Analysis of Bromine-Mercury Reactions in Flue Gas

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Outline

- Objectives
- Introduction
- Kinetics and modeling of Hg-Br reactions
- Experimental
  - Sample conditioning
  - Homogeneous oxidation by Cl and Br
- Conclusions

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Project Objectives

- Collect data, develop models that allow prediction of extent of reaction between bromine and mercury in flue gas.
- Homogeneous and heterogeneous reactions.

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Introduction - Coal Composition

Sample Description	Elkhor/Hazard low S bit	**Pittsburgh med S bit**	Illinois 6 high S bit	Wyodak PRB	**Wyodak PRB**	Ohio 5,6,7 high S bit	ND Lignite lignite
ANALYSIS (As Received):							
Carbon	74.87	**76.62**	67.70	53.20	**51.19**	71.07	38.57
Hydrogen	4.59	**4.80**	4.73	4.59	**3.64**	4.81	2.60
Oxygen	8.38	**6.91**	9.19	20.74	**12.29**	8.10	12.52
Nitrogen	1.43	**1.48**	1.18	0.83	**0.72**	1.37	0.42
Sulfur	0.82	**1.64**	3.60	0.22	**0.32**	2.62	0.63
Ash	7.41	**7.01**	10.26	7.36	**6.03**	9.70	9.38
Moisture	2.33	**1.44**	3.31	13.06	**25.81**	2.33	35.88
Total	99.83	**99.89**	99.96	100.00	**100.00**	100.00	100.00
Hg, ug/g	0.13	**0.11**	0.22	0.19	**0.13**	0.15	0.13
Cl, ug/g	1660	**976**	338	**	**26**	974	36
Br, ug/g	25.0	**17.0**	3.7	2.4	**1.2**	23.0	1.9
Cl/Br	66	**57**	91	--	**22**	42	19

Analyses from DOE Toxics program. Equilibrium calculations use Pittsburgh bituminous, 3% O_2.

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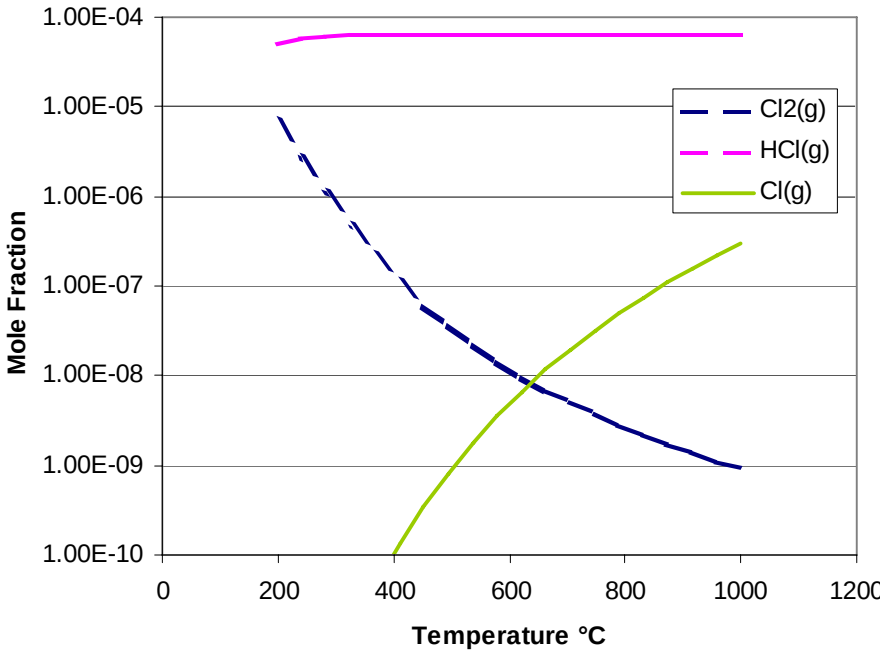
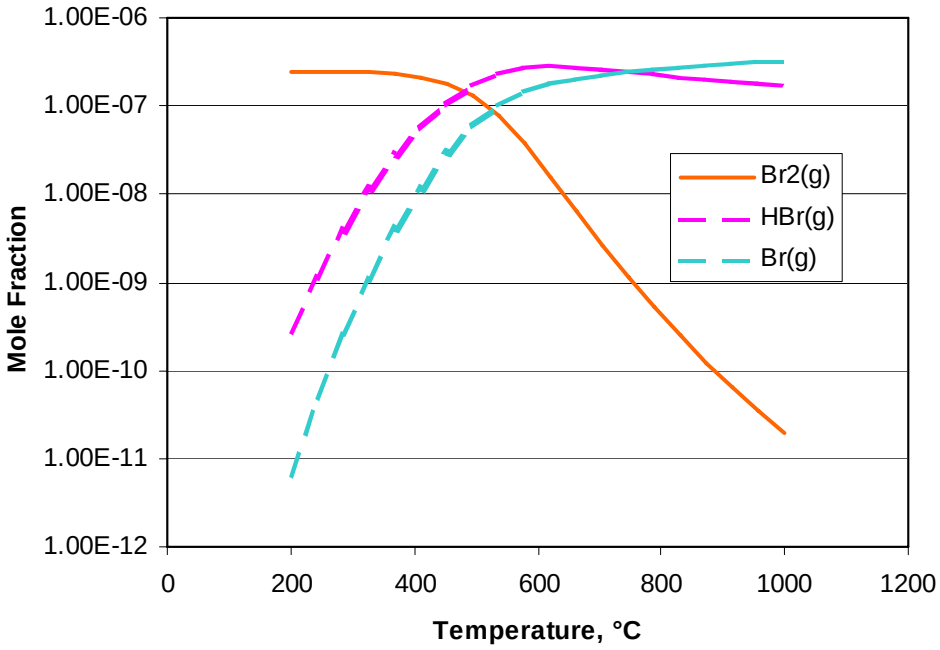
Introduction - Thermodynamics of Cl and Br





HCl is dominant species at all T.

Br_2 is dominant species below 400°C.

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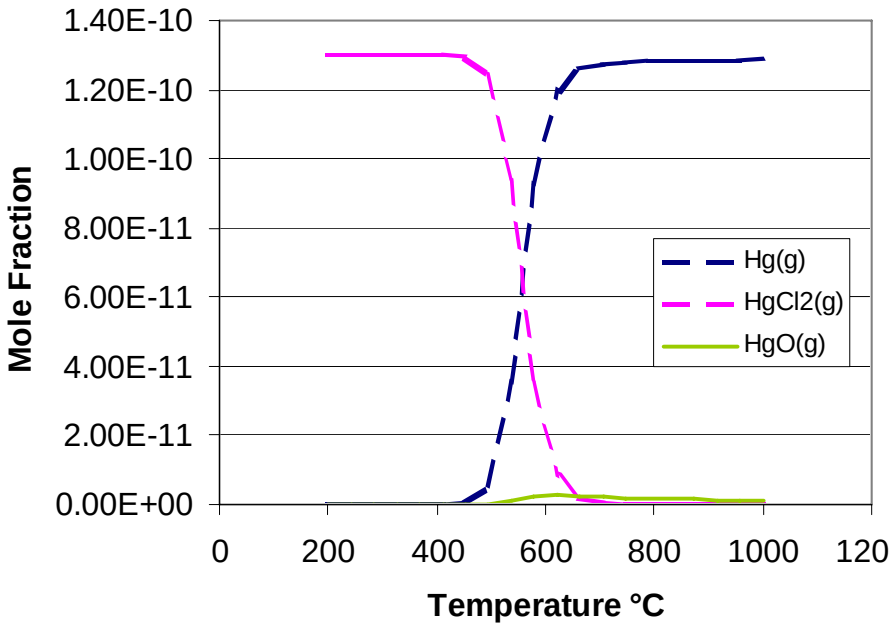
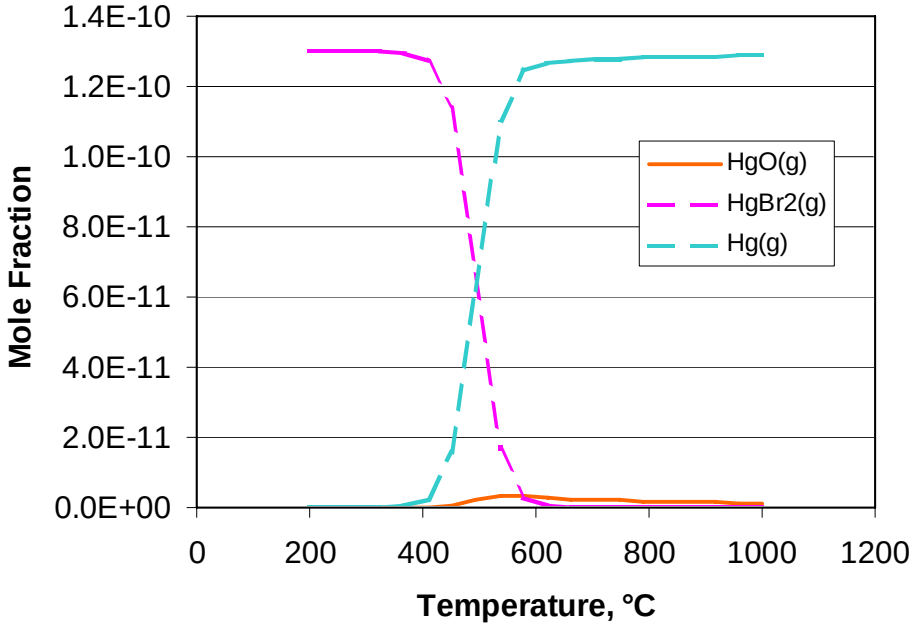
Introduction - Thermo of Hg/Cl, Hg/Br





