Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

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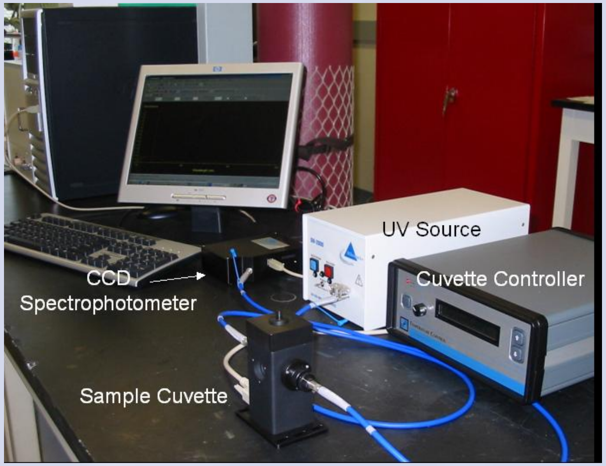
Introduction

- **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
  - Overall reaction:
    - $Hg^{+2} + HSO_3^- + H_2O \rightarrow Hg^o\uparrow + SO_4^{-2} + 3\ H^+$
  - Limits overall Hg removal by FGD system
- **Expected Benefits** – the ability to predict FGD re-emissions, and change or optimize FGD conditions to minimize or eliminate them

Technical Approach

- UV, CVAA, electrochemical, and bench-scale wet FGD tests conducted to develop Hg re-emission reaction mechanisms
  and kinetics



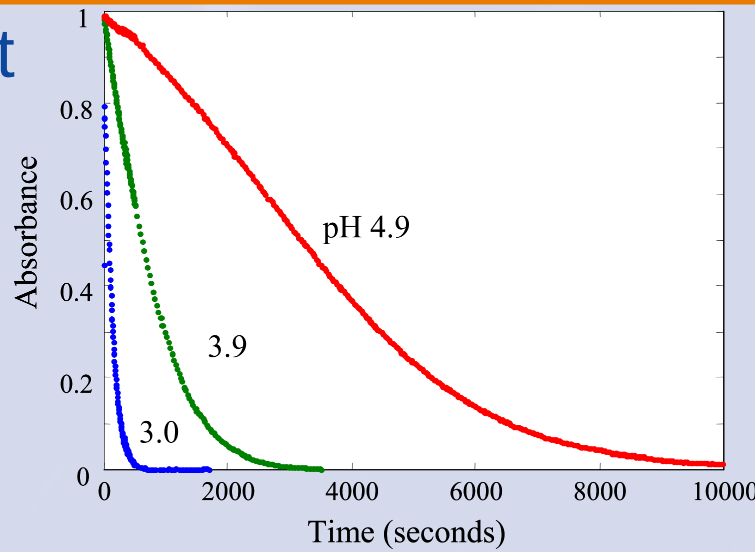
- Development of a kinetics model
- Additional bench-scale wet FGD tests to:
  - Verify model predictions
  - Evaluate re-emission additives (e.g., TMT-15)
  - Evaluate solids and other effects on re-emission

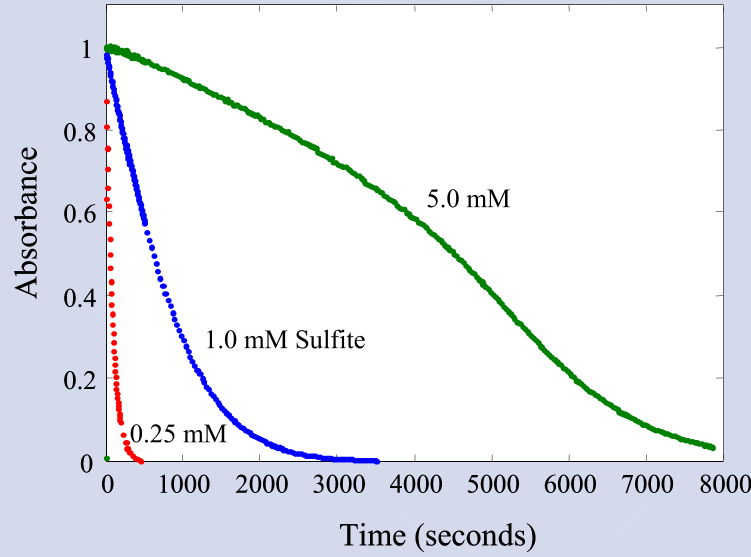
UV and CVAA Spectroscopic Results

- Found large effect of chloride
  - Identified a new re-emission mechanism involving chloride rather than sulfite alone
  - Reduction of oxidized mercury to Hg^0 occurs through formation of Hg^{+2}/sulfite/ chloride complexes and decomposition of complexes to form Hg^0
- pH, sulfite, and chloride concentrations can greatly affect re-emission rates

Summary of Sulfite / pH Results

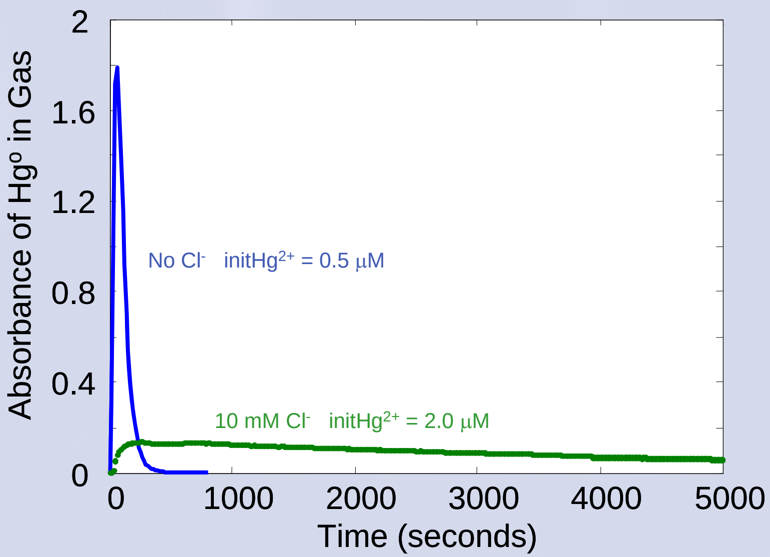
- Results show significant pH effect between pH 3-6, with faster mercury reduction at lower pH
- Rates generally decrease at higher sulfite concentration
  - Formation of $Hg(SO_3)_2^{-2}$ which is more stable than $HgSO_3$
- Trends suggest higher re-emissions from lower pH, lower sulfite FGD systems (e.g., LSFO)
  - Notwithstanding chloride/other effects





