Development of Novel CO_2-Selective Membrane for H_2 Purification

W.S. Winston Ho

The Ohio State University, Columbus, OH

DOE Program Manager: Nancy L. Garland

ANL Technical Advisor: Thomas G. Benjamin

2004 Program Review, Philadelphia, May 24 - 27, 2004

Objectives

- **Produce Enhanced H_2 Product with <10 ppm CO at High Pressure Used for Reforming**
- **Overcome Fuel-Flexible Fuel Processors Barrier L: H_2 Purification/CO Clean-up**
- **Achieve Target: <10 ppm CO in Product Stream**

Budget

- **Total Funding for the Project**
  - **$880,000 (10/01/01 – 09/30/04)**
  - **DOE Share = $704,000**
  - **Contractor Share = $176,000**

- **Funding for FY04 = $346,250**
  - **DOE Share = $277,000**
  - **Contractor Share = $69,250**

Technical Barrier and Target

- **DOE Technical Barrier for Fuel-Flexible Fuel Processors**
  - **L: H_2 Purification/CO Clean-up**
- **DOE Technical Target for Fuel-Flexible Fuel Processors for 2010**
  - **< 10 ppm CO in Product Stream**

Approach

Use CO_2-Selective Membrane to:

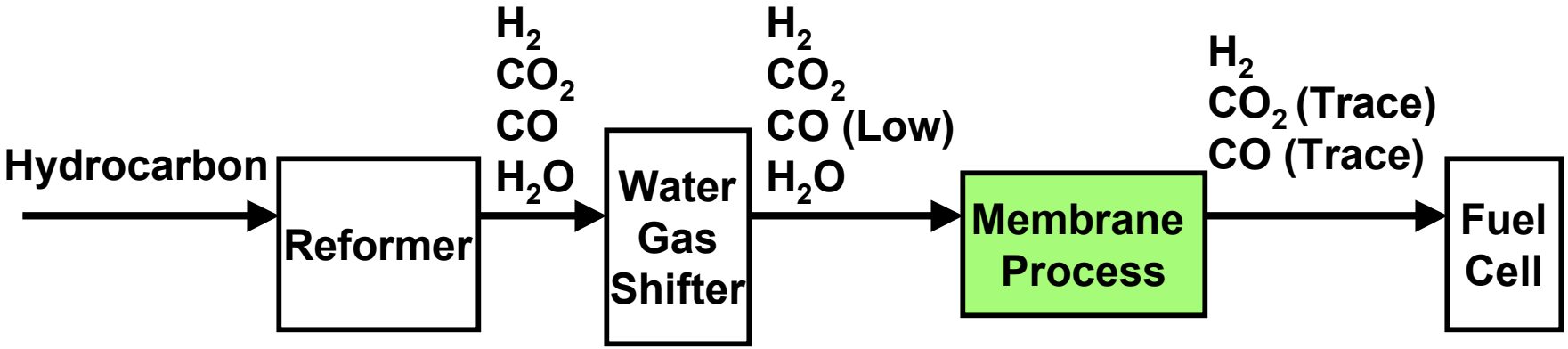
- Remove CO_2 for H_2 Enhancement
- Drive Water-Gas-Shift (WGS) Reaction to Product Side

$$CO + H_2O \rightarrow H_2 + CO_2 \uparrow$$

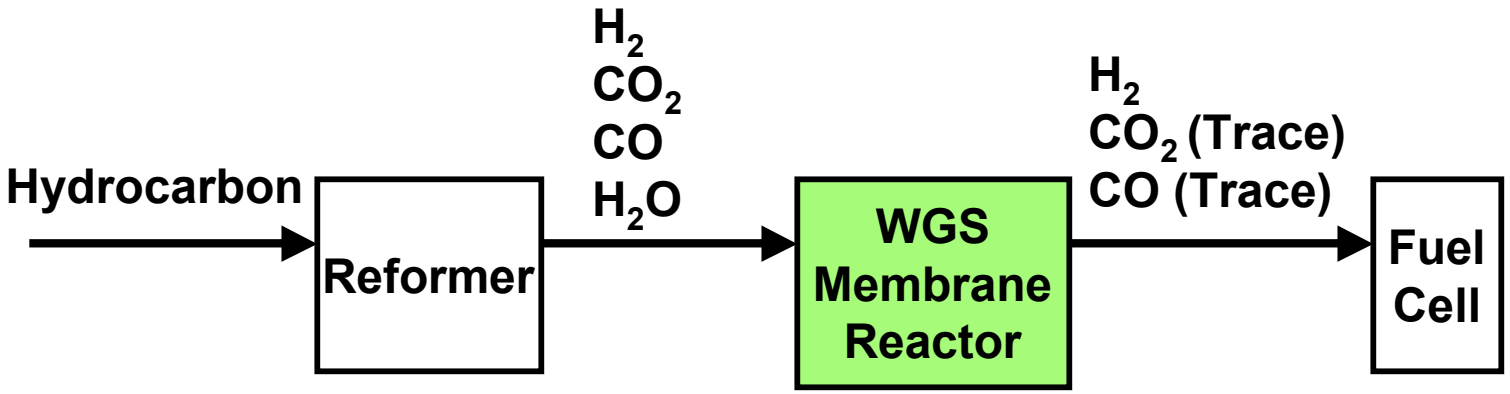
- Decrease CO to <10 ppm via CO_2 Removal

Fuel Processing with CO_2-Selective Membranes for Fuel Cells

- Low Temperature CO_2-Selective Membrane



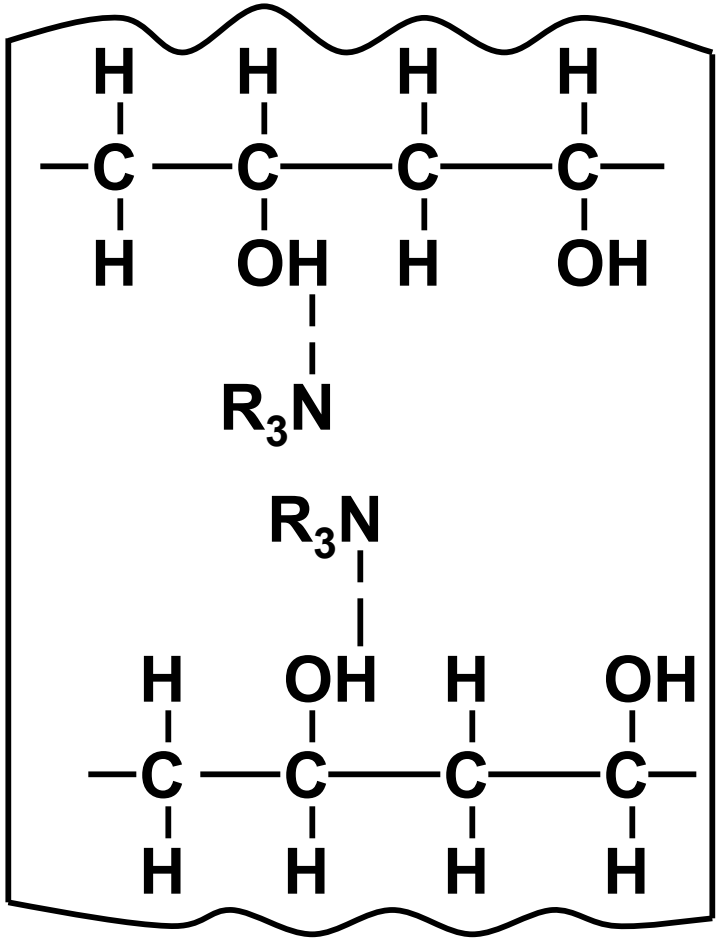
- High Temperature CO_2-Selective Membrane