$HgCl_2$ stable below 550°C.

$HgBr_2$ stable below 500°C. Chlorine excluded from this calculation.

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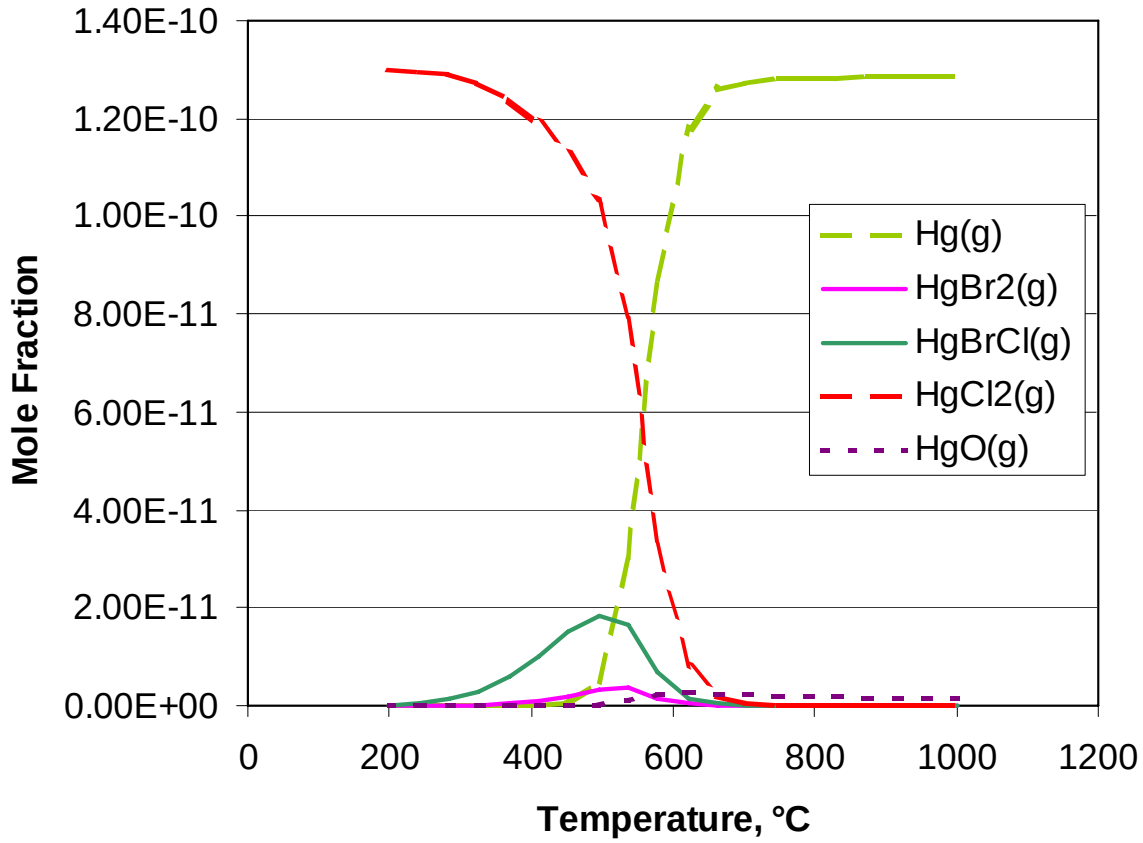
Introduction - Thermodynamics of Hg/Cl/Br



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Introduction - Hg/Br Reactions

- Chemists first observed depletion of atmospheric mercury in the Arctic, initiated by the polar sunrise, in late 1990's.
- Theoretical and experimental studies support the following mechanism (Balabanov, et al., 2005), with the source of the Br being sea salt aerosols (NaBr).

$$Br_2 + h\nu \rightarrow 2Br$$
$$Hg + Br \rightarrow HgBr$$
$$HgBr + Br \rightarrow HgBr_2$$
$$HgBr + Br_2 \rightarrow HgBr_2 + Br$$

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Introduction - Hg/Br reactions

- Atmospheric chemists - oxidation of mercury occurs heterogeneously and homogeneously.
- Vosteen et al. – Br, added as bromide salts to fuel or flame much more effective on weight basis than Cl.

Introduction - Hg/Br reactions

- Alstom KNXTM boiler additive (bromine salt) increases Hg oxidation in flue gas and improves capture of Hg^0 by activated carbon in low-halogen flue gas
- Bromine-impregnated activated carbon shows 40-80% capture of mercury with hot-side ESP and >90% capture of mercury with cold-side ESP in low-halogen flue gas

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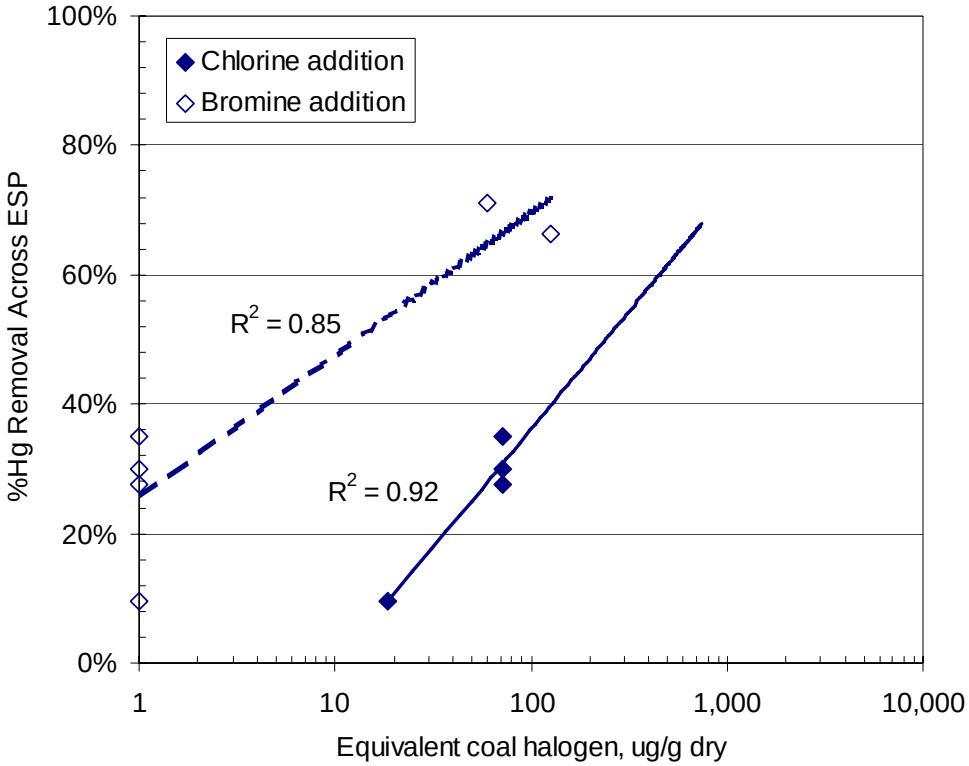
Introduction – Halogen Addition