Summary of Chloride Effect

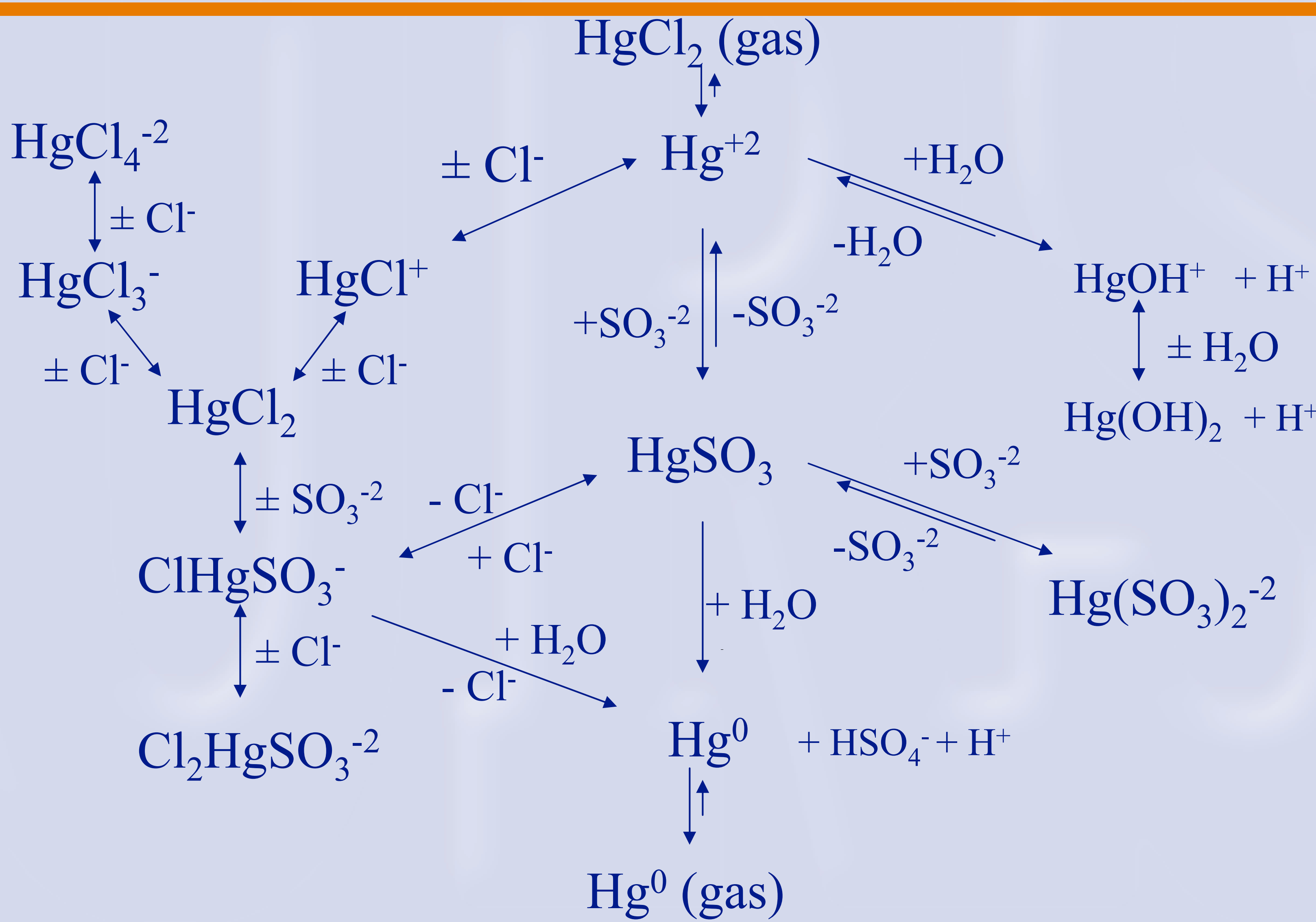
- Chloride slows re-emissions dramatically through change of reaction mechanism, formation of new intermediate: $ClHgSO_3^-$
- $ClHgSO_3^-$ decomposes to Hg^0, but much more slowly than $Hg(SO_3)_2^{-2}$ or $HgSO_3$
- $Cl_2HgSO_3^{-2}$ is formed reversibly at higher chloride, does not decompose to Hg^0 (i.e., low re-emissions at higher Cl concentration)



Kinetics Model Development

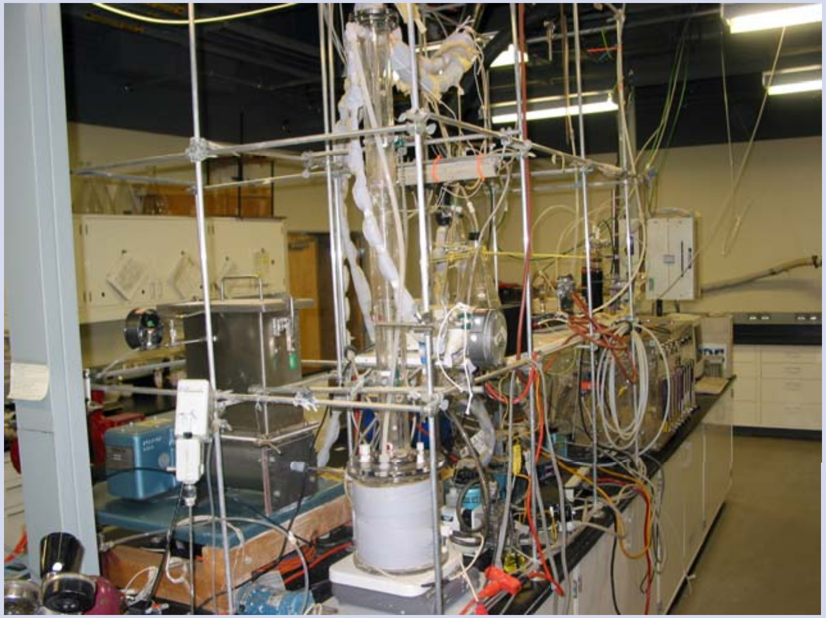
- Kinetics model generally reproduces observed trends of mercury reduction rates vs. pH and sulfite
- Current interpretation of modeling results:
  - Re-emissions rate is controlled by mercuric chloro-sulfite complexes at pH near 4
  - Controlled by mercuric sulfite complexes at higher pH
- Model indicates the concentration of the aqueous species "sulfite" (SO_3^{-2}) is of major importance
  - Species that form ion pairs with sulfite (e.g., calcium, magnesium) can lower SO_3^{-2} concentration, affect mercury reduction rates

