Water-Gas Shift Membrane Reactor Studies

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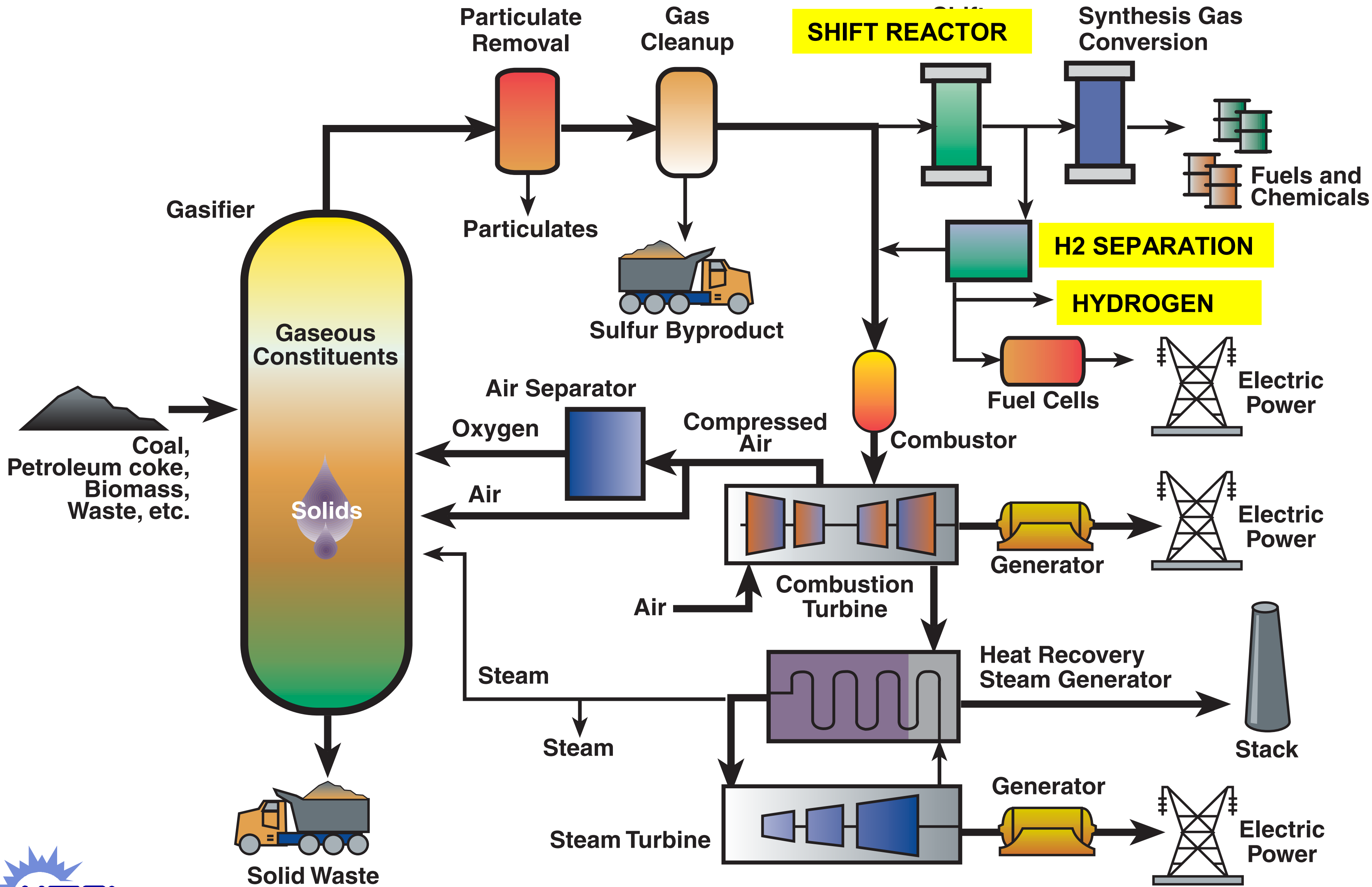
NETL's Hydrogen Program

- **Vision**
  - Fossil fuel resources are the transition feedstocks for the production of hydrogen for broad-based applications in the "Hydrogen Economy"
- **Mission**
  - Develop and demonstrate technology to produce and to separate hydrogen for downstream uses, both in advanced energy plant applications and in off-site applications
- **Program Directions**
  - Clean hydrogen for downstream processes
  - Transition to the Hydrogen Economy
  - CO_2 capture and sequestration

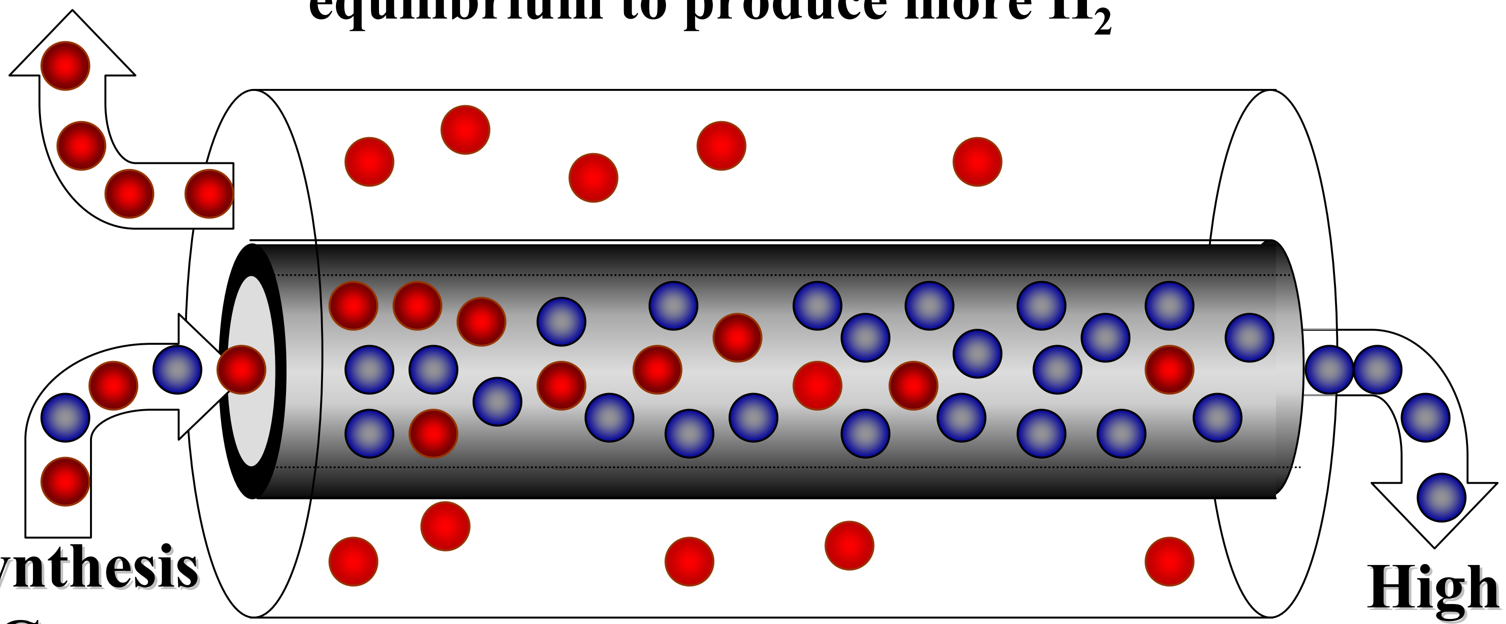
Coal Gasification Technology Options



H_2 Membrane Reactor Concept

*WGS Reaction: $CO + H_2O \boxtimes CO_2 + H_2$
*High-T for favorable kinetics
*Membrane removes H_2 to "shift" unfavorable equilibrium to produce more H_2

