Homogeneous Promotion of Mercury Oxidation

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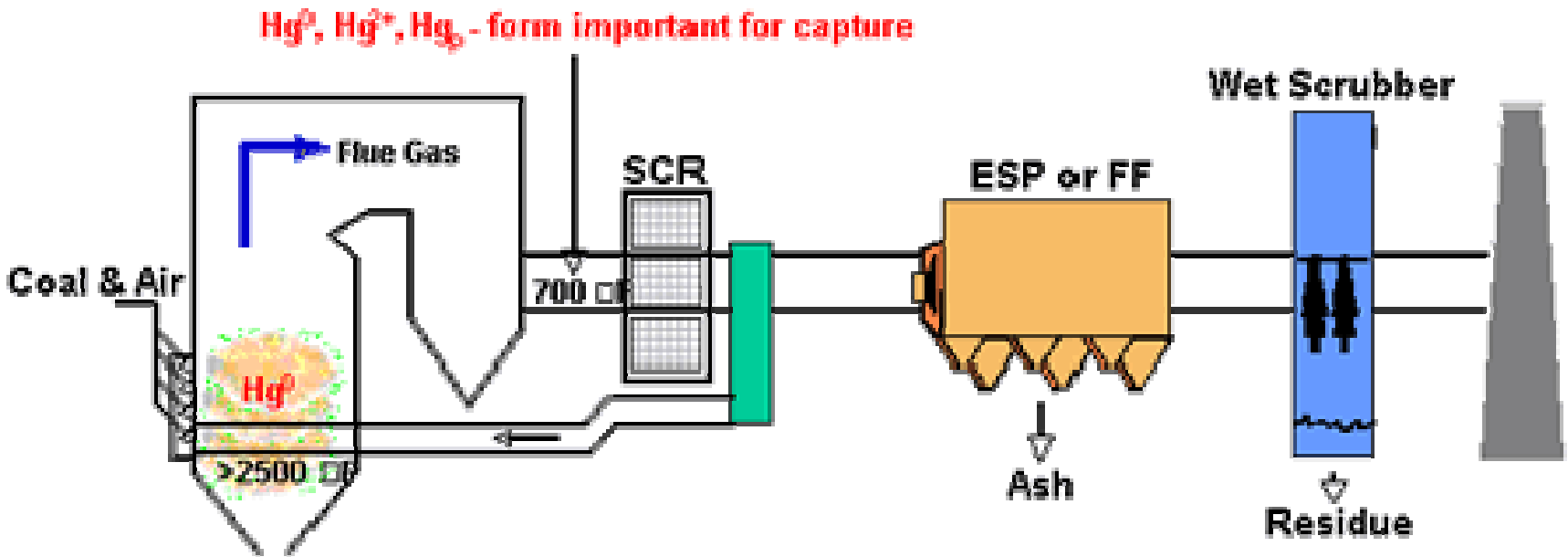
Mercury in Coal Plants

- About 75 tons Hg mined per year
- 50 tons emitted, rest captured
- Oxidized Hg key
- Role of SCR



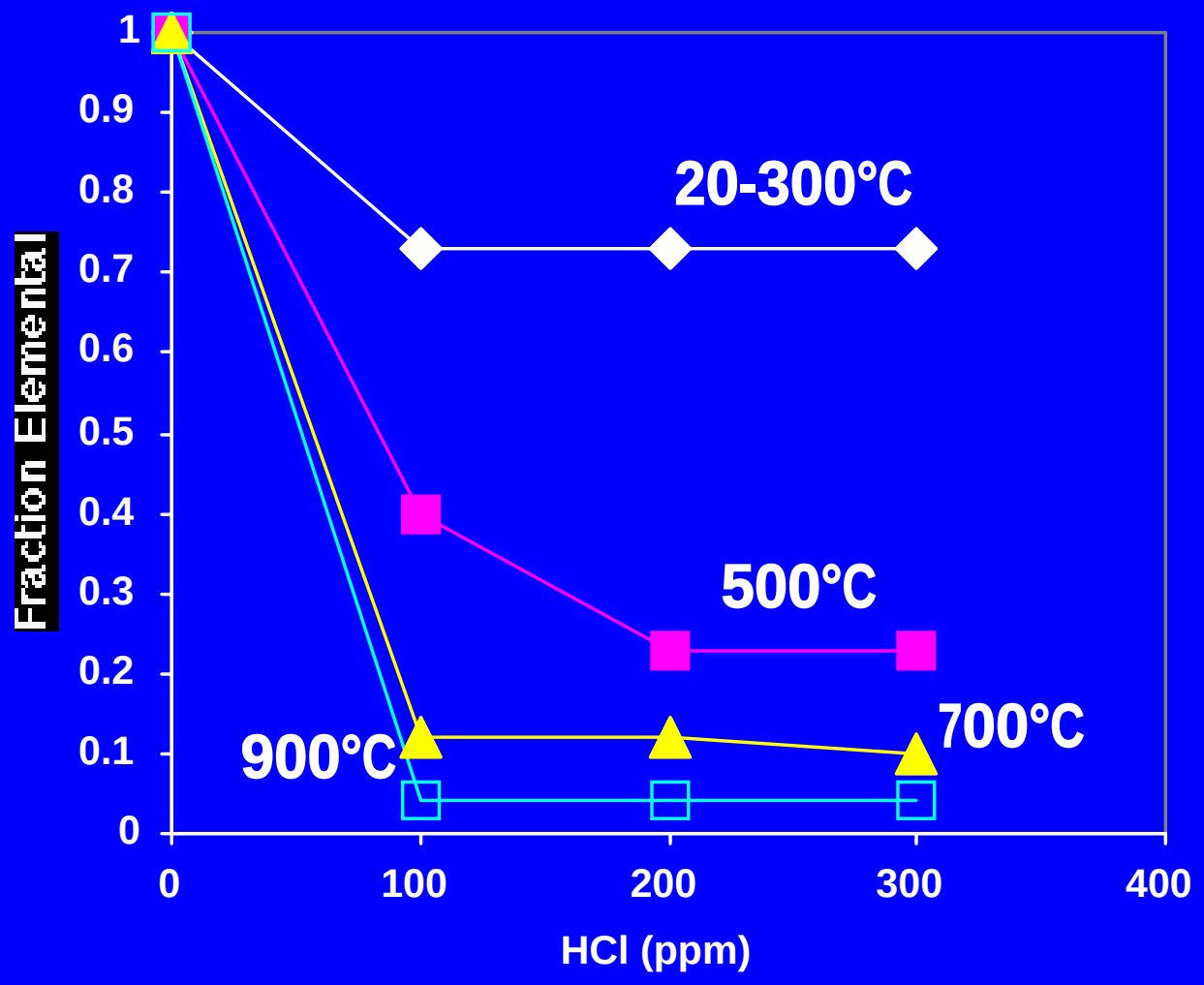
Regulatory Forcing

- EPA Regs.: Phase I: 50 --> 38 tons
- Phase I focuses on using existing SOx/NOx control equipment
- Niche for low-cost means of promoting oxidation?
- Phase II: 38-18 tons (2018)

