

# Integration of a Structural Water Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device

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Project ID #  
**PD\_49\_Barton**

## Timeline

- Start - 7/1/05
- End – 6/30/09
- 95% complete

## Budget

- Total project funding
  - \$1,445,427 DOE share
  - \$361,357 Contractor share

## Barriers

- Water gas shift capital costs for IGCC
- Hydrogen transport membrane cost

## Collaborators

- University of Wyoming
- Chart Energy and Chemicals
- REB Research and Consulting
- USDoE Ames Laboratory

# Objectives

## 2006

- **Develop a structural water gas shift catalyst capable of withstanding compressive forces.**
- **Develop vanadium alloy hydrogen separation membranes for fabrication of devices by brazing.**

## 2007

- **Integrate the WGS catalyst and metallic membranes into a device and test under gasifier conditions.**

## 2008

- **Build a modular WGS/membrane integrated device capable of producing 10,000 l/day hydrogen from coal derived syngas.**

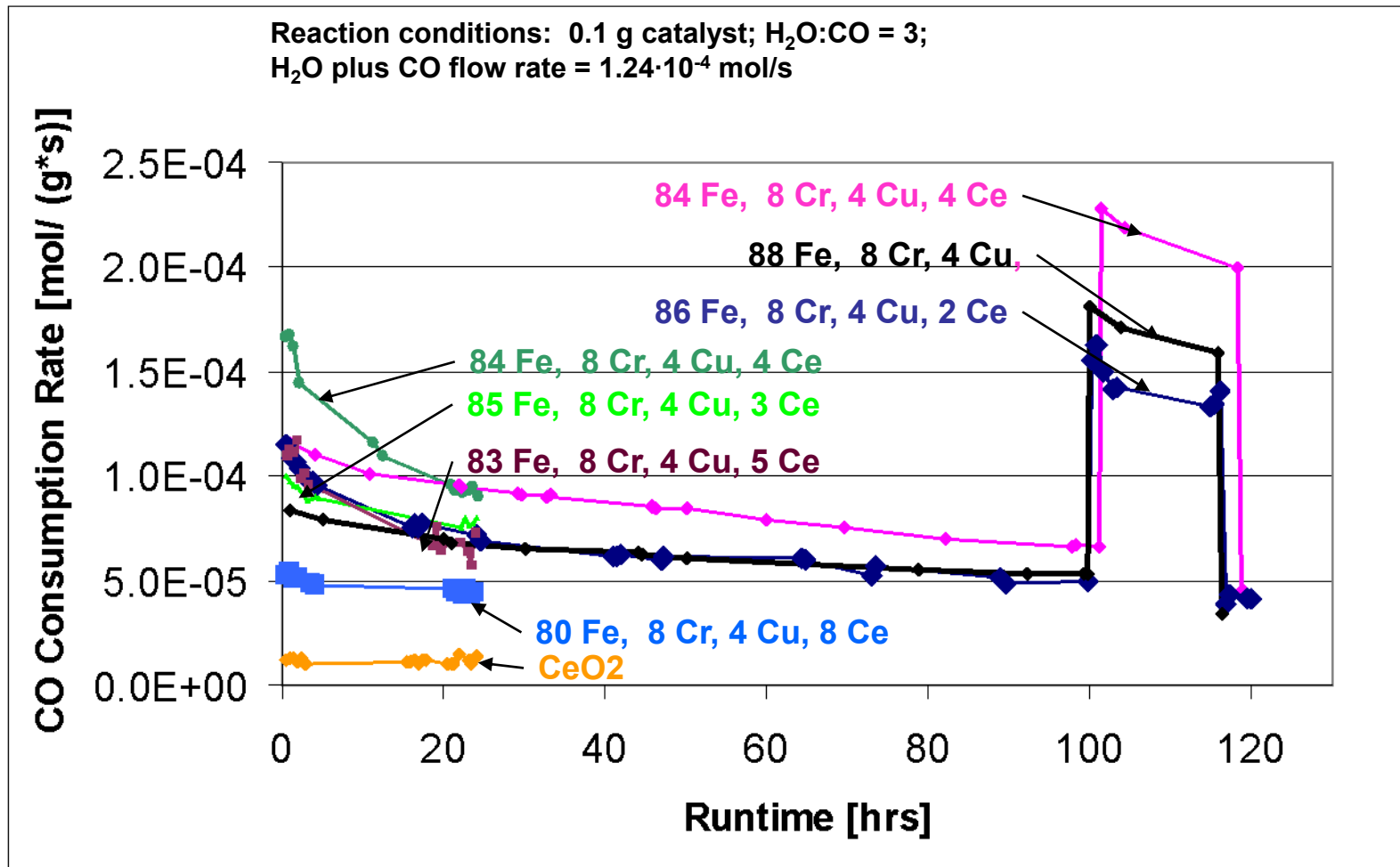
# Approach

- **Task 1 Water Gas Shift Catalyst (100%)**
  - Alumina and ceria
  - Monoliths
- **Task 2 Scale Up Integrated Devices (100%)**
  - Chart Energy and Chemicals
  - REB Research and Consulting
- **Task 3 Gasifier Testing (90%)**
  - Fluidized bed coal gasifier
- **Task 4 Economics (50%)**
  - Subcontract to University of Wyoming