- Increase halogen content
  - Addition of chlorine or bromine to fuel or boiler



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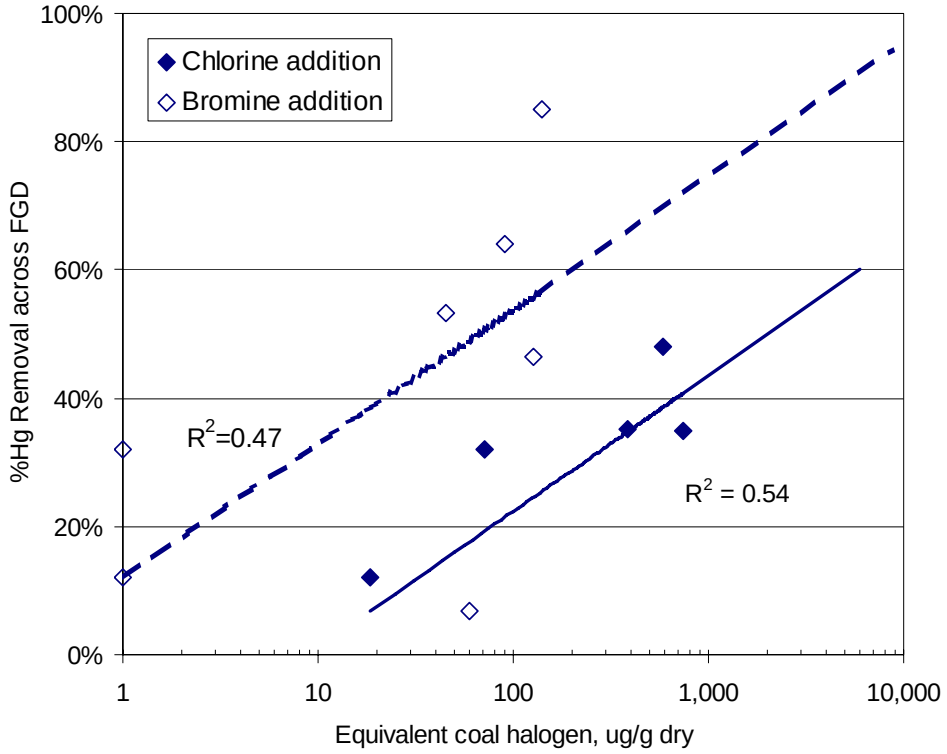

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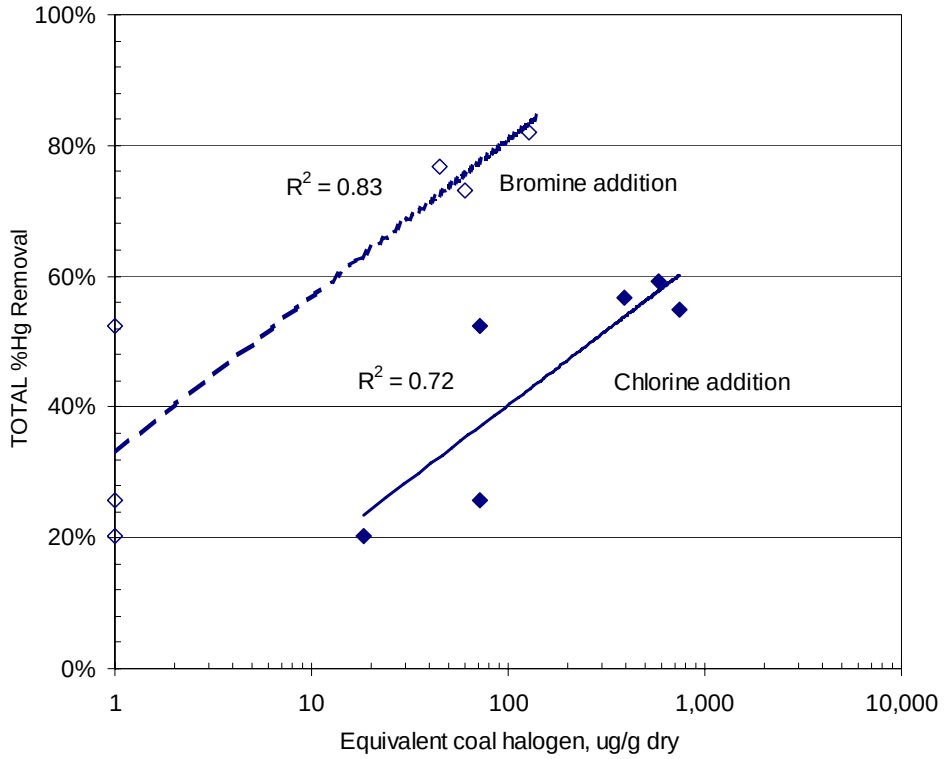

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Kinetics and Modeling

- Modeling of homogeneous Hg-Cl and Hg-Br reactions
  - 468 reactions, 127 species
  - NOx, SOx, Br, Cl chemistry
  - Br chemistry from NIST website
  - Br-Hg chemistry developed for this work
  - 3% excess air, Pittsburgh bituminous

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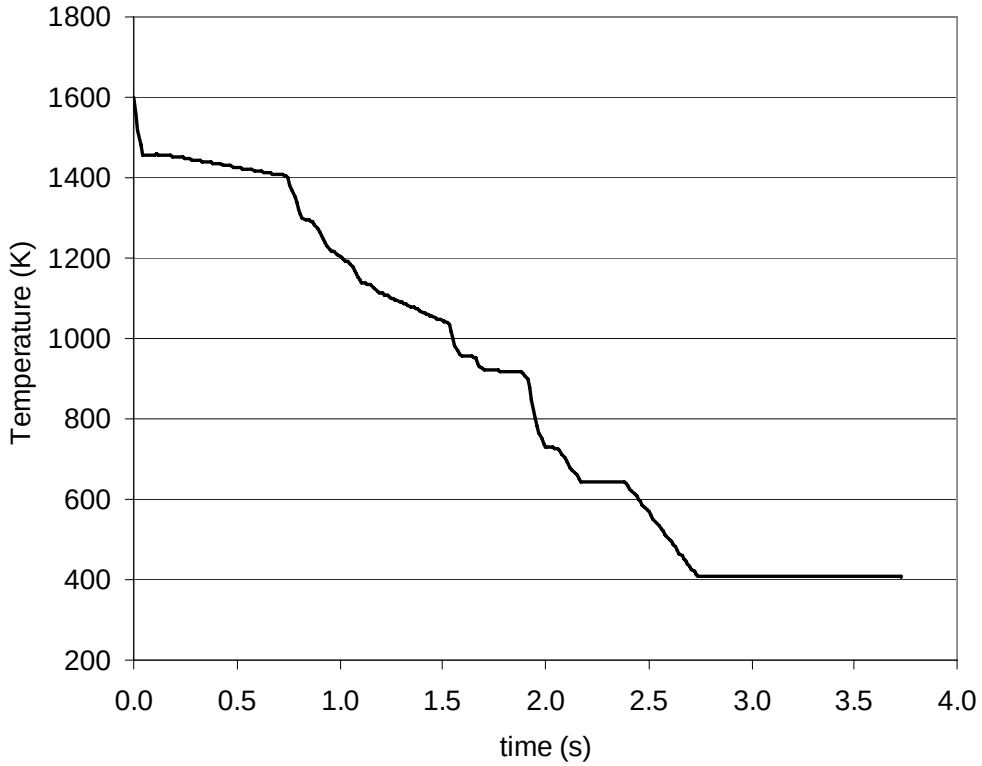
Kinetics and Modeling