Pure Hydrogen

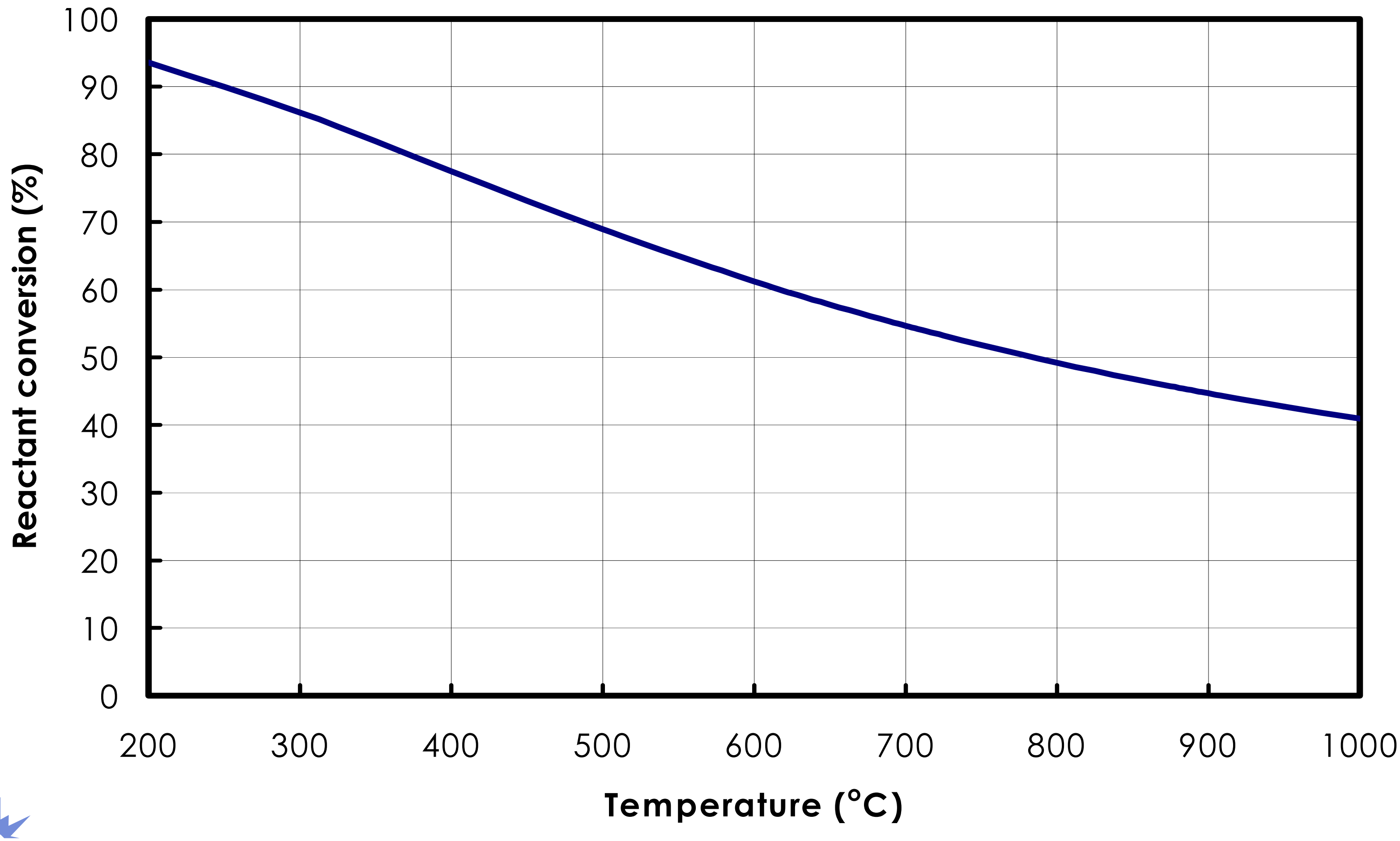


Synthesis Gas...
(H_2, CO_2, CO, plus H_2O,)

High Pressure CO_2

Equilibrium Conversion for the Water Gas Shift Reaction

$[CO]_0=[H_2O]_0$, $[CO_2]_0=[H_2]_0=0$



Project Rationale

- **Designing WGS Membrane Reactors Requires the Consideration of Reaction Kinetics and Mass Transport Phenomena**
  - Forward Water-Gas Shift Kinetics
  - Reverse Water-Gas Shift Kinetics
  - Catalytic Effect of Reactor Materials, Membrane Materials & Heterogeneous Catalyst Particles
  - Heterogeneous Catalysis May Not Be Needed
  - Hydrogen Flux Through Membrane
  - Hydrogen Selectivity of Membrane
  - Durability of Membrane in Extreme Environments

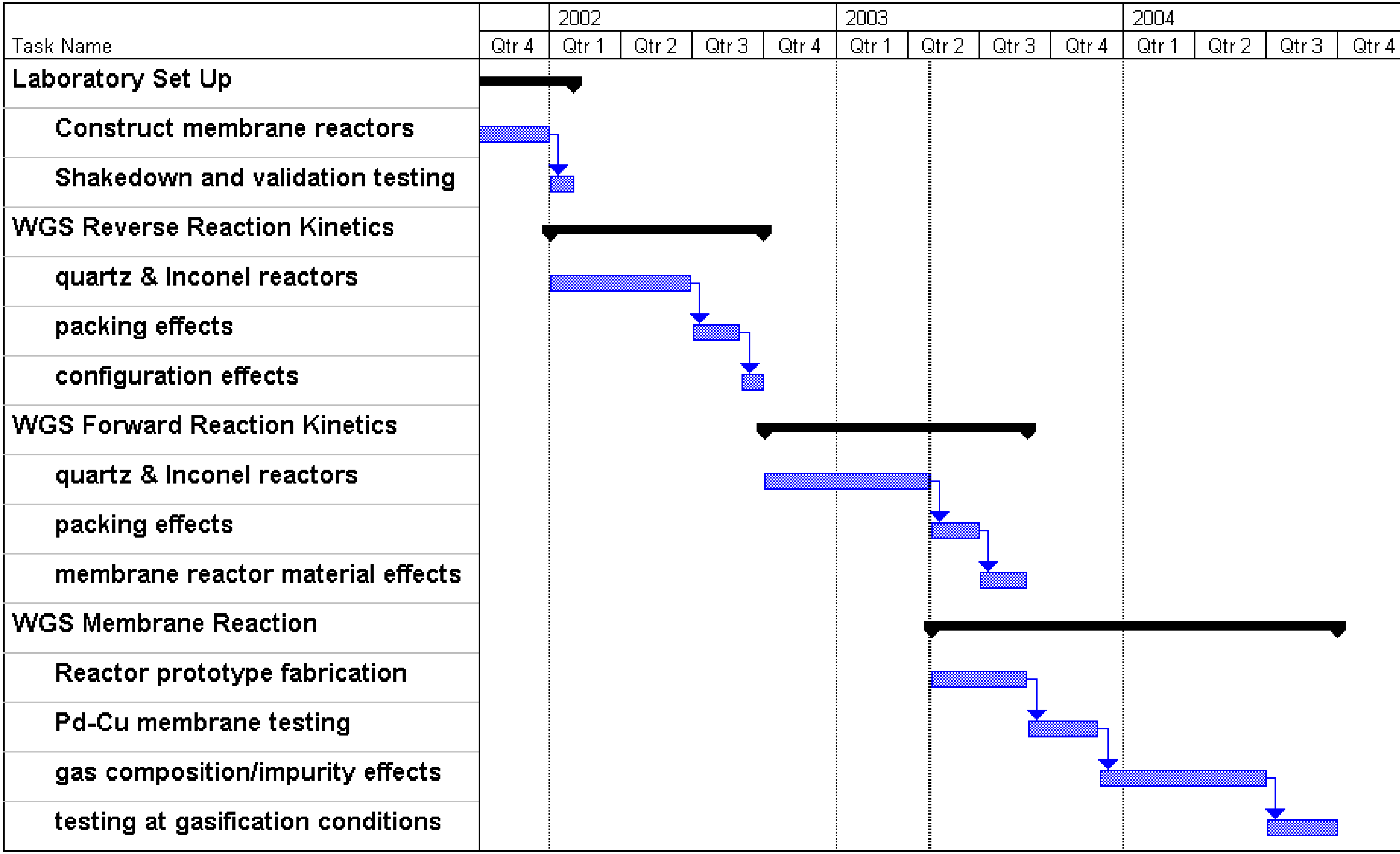
Relevance to EE H2 Production R&D Plan

- Project falls within the Technical Objective to develop technology to produce pure H_2 from coal using a 600ºC membrane system at a cost of $0.79/kg by 2015
- Related Technical Targets are based on use of a membrane water-gas shift reactor in the system
- Project addresses Technical Task 4 on "Alternative and Improvements to Conventional Water-Gas Shift" and related technical barriers

FY03 Approach

- **Goal: evaluate WGS kinetics and membrane flux using industrial gas mixtures and conditions**
  - complete reverse kinetics and CFD modeling to optimize reactor geometry for forward reaction
  - measure forward kinetics in quartz & Inconel reactors to determine reactor wall catalysis
  - measure forward kinetics in reactor lined with membrane material to determine catalytic activity
  - measure membrane H_2 permeability in presence of clean syngas components (CO_2, H_2O, CO)
  - conduct forward WGS using a membrane reactor at favorable conditions