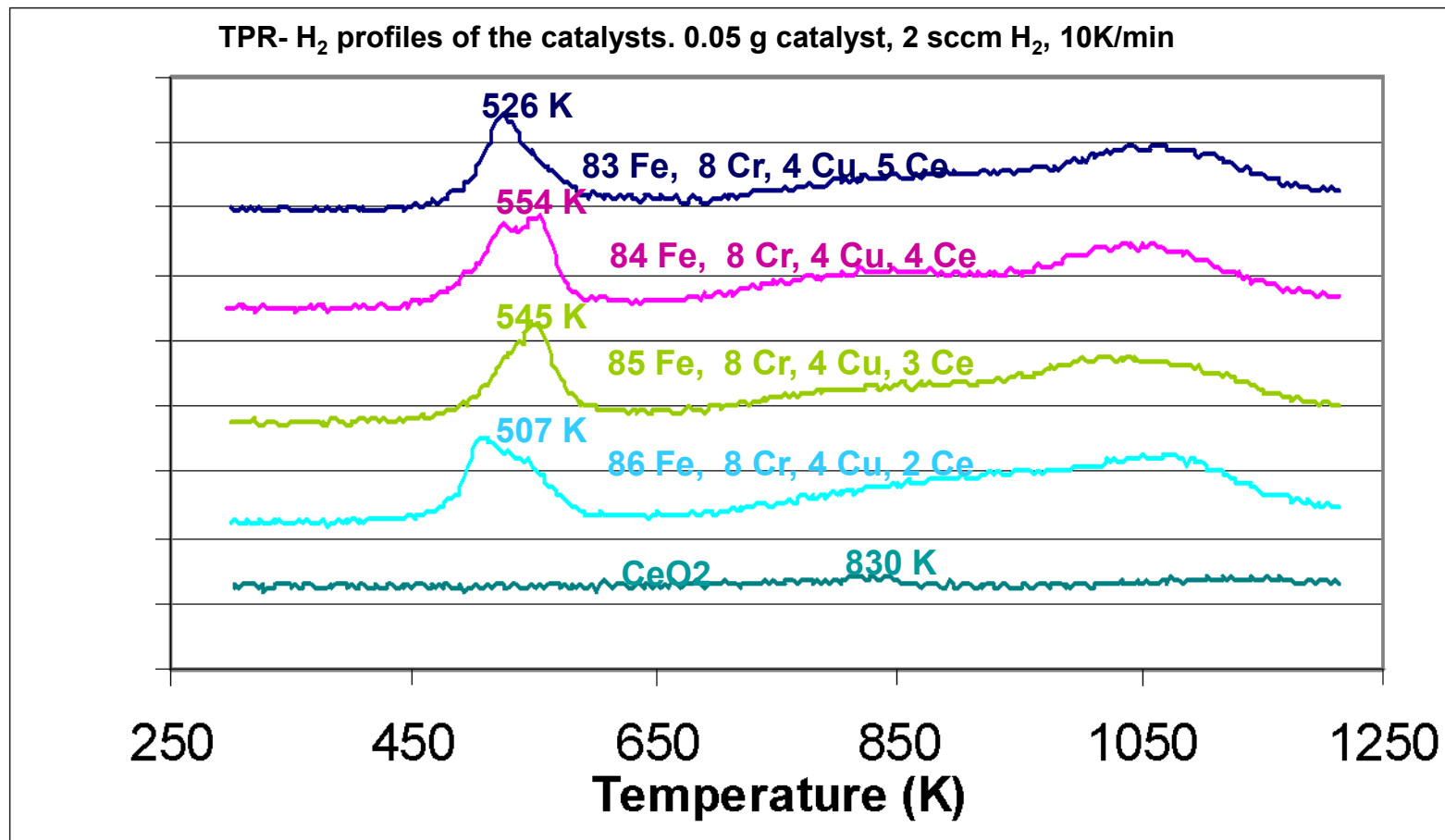
# Results

- **Task 1 Structural Water Gas Shift Catalyst**
  - Focus of the chemistry of the water gas shift catalyst has been on Fe-Al-Cr-Cu-Ce system
  - Catalysts have been tested by impregnation into porous mullite substrates and cordierite monoliths

## Among Fe-Cr-Cu-Ce-O catalysts, those with 4 wt% ceria are the most