- Typical time-temperature history in boiler

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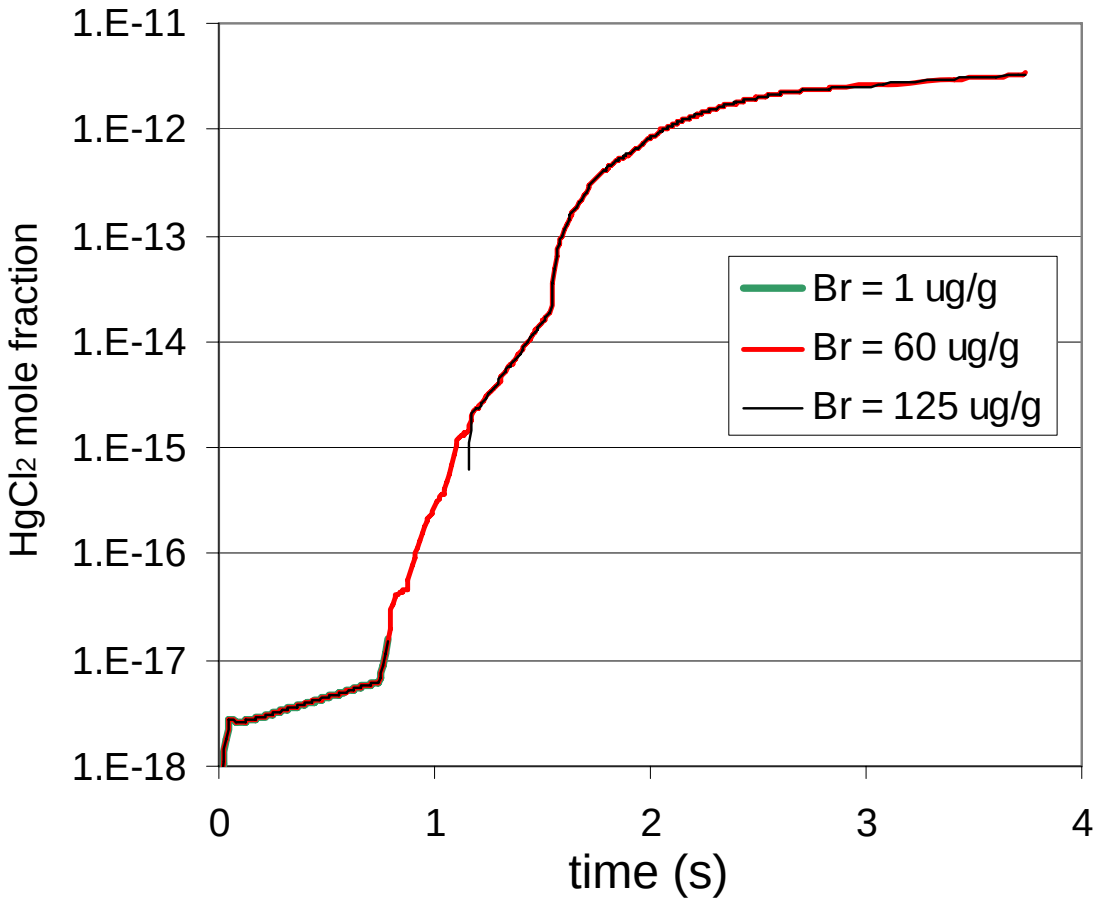
Kinetics and Modeling

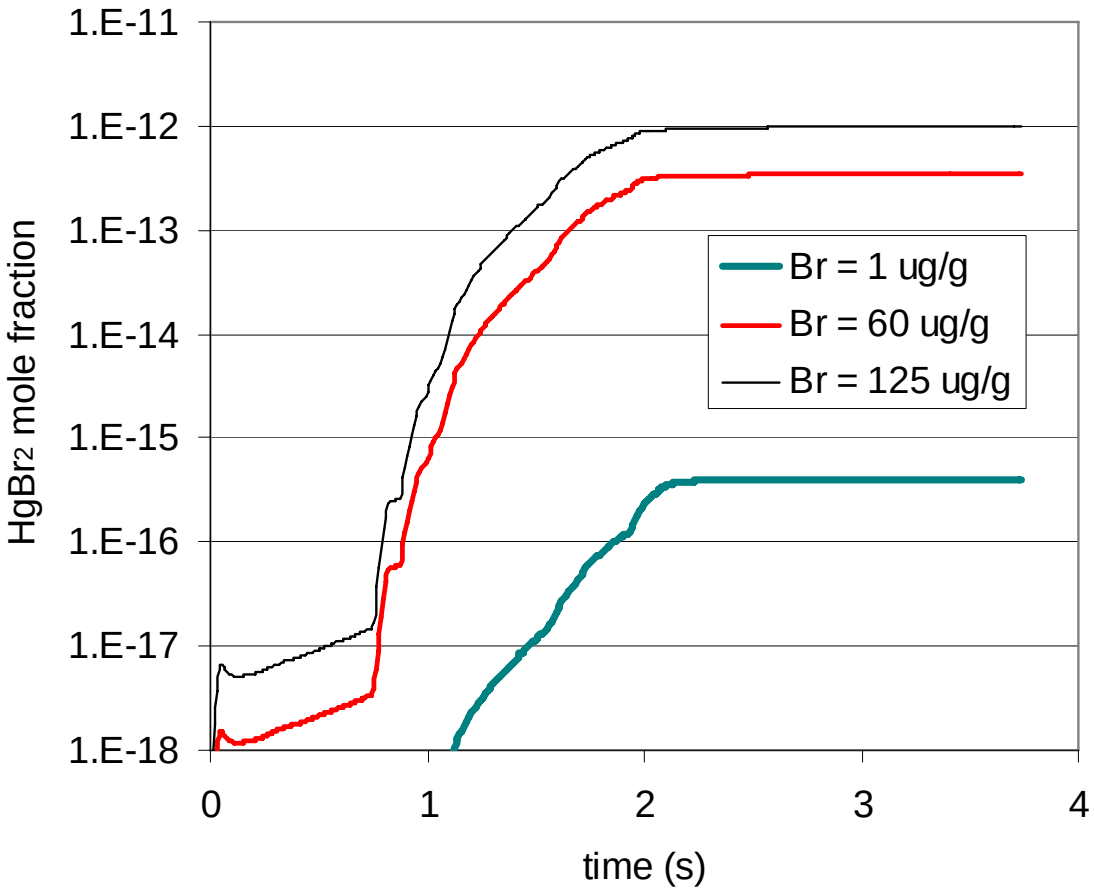
- The Cl/Br ratio has little impact on $HgCl_2$



- Equivalent coal halogens:
  - 70 ug/g Cl
  - 1, 60, 125 ug/g Br
- Equivalent flue gas halogens (as HX):
  - 5.7 ppmv HCl
  - 0.38, 2.3, 4.6 ppmv HBr
- Cl/Br molar ratios: 150, 2.5, 1.2