Project Timeline



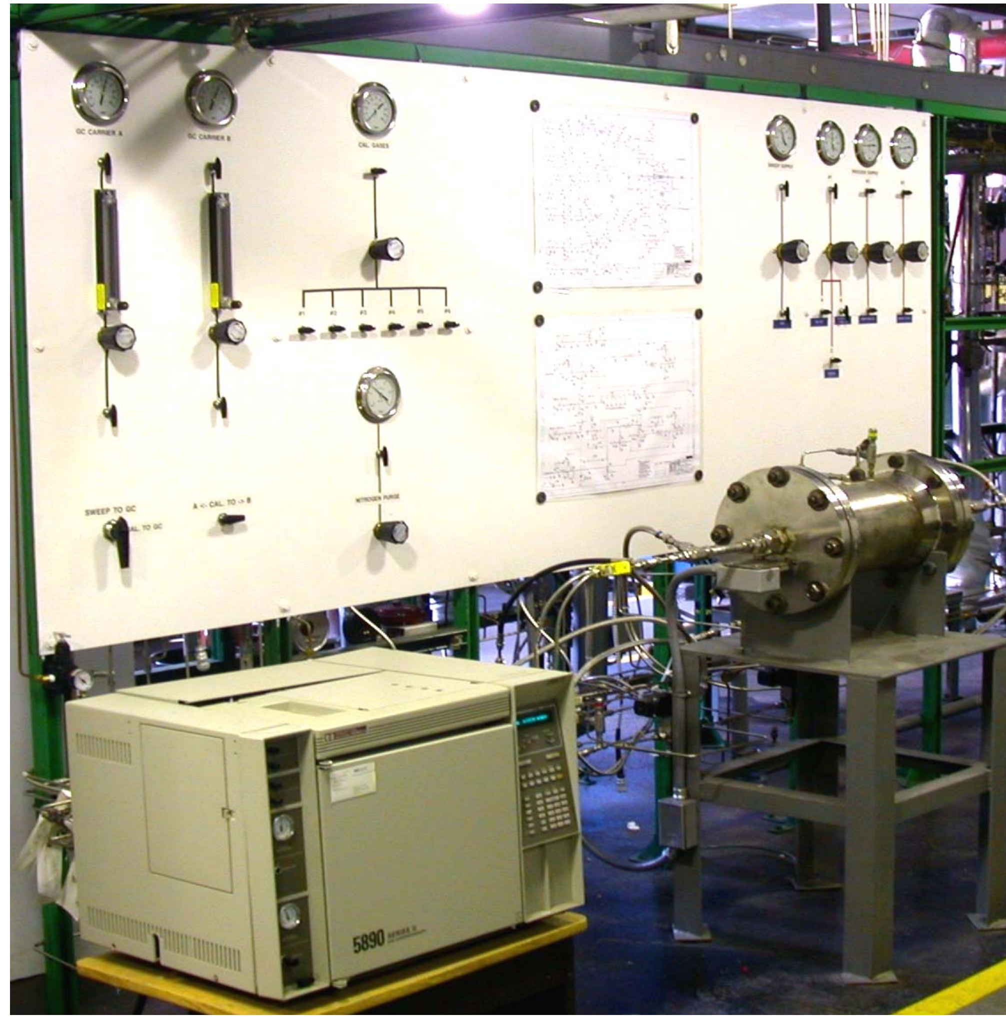
FY02 & FY03 Accomplishments

- **High-T water-gas-shift (WGS) reaction concept:**
  - conducted first-ever hi-T and hi-P reverse WGS reaction kinetics study
  - reverse WGS significantly catalyzed by Inconel reactor wall
  - conducted CFD simulations for effect of reactor geometry on kinetics
  - completed intrinsic kinetics testing of forward WGS reaction
- **Designed & constructed HMT3 unit with enhanced features for membrane reactor testing**
- **F. Bustamante et al., "Very High-T, High-P Homogeneous WGS Reaction Kinetics," AIChE Mtg., Reno NV, 11/01**
- **F. Bustamante et al., "Kinetic Study of the Reverse WGSR in Hi-T, Hi-P Systems," ACS H_2 Symp., Boston MA, 08/02**
- **F. Bustamante et al., "Kinetics of the Homogeneous WGS Reverse Reaction at Elevated Temp.," AIChEJ (in press, 2003)**

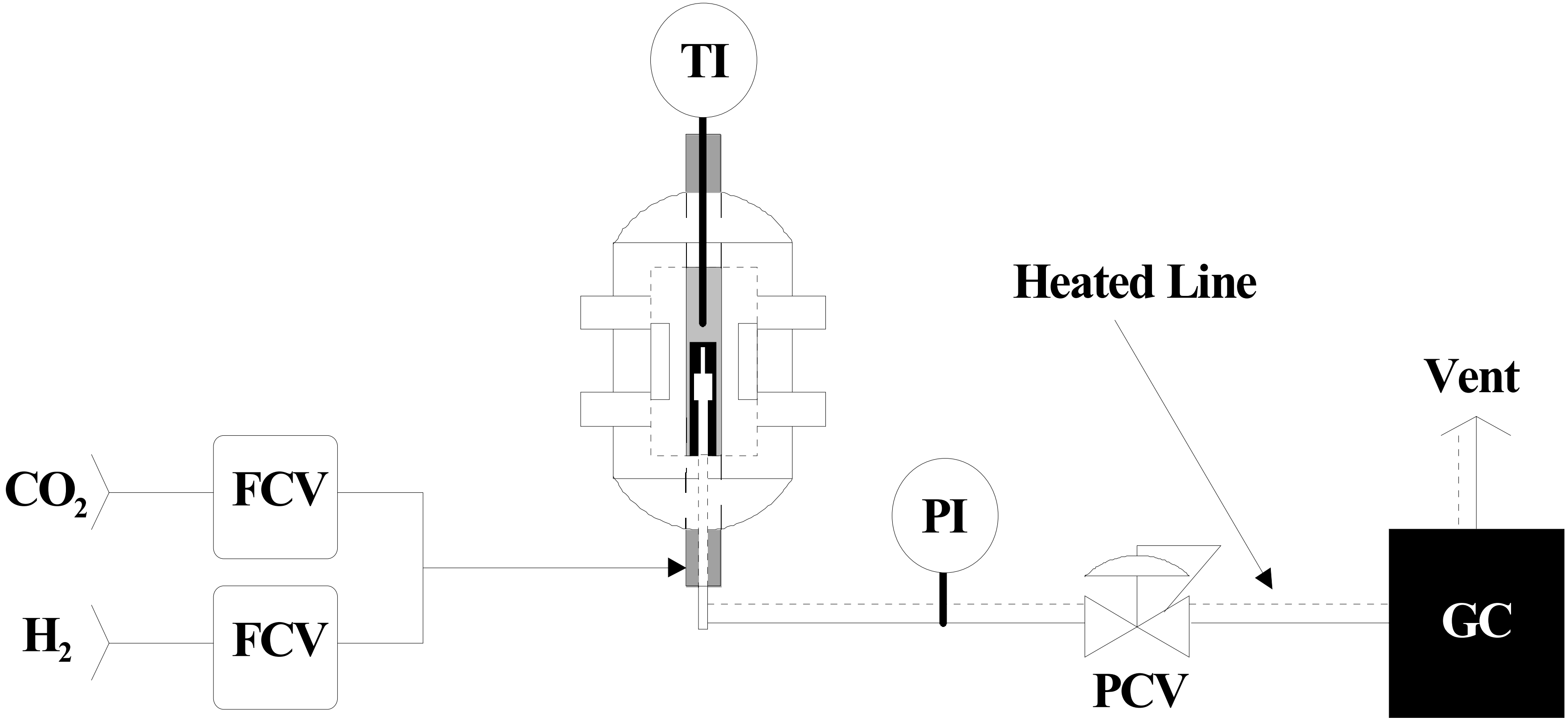
NETL

NETL Hydrogen Separation Facilities

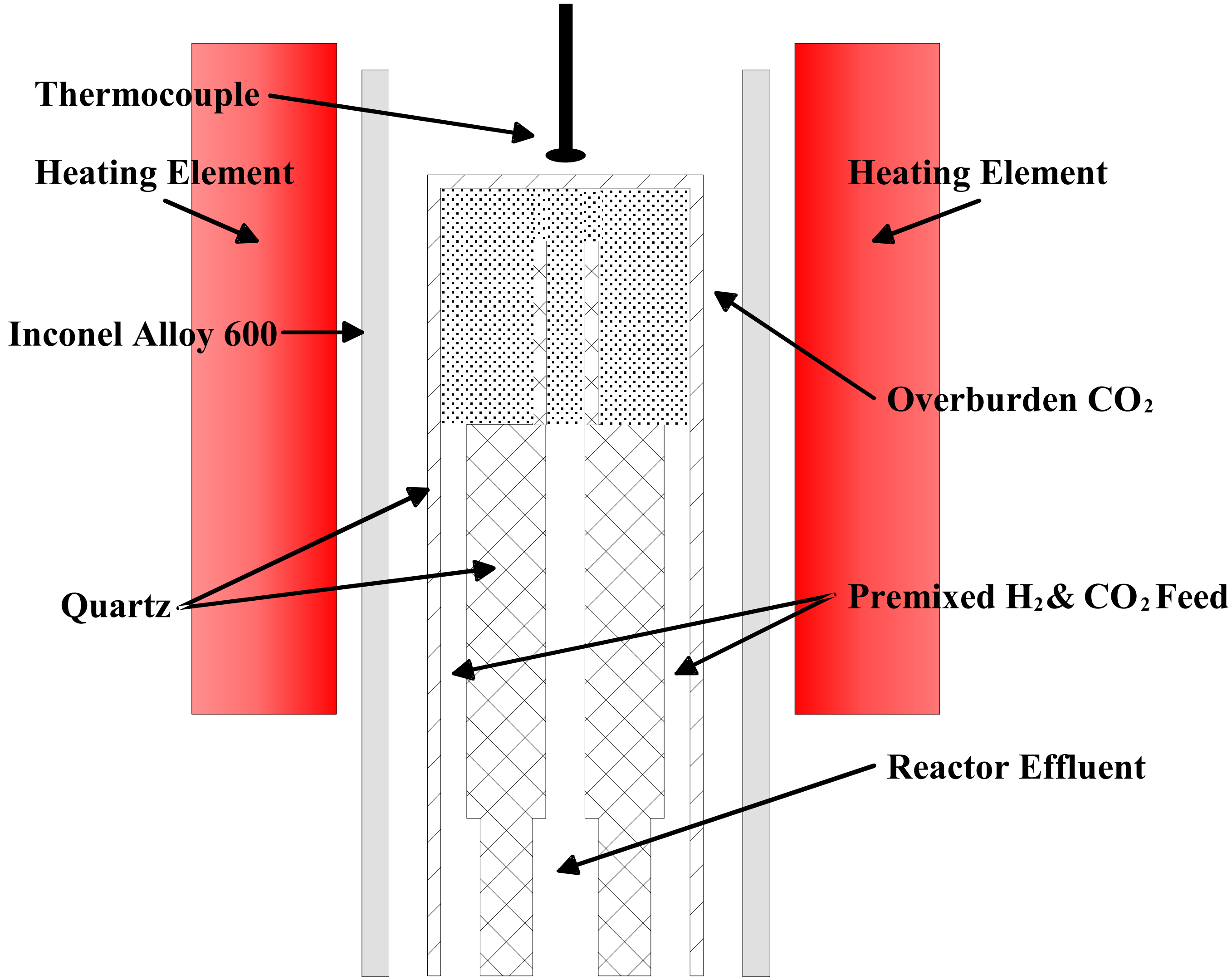
- 3 H_2 Membrane Test Units
- Constructed FY99 to FY02
- Temperatures to 900°C
- Pressures to 400 psi
- Disk & tubular membranes
- 1/4” to 1/2” membranes
- Feed gas flexibility
- Membrane separation & reactor configurations
- “Clean” and “sulfur-laden” gas feedstocks
- Online analysis of products by GC