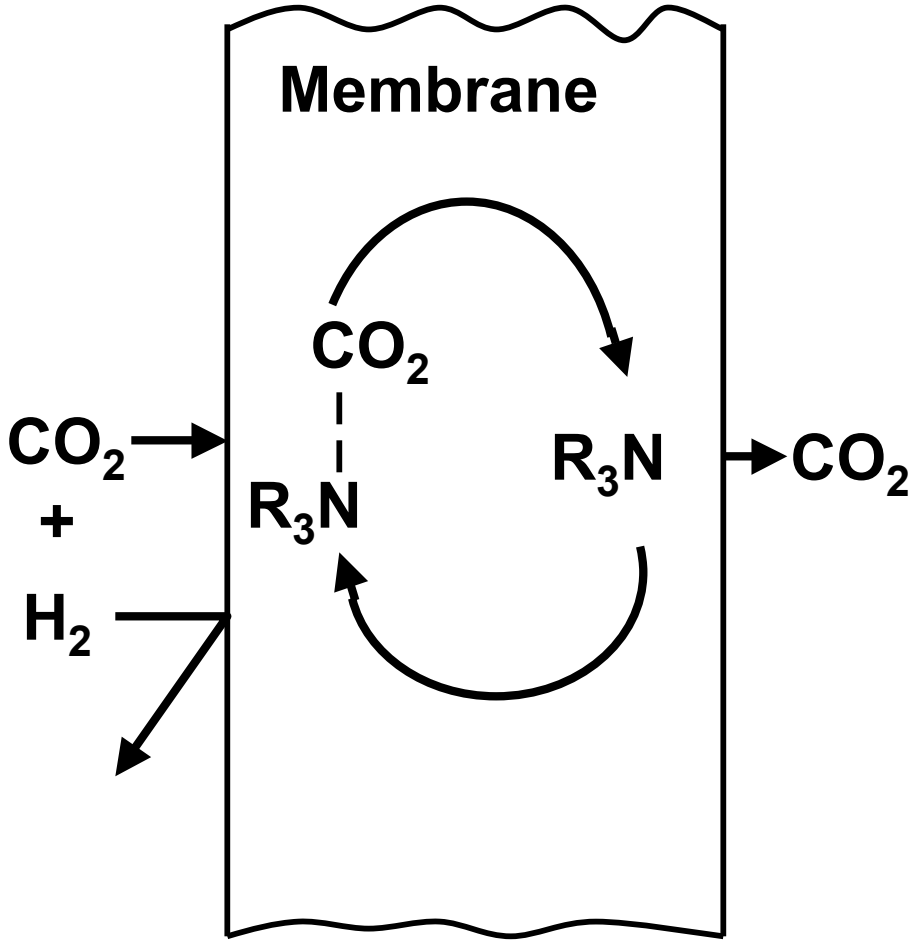


$$CO + H_2O \rightarrow H_2 + CO_2 \uparrow$$

CO_2-Selective Membranes by Incorporating Amines in Polymer Networks … Facilitated Transport

Example: Polyvinylalcohol-Containing Amine Membrane





Project Safety

- **CO Monitor / Alarm Installed Next to Membrane Units for Personnel Safety**
  - **Alarm Never Sounded So Far for >2.5 Years of Membrane Operations (MOs), Indicating Safe MOs**
- **N_2 Purging Used in Ovens to Prevent CO / H_2 Accumulation from Any System Leakage**
  - **Ovens Provide Precise Temperatures for Membrane Units for Accurate Exp. Measurements**
  - **Locking Device Installed to Prevent N_2 Purging from Accidental Shutdown**
- **Membrane Units Housed in a Hood**
  - **Locking Device Installed to Prevent Hood from Accidental Shutdown**
- **Safety Vulnerability Techniques Used (HAZOP, FMEA)**