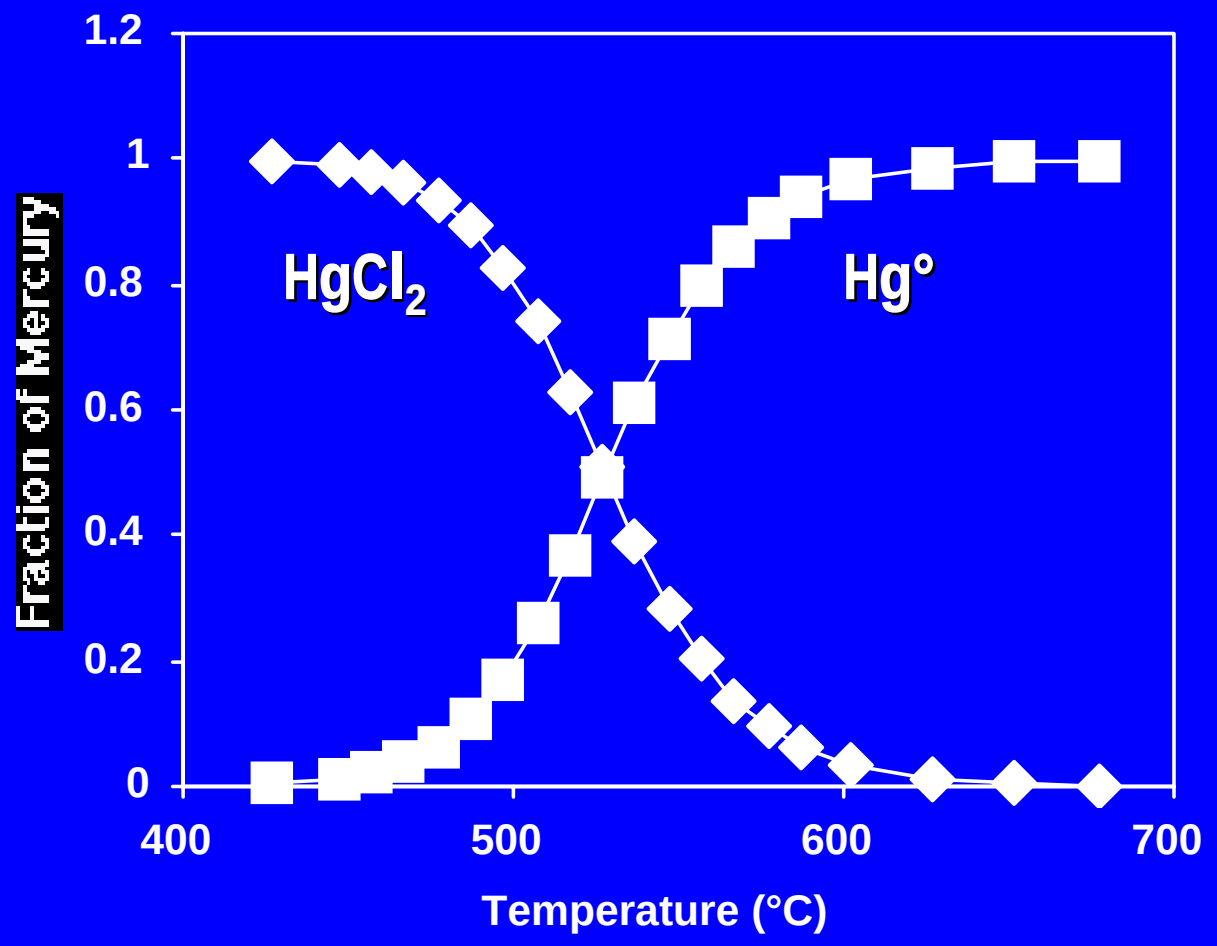
Objectives/Overview

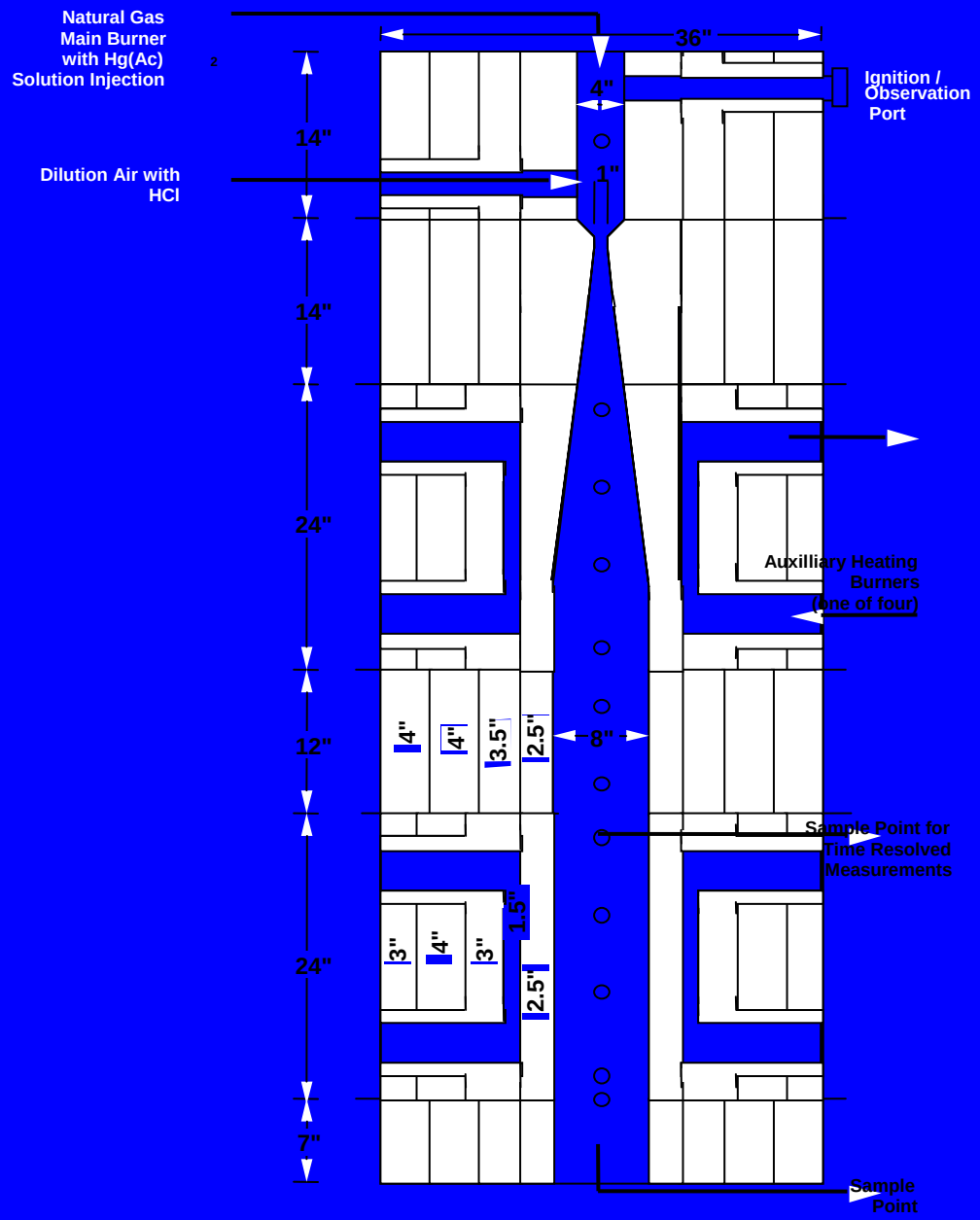
- Identify the mechanism(s) responsible for oxidation
- Make use of this to promote oxidation in low cost/low impact way