Kinetics and Modeling

- $HgBr_2$ is formed



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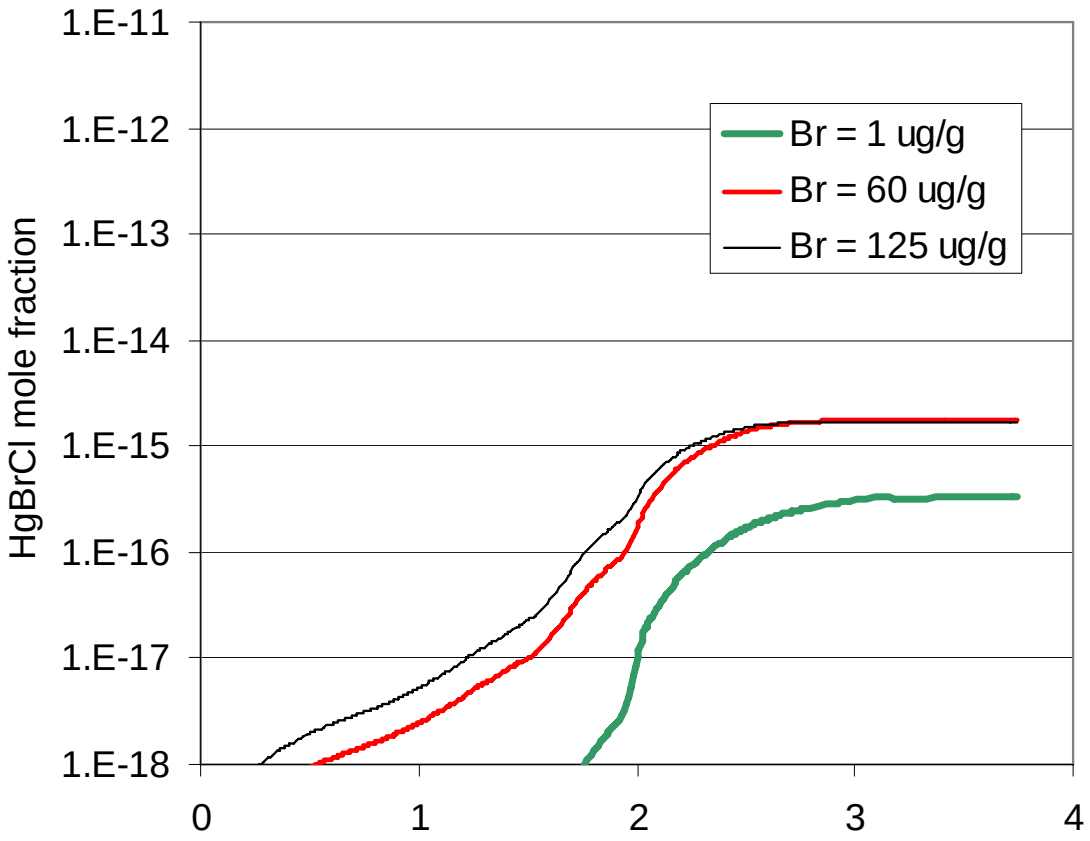
Kinetics and Modeling

- HgBrCl is formed at low levels



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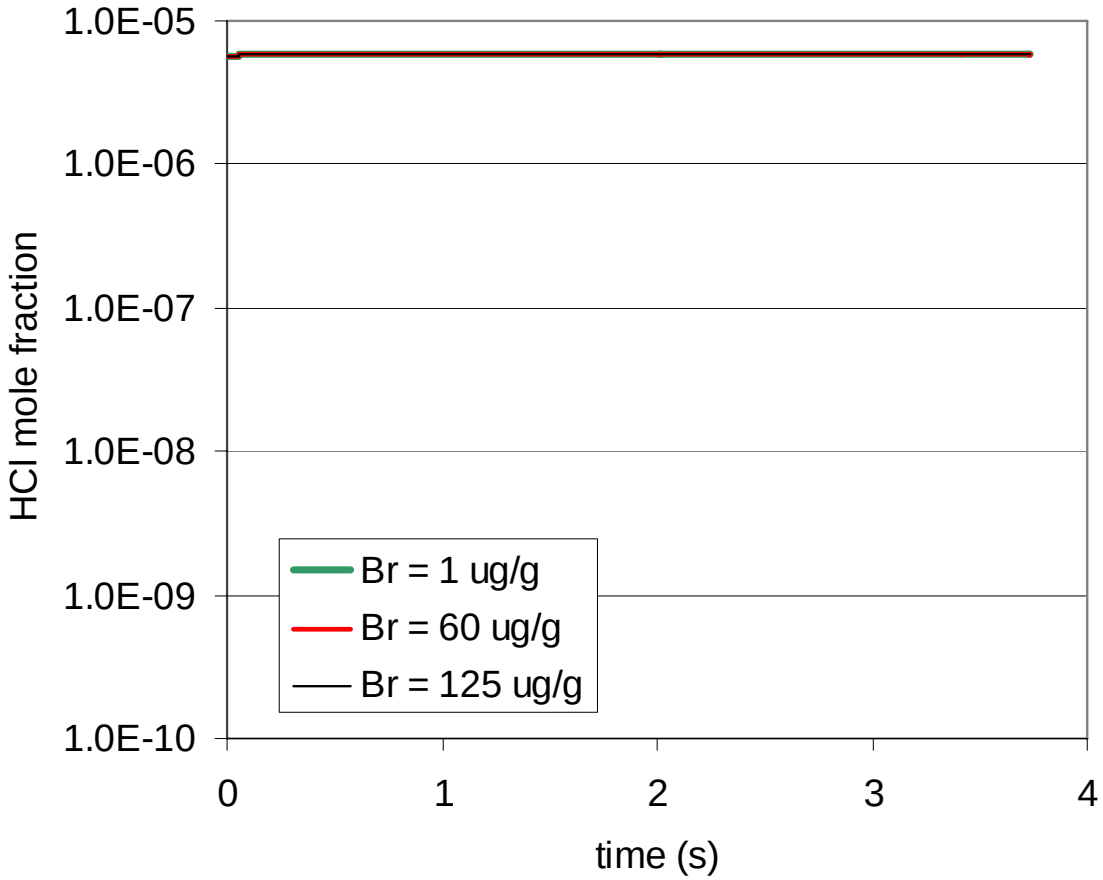
Kinetics and Modeling

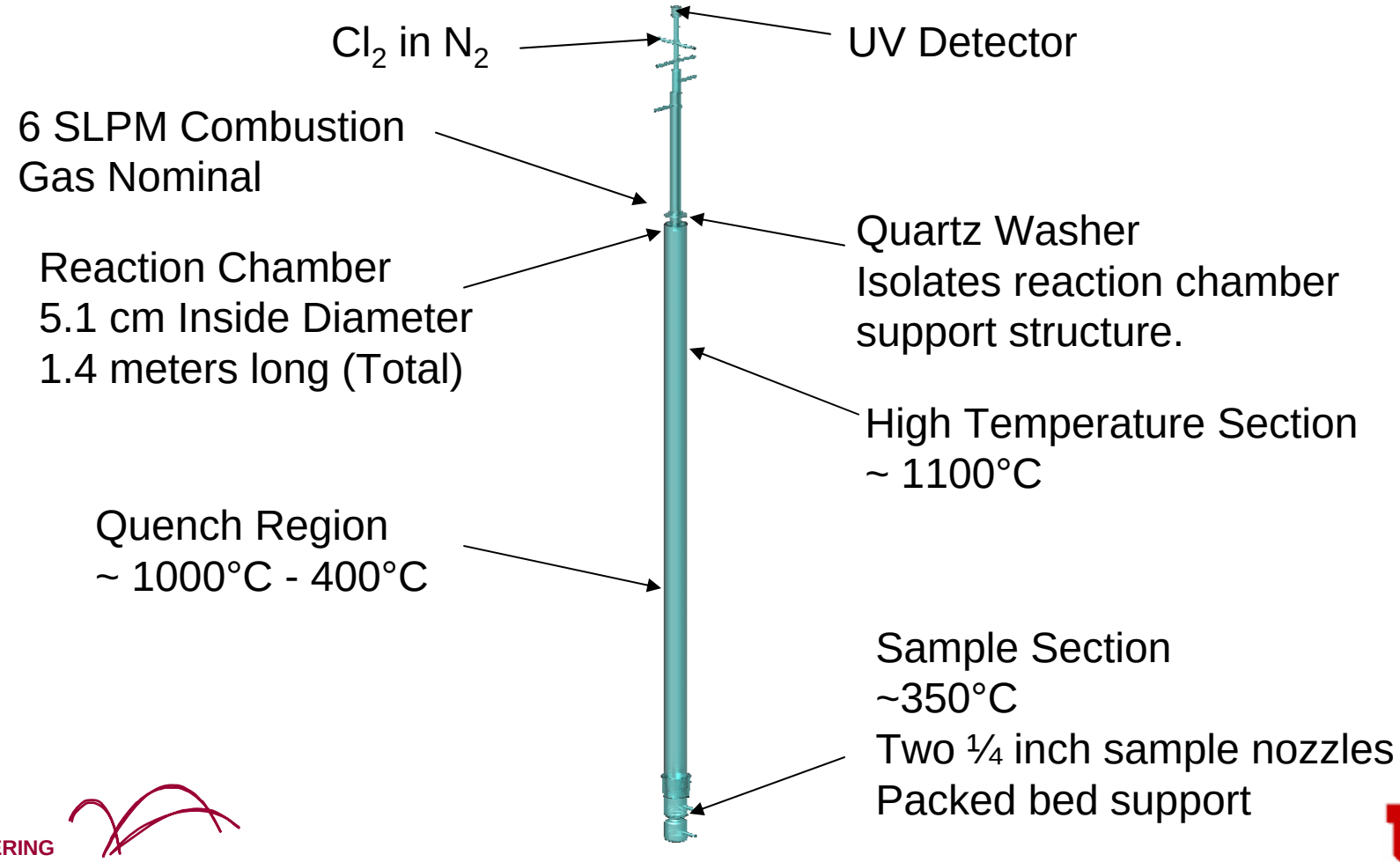
- Homogeneous oxidation is negligible
  - This suggests oxidation is heterogeneous