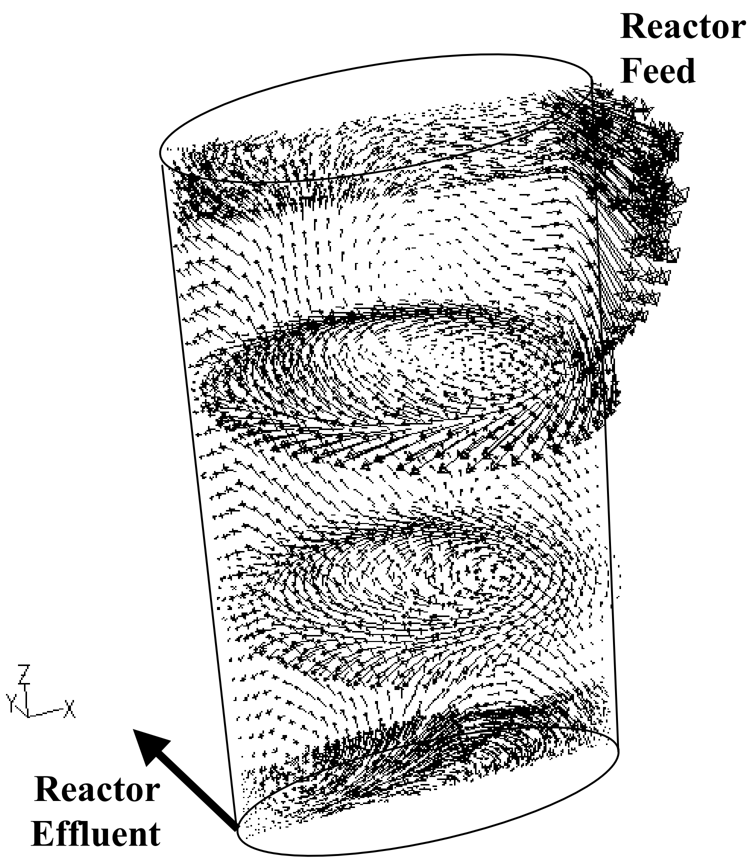
Experimental Setup



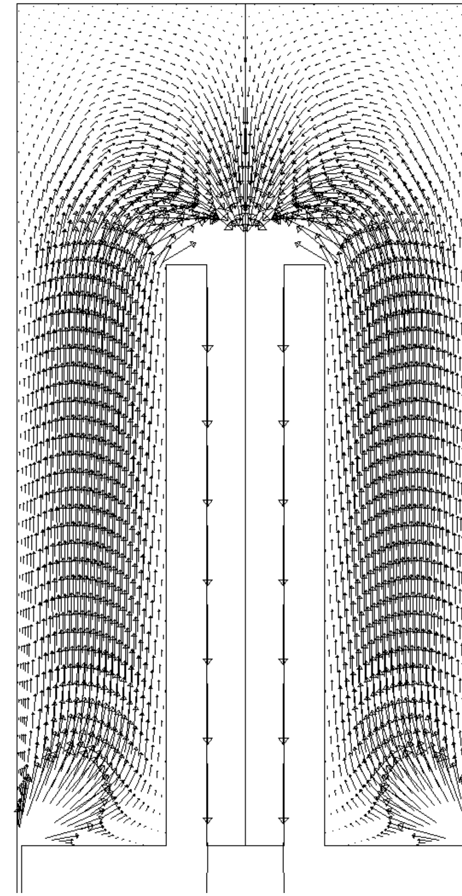
Quartz Reactor



High-T, Low-P <u>Reverse</u> WGS Kinetics
CFD Modeling of Flow Patterns in Reactor



Graven & Long, 1954



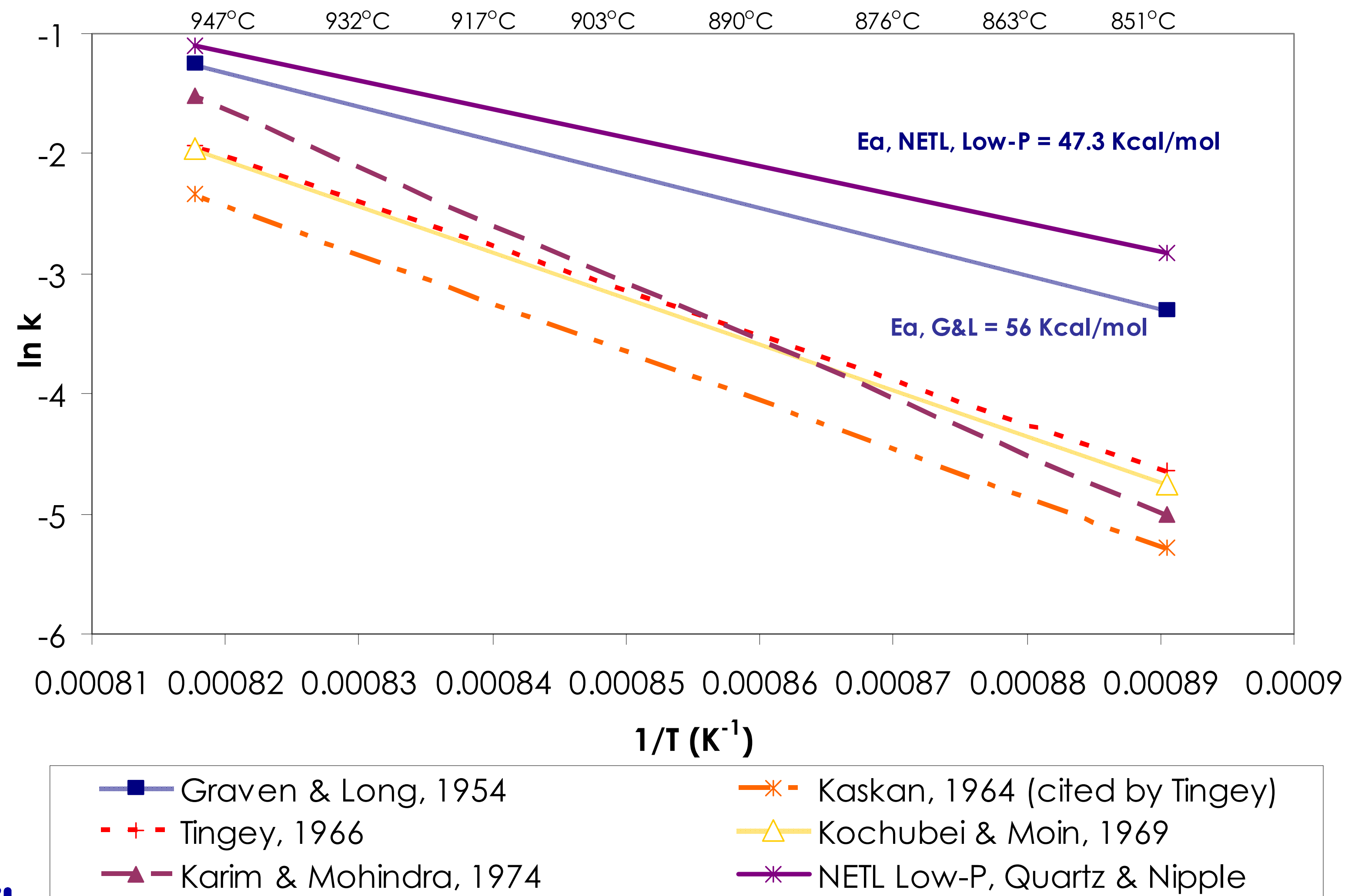
NETL, 2002

Simulations performed by S. Shi (Fluent) and B. Rodgers (NETL)