Diagram of Main Reaction Pathways in Kinetics Model

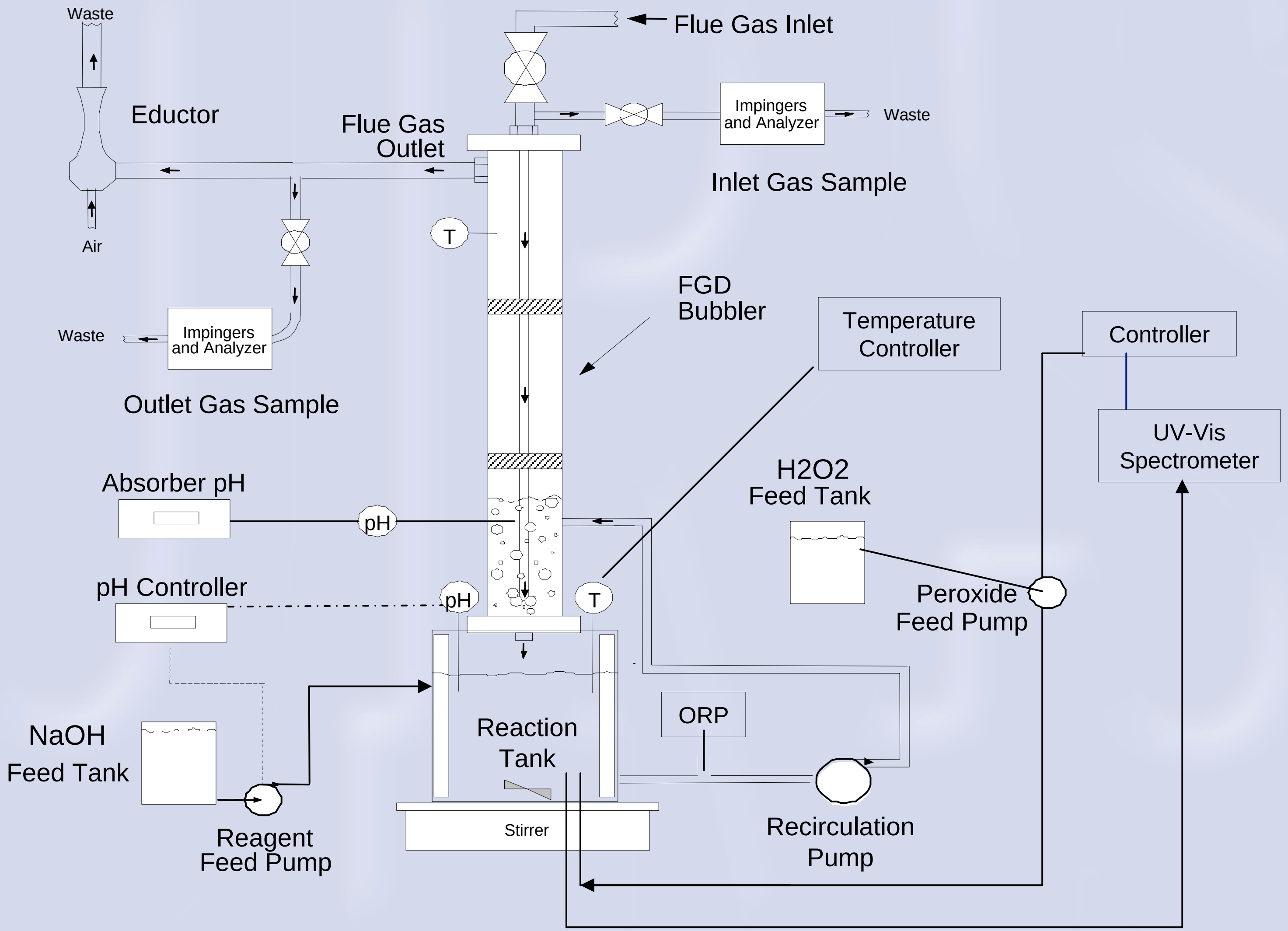


Bench-scale FGD Test Series

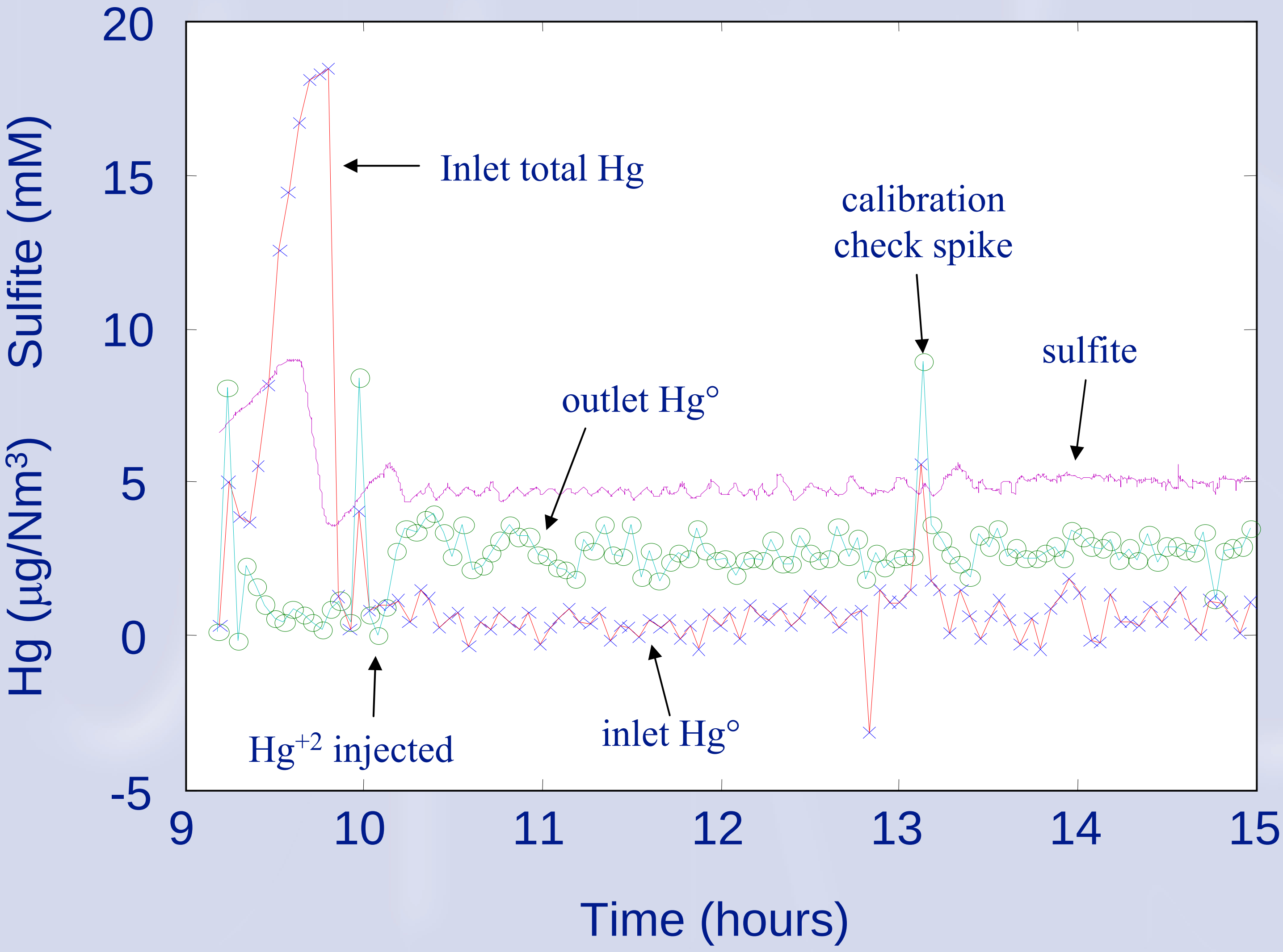
- Use simulated flue gas containing SO_2, $HgCl_2$, CO_2, O_2, HCl, N_2
- Most tests use clear liquor (NaOH for pH control), real-time sulfite monitoring and H_2O_2 for sulfite control
- First test matrix evaluated pH/sulfite/chloride effects
- Later tests investigating other chemical and physical variables



