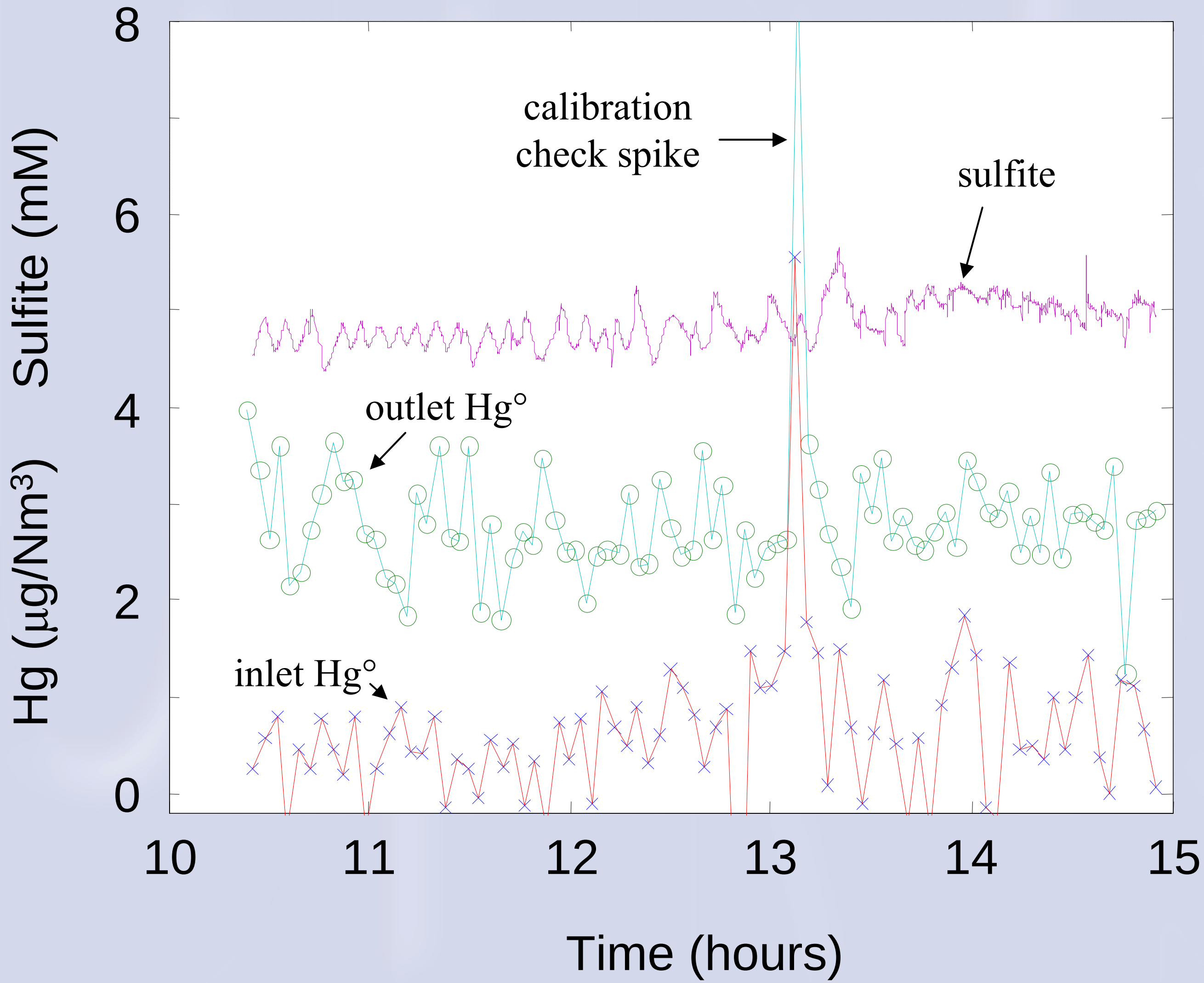


Bench-scale Run at pH 5.0, 5 mM Sulfite, 100 mM Chloride

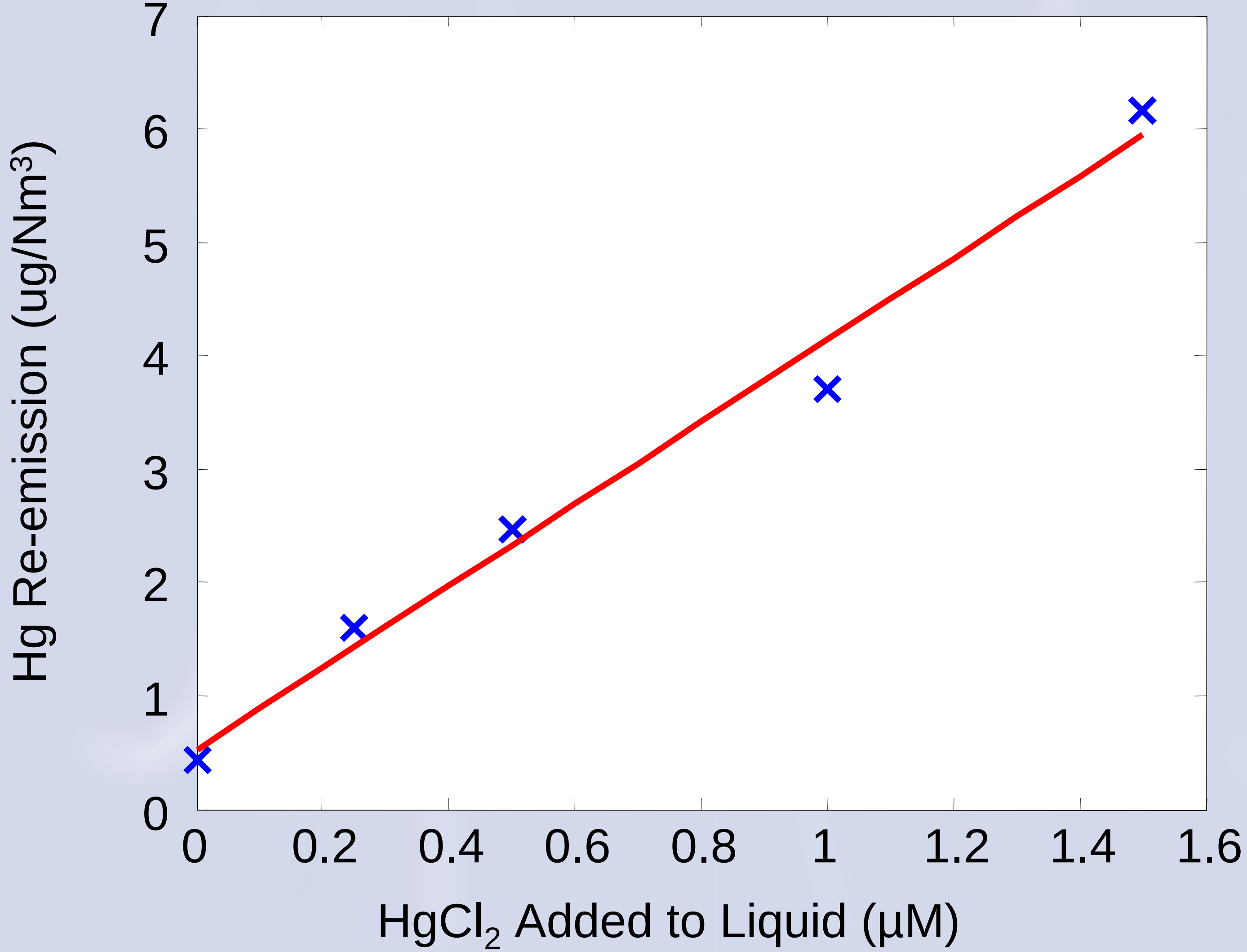


Bench-scale Run at pH 5.0, 5 mM Sulfite, 100 mM Chloride: Re-emissions Region

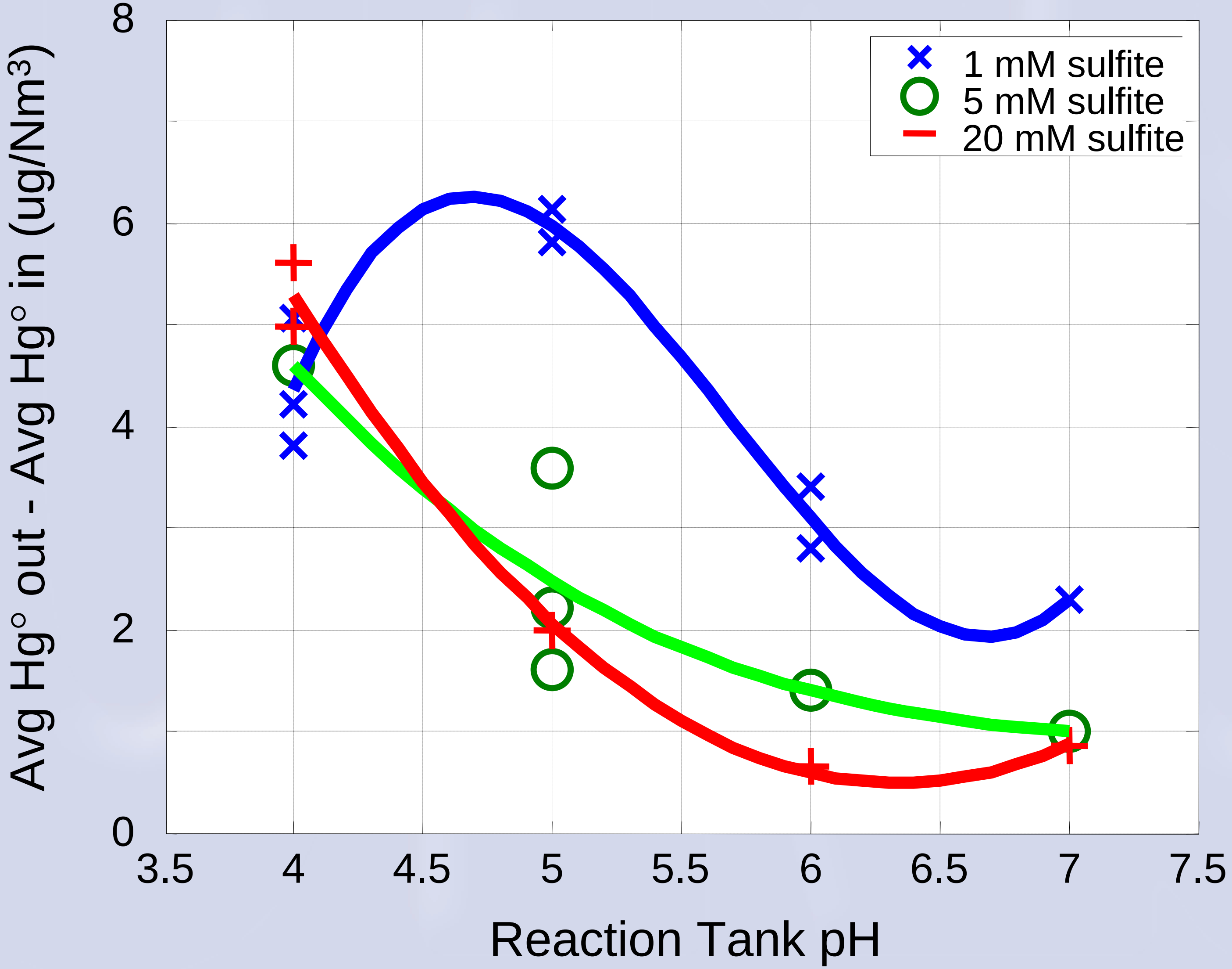
Average re-emission = [average elemental Hg in outlet] – [average elemental Hg in inlet]



Variation of Re-emissions with Hg^{+2} in Liquid: Bench-scale Runs at pH 5.0, 5 mM Sulfite, 100 mM Chloride



Bench-scale Runs at Varied pH and Sulfite Concentration with 100 mM Chloride



Effects of TMT Re-emission Additive (Preliminary results)

- Have observed periods of very low re-emissions for scrubber liquors containing TMT
- But have also observed initial periods of very high re-emissions when TMT present
- TMT solutions have a more reducing ORP than normal - may be reason for high emissions,
- Emissions would decrease as precipitation of TMT-Hg solid removes oxidized Hg from solution
- Implies precipitation kinetics may be key to using TMT - can study using the bench-scale apparatus

Project Status and Conclusions

- Developed experimental methods for following reactants and products independently
- Chloride, sulfite, and pH have major effects on reaction rates and mechanism - model developed to capture these trends
- Used bench-scale FGD system to:
  - Verify pH, sulfite, chloride effects

Future Work

- Conduct further bench-scale FGD tests to:
  - Determine effects of cations and other species which affect effective sulfite concentration
  - Determine effects of halide and other inhibitors, Hg precipitants, organic acids, NO_x , along with other species and physical conditions