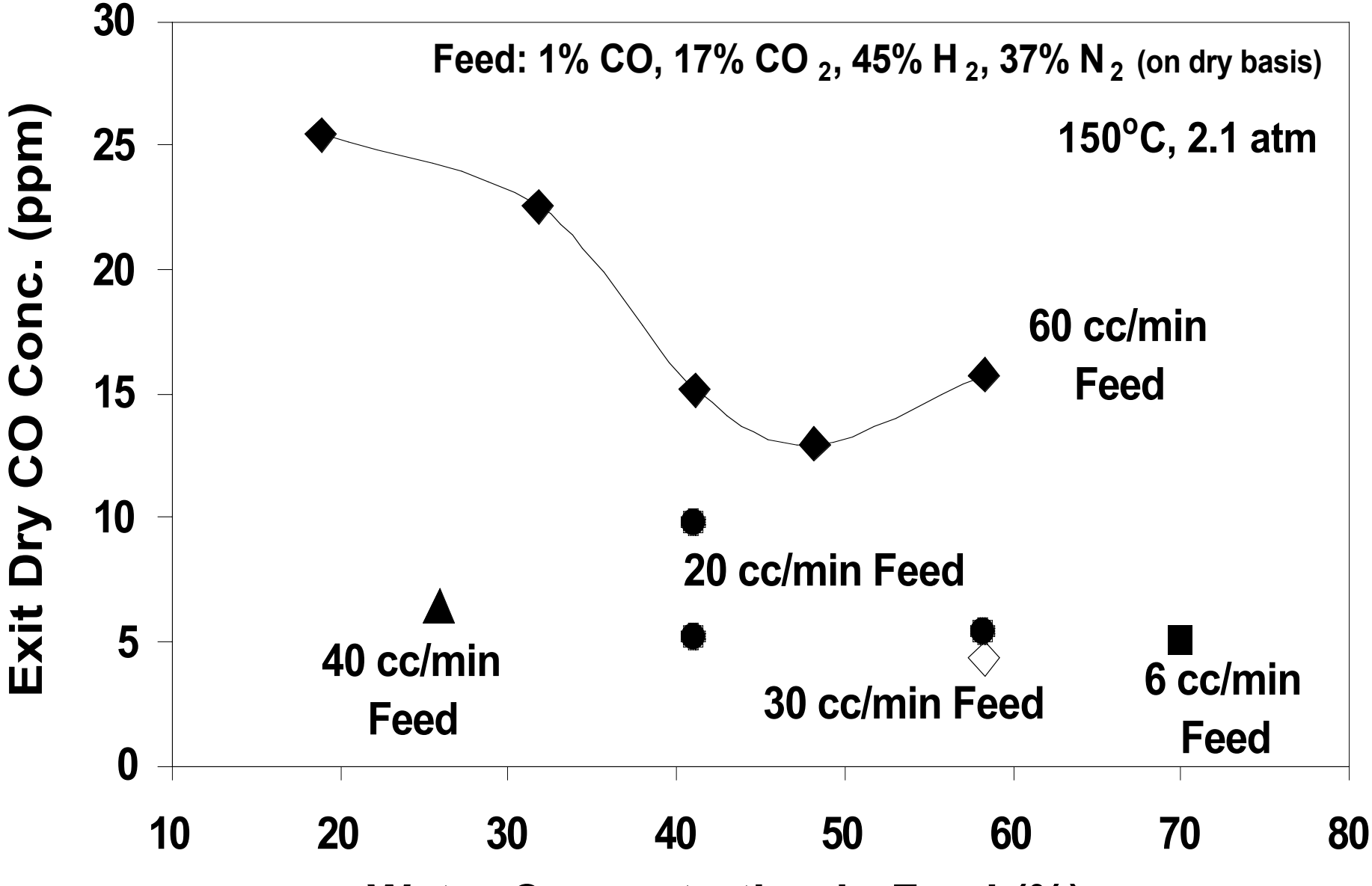
Project Timeline

Task	2001 4Q	2002 1Q	2002 2Q	2002 3Q	2002 4Q	2003 1Q	2003 2Q	2003 3Q	2003 4Q	2004 1Q	2004 2Q	2004 3Q
Phase 1												
1. Modeling Study to Show <10 ppm CO Feasible	———	———	———	———	Δ							
2. Synthesis of Novel Membranes	———	———	———	———								
Phase 2												
3. Characterization of Membranes					———	———	———	———				
4. Set-up of Lab Reactor					———	———						
5. Membrane Fabrication					———	———	———	———				
6. Proof-of-Concept Demo							———	———	Δ			
Phase 3												
7. Set-up of Membr. Reactor									———	———		
8. Fabrication of Membrane Module/Device									———	———	———	———
9. Membrane Reactor Demo											———	Δ

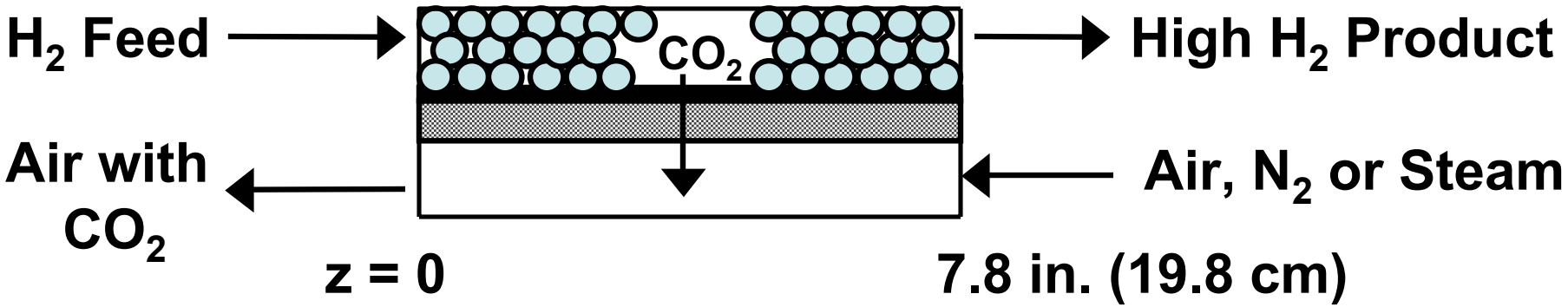
Technical Accomplishments

- **WGS Membrane Reactor Experiments Showed**
  < 10 ppm CO – Project Milestone Achieved
  - **Small Cell: Circular (Laboratory Membrane Cell)**
  - **Big Cell: Rectangular with Well-defined Flow (7.5X Small Cell)**
    + **Data in Line with Model**
- **CO_2 Removed Effectively to ~30 ppm**
  - **In Line with CO_2 Model Developed**
- **Membranes with High CO_2/H_2 & CO_2/CO Selectivities & High CO_2 Flux Synthesized**
- **<10 ppb H_2S Achieved Experimentally (Outside Project Scope)**
  - **H_2S Model Developed Shows This H_2S Achievable in Entrance Section**

WGS Membrane Reactor Experiments Showed < 10 ppm CO: Small Cell



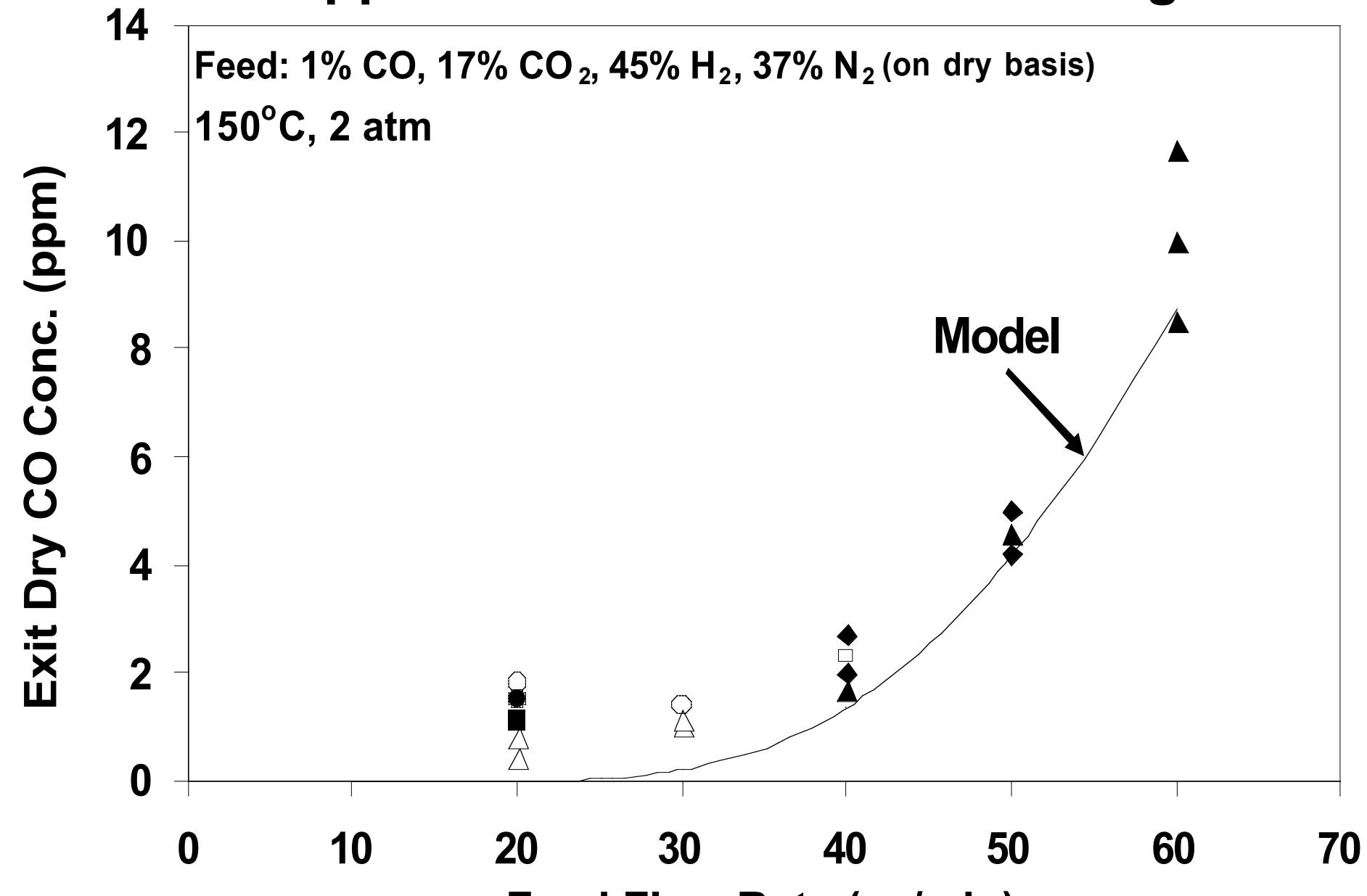
CO_2-Selective Membrane Reactor: Experiments and Modeling