active and stable for WGS



## Optimum ceria addition (4% CeO<sub>2</sub>) produces the most reducible catalyst based on H<sub>2</sub> TPR peak areas



The initial peaks correspond to the transformation of Fe<sub>2</sub>O<sub>3</sub> into Fe<sub>3</sub>O<sub>4</sub>

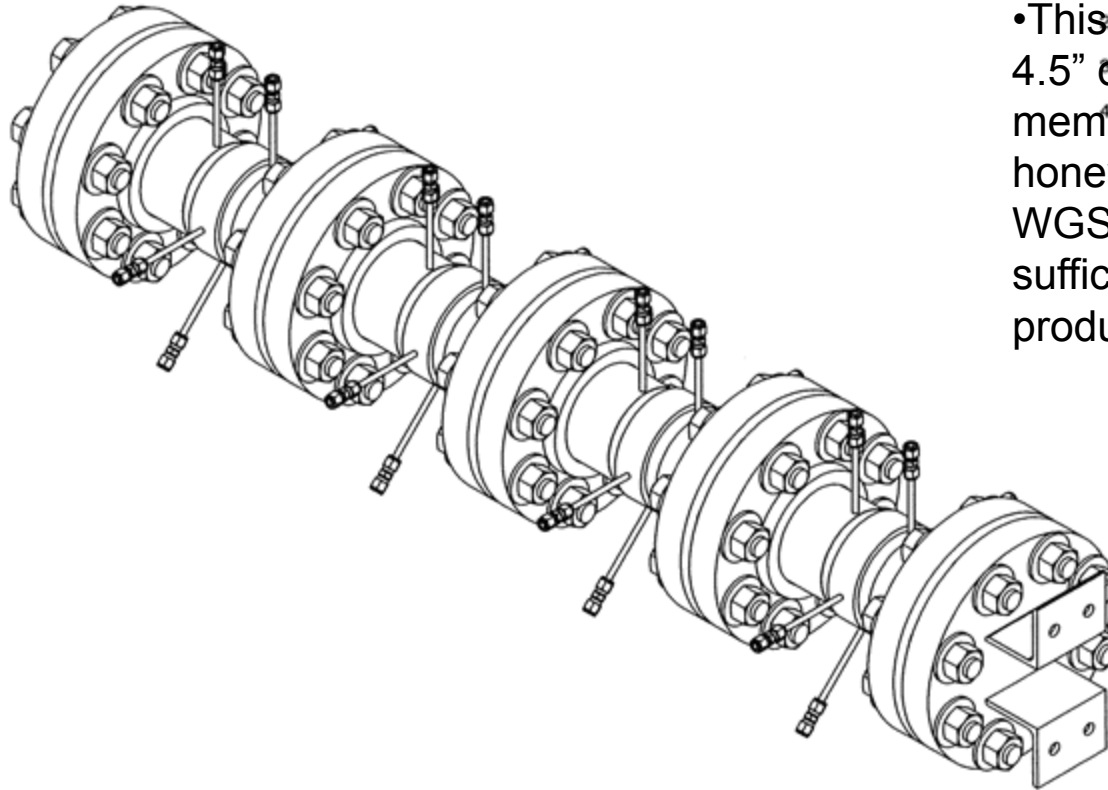
# Ceramic honeycomb monolith impregnated with WGS catalyst