- Equivalent coal halogens:
  - 70 ug/g Cl
  - 1, 60, 25 ug/g Br
- Equivalent flue gas halogens (as HX):
  - 5.7 ppmv HCl
  - 0.38, 2.3, 4.6 ppmv HBr
- Cl/Br molar ratios: 150, 2.5, 1.2

Experimental - Quartz Tubular Reactor

- 300 W (1000 Btu/h), methane-fired



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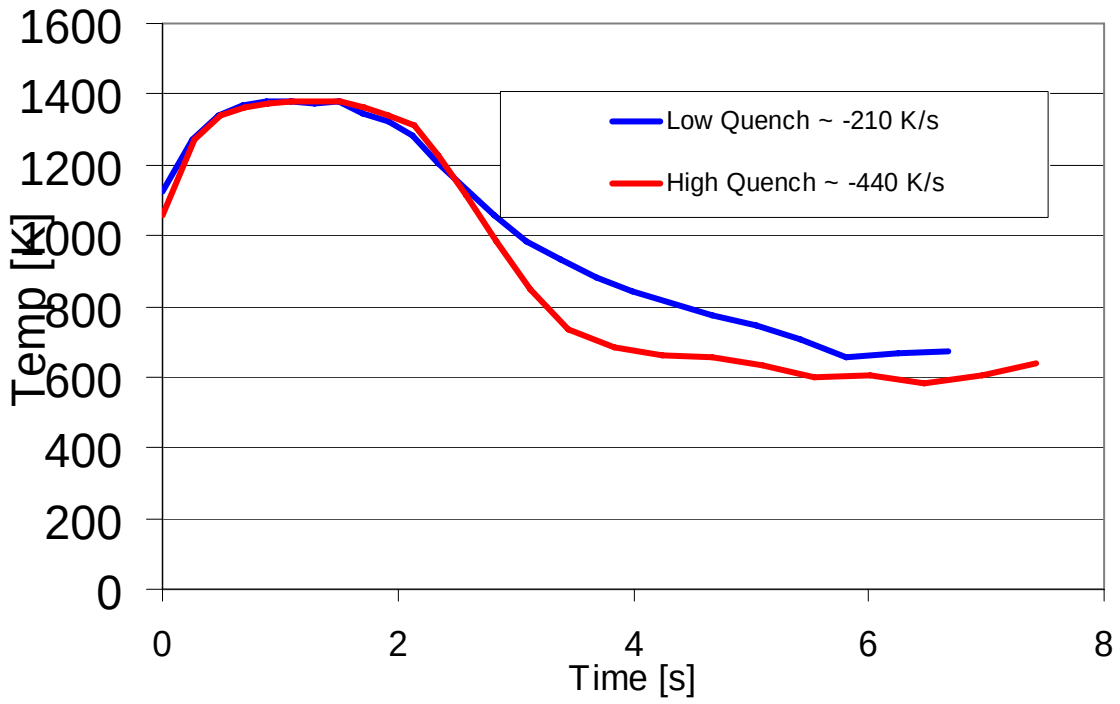
Experimental - Quartz Tubular Reactor

- Temperature profiles



- Similar to industrial profiles
- Produced by changing the temperature setting of quench section heat tape

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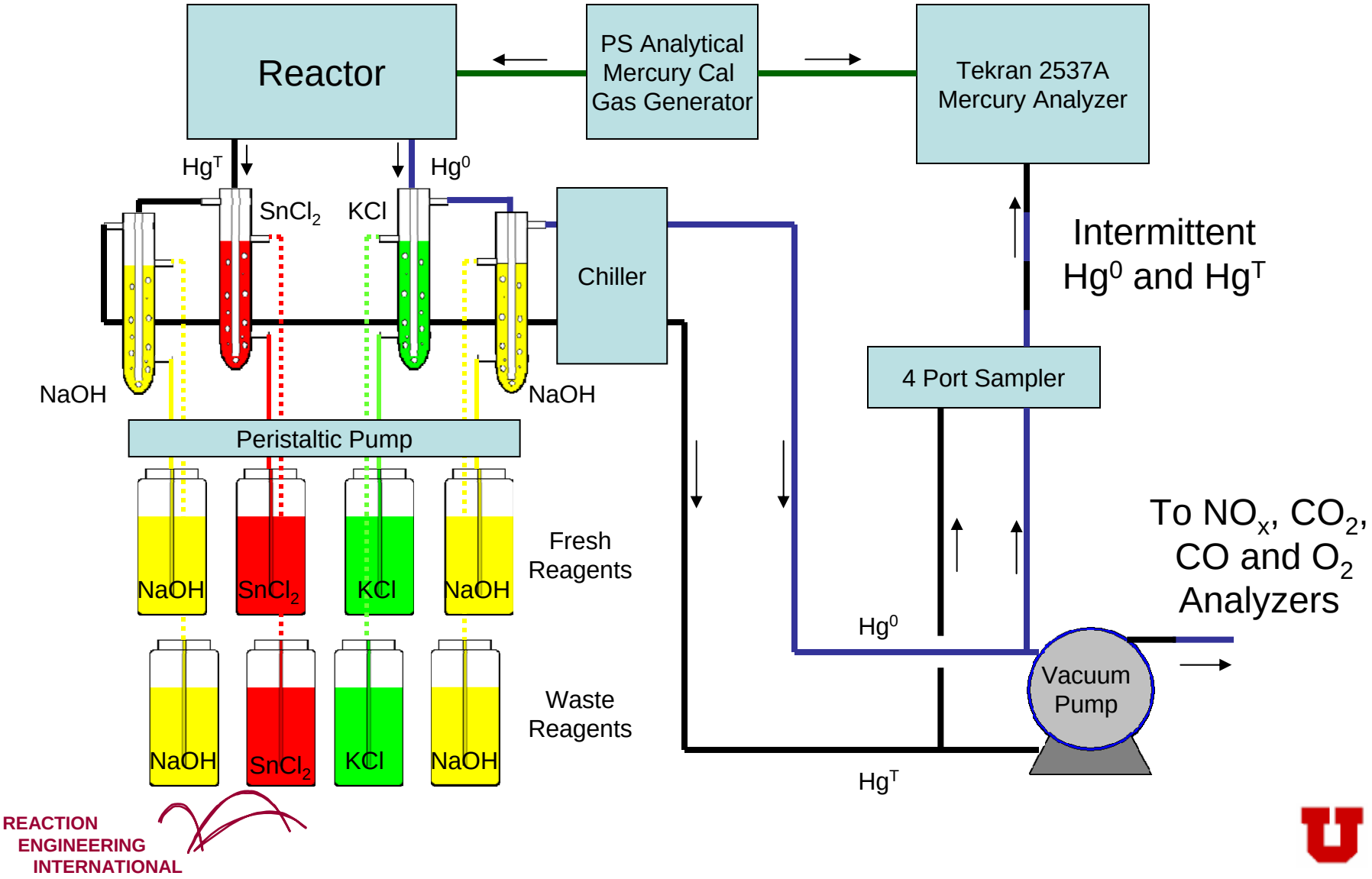
Experimental – Sample Conditioning System