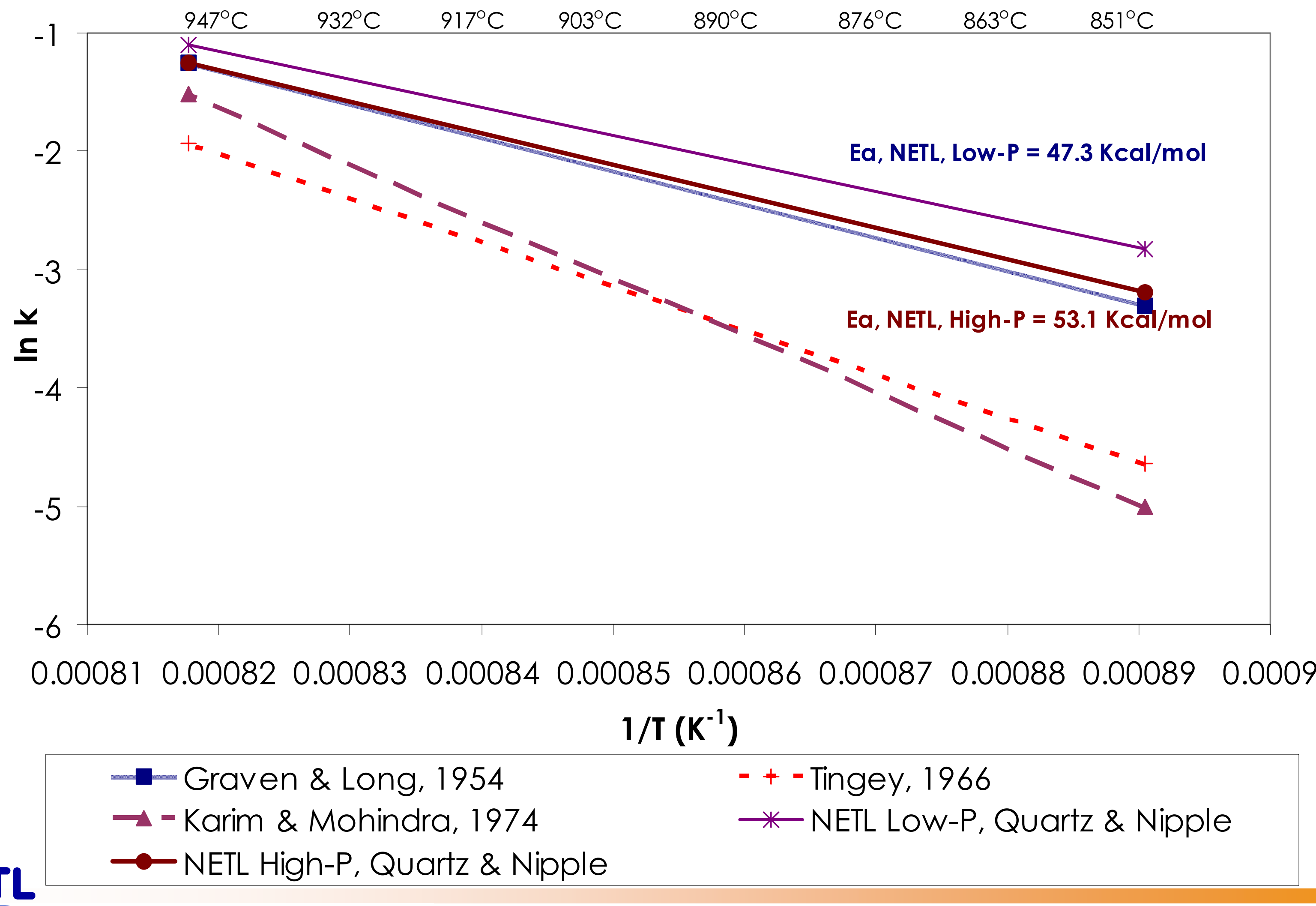
Kinetic Expression for the Reverse WGS Reaction Based on the Bradford Mechanism

- ***Reverse* Reaction**
- $CO_2 + H_2 \longrightarrow H_2O + CO$
- $r = - k_r [H_2]^{0.5}[CO]^1$
- $k_r = k_{ro} \exp(-E_a/RT)$

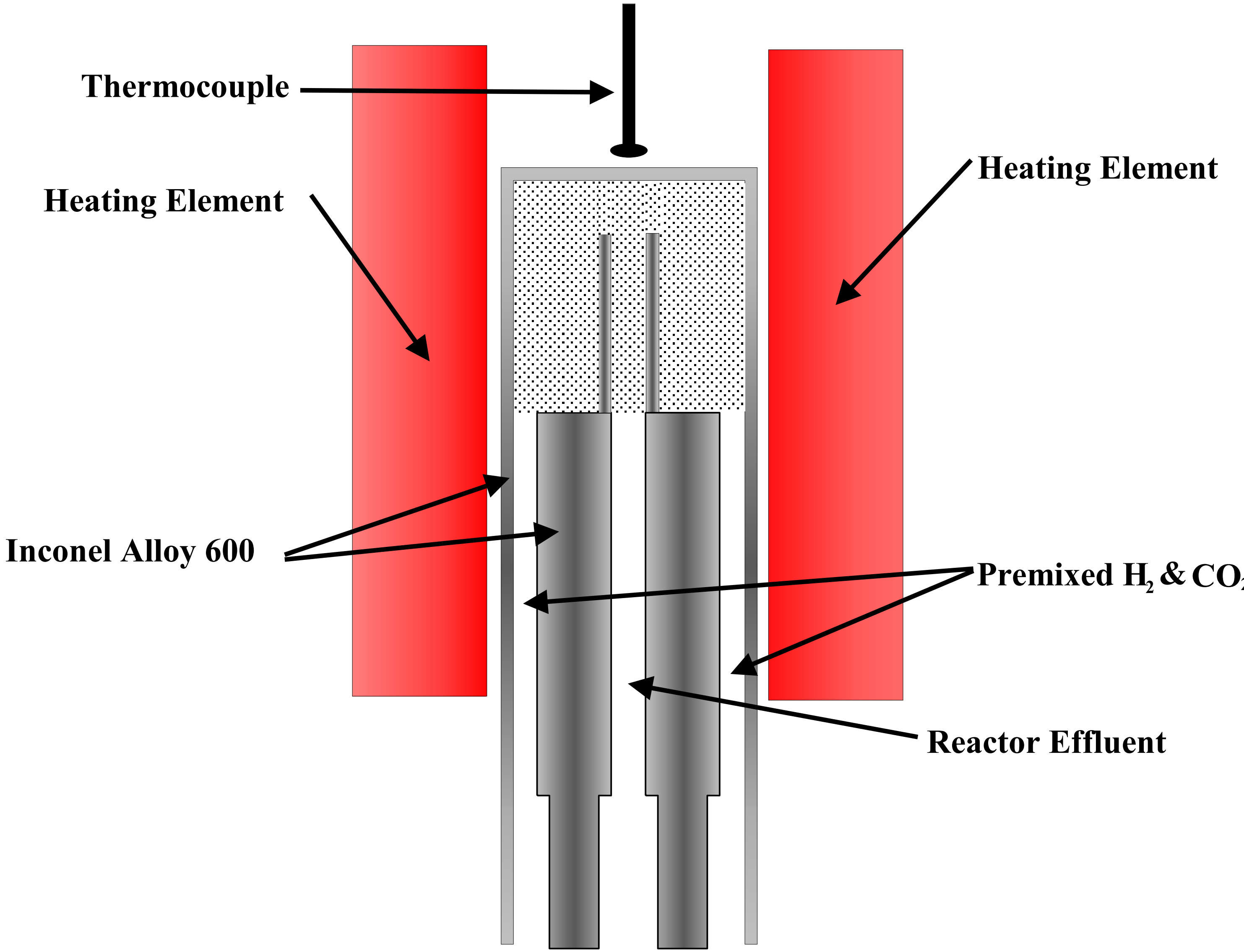
High-Temperature (>850°C), *Low-Pressure* (1 atm) <u>Reverse</u> WGS Quartz Reactor