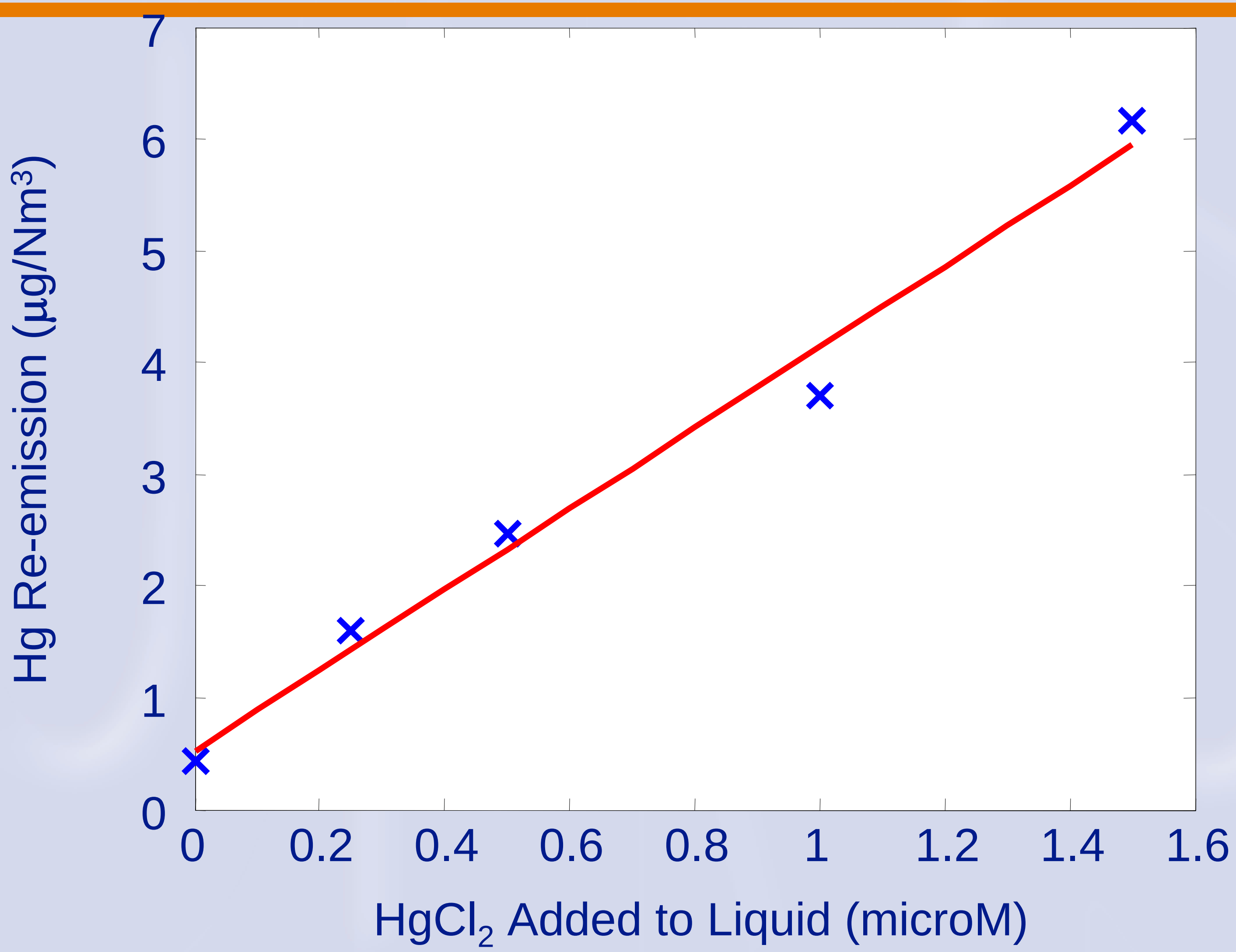
Bench-scale FGD System



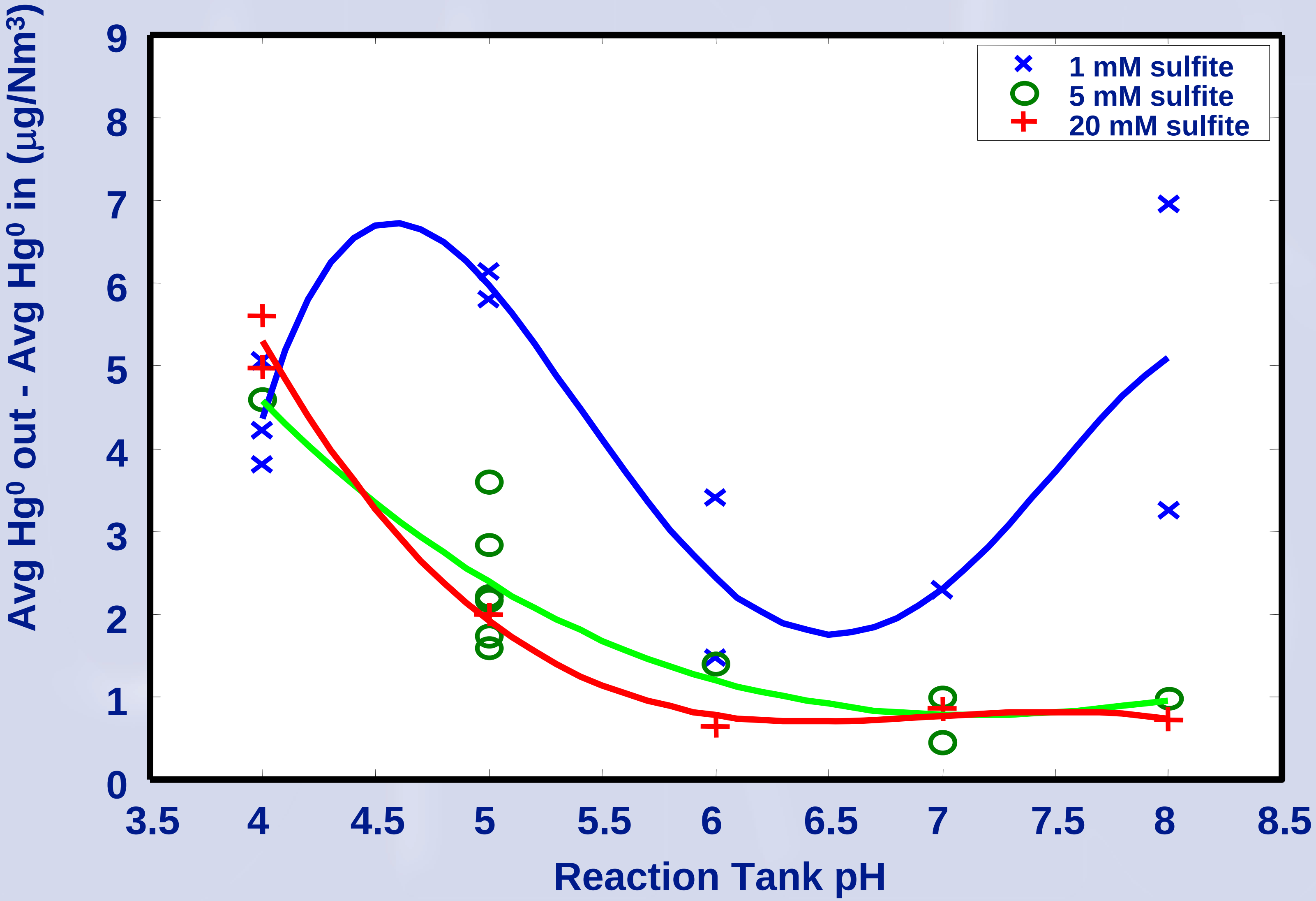
Complete Run Sequence for Bench-scale Run at pH 5.0, 5 mM (400 ppm) sulfite, 100 mM (~3600 ppm) chloride



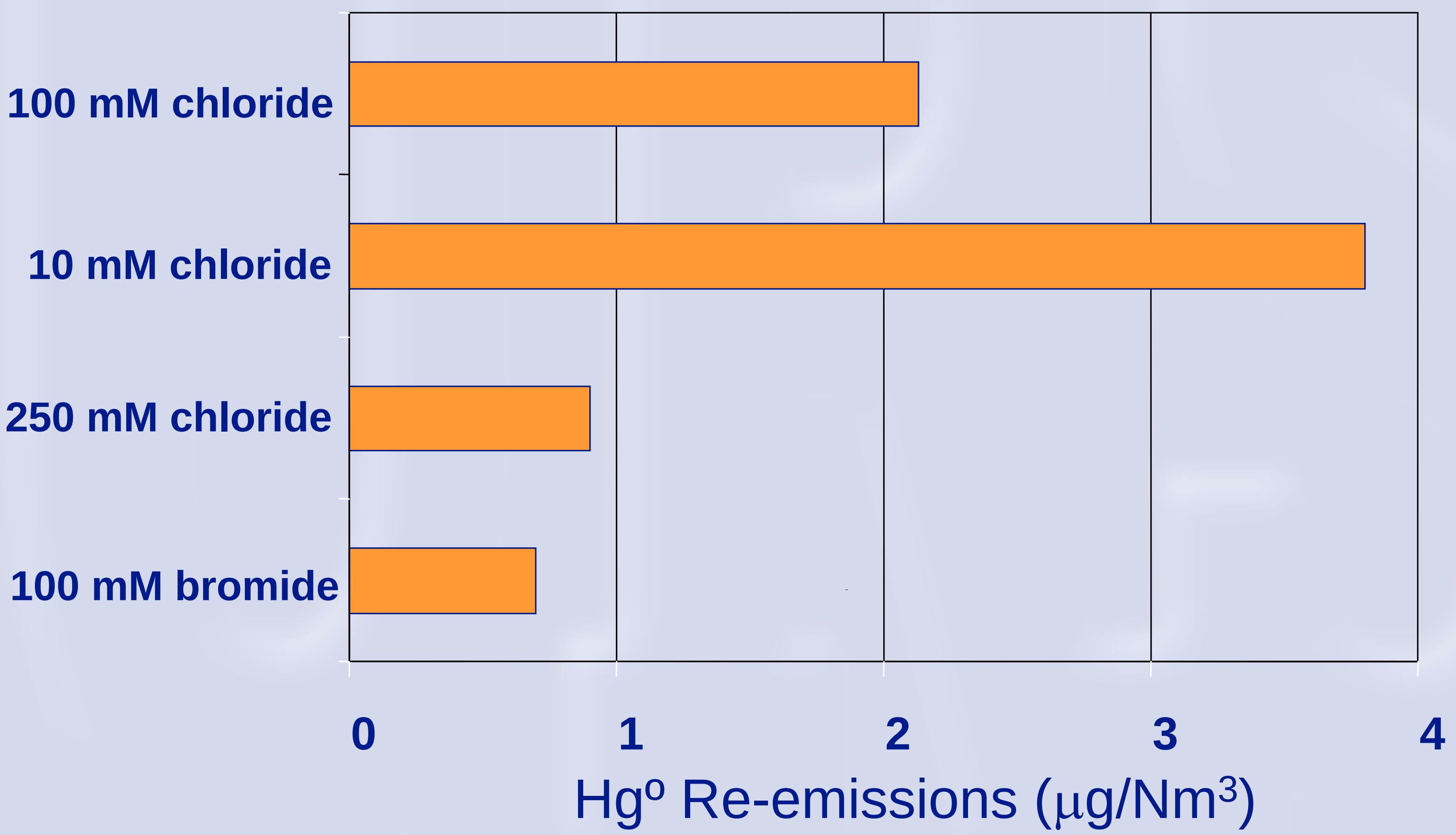
Variation of Re-emissions with Hg^{+2} in Liquid Phase (bench-scale runs at pH 5.0, 5 mM sulfite, 100 mM chloride)