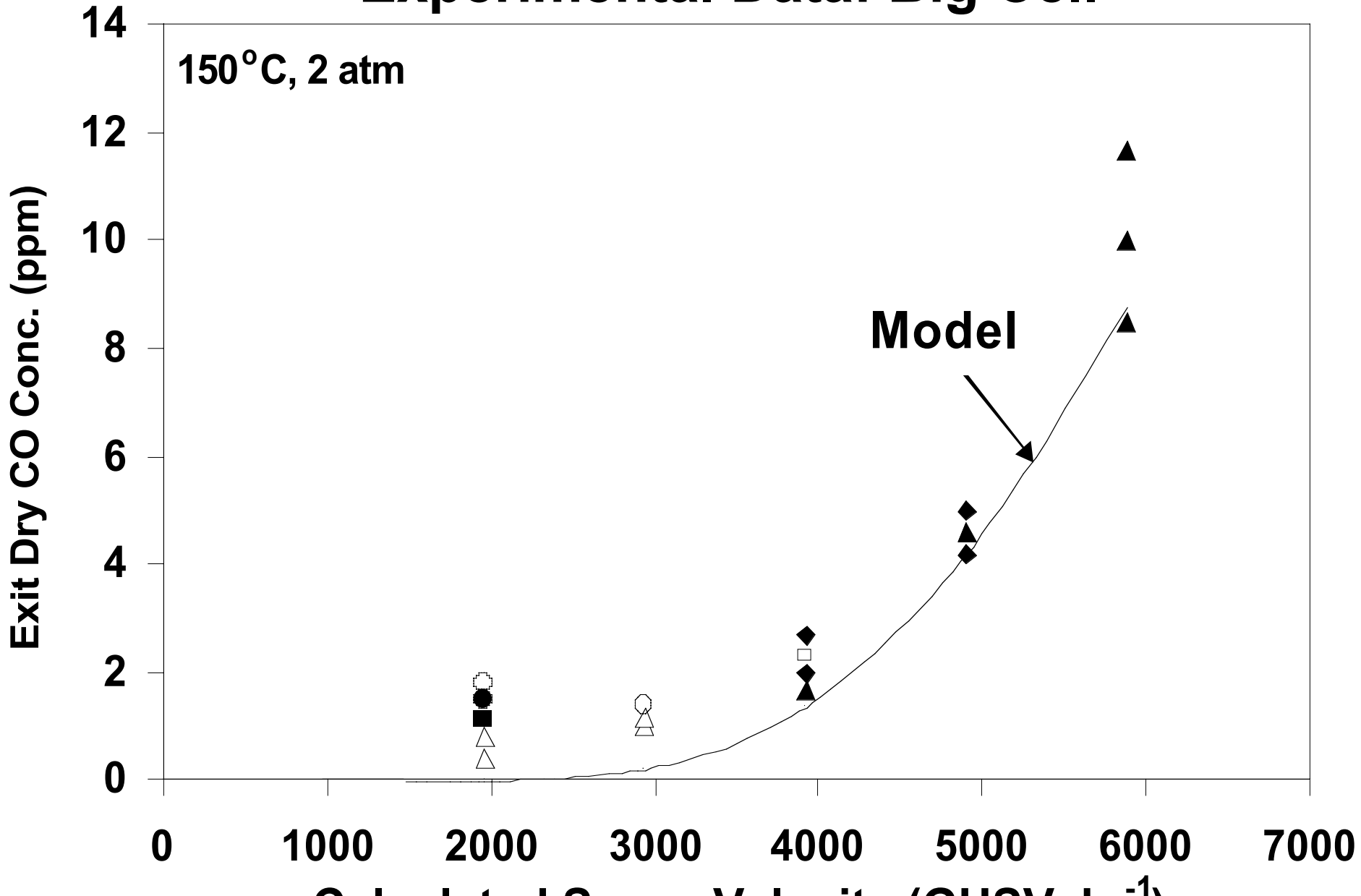
Big Cell

- Well-defined Gas Flow and Velocity
- Suitable for Modeling and Scale-up

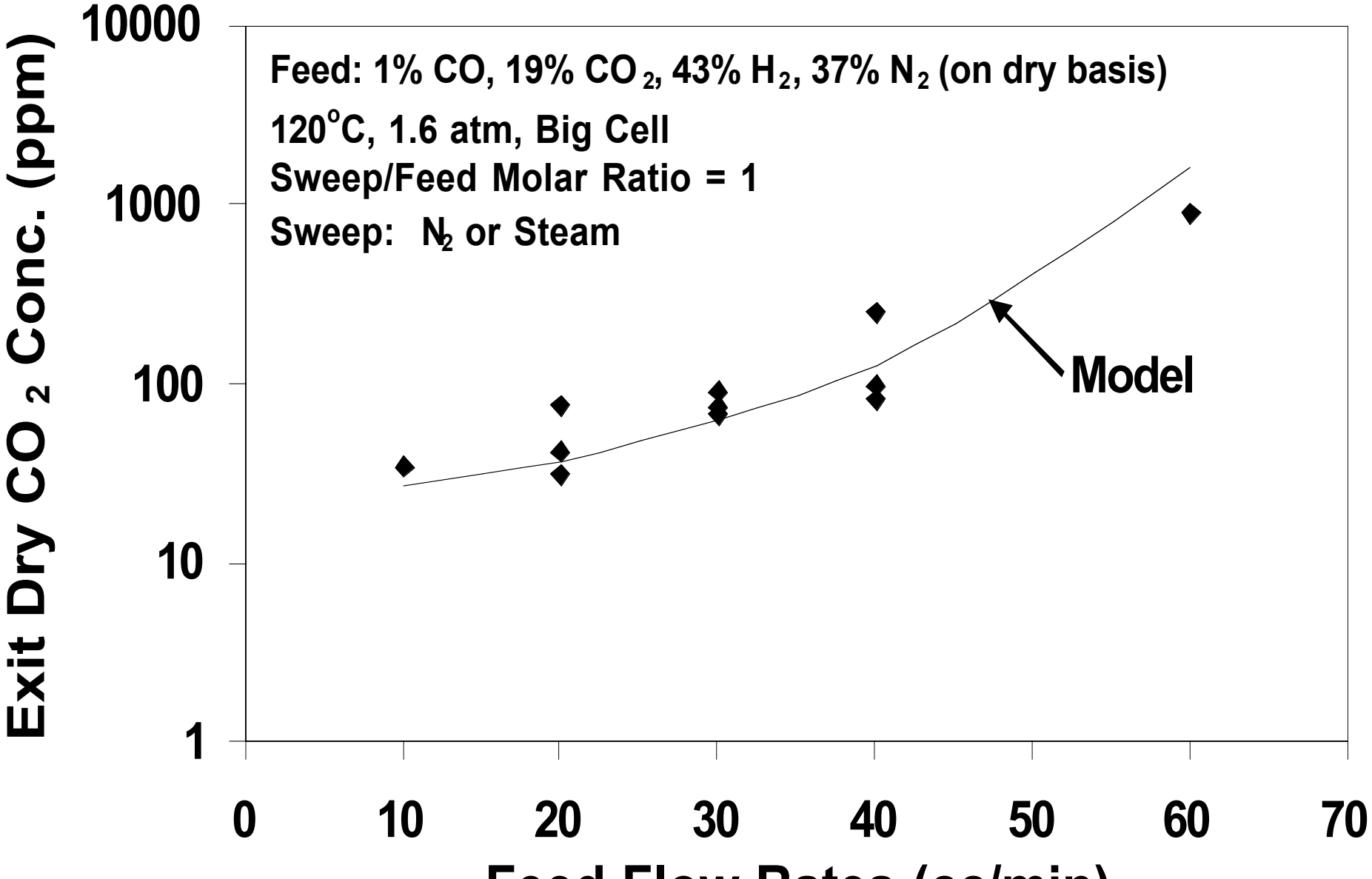
WGS Membr. Reactor Experiments Showed < 10 ppm CO in Line with Model: Big Cell