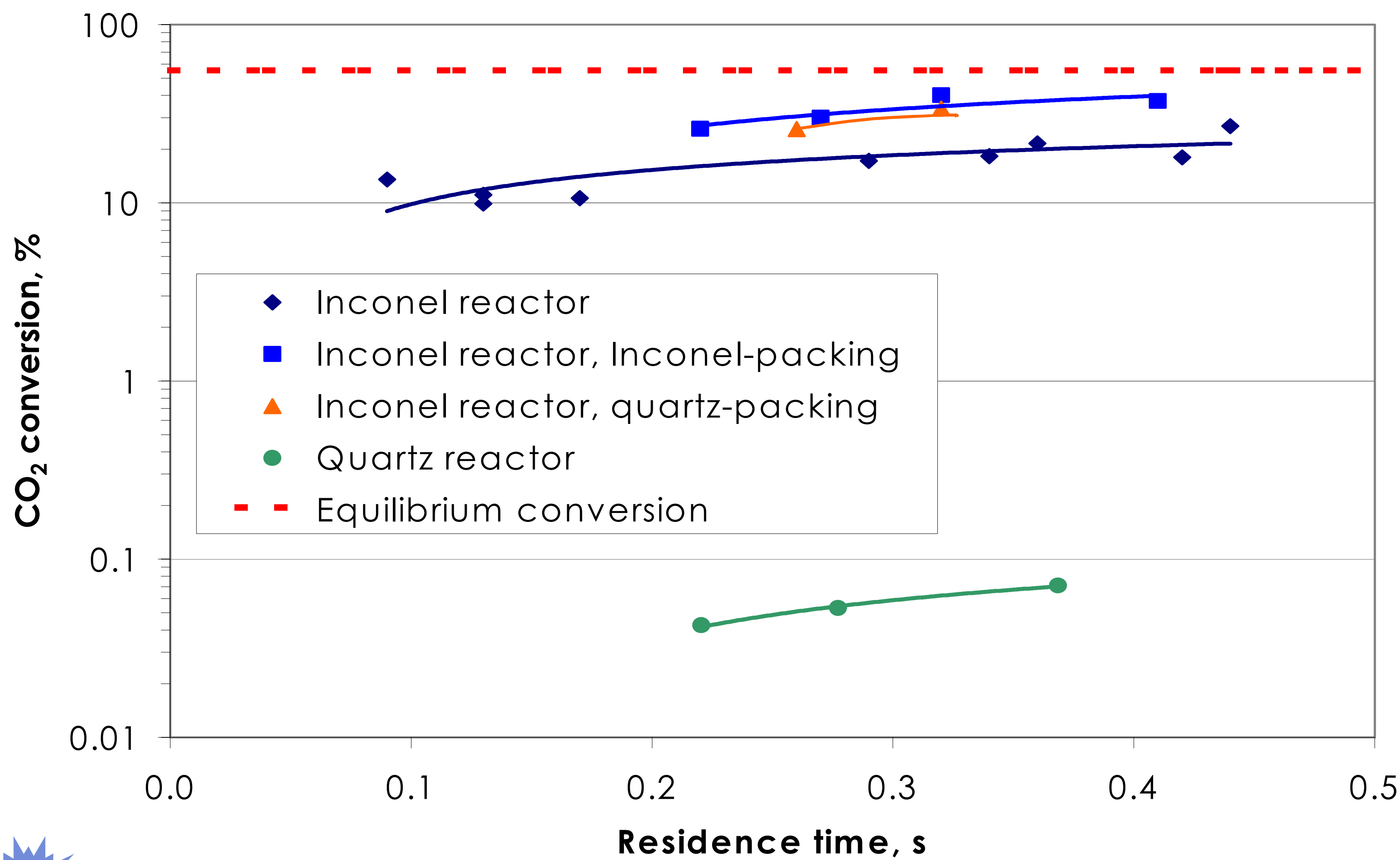
High-Temperature (>850°C), *High-Pressure* (16 atm) Reverse WGS in a Quartz Reactor



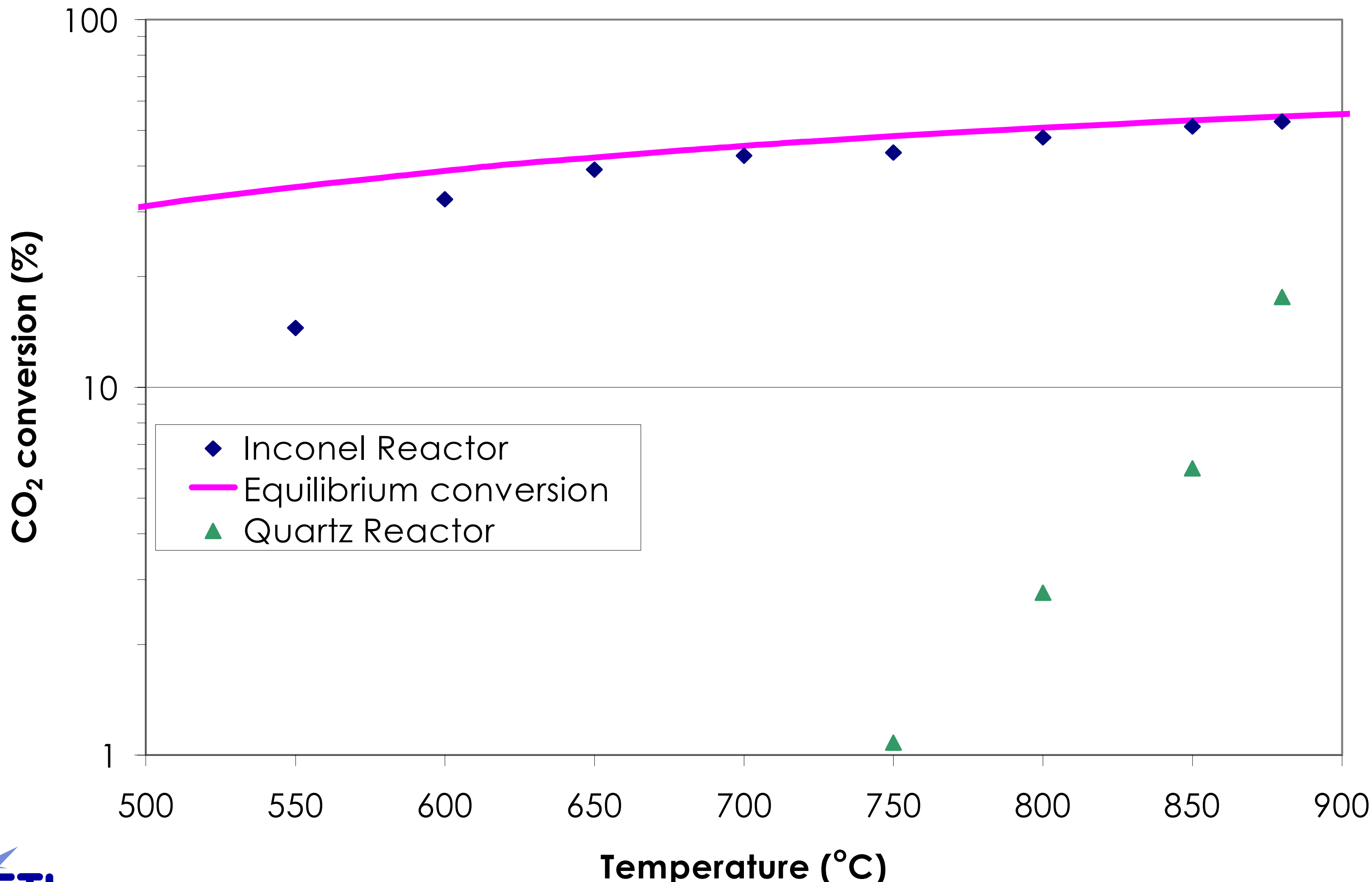
Inconel Reactor



WGS Reverse Reaction Test Data (Inconel reactor, 900°C, 101.3 kPa, Equimolar H_2 and CO_2 feed)



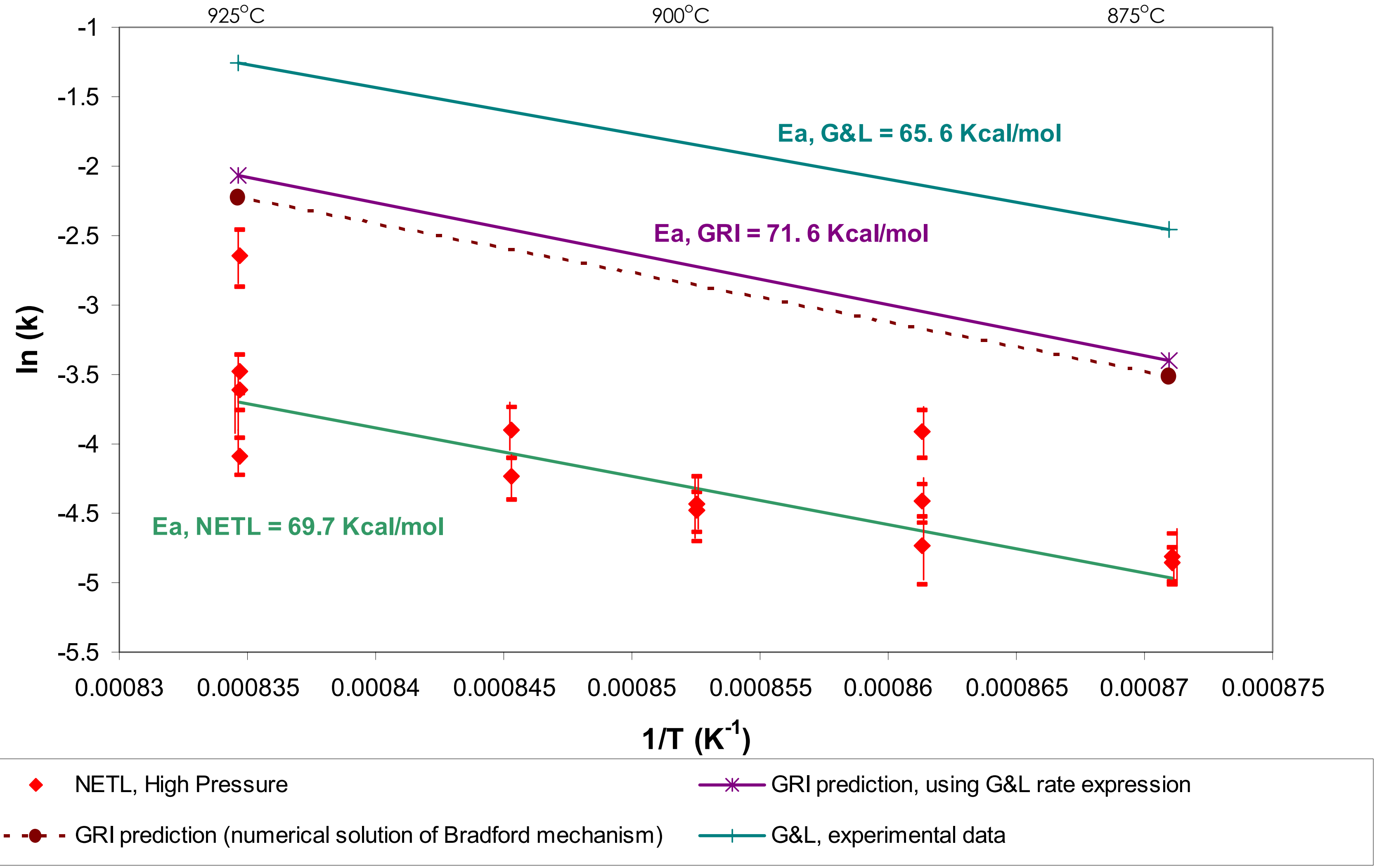
High-Pressure (16 atm), High-Temperature Reverse WGS in an Inconel Reactor