Bench-scale Re-emissions as a Function of pH (100 mM Cl^-)



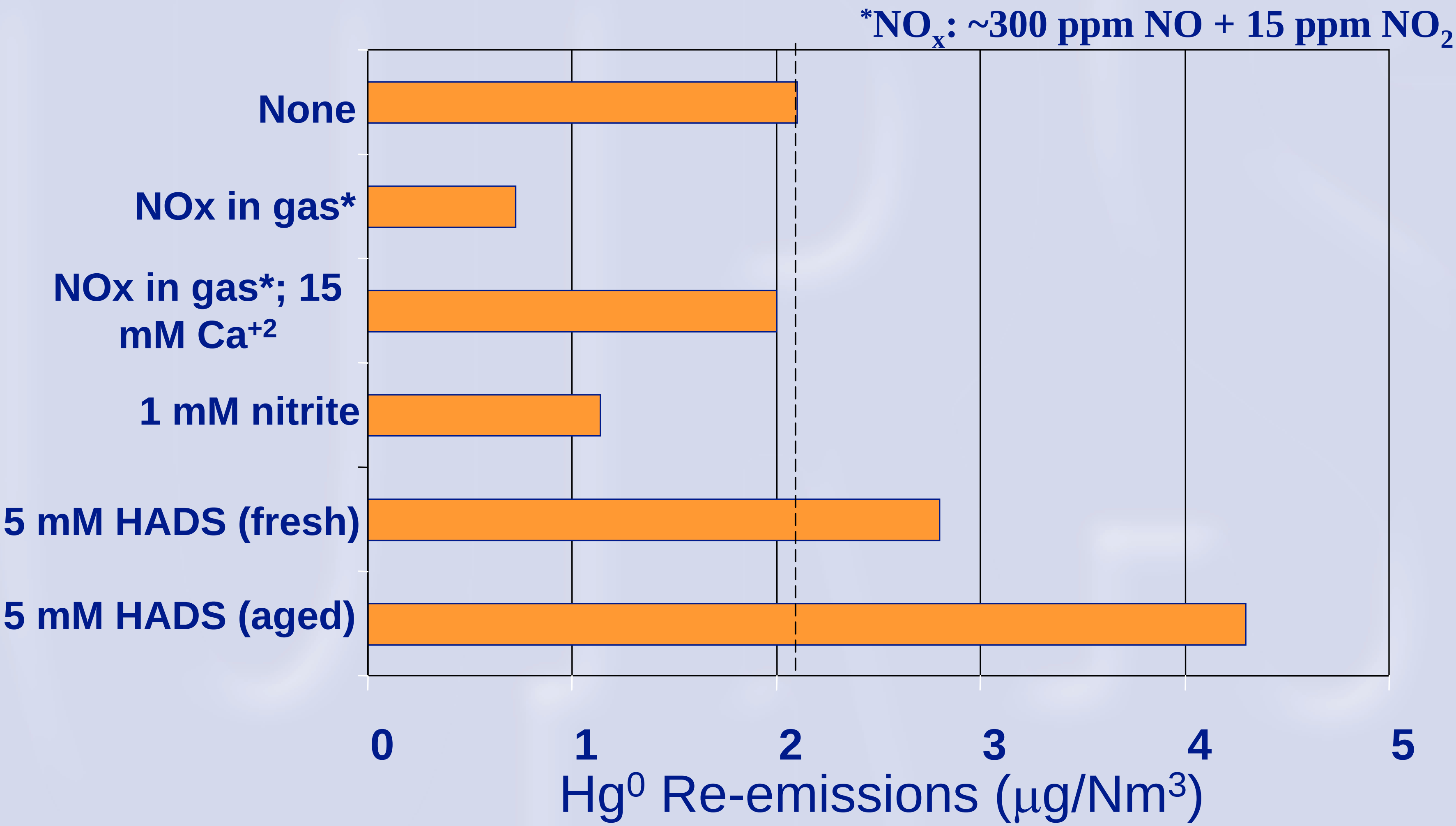
Effect of Chloride and Bromide on Hg^0 Re-emissions at 5 mM sulfite, pH 5.0



NO_X Effects

- Bench FGD re-emissions lower with NO_X in inlet gas
  - Contrary to full-scale observations (higher re-emissions with SCR out of service & higher NO_X)
  - But NO_X in flue gas also leads to S-N species in FGD liquor
- Tests with synthetic S-N (HADS, possibly HATS) in bench FGD liquor showed higher re-emissions
- Tests needed with NO_X in inlet gas, HADS in liquor
- Incorporation of S-N species into kinetics model possible