## Task 2

# Scale Up Integrated Device #1



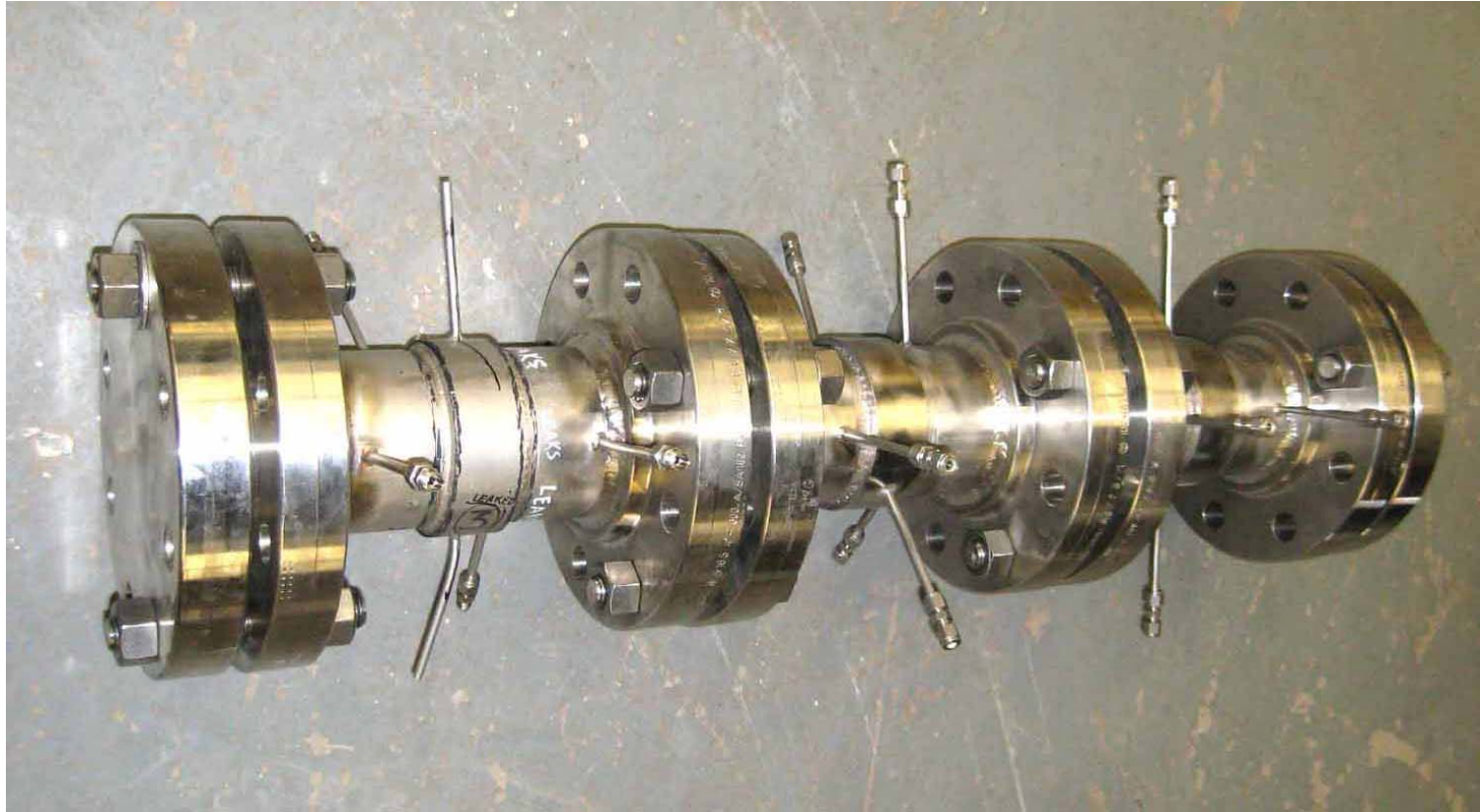
- This integrated device has eight 4.5" diameter vanadium alloy membranes sandwiched with honeycomb ceramic supported WGS catalyst to provide sufficient working area to produce 10,000 l/day hydrogen.