Early Oxidation Data

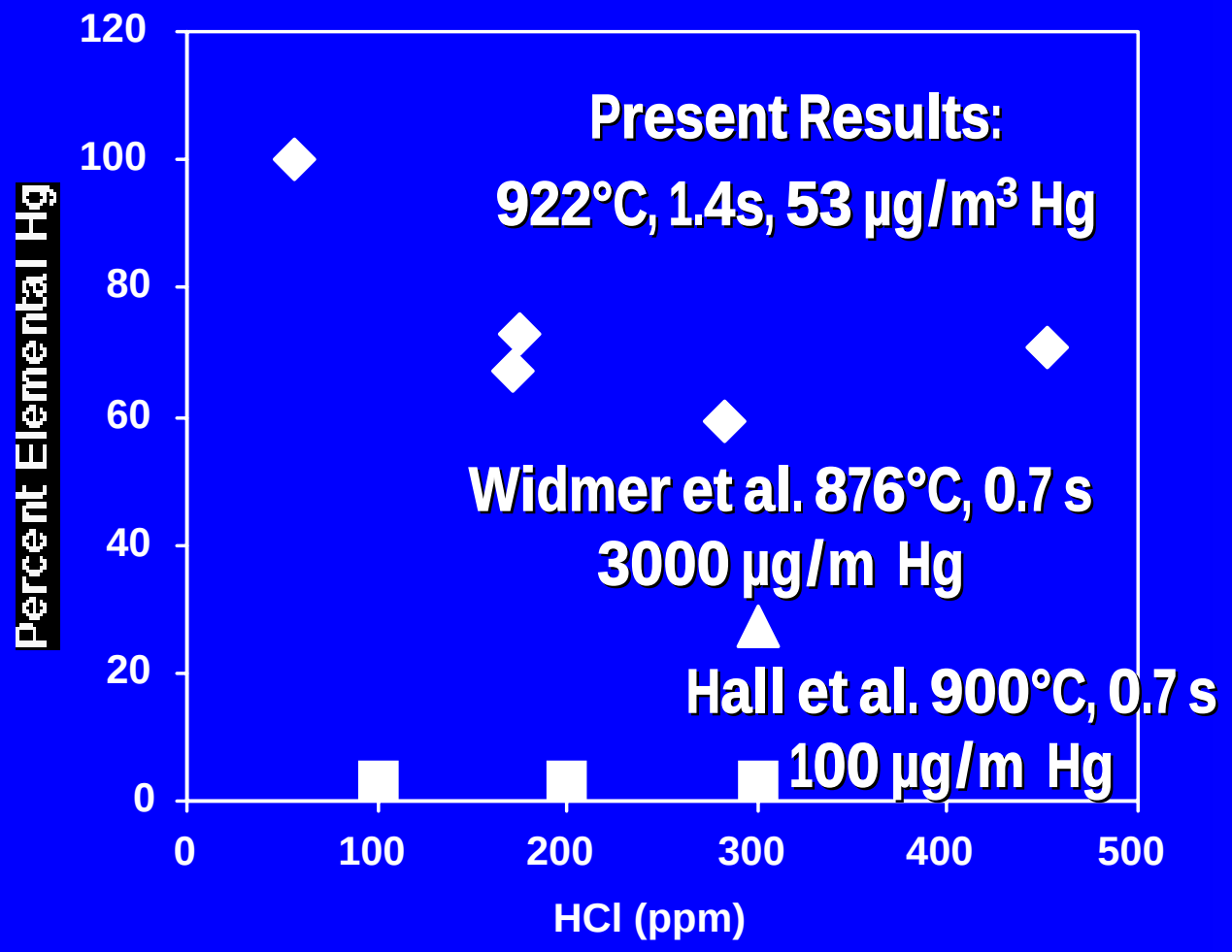


Equilibrium




Natural Gas
Main Burner
with Hg(Ac)
Solution Injection
2
36"
4"
Ignition /
Observation
Port
14"
Dilution Air with
HCl
1"
14"
24"
Auxilliary Heating
Burners
(one of four)
12"
4"
4"
3.5"
2.5"
8"
Sample Point for
Time Resolved
Measurements
1.5"
3"
4"
3"
24"
2.5"
7"
Sample
Point