Calculated Space Velocity Based on Experimental Data: Big Cell

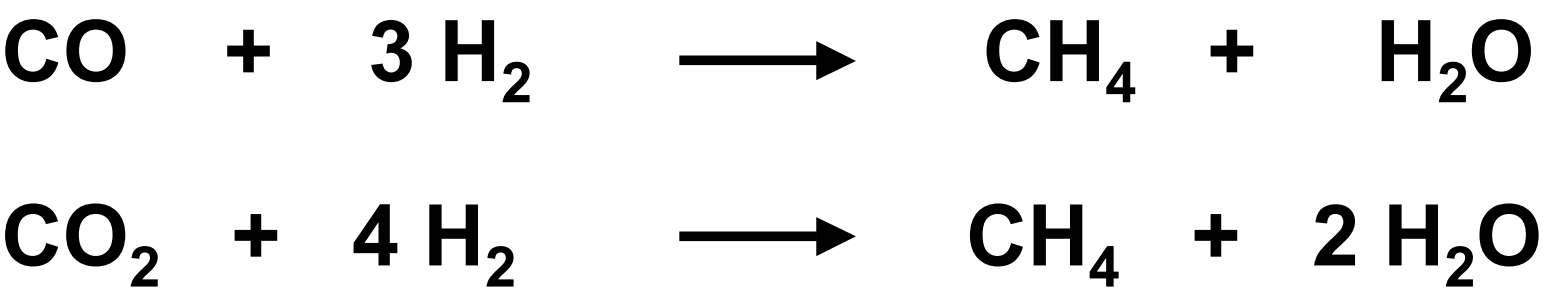


CO_2 Removed Effectively -- CO_2 Concentration in Retentate



Methanation Readily Converts Carbon Oxides to Methane

- **Methanation (at ~160 – 180°C)**



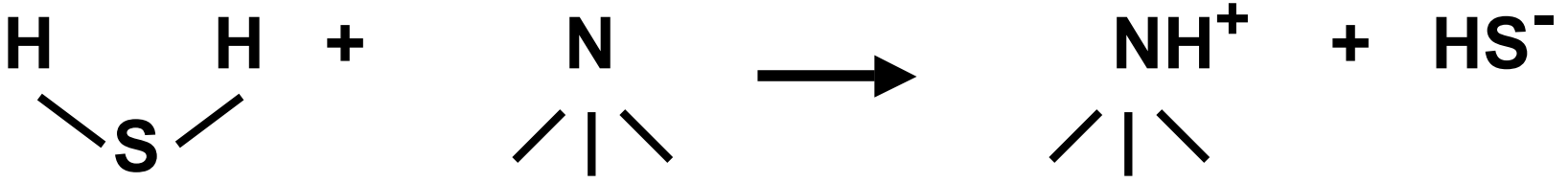
- **Important to Remove CO_2 as Much as Possible before Methanation**
- **Exit CO Concentration < 5 ppm**

H_2S Removal Rate Expected to be Faster than CO_2 Rate
(Outside the Project Scope)

- CO_2 Reaction via Mainly Carbamate Formation

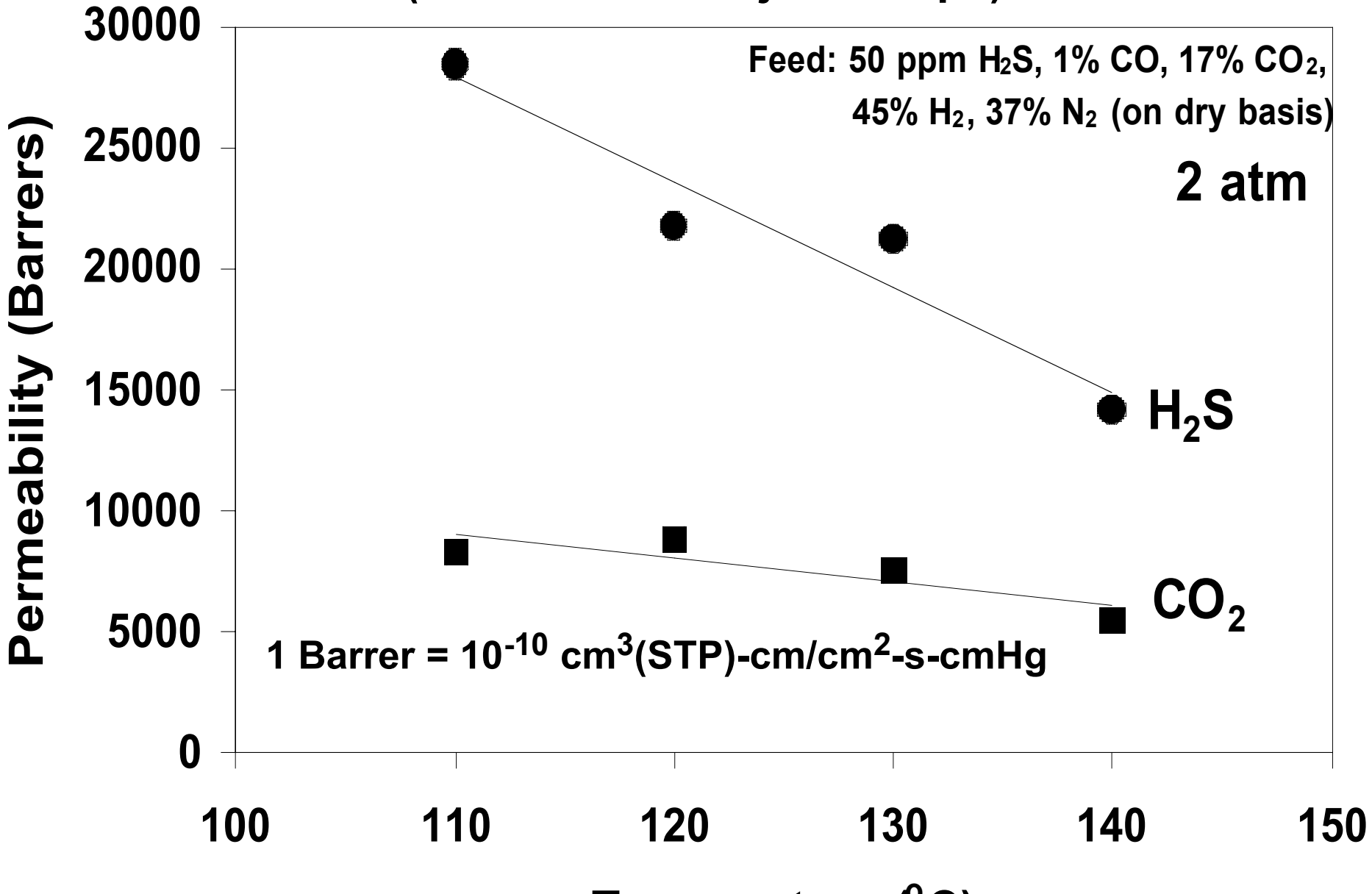
$$2\ R\text{-}NH_2 + CO_2 \rightarrow R\text{-}NH\text{-}COO^- + R\text{-}NH_3^+$$