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# Chart Three Module Membrane - WGS Reactor



# Heating the Membrane – WGS Module



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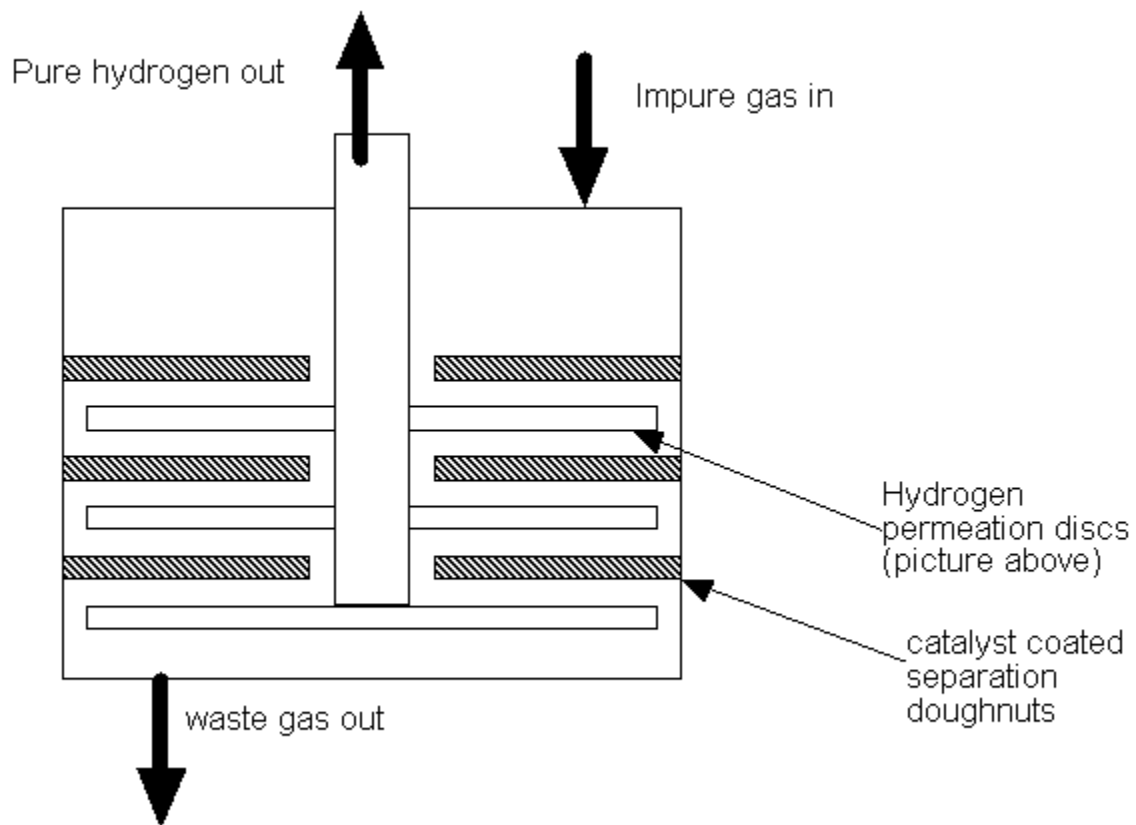
## Task 2      Scale Up Integrated Device #2

