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Abstract

The synthesis of composite Pd membranes has been modified by the addition of a Al(OH)_3 graded layer and sequential annealing at high temperatures to obtain membranes with high permeance and outstanding selectivity stability for over 4000 hours at 450°C . Most of the membranes achieved in this work showed H_2 flux well above 2010 DOE targets and in some case, also above 2015 DOE targets. Similar composite membranes were tested in water gas shift reaction atmospheres and showed to be stable with high CO conversion and high hydrogen recovery for over 1000 hours. The H_2 permeance of composite Pd-Au membranes was studied as well as its resistance in H_2S containing atmospheres. H_2S poisoning of Pd-based membranes was reduced by the addition of Au and the loss undergone by membranes was found to be almost totally recoverable with 10-30 wt%Au. PSA technique was studied to test the possibility of H_2S and COS removal from feed stream with limited success since the removal of H_2S also led to the removal of a large fraction of the CO_2 . The economics of a WGS bundle reactor, using the information of the membranes fabricated under this project and integrated into an IGCC plant were studied based on a 2D reactor modeling. The calculations showed that without a government incentive to impose a CO_2 tax, application of WGS membrane reactors in IGCC would be not as economically attractive as regular pulverized coal plants.

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Executive Summary

High pressure hydrogen flux measurement for the membrane 029 was close to the DOE-NETLs 2010 targets. The long-term H_2 permeation and the selectivity stability testing of membrane 029 was carried out for over 175 days (~4270 hours) in the temperature range of 400-450°C. The He leak of the membrane 029 was not detectable, indicating an essentially infinite H_2 /He selectivity that remained stable. The final He leak at 450°C and at a ΔP of 35 psi ($P_{High}=50$ psia & $P_{Low}=15$ psia) was as low as 0.016 scfh/ft² (<0.1 sccm), which corresponded to a H_2 /He selectivity of ~6000 (4200 hours).

Similar high selectivity stability results were reproduced with membranes #030, #031 and #033 indicating that 2-3 annealing at 550°C in He with polishing steps is an effective technique to mitigate the He leak development at 450°C. Yet, it appeared that all membranes which underwent annealing at 550°C have in general a lower permeance than membranes without annealing steps.

High permeances were obtained on membranes prepared on $Al(OH)_3$ graded supports (#025, #032, #036, #038, #039 and #053). However, their permeance was seen to decrease after 2-3 annealing steps at 550°C in He. It was concluded that densification of the $Al(OH)_3$ layer might have caused the permeance loss even though intermetallic diffusion could also possibly have played an important role at such high temperatures.

Mixed Gas experiments were carried out by utilizing a 18.1 μm thick Pd/Inconel membrane AA-6 with four different gas mixtures all containing the same fraction of hydrogen along with He, CO_2 , CO_2/CO , and H_2O at three different temperatures; 350, 400, and 450°C. Mass transfer resistance due to concentration polarization was found to be significant over the whole range of feed flow rates studied (up to 20 scfh), lowering the H_2 flux by at least 20%. Inhibitory effects were also observed due to reversible surface binding of the non-permeable gases such that the inhibition by CO was approximately 3 times greater than that of H_2O , and H_2O 4 times greater than CO_2 .

Packed bed WGS reactions were done at 305, 351, 400, and 451°C with identical feed conditions. It was found that incomplete conversion of 37% below equilibrium occurred at the lowest temperature of 305°C. At 351, 400, and 451°C, a conversion within 1.6% of the equilibrium conversion was observed for all cases. The carbon balance for the lowest temperature was low, 94.6%, but the carbon balances for the other 3 cases were within 3%.

WGS reactions were performed in a catalytic membrane reactor with several feed conditions; a pressure of 212 psia, temperatures of 350-500°C, GHSV's of 2100 and 2900 hr^{-1} , and H_2O/CO ratios of 1.1, 1.6, and 2.6. The membrane permeance declined slowly during reactions conducted at H_2O/CO ratios of 1.6 or less, probably due to coke formation. Steady state conditions were maintained during all the experiments performed with a H_2O/CO ratio of 2.6. The CO conversions as high as 98.2% were achieved with temperature of 450°C, pressure of 212 psia, steam to CO ratio of 2.6:1, and GHSV of 2900 hr^{-1} . The maxima observed in the CO conversion versus temperature plots in the range of 400-500°C, for both sets of feed conditions, indicated the likely presence of an optimal operating temperature in that range.

WGS reactions were performed in a catalytic membrane reactor with a simulated syngas mixture: 22.7% CO , 22.0% H_2 , 9.9% CO_2 , and 45.4% H_2O . The reactions were performed with a variety of feed conditions; a pressure of 212 psia, temperatures of 350-450°C, GHSV's of 1100, 2100, 3400, 4500, and 5400 h^{-1} , and steam to CO ratios of 2:1. CO Conversions as high as 97.9% (15% over the equilibrium conversion) were achieved at a temperature of 400°C and a GHSV of 1100 h^{-1} .

The Pd/alloy-based membrane reactor performance both for the laboratory and industrial scale applications were assessed with the aid of membrane reactor simulations and a process intensification methodology for the water gas shift membrane reactor in three main areas namely process enhancement, control, safety and economics, was proposed. Both H_2 purity of 99.99% and flux target of 250 scfh/m² specified by the DOE could be easily achieved by using a Pd-based membrane having ~34 ft³/[ft²-h-psi^{0.5}] H_2 permeance and ~8000 ideal H_2 /He selectivity, prepared

through the current membrane synthesis technology developed in the Center for Inorganic Membranes Study (CIMS) laboratory, WPI.

Results on Pd-Au composite membranes showed that the H_2 permeance increased with the decrease of activation energy as Au content was increased up to ~5 wt%. Subsequently, further increase of Au composition (> 8 wt %) of the Pd-Au membrane caused the decrease of permeance as well as the increase of activation energy in comparison to the pure-Pd membranes. The H_2S poisoning tests showed that Pd-Au membranes having higher Au content exhibited better sulfur resistance with less permeance loss. The optimum Au composition in terms of H_2 permeance was determined to be within 10 - 30 wt%. The permeance of Pd - 12.3 wt% Au and Pd - 16.7 wt% Au remained over 50% of the original H_2 permeance in the presence of H_2S up to 5 ppmv at 400°C, and the permeance loss was recoverable. The bulk sulfidation of Pd was found to be reversible with irreversible surface sulfide remaining on the surface. Sulfides formation increased with lower temperatures, longer exposure time, and higher H_2S concentrations as confirmed by the XPS analysis. The Pd/Au alloy surfaces showed a significantly lower tendency to form sulfides when compared to pure Pd samples. Sulfide was only present on the surface and no sulfide was detected in the bulk. In a Pd-