- H_2S Reaction via Small Proton Transfer
  … Very High Rate



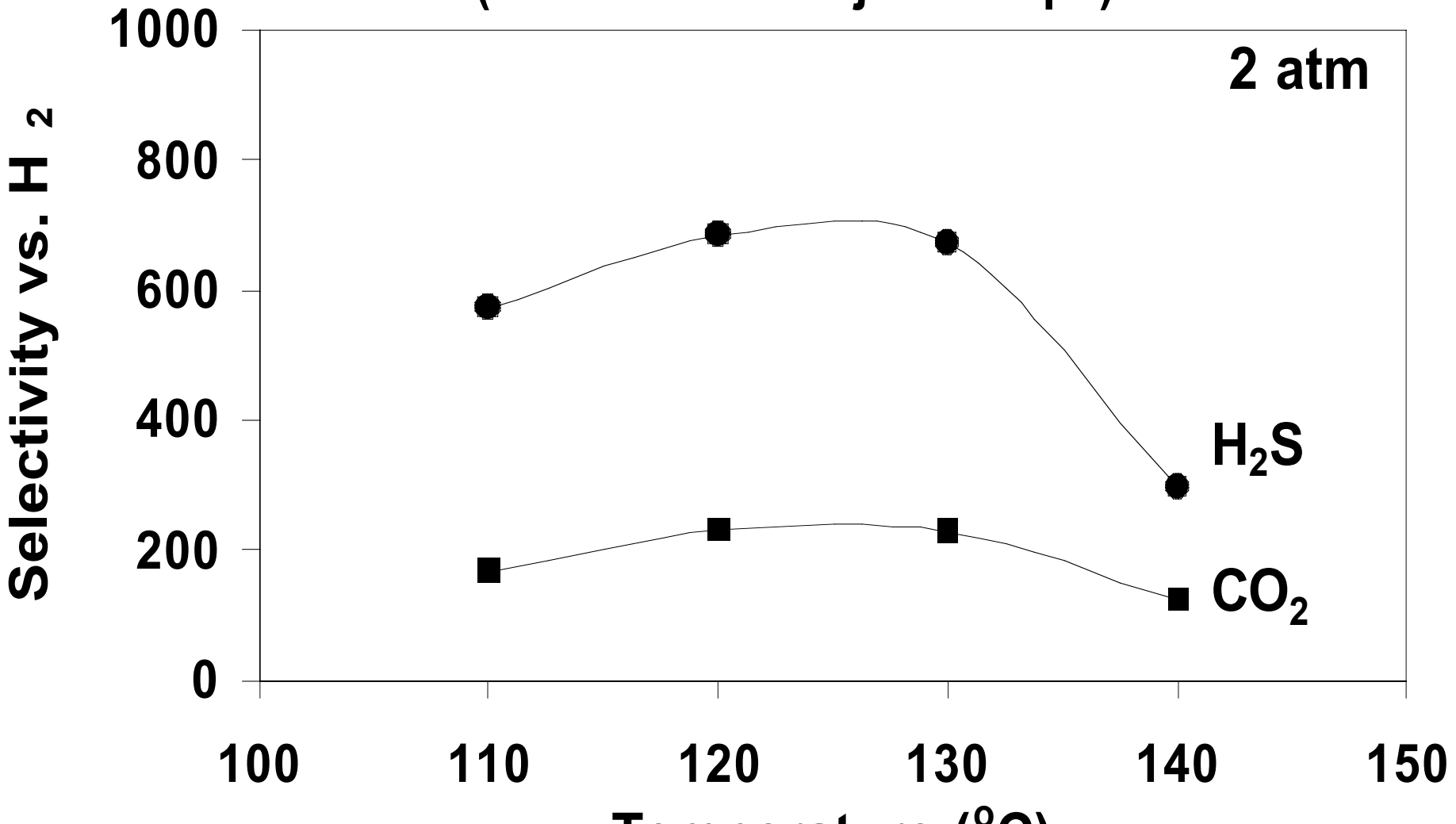
H_2S Has Higher Permeability than CO_2

(Outside the Project Scope)



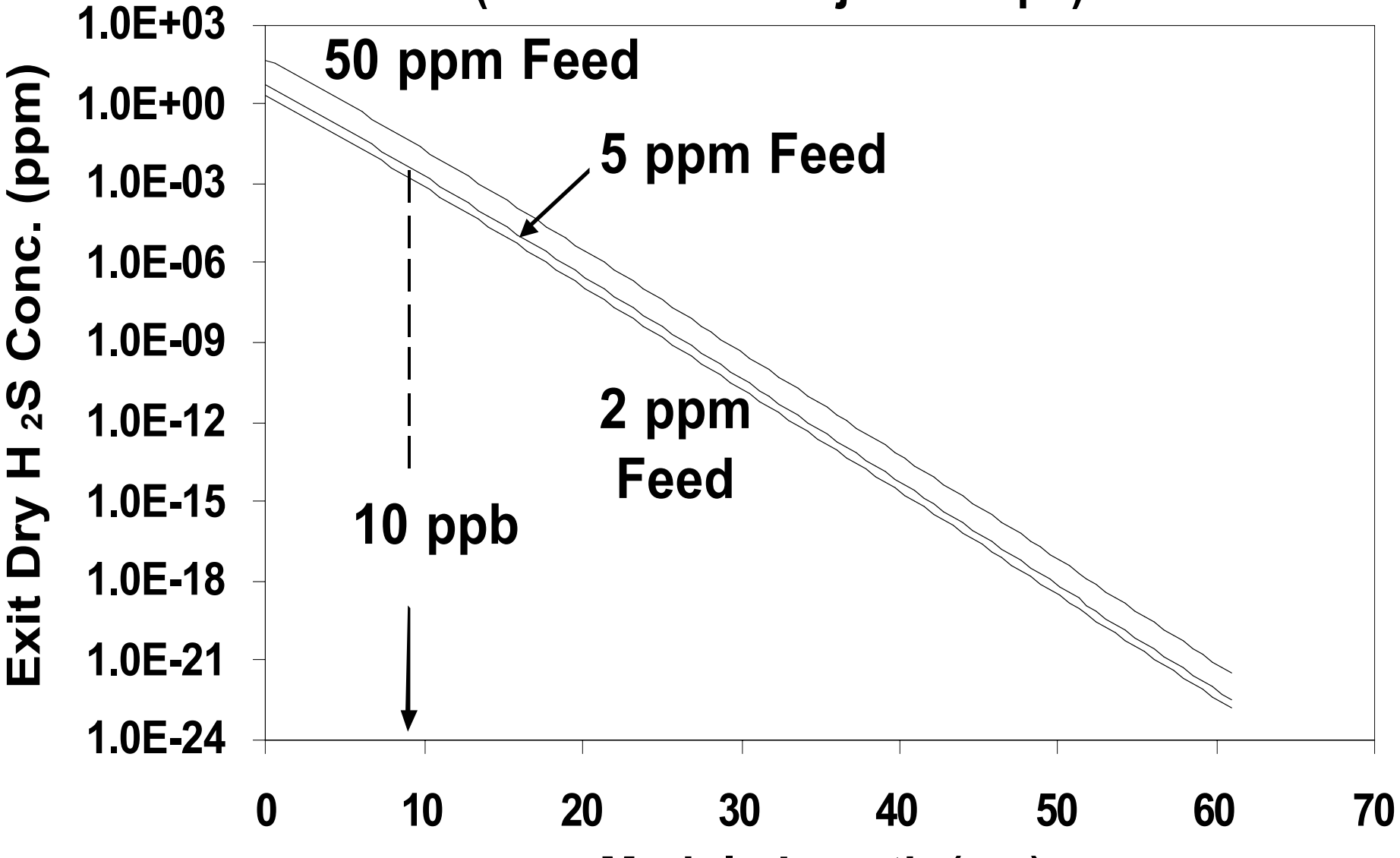
H_2S/H_2 Selectivity Higher than CO_2/H_2 Selectivity