Data Comparison



Mechanism

$Hg + HCl \rightarrow HgCl + H$

$Hg + Cl_2 \rightarrow HgCl + Cl$

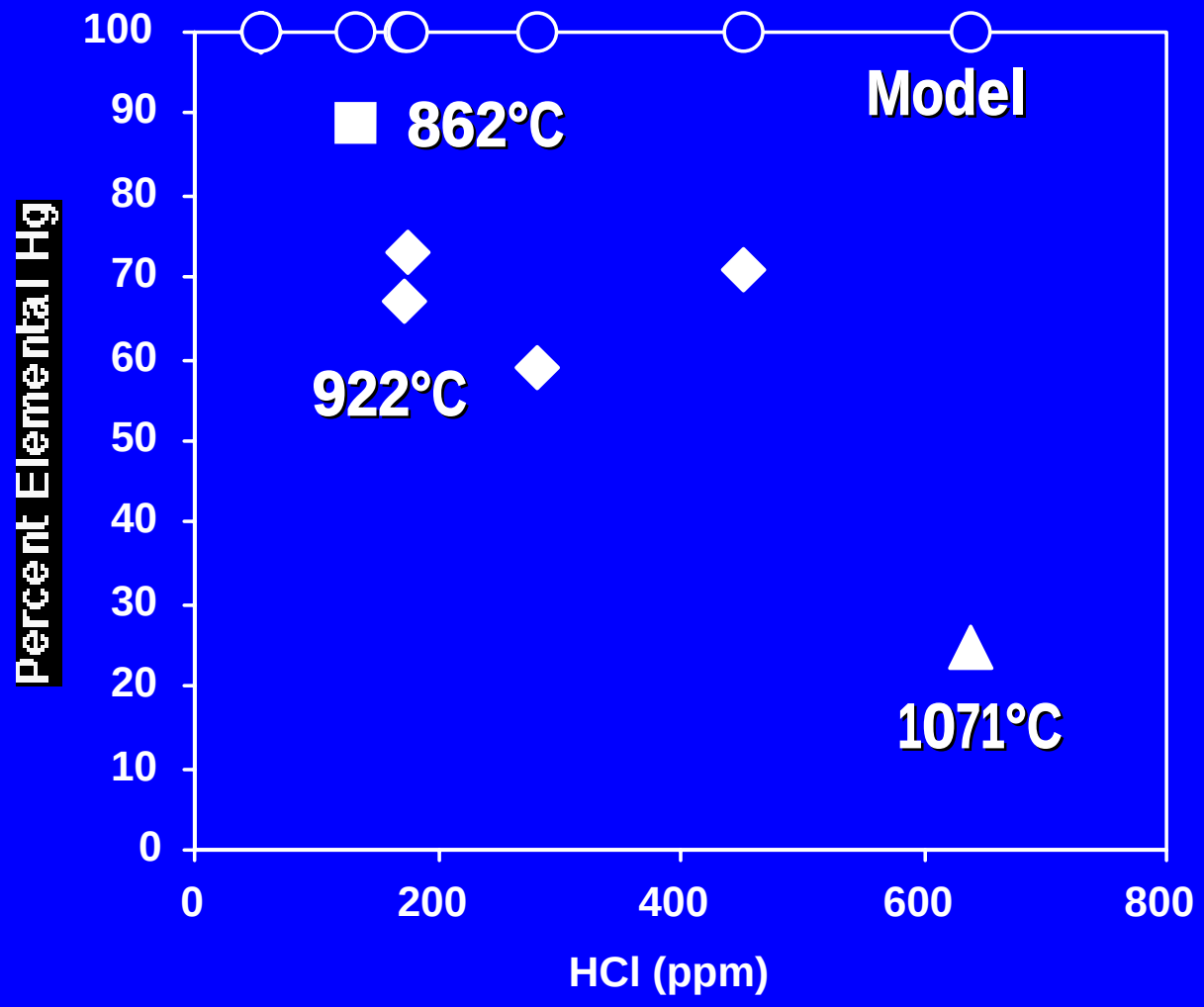
$Hg + Cl + M \rightarrow HgCl + M$

$HgCl + HCl \rightarrow HgCl_2 + H$

$HgCl + Cl_2 \rightarrow HgCl_2 + Cl$

$HgCl + Cl + M \rightarrow HgCl_2 + M$

Data vs. Model



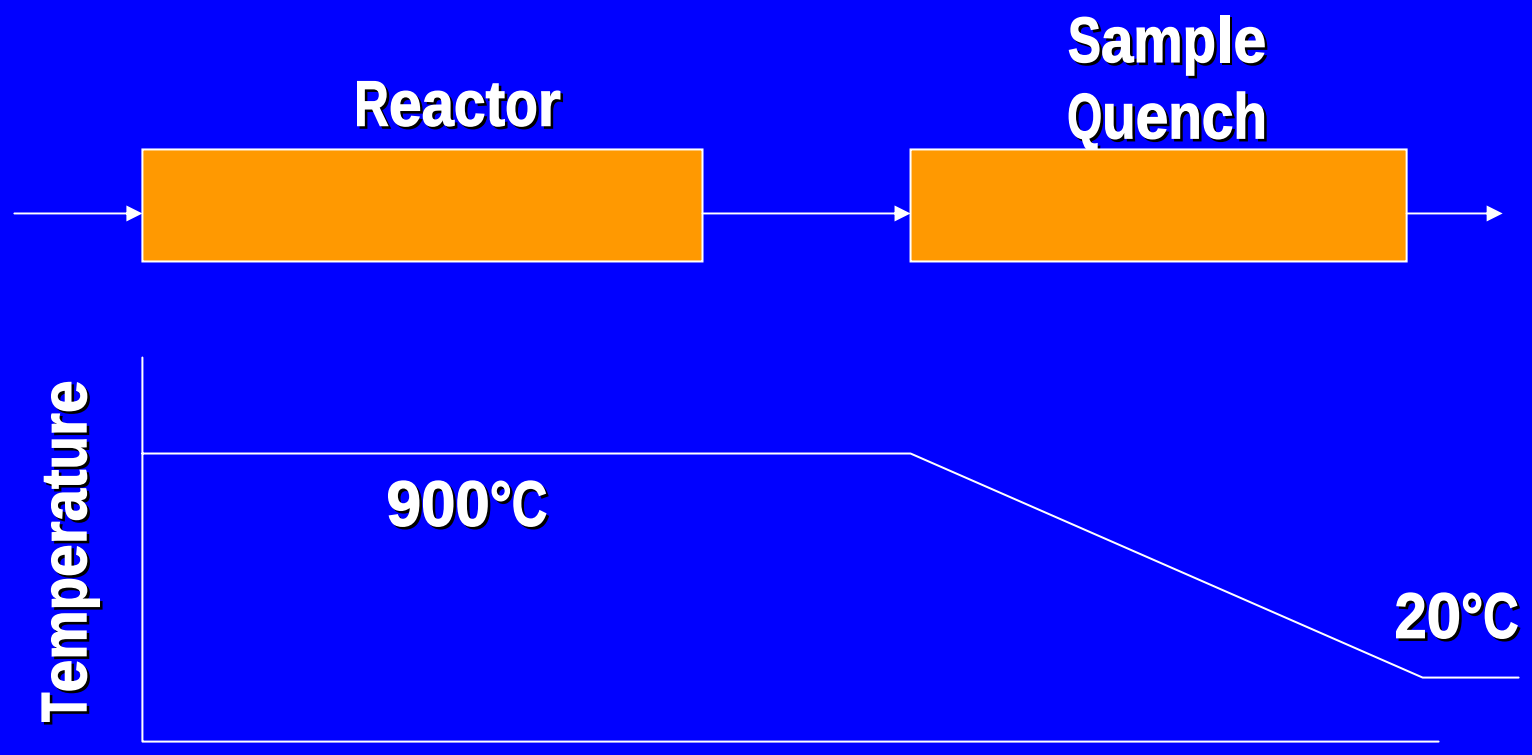
Mechanism

$Hg + HCl \rightarrow HgCl + H$	Energy Barrier too High
$Hg + Cl_2 \rightarrow HgCl + Cl$	No Cl_2 at High Temperatures
$Hg + Cl + M \rightarrow HgCl + M$	At collision limit at room T
$HgCl + HCl \rightarrow HgCl_2 + H$	Detailed analysis, too slow
$HgCl + Cl_2 \rightarrow HgCl_2 + Cl$	No Cl_2
$HgCl + Cl + M \rightarrow HgCl_2 + M$	Unknown rate, but must be fast

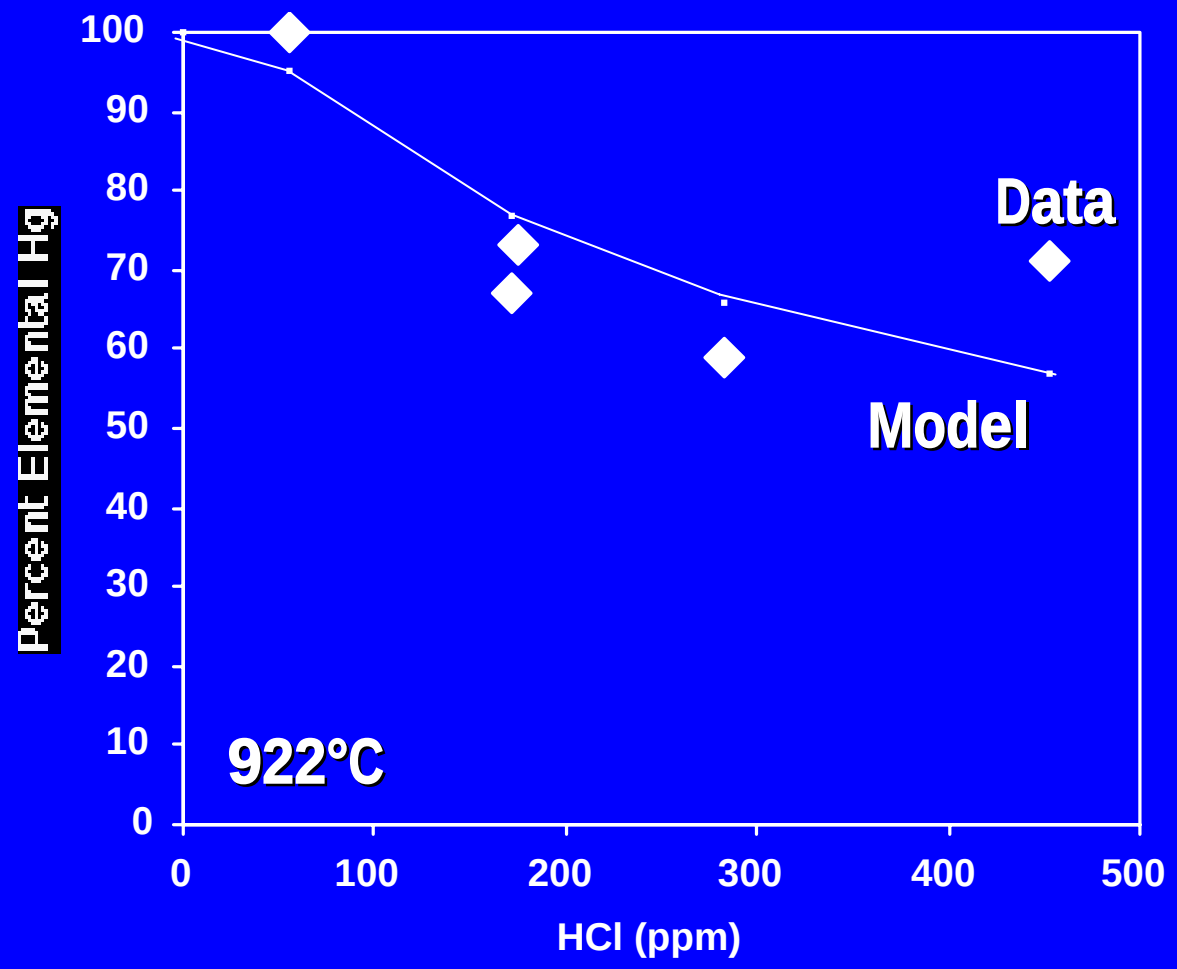
Back Reactions Fast

- $HgCl + H \rightarrow Hg + HCl$
- $HgCl + OH \rightarrow Hg + HOCl$
- Reactions too fast to allow any $HgCl_2$ to survive at 900°C
- Consistent with equilibrium
- Not consistent with data