The second scale up unit is based on a “disc and doughnut” design produced by R. Buxbaum of REB Research and Consulting. In this design, the vanadium alloy membranes are joined in pairs into a structural component capable of withstanding differential pressure.

### Disc and doughnut design of a hydrogen separation system



# Disc and Doughnut Schematic



# Double Stacked Membrane – WGS Reactor



## • **Task 3 Gasifier Testing of WGS-Vanadium**

- **WRI operates a steam/oxygen blown 7 inch fluidized-bed coal-gasifier using Wyoming Powder River Basin coals at 35 lbs/hour.**
- **Temperature control allows some hydrogen/carbon monoxide ratio adjustment (40/60 to 60/40).**
- **A 90 to 120 scfh syngas slipstream can be cleaned for particulates, condensate, sulfur and mercury.**
- **Secondary vessel is heated and the syngas compressed for testing catalysts, membranes or integrated system.**
- **The operational temperature is 350 - 450°C, the testing pressure is 115 psia.**

# Gasifier Test Data

- **Inlet gas dry composition**
  - $H_2 = 37\%$
  - $CO = 27\%$
  - $CO_2 = 30\%$
  - $CH_4 = 3\%$
  - **Steam excess**
- **Single module hydrogen production (100 psig)**
  - **2.3 scfh at 400°C**
  - **1.5 scfh at 350°C**
  - **Extrapolation for 4 module unit is 12,000 l/day hydrogen at 400°C**
- **Flux Value at 400°C corresponds to 52 scfh/ft<sup>2</sup> with a driving pressure of 250  $((P_f^{0.5} - P_s^{0.5}) \times P_a^{0.5})$**
- **Longevity and sulfur testing ongoing**



# Conclusions

- The structural water gas shift catalyst developed with Al and Ce shows higher activity and is more appropriate for the integrated WGS - membrane device than the commercial catalyst.
- The vanadium alloy membranes are challenging to manufacture, but the alloys bond extremely well with structural components using standard manufacturing methods.
- Our project was not primarily a membrane development project. The vanadium alloy membranes do not yet meet the 2010 flux or cost targets but the performance results are similar to 2007 targets.
- Two integrated devices were constructed that met the 10,000 liter per day hydrogen goal at 600 psig and 400°C in coal derived syngas. One device was constructed to incorporate anyone's best membrane material. A comparison of the two approaches is part of the economic analysis.

# Future Work

- Commercialization of the water gas shift catalyst monolith will be pursued with the assistance of a catalyst manufacturer.
- We need to improve vanadium alloy membrane production for large scale manufacturing.
- Completion of the testing of the two scaled integrated devices will be followed by the design and fabrication of the 10x assembly based on the economic and performance data for testing under coal gasification conditions.