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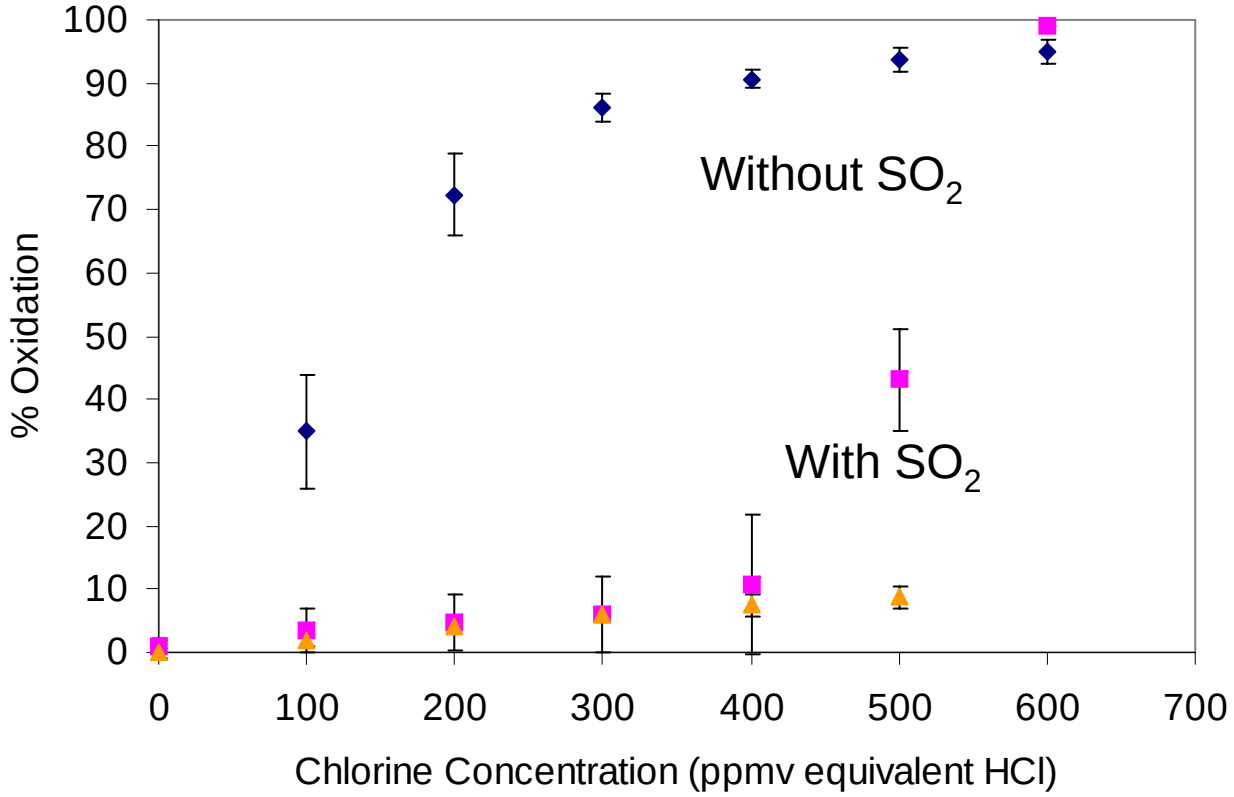
Experimental – Sample Conditioning

- Oxidation of Hg with and without SO_2



25 μg/m³ Hg
440 K/s quench

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Experimental – Sample Conditioning

- Elemental mercury is oxidized by hypochorite in KCl impinger

$$Cl_2 + 2H_2O = HOCl + H_3O^+ + Cl^-$$

- Sodium thiosulfate ($Na_2S_2O_3$) removes chlorine from solution

$$Na_2S_2O_3 + 8Cl + 5H_2O = 2NaHSO_4 + 8\ HCl$$

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + S + SO_2$$

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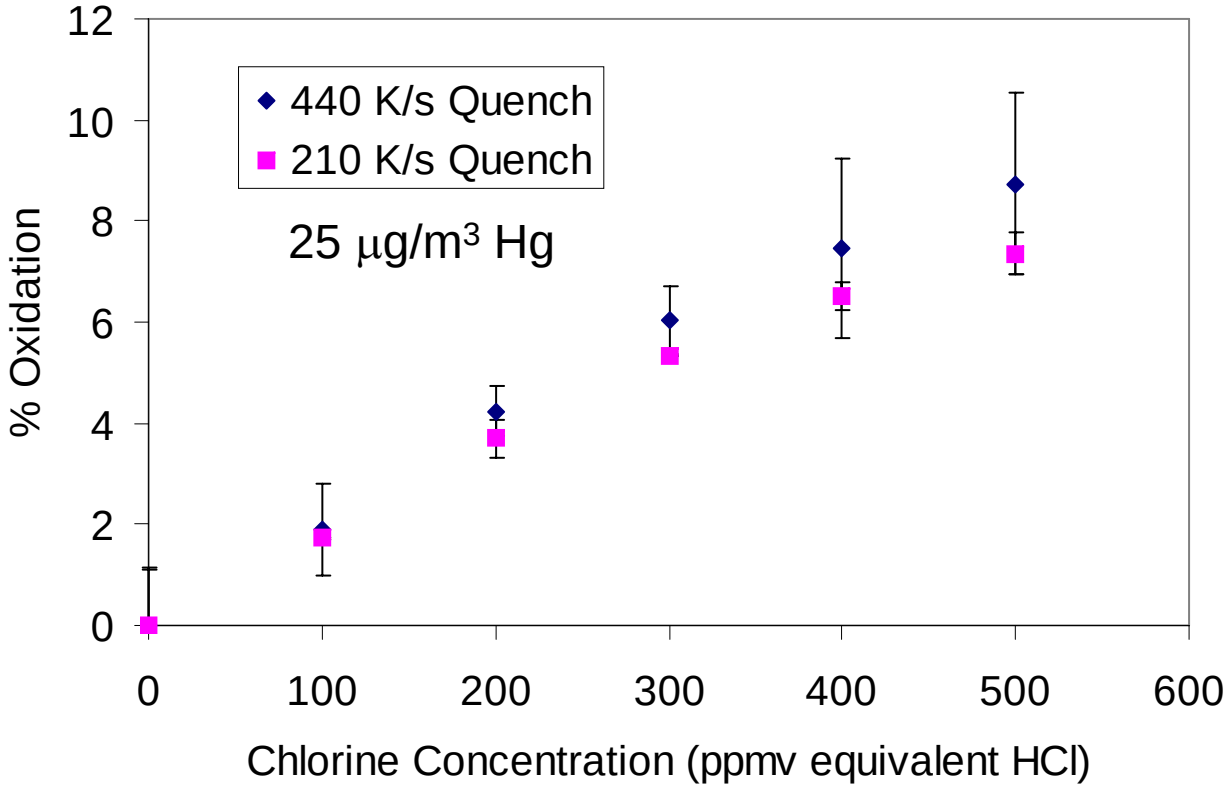
Experimental – Sample Conditioning