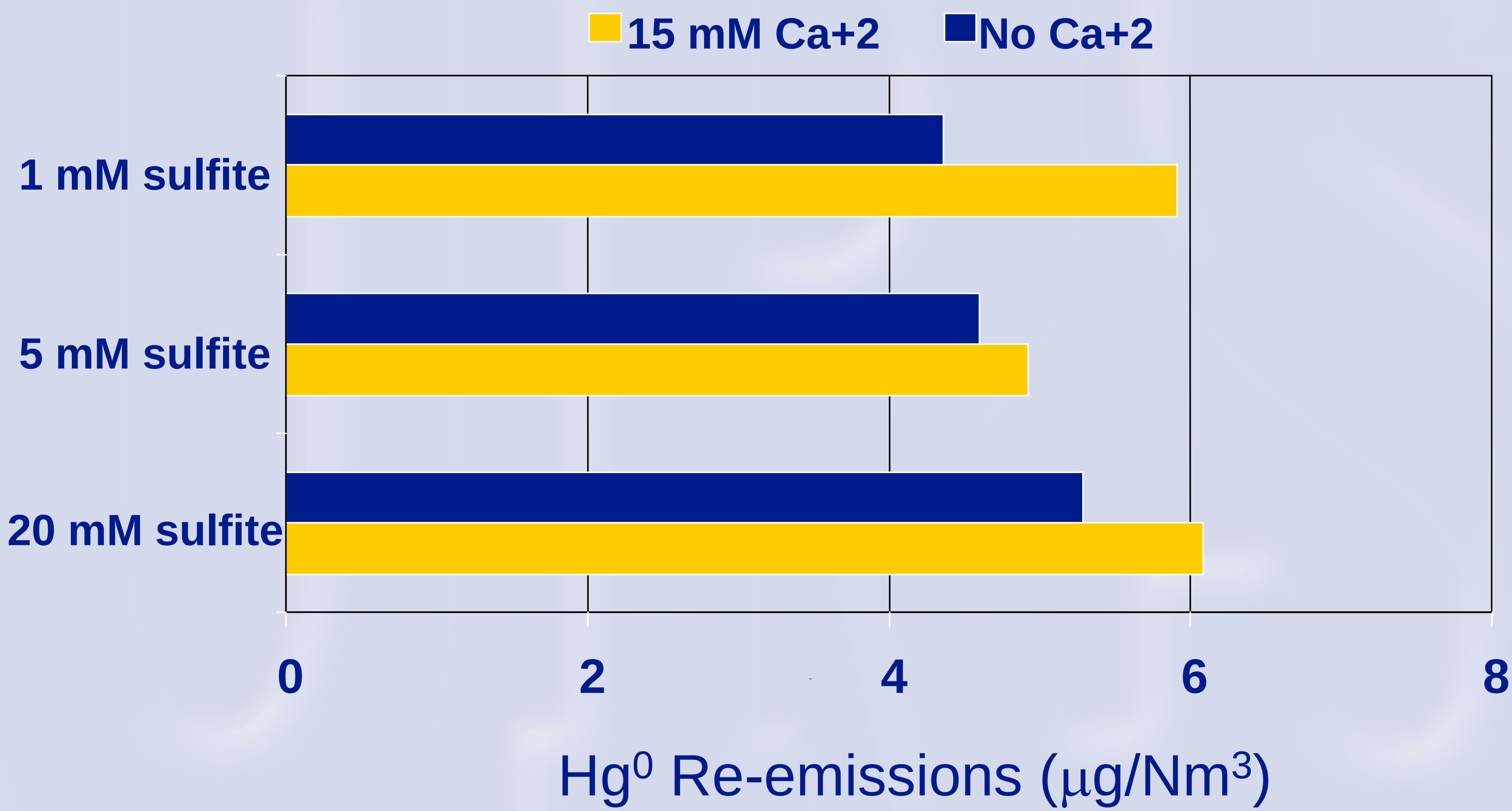
Effect of N-containing Species on Hg^0 Re-emissions at 5 mM sulfite, pH 5.0, 100 mM chloride



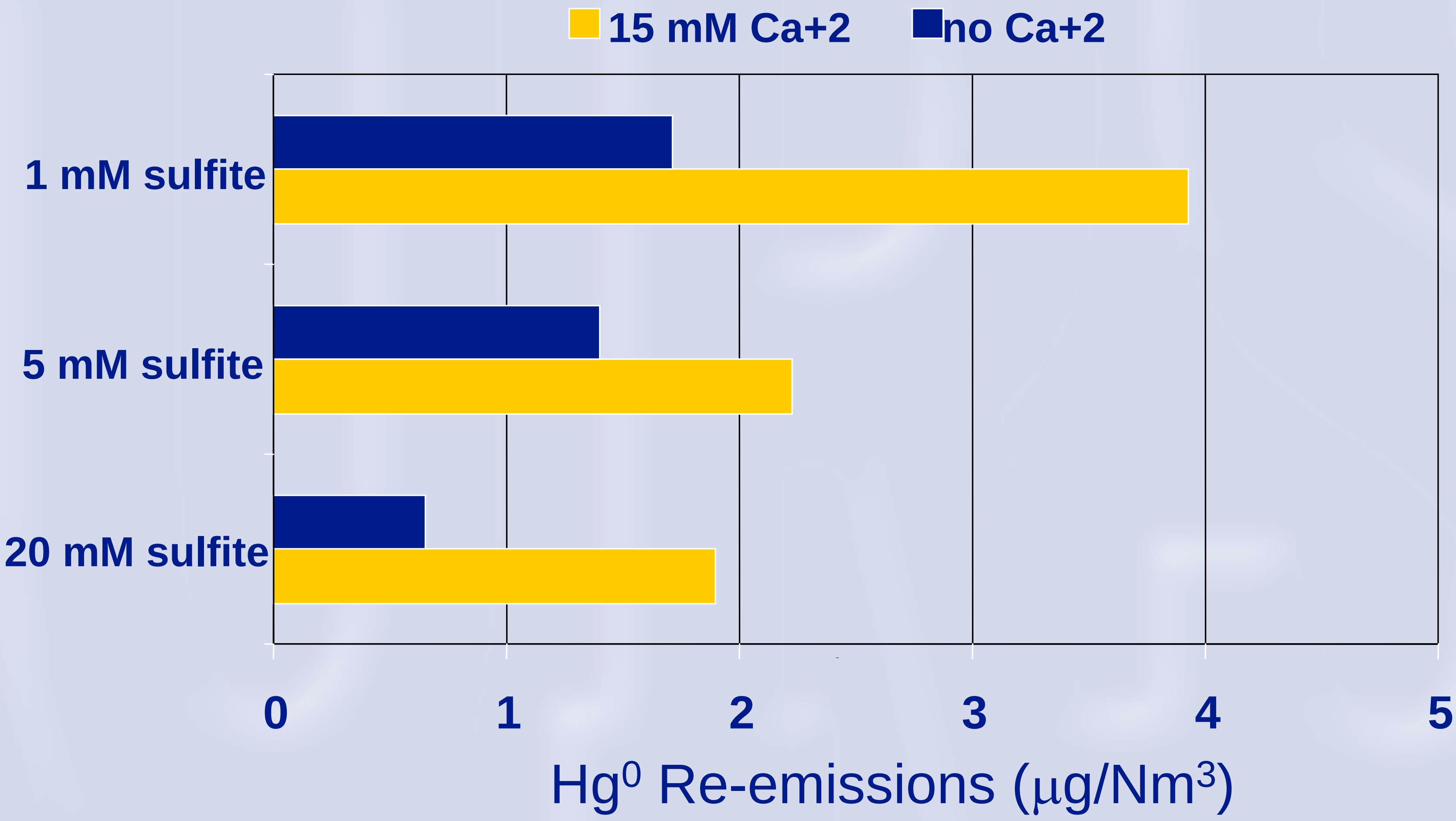
Effects of Calcium Ion (most tests have been run in clear Na solution)

- More complicated than expected
- Appears to depend on pH and perhaps sulfite concentration
- May involve formation of gypsum or other calcium solids
  - Sulfate increases during run to levels close to gypsum saturation