# WGS Catalyst Development Future Work

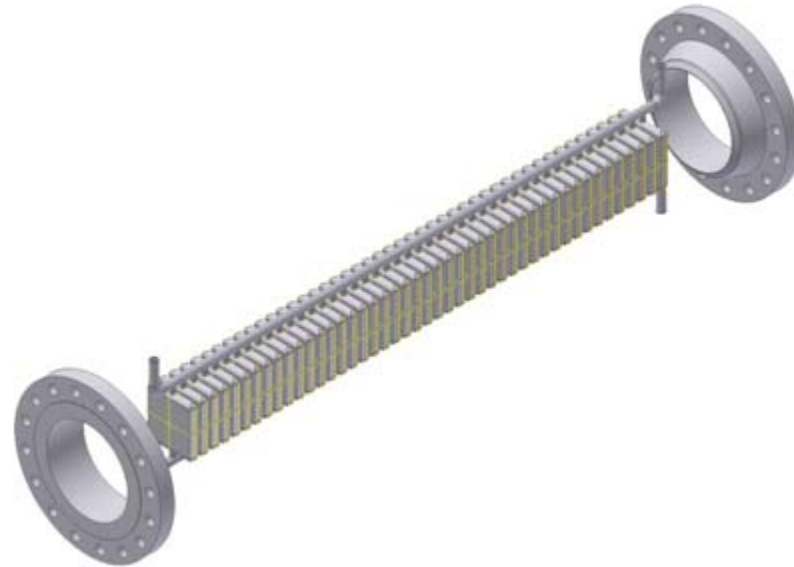
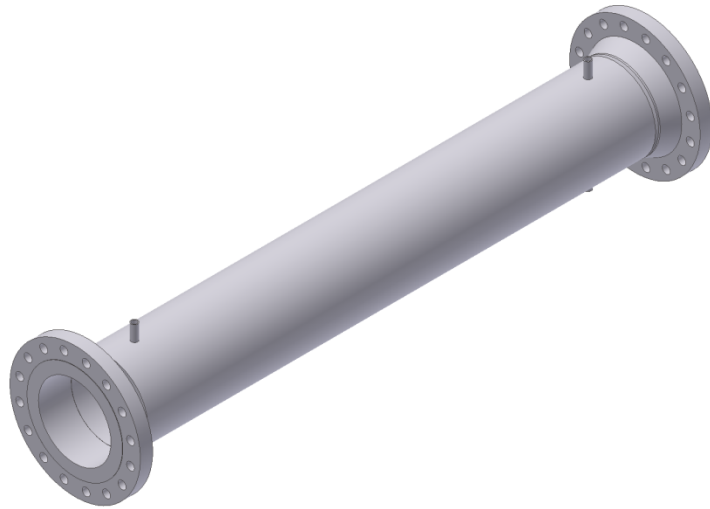
New methods of depositing the catalyst on the monoliths should involve a single step that deposits sufficient mass in the correct phase to maintain catalyst activity and stability. Single step liquid-phase impregnation is the most likely candidate. The research will focus on determining the optimum precursor chemicals and solvents that will permit sufficient solution concentration to deposit the required amount of catalyst. The optimum thermal treatment and activation methods will be sought. Methods for preventing pore mouth plugging will be developed, such as modifying the liquid-phase chemistry with addition of surfactants, as part of the catalyst loading and pretreatment methods.

# Additional WGS Catalyst Future Plans

- Increase catalyst stability and resistance to syngas impurities/poisons via inclusion of traps capable of regeneration.
- Further increase high temperature activity and stability to match increases in H<sub>2</sub> membrane performance.
- Examine surface coatings for additional water gas shift activity.

# 10,000 cm<sup>2</sup> Membrane – WGS Reactor

The WGS reaction takes place in annular space of a 12" diameter pipe, and hydrogen is collected through a manifold system. Modules are 15 cm x 15 cm with vanadium alloy membranes on both sides; configuration will meet target of 10,000 square cm of surface area. Overall length of the vessel is 90 inches.



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# Project Summary

**Approach:** The key to a commercially scaled device that integrates metallic hydrogen transport membranes and water gas shift catalyst will be a catalyst with high compressive strength and no friability and a practical low cost method to attach the membranes to structural alloys.

**Conclusions:** The ceramic catalysts developed are superior to commercially available WGS materials with respect to survival in a pressurized device. Two different viable integrated device designs using vanadium membranes have been tested that should meet scalability issues and performance criteria. Membrane performance is not yet high enough, but manufacturability goals have been met.

**Future Work:** Successful testing of the integrated devices in coal derived synthesis gas will be followed by scale up by 10x. Commercialization of the WGS catalyst monolith will be pursued.