Add the Cool-Down Region



Data vs. Model



Two Zones Needed

Hot: $HCl + OH \rightarrow Cl + H_2O$

Reach equilibrium Cl

$Hg + Cl + M \rightarrow HgCl + M$ fast, but

$HgCl + H \rightarrow Hg + HCl$ much faster

Two Zones Needed

Cold: $Cl + Cl + M \rightarrow Cl_2 + M$

This is slow, and leaves a large Cl population in cold zone

$Hg + Cl + M \rightarrow HgCl + M$

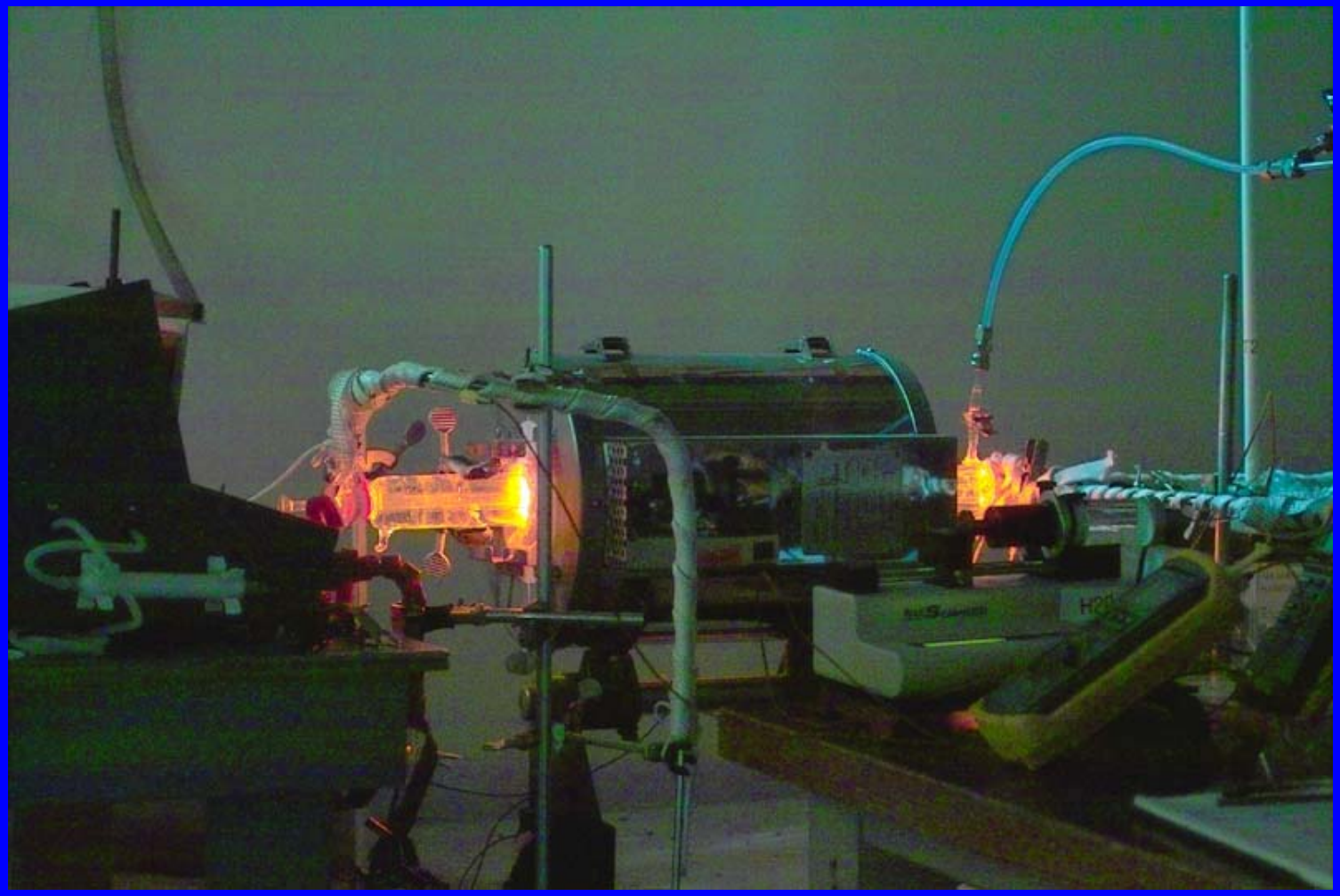
$Hg + Cl_2 \rightarrow HgCl + Cl$
$HgCl + Cl + M \rightarrow HgCl_2 + M$
$HgCl + Cl_2 \rightarrow HgCl_2 + M$

Reverse reactions are now stopped due to cold temperatures

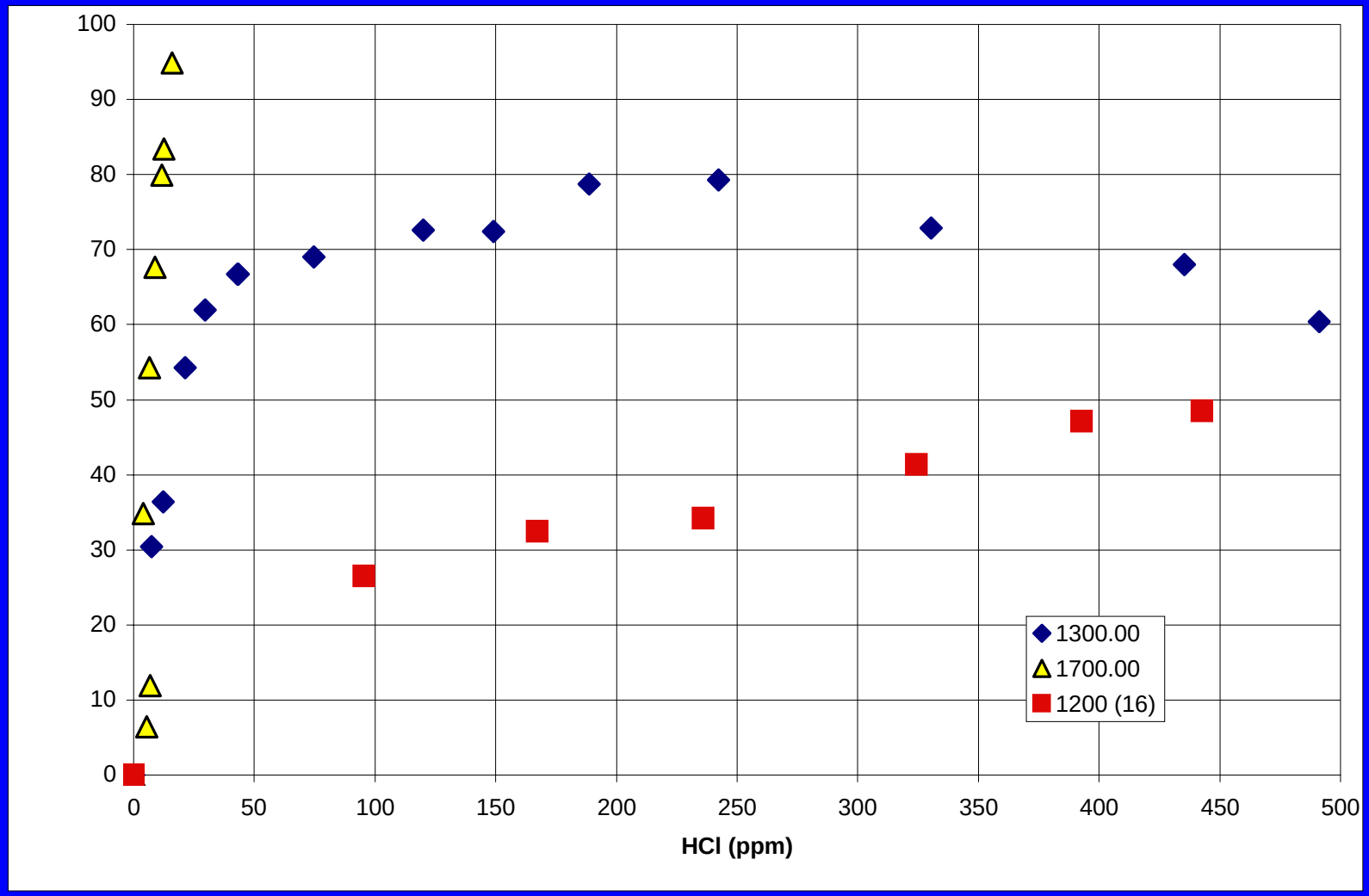
Implications

- No $HgCl_2$ exists in any of the hot experiments
- It is all made during quench
- But, high temperature is needed to prepare the oxidizing agent
- How can this be used to promote oxidation?
- Need for more flexible experiment