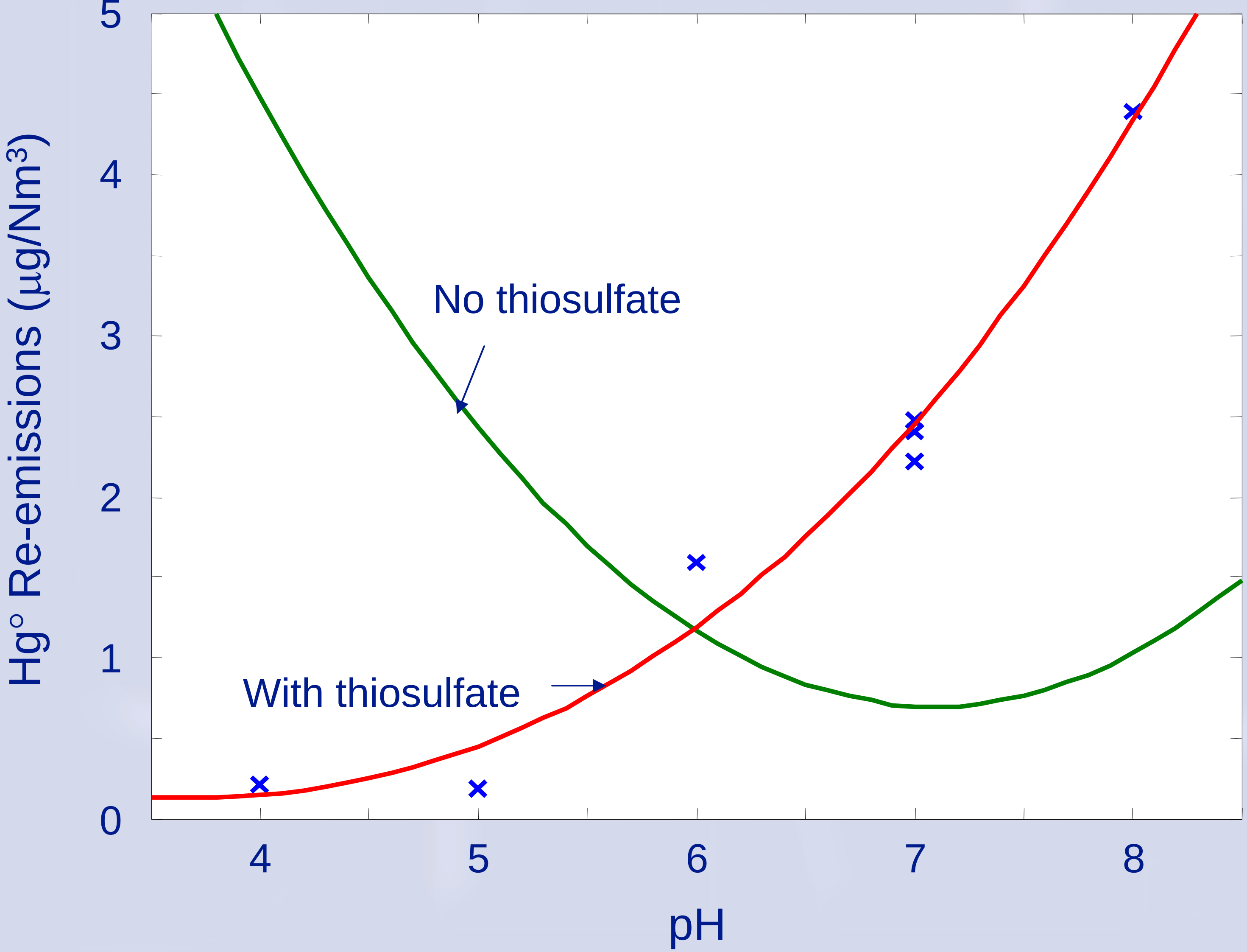
Effect of Calcium on Hg^0 Re-emissions at pH 4.0, 100 mM chloride



Effect of Calcium on Hg^0 Re-emissions at pH 6.0, 100 mM chloride



Effect of 1 mM Thiosulfate on Hg^0 Re-emissions as a Function of pH; 5 mM sulfite, 100 mM chloride



Re-emission Inhibitors – TMT-15

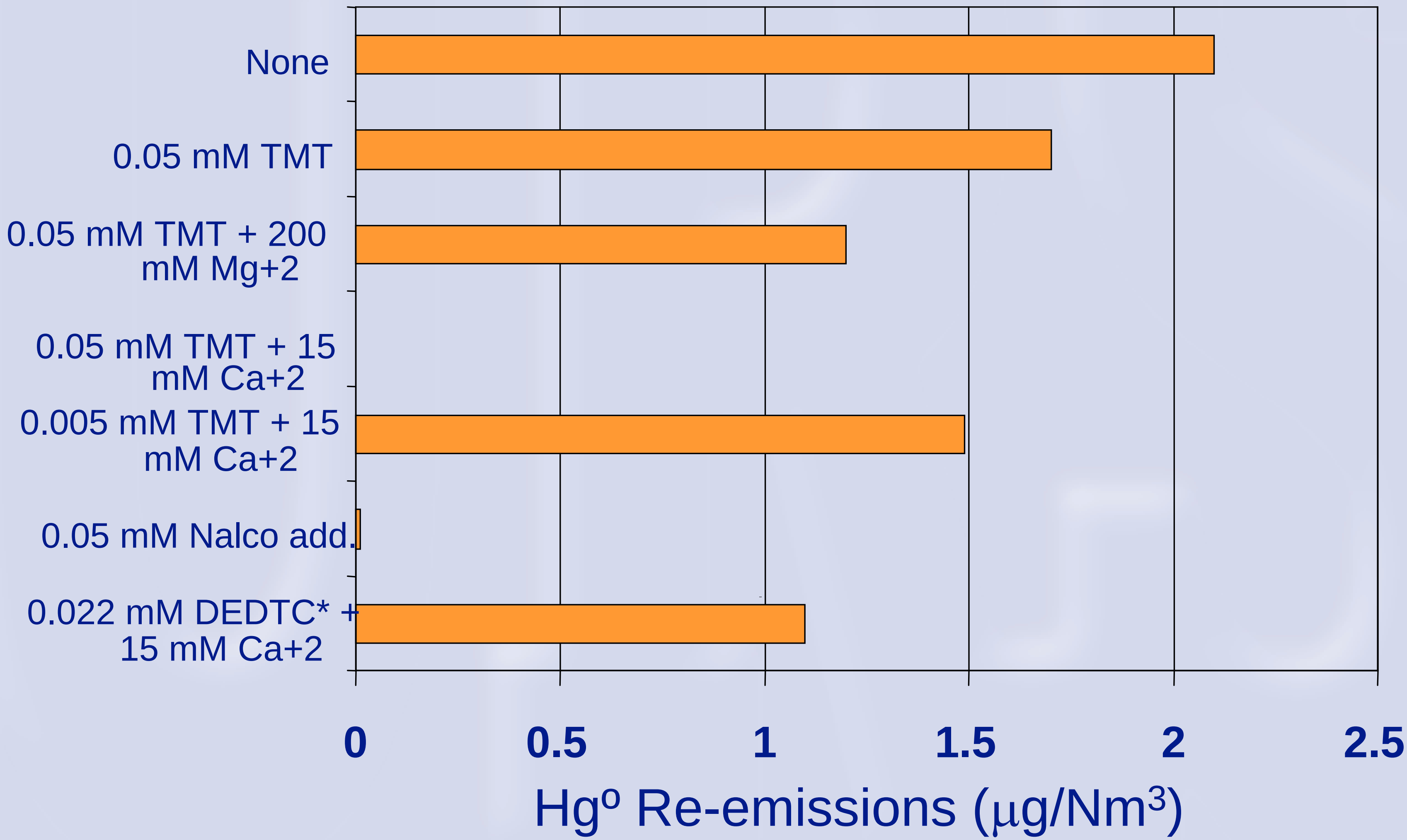
- Complex behavior observed with TMT
  - Some tests showed very low re-emissions
  - Have also seen initial periods of very high re-emissions when TMT present
  - TMT can act as a reducing agent - may cause high re-emissions under some conditions
  - Re-emissions apparently decrease as precipitation of TMT-Hg solid lowers Hg^{+2} concentration in solution
  - Complex behavior seen with Ca, Mg in liquors

Re-emission Inhibitors (continued)

- Nalco additive worked well in one test; more testing needed to characterize
- Diethyldithiocarbamate showed some effectiveness, but not as effective as Nalco additive
- Tests continue with other additives (e.g., Vosteen Consulting's "PRAVO")