(Outside the Project Scope)



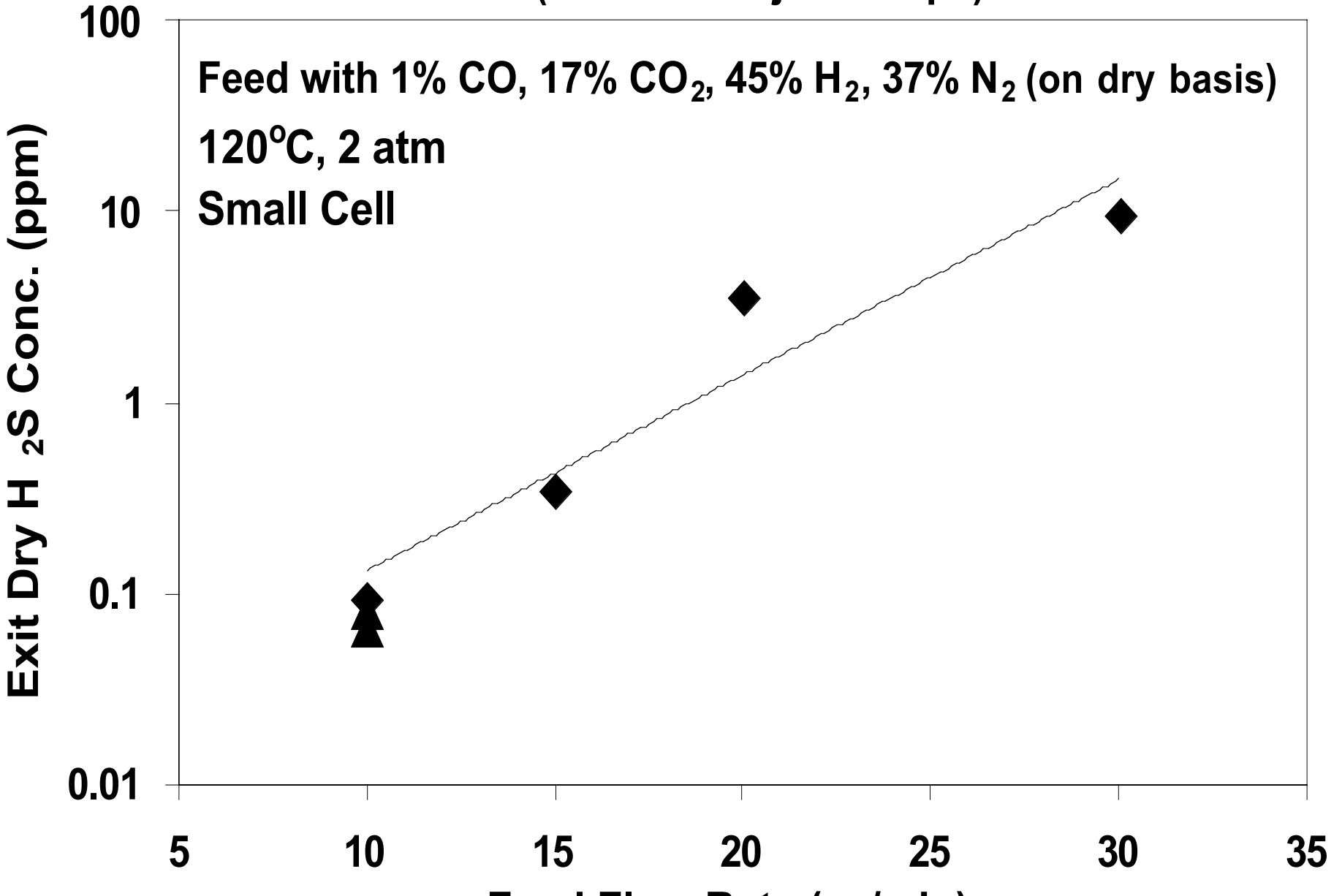
Modeling Shows <10 ppb H_2S Achievable in Entrance Section

(Outside the Project Scope)



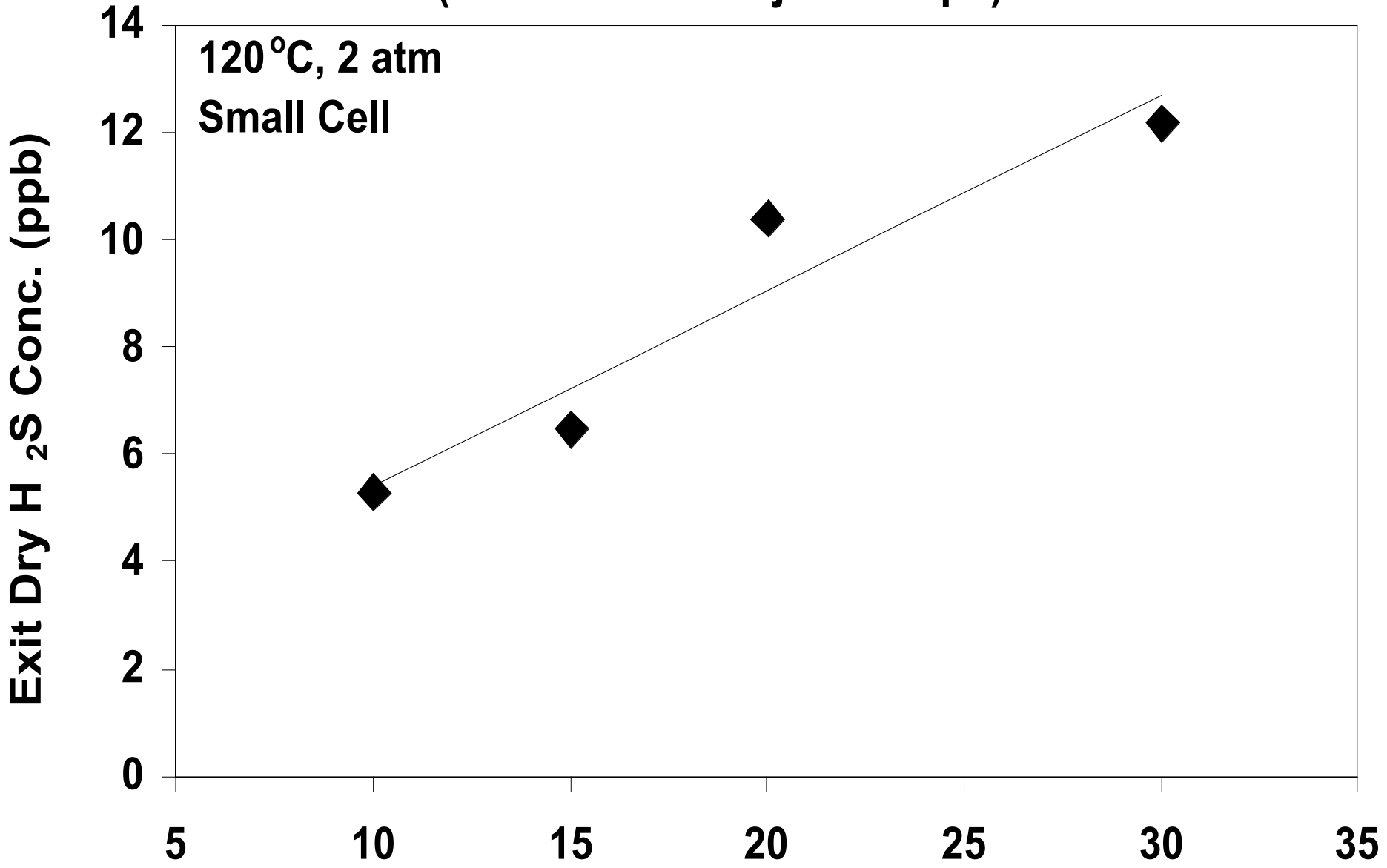
H_2S Removed Effectively: 50 ppm H_2S Feed