- Oxidation of mercury with $Na_2S_2O_3$ added to KCl impinger



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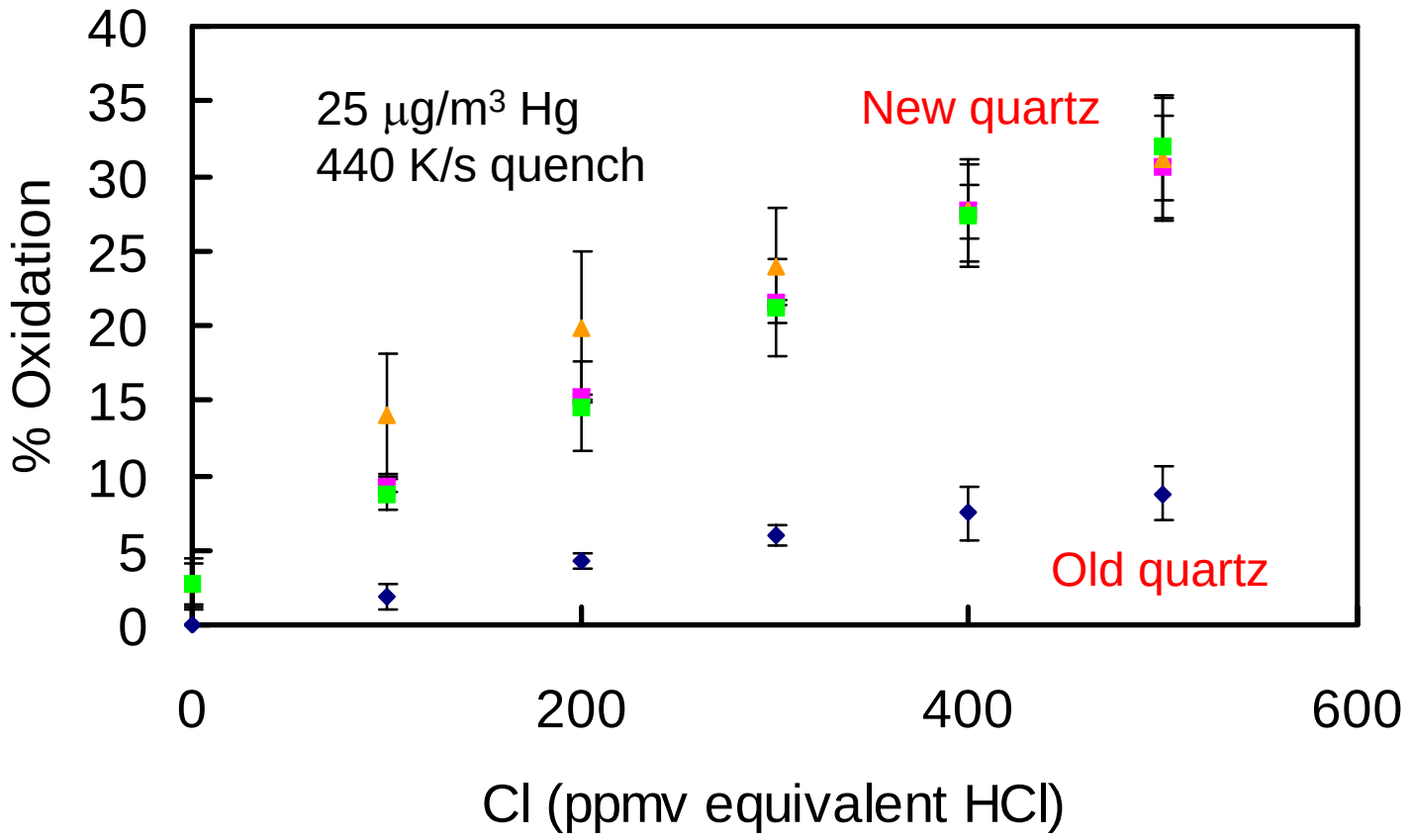
Experimental – Homogeneous Oxidation

- Effect of new quartz walls on oxidation by Cl



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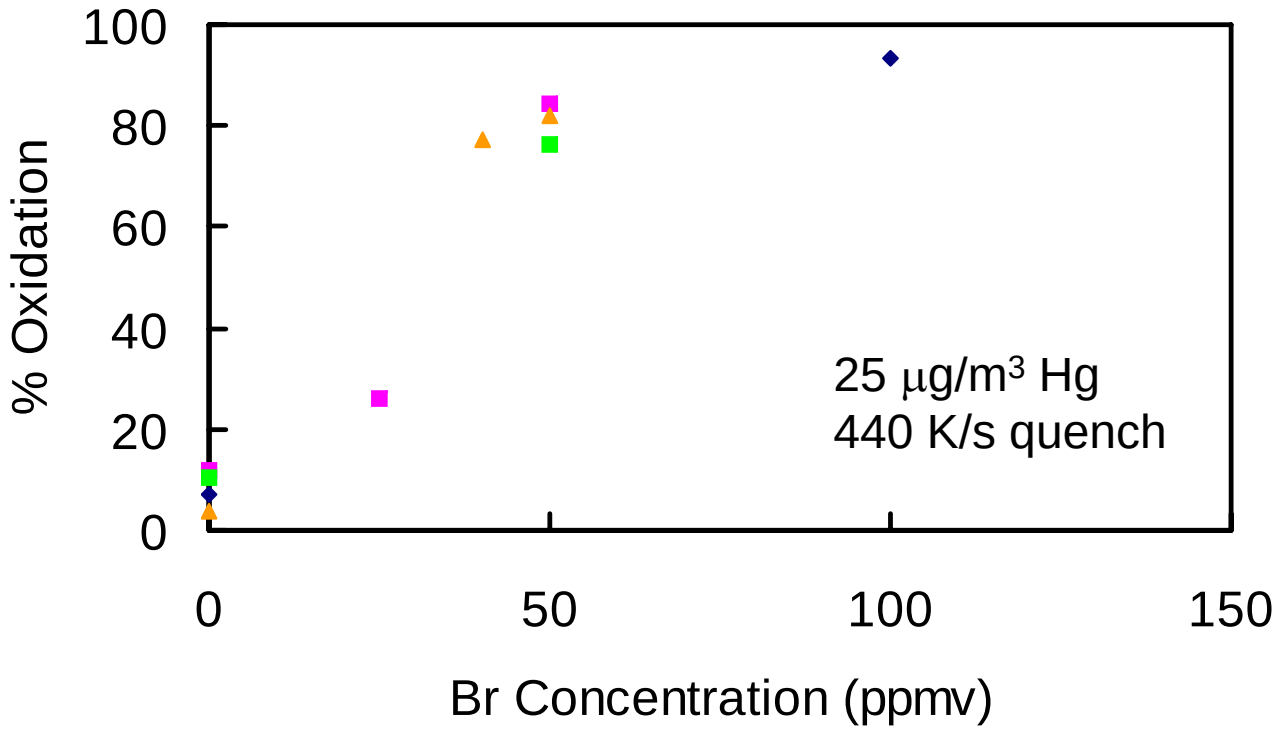
Experimental – Homogeneous Oxidation

- Oxidation by Br with new quartz in use



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Conclusions

- Thermodynamic and kinetic calculations show HCl and Br_2 dominant below 500°C.
- Field tests show significant increases in Hg removal with halogen addition.
- Kinetic calculations suggest oxidation by Cl and Br dominated by heterogeneous paths.
- Sample conditioning in presence of Cl may give high apparent oxidation.
- Br appears more effective than Cl.

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Future Work

- Include heterogeneous processes in modeling.
- Further study effects of reactor surface to volume ratio.
- Fixed-bed studies using fly ash, activated carbon, and bromine impregnated AC.

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