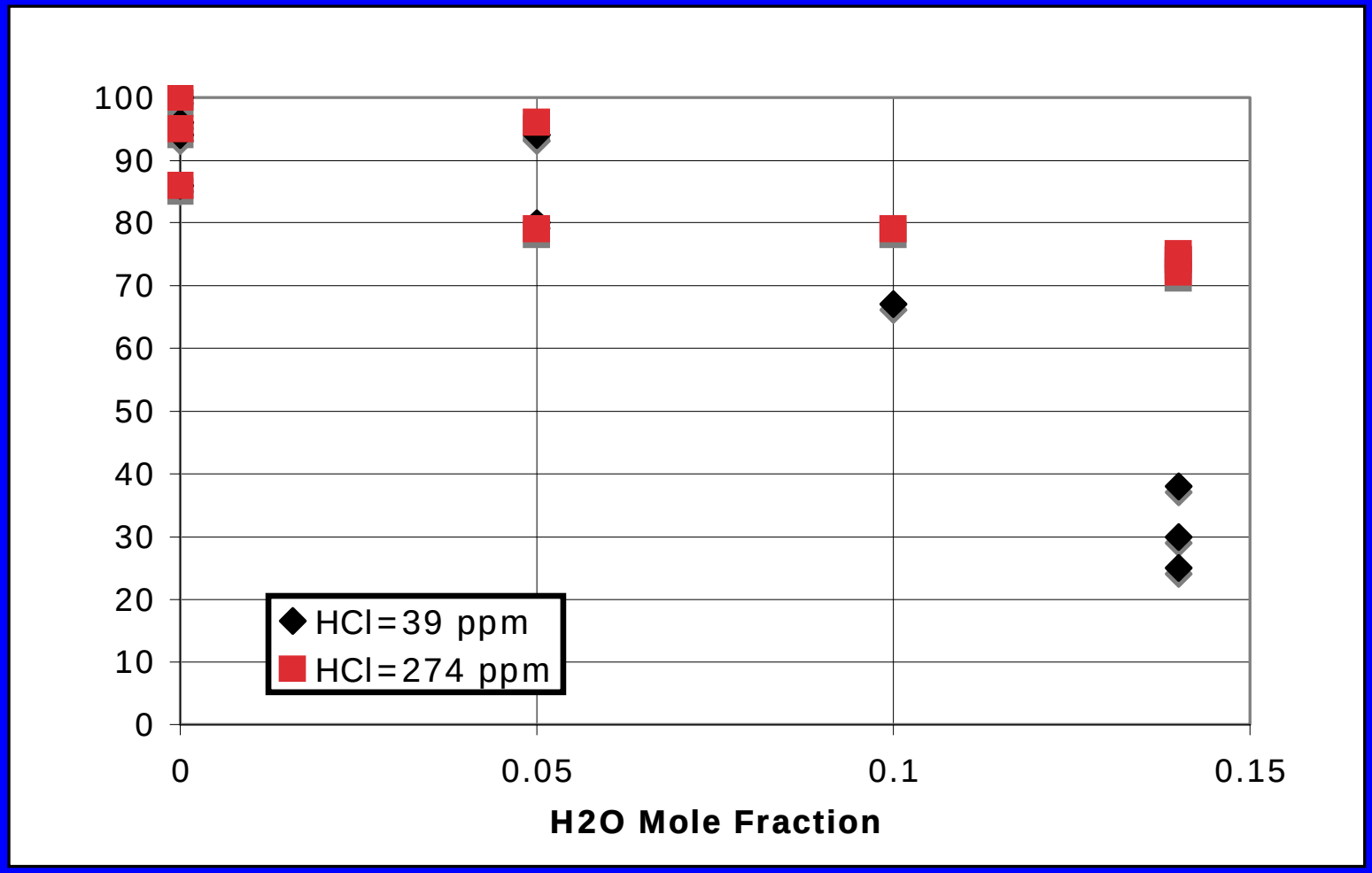
Quartz Flow Reactor



Oxidation by HCl



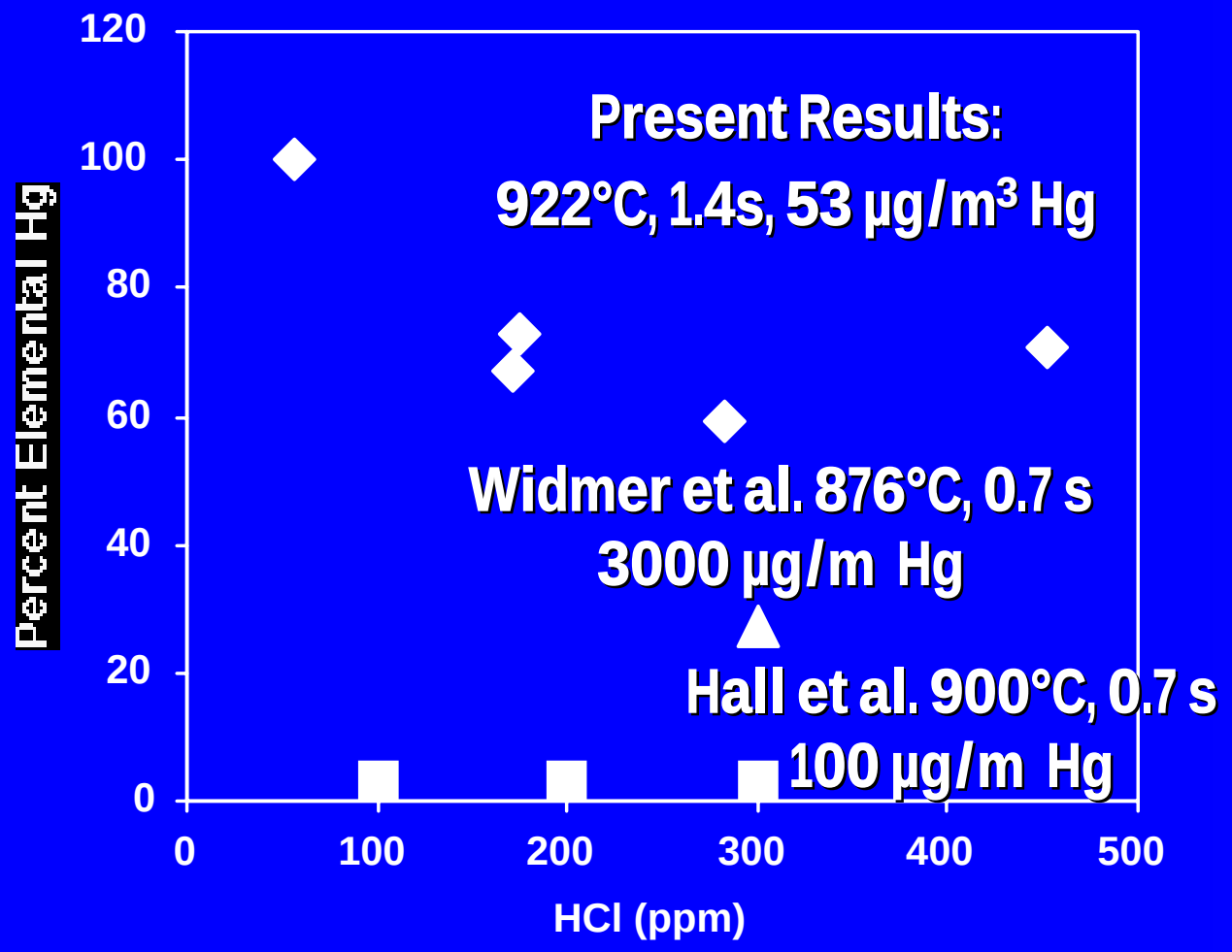
Water Vapor


100
90
80
70
60
50
40
30
20
10
0
0
0.05
0.1
0.15
H2O Mole Fraction
HCl=39 ppm
HCl=274 ppm

Kinetics

- In dry gas, equilibrium Cl is 20x higher than in wet gas at 922°C
- This rationalizes why the Hall *et al.* data are so reactive
- $HCl + OH = Cl + H_2O$ goes to left

Data Comparison



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How to Promote Oxidation?