(Outside Project Scope)



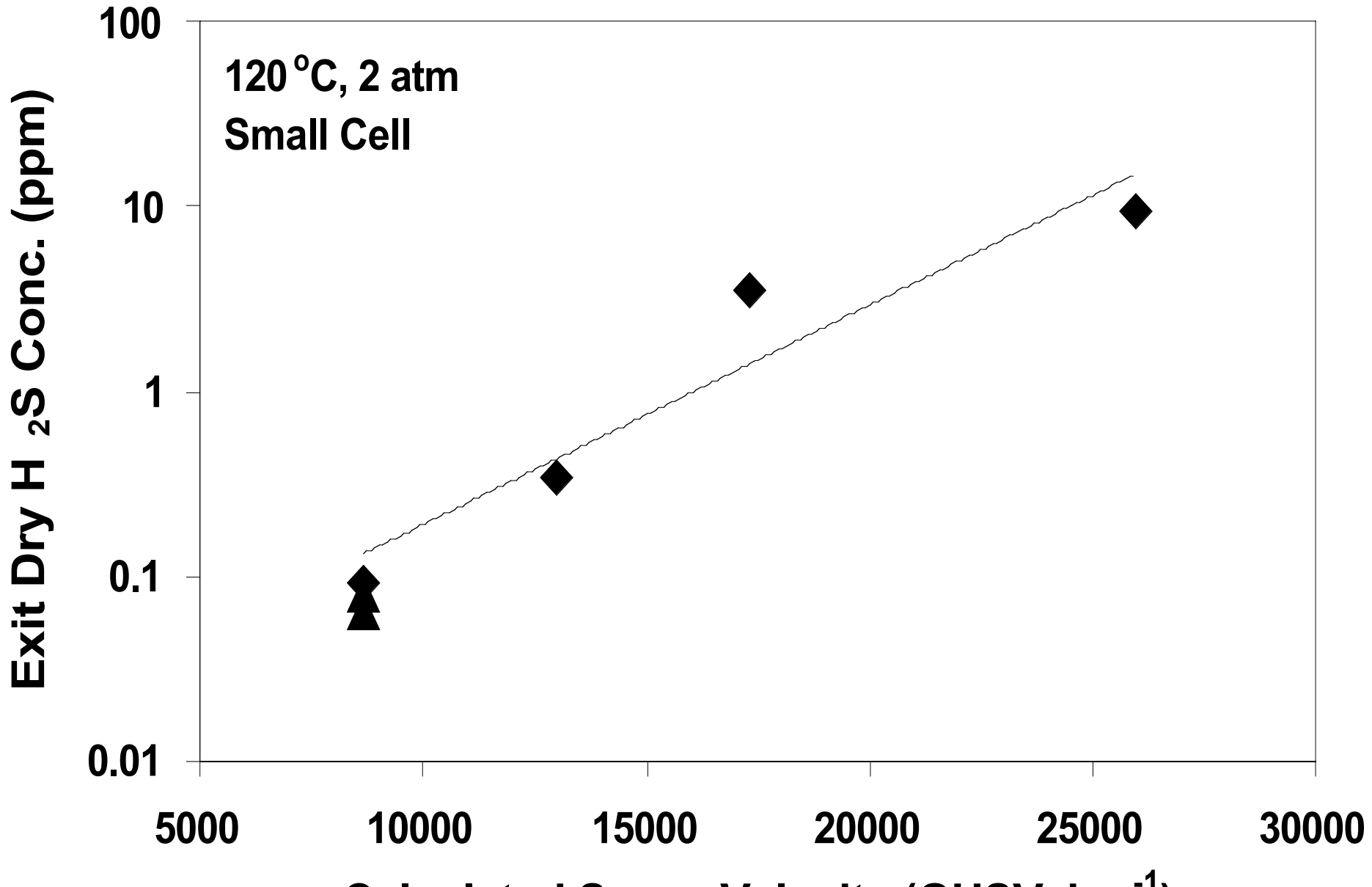
H_2S Removed Effectively: 100 ppb H_2S Feed

(Outside the Project Scope)



Calculated Space Velocity Based on Exp. Data

50 ppm H_2S Feed (Outdise the Project Scope)



Significant Interactions/Collaborations

- **Work with Unitel Technologies / H2fuel on Membrane Scale-up**
  - **Discussions with Auto Companies**
- **Collaboration with H_2 Supplier for Fuel Cell Applications**
- **Presentations / Publications on CO_2-Selective Membranes**
  - **2 at AIChE 2003 Annual Meeting**
  - **6 Seminars at Universities / Companies**

Responses to Reviewers' Comments

- **Recommend to Identify High-Temp Membrane**
  - **Continued to Synthesize / Characterize Membranes with Improved Thermal Stability**
- **Investigate Membrane Reactor Scale-up**
  - **Built a Big Cell (7.5X Small Cell) with Well-defined Flow Suitable for Modeling/Scale-up**
  - **Showed Data in Line with Model Developed**
- **Generate a Detailed Model (Experimental)**
  - **Developed WGS / CO_2 Removal Models**
  - **Showed Good Agreements between the Models and Experiments**

Future Plans

- **Continue to Synthesize / Characterize Membranes with Improved Properties**
- **Investigate Membrane Stability**
- **Complete Membrane Reactor Demonstration**
- **Demonstrate <10 ppm CO via CO_2 Removal and Methanation for Fuel Cells**
- **Look into More Active WGS Catalysts**