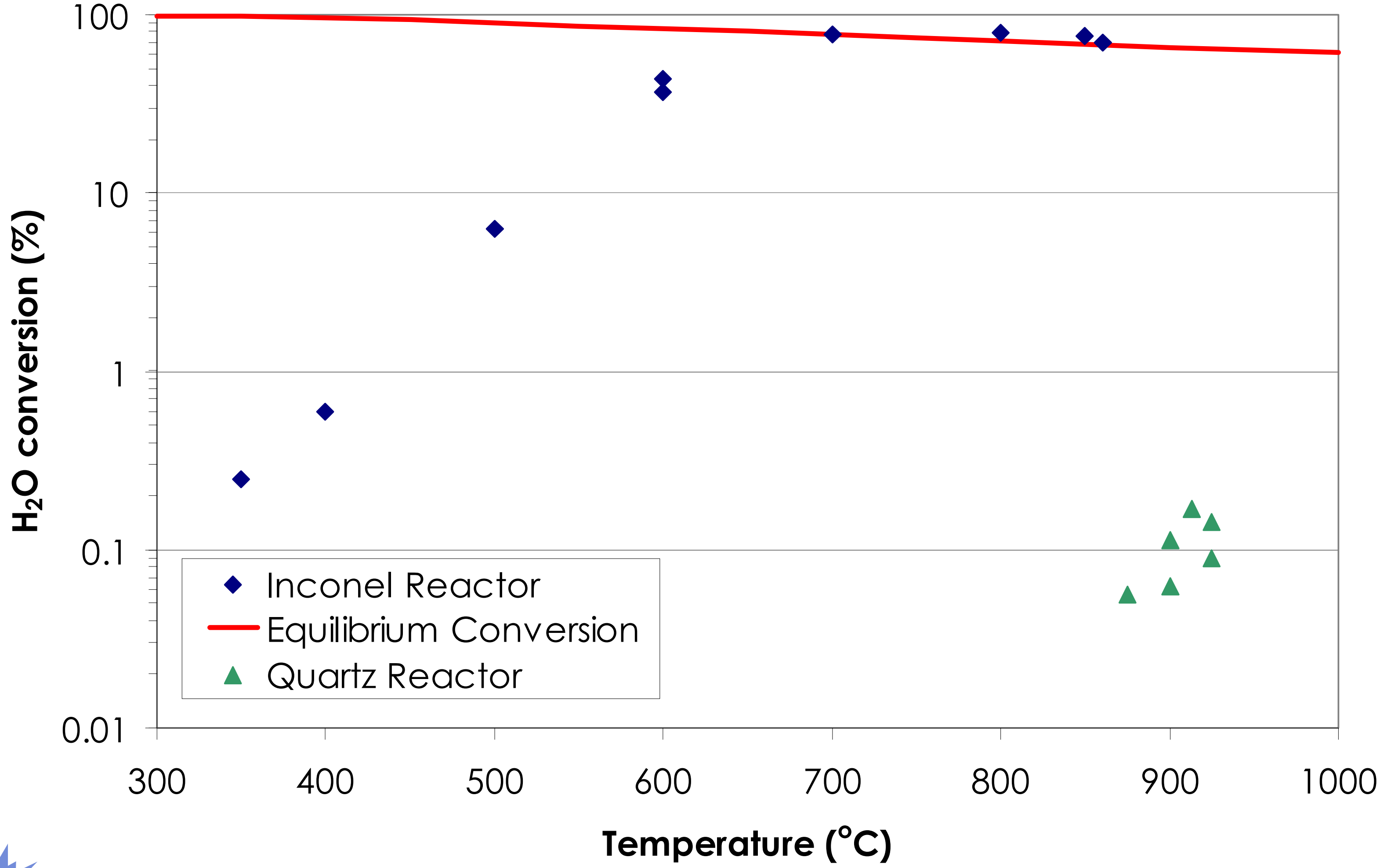
Kinetic Expression for the Forward WGS Reaction Based on the Bradford Mechanism

- ***Forward Reaction***
- $H_2O + CO \longrightarrow CO_2 + H_2$
- $r = -k_f [H_2O]^1[CO]^{0.5}$
- $k_f = k_{fo} \exp(-E_a/RT)$
- Exponents of 1 and 0.5 verified
- Boudouard reaction produces C
- 2CO = C + CO2
- Suppress C deposits via short reaction runs
- Removal of C deposits via overnight O_2 purge to produce CO_2

High-Temperature (>850ºC), *High-Pressure* (16 atm) Forward WGS in a Quartz Reactor



Ambient-P, *Forward* WGS – Inconel Reactor Wall Effects

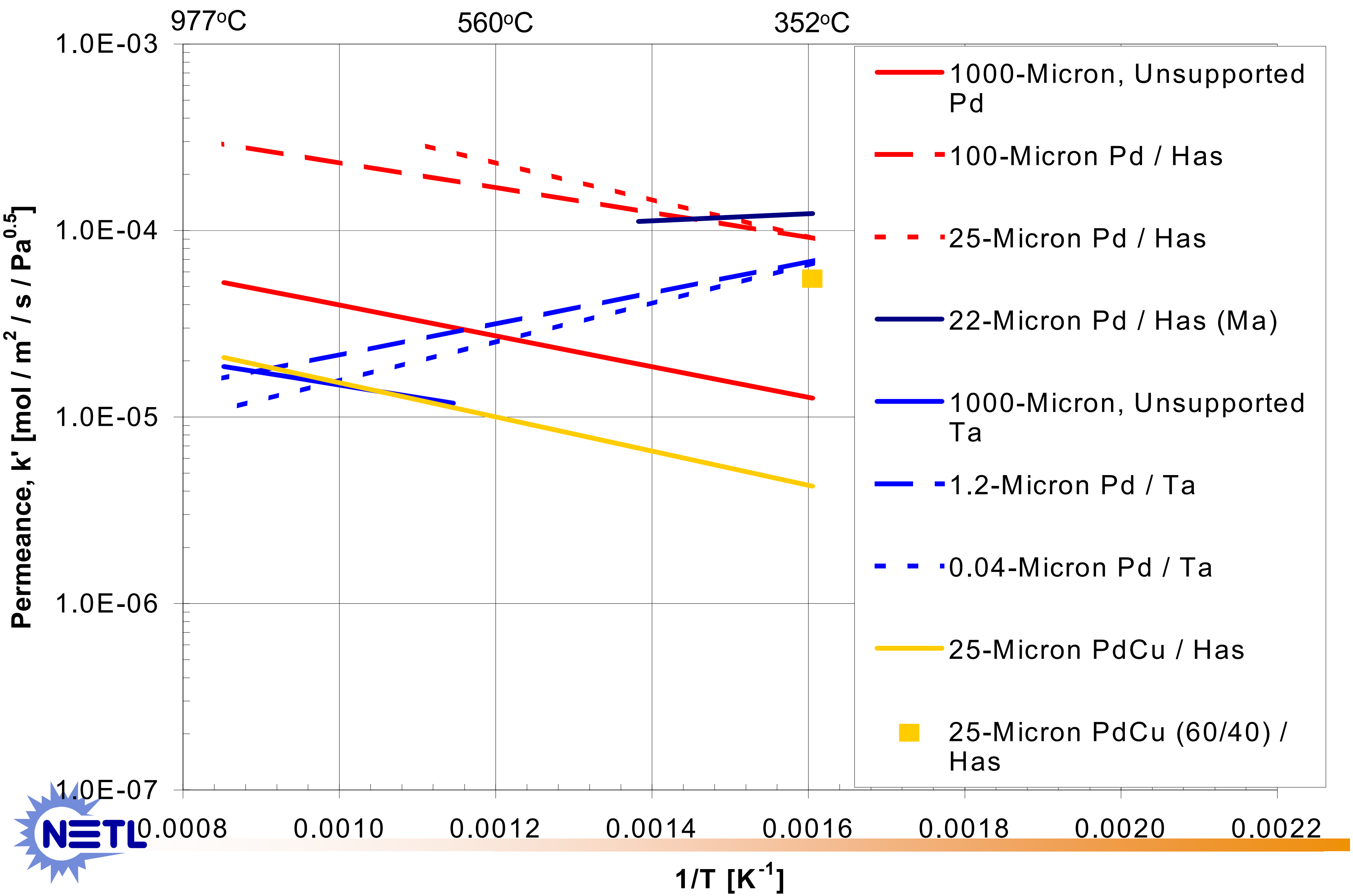


$(x_{CO})_0 = 0.72$, $(x_{H2O})_0 = 0.28$, $(x_{CO2})_0 = (x_{H2})_0$, $\tau \sim 0.5 – 1$ s