- Increase amount of Cl entering the quench zone
- Promote decomposition of HCl:

$$HCl + OH \rightarrow Cl + H_2O$$

$$HCl + H \rightarrow Cl + H_2$$

$$HCl + O \rightarrow Cl + OH$$

- Provide free radicals via addition of chain-branching species

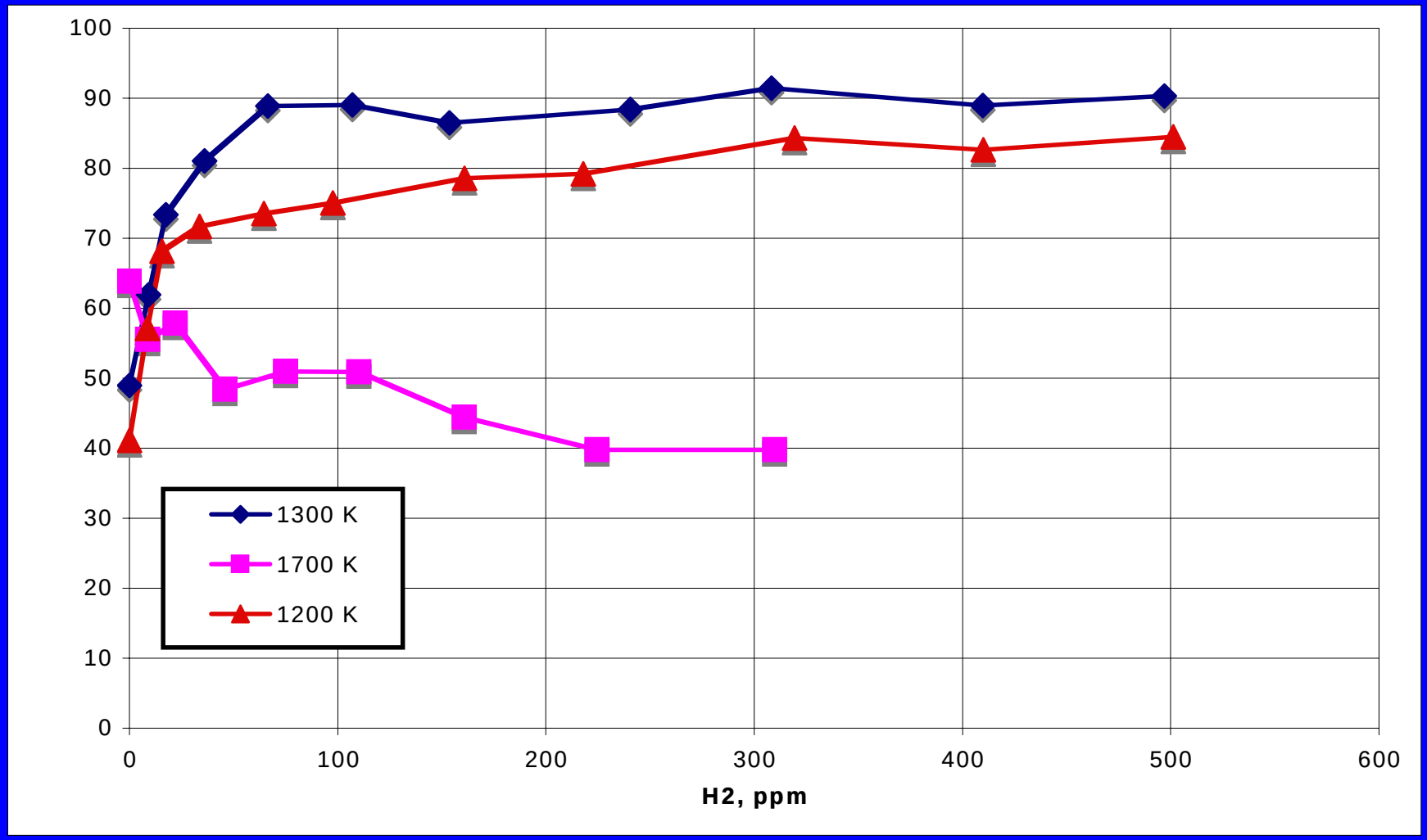
Hydrogen Promotion

- $H_2 + OH \rightarrow H + H_2O$
- $H + O_2 \rightarrow OH + O$
- $O + H_2O \rightarrow OH + OH$

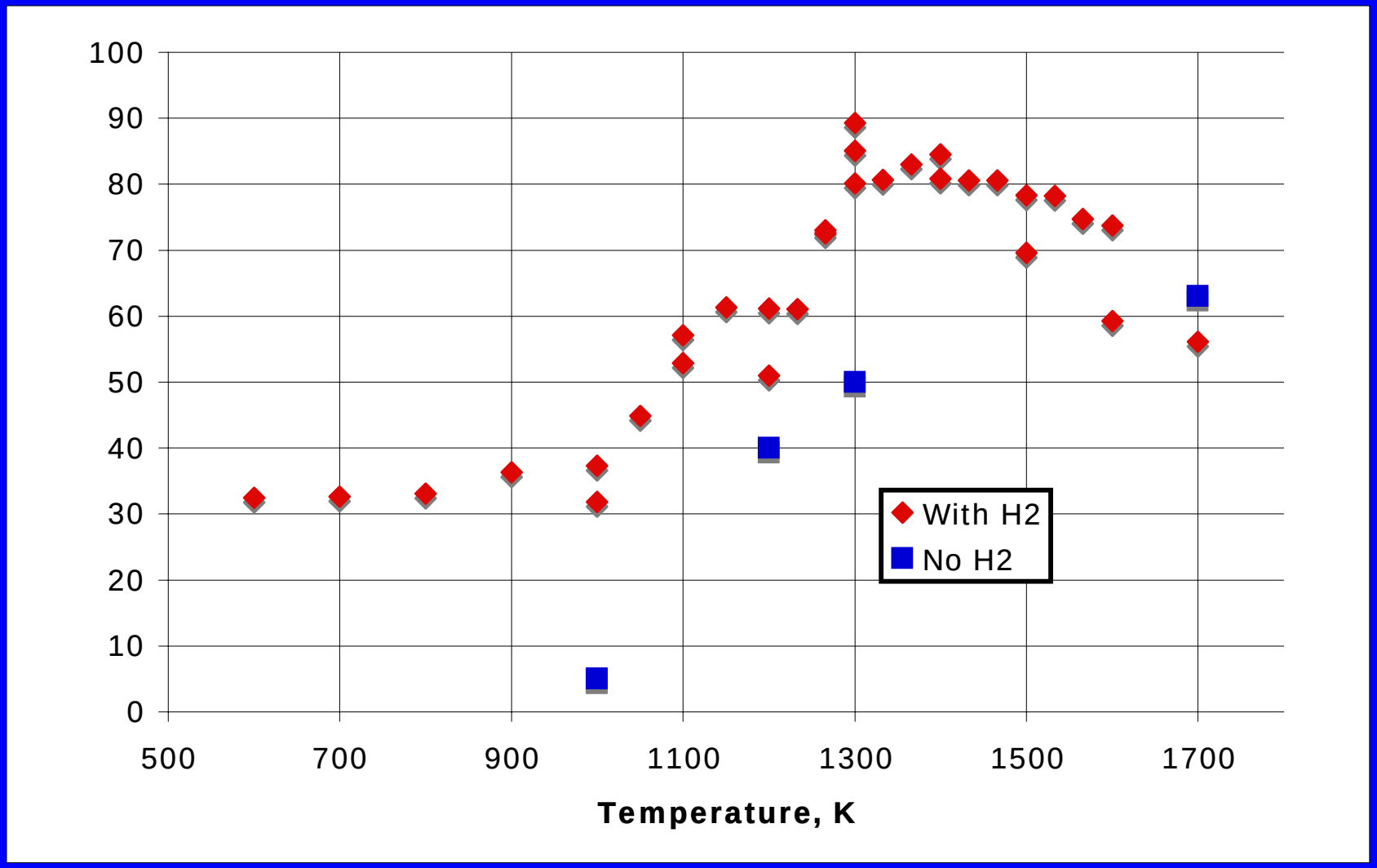
--> Net 2 OH generated per H_2 consumed, but:

- $H_2 + Cl \rightarrow HCl + H$ competes with
- $HCl + OH \rightarrow Cl + H_2O$

Hydrogen Promotion



Temperature Dependence



Observations and Kinetics

- Increase conversion at lower temperatures
- Possible deactivation at higher temperatures
- Very low temperature oxidation an open issue