Effect of Potential Re-emission Inhibitors; pH 5, 5 mM sulfite, 100 mM chloride

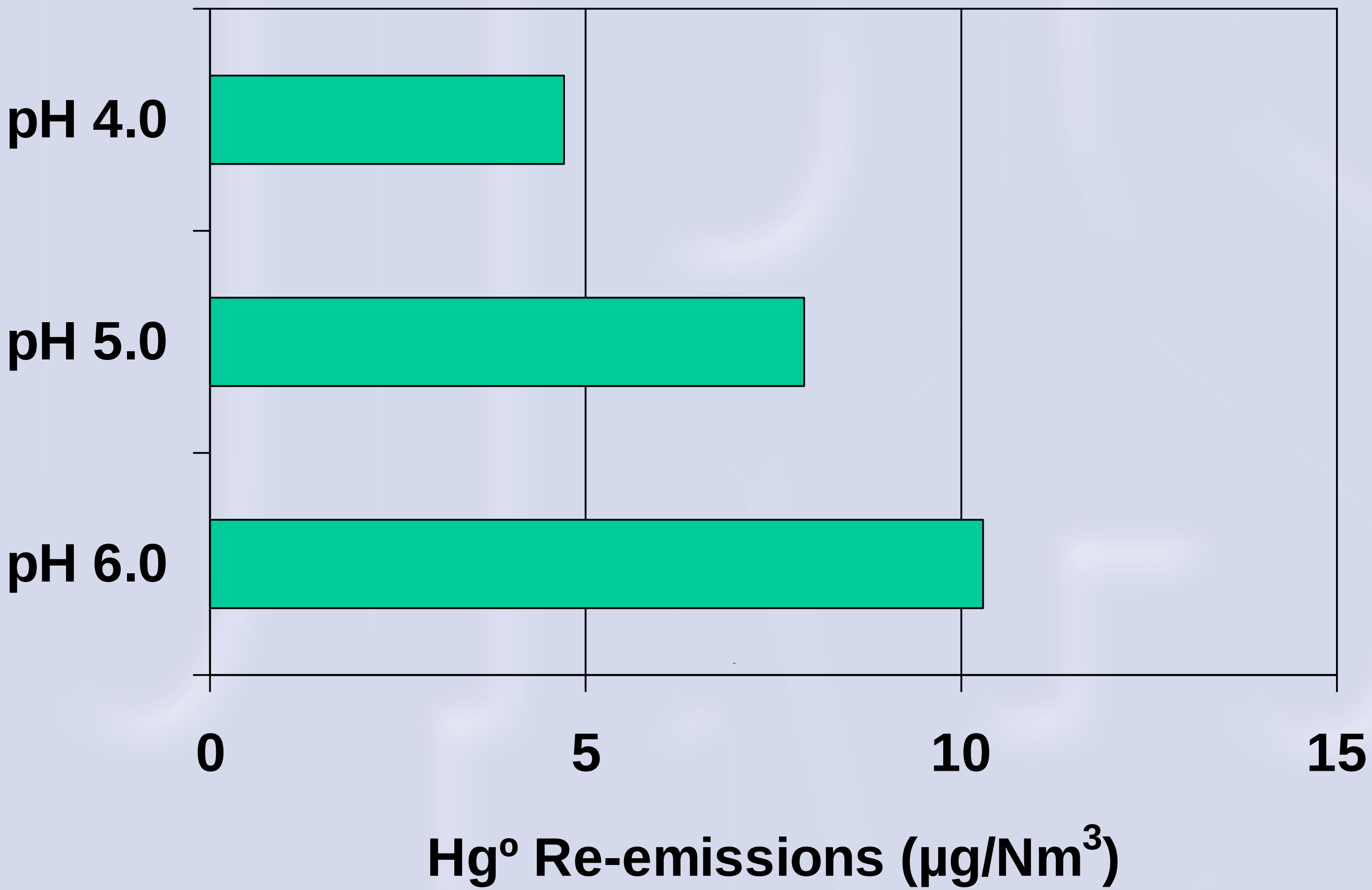
*DEDTC: diethyldithiocarbamate



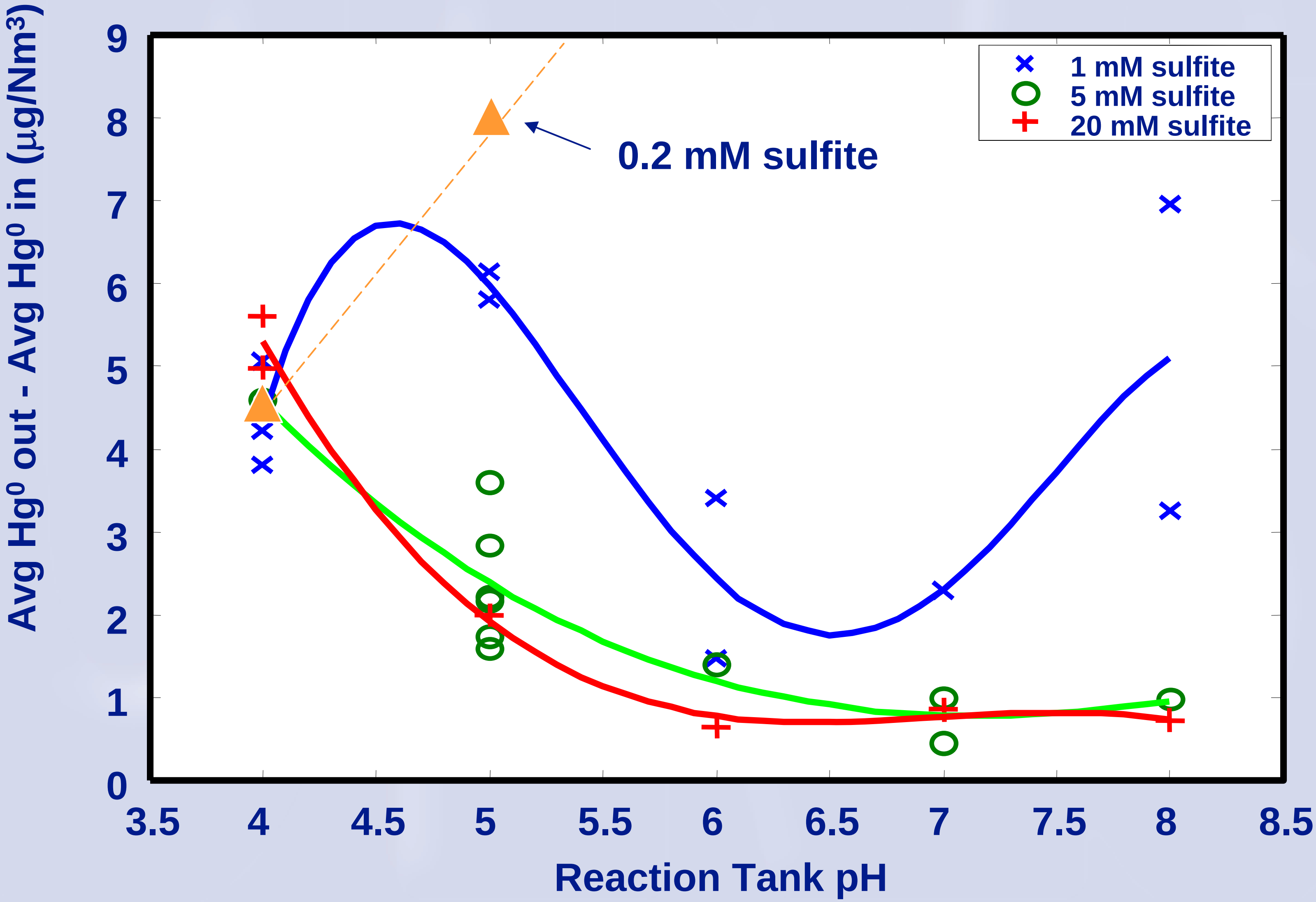
Re-emission at Very Low Sulfite

- Very low sulfite values of interest since typical of forced oxidation FGD systems and lower sulfites expected to give higher re-emissions
  - 0.2 mM is the lowest that can be measured and controlled in bench-scale system
- At 0.2 mM sulfite, re-emissions increase with pH, unlike at higher sulfite
- The change in pH effect is also seen in model simulations but to a lesser extent

Effect of pH on Re-emissions at 0.2 mM Sulfite, 100 mM Chloride



Bench-scale Re-emissions as a Function of pH (100 mM Cl^-)



Project Status and Conclusions

- Determined that chloride, sulfite, and pH have major effects on reaction rates and mechanism
  - Model developed captures these trends
  - Higher Cl^- typically lowers re-emission
  - pH – sulfite relationship is complex
- Bench-scale FGD system used to verify and extend results, determine effects of Ca^{+2}, Mg^{+2}, thiosulfate, halides, Hg precipitants/inhibitors, organic acids, NO_x, HADS, others
- Final report due in March 2008
- More work needed to verify model at full scale