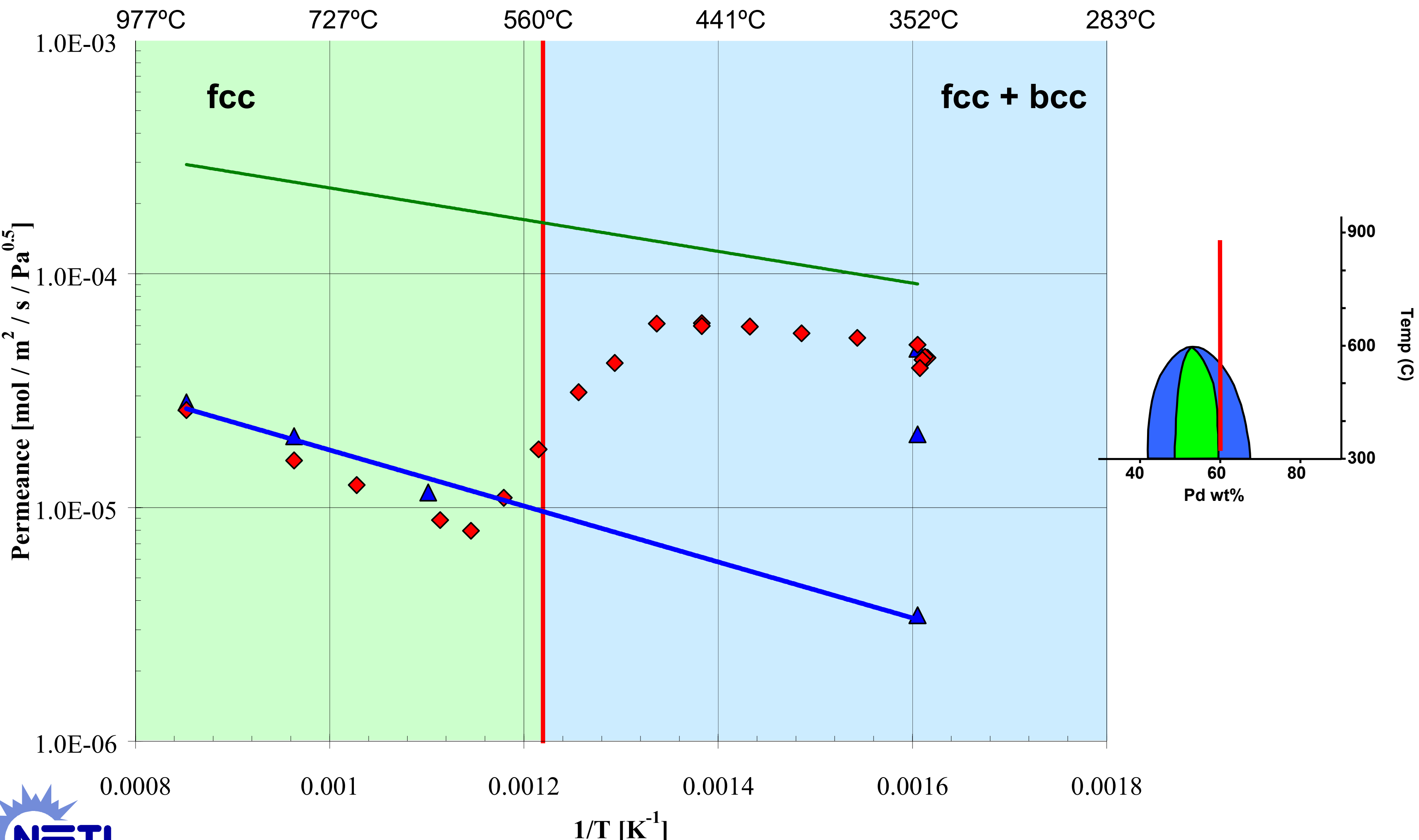
Related Project Activities Funded by DOE-FE

- Development of membrane reactors requires knowledge of both reaction kinetics and membrane performance
- Membranes will be evaluated over a wide range of T (up to 900° C) and P (up to 400 psia)
- The H_2 permeance and selectivity of dense membranes and porous membranes will be investigated
- The effect of CO_2, H_2O and CO on permeance and selectivity will be determined
- The effect of gaseous contaminants (e.g. H_2S) on membrane performance will be evaluated

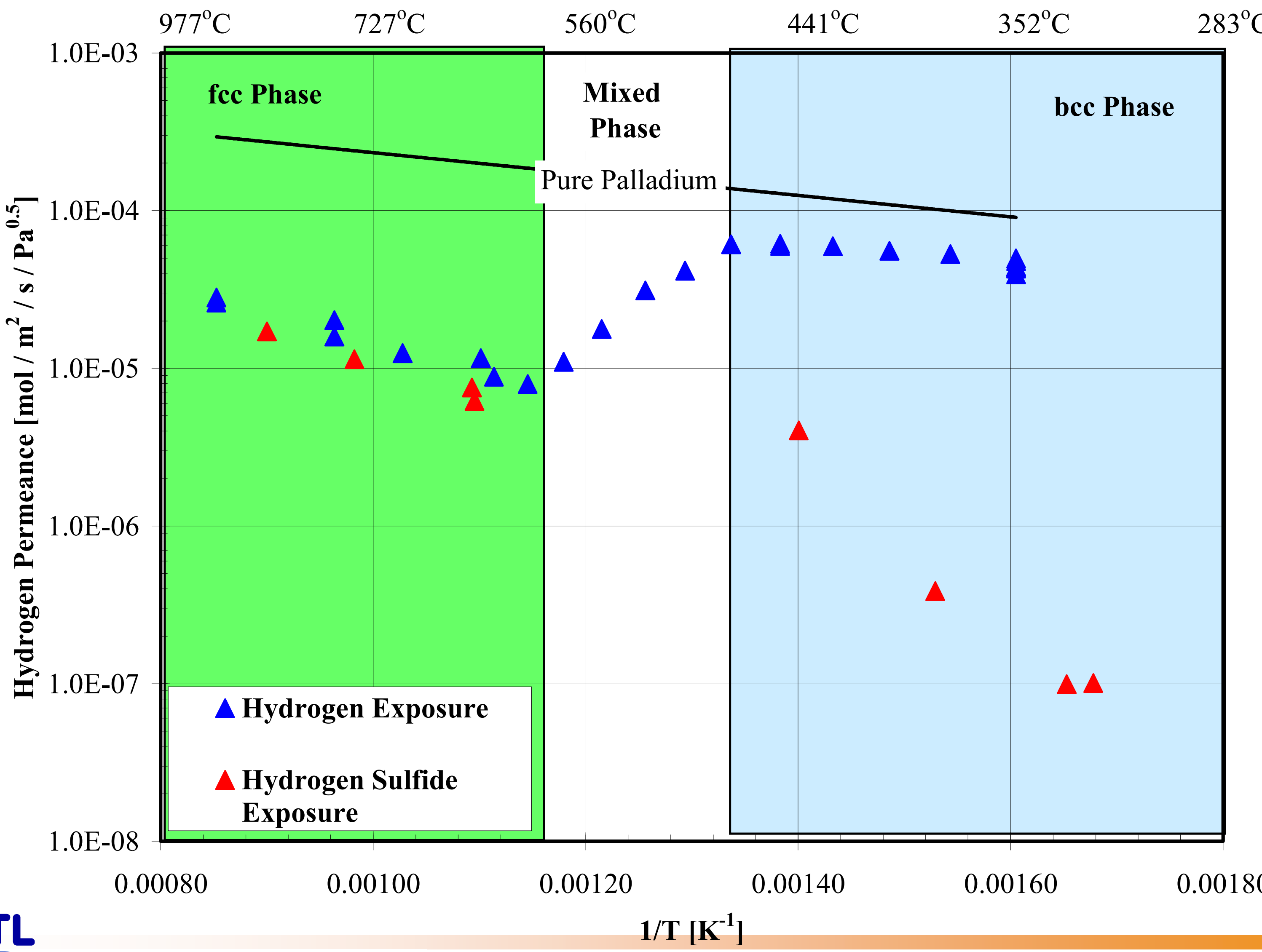
Summary of Membrane Permeability Test Data



60%Pd-40%Cu Alloy Permeance Through Phase Transition



Sulfur Tolerance of 60/40 Pd-Cu



Future Plans

- Kinetics studies of the forward WGS reaction
- Effect of membrane materials on reaction kinetics, e.g. Pd, PdCu alloys
- Effect of sulfur poisoning on catalytic reactor materials, membrane materials, or heterogeneous catalyst particles
- Construction of a sulfur-resistant membrane reactor for the forward water-gas shift reaction
- Incorporation of all reaction kinetics results and permeability results into a high T, high P WGS membrane reactor model