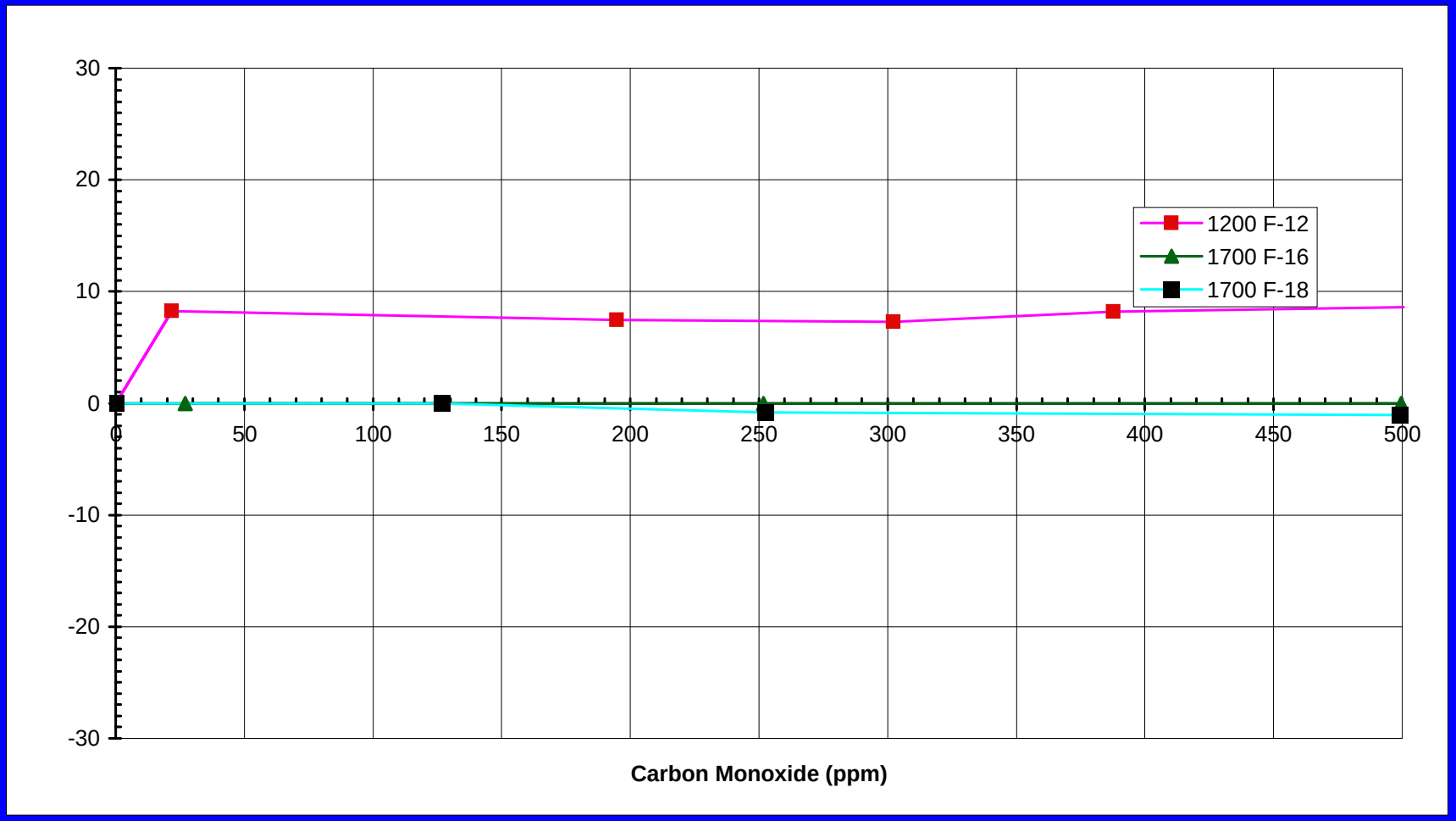
Carbon Monoxide

- $CO + OH \rightarrow CO_2 + H$
- $H + O_2 \rightarrow OH + O$
- $O + H_2O \rightarrow OH + OH$

→Achieve excess OH concentrations

→Higher temperature needed?

CO and Hydrogen



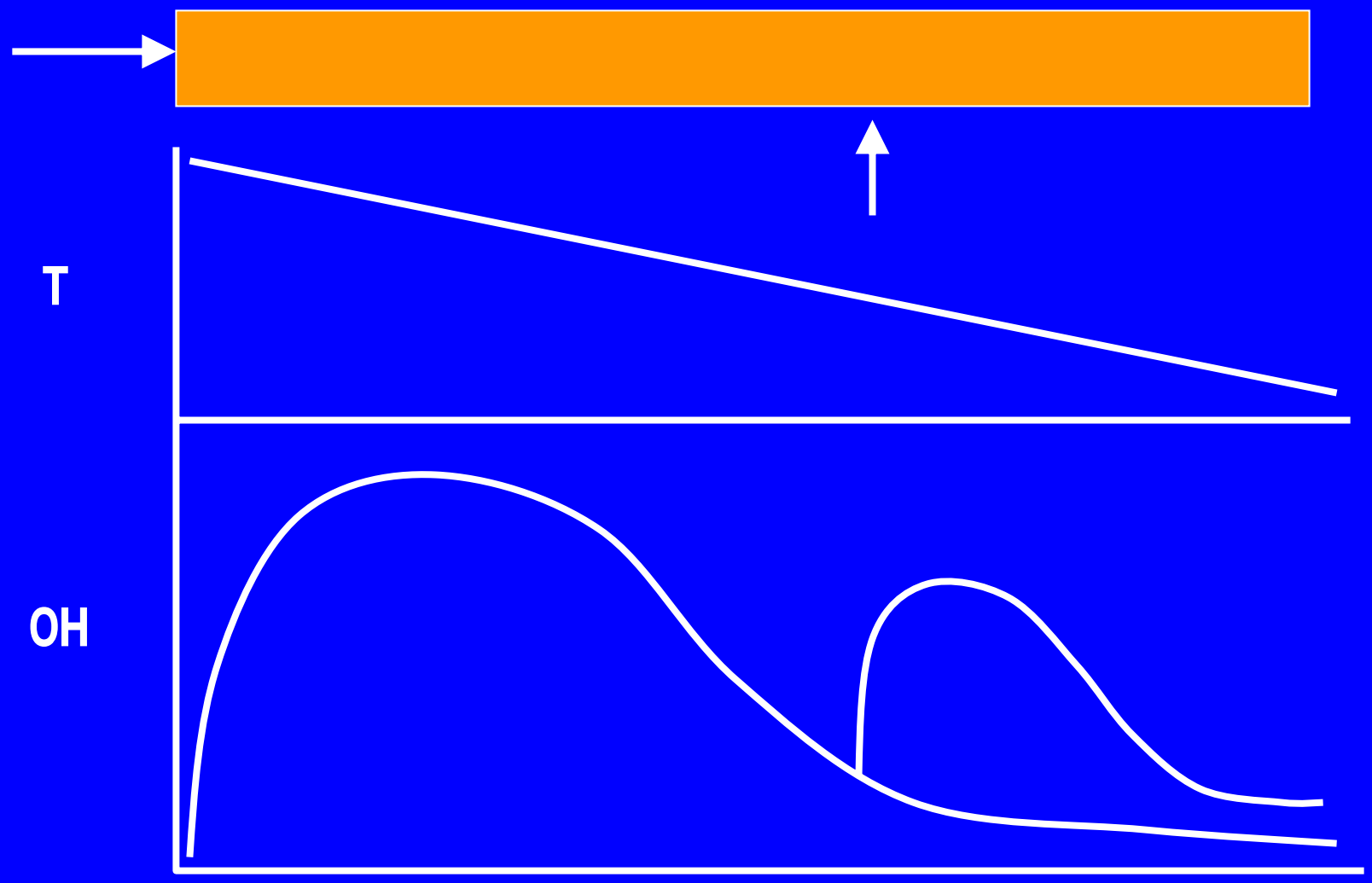
Conclusions

- Promotion of homogeneous oxidation can be done with very small amounts of additive
- Mechanism appears consistent with our present understanding
- Ongoing work focuses on key issues

Extend Chemical Kinetics

- $NO + OH + M \rightarrow HONO + M$
- $Hg + ClO \rightarrow HgO + Cl$
- Sulfur reactions

Behavior in Realistic Quench



In Practice

- Generate CO/H_2 mix via natural gas reformer (no water gas shift needed)
- Fuel costs low: ~$75,000/yr for 600 MWe plant @ 50 ppm H_2 and $5/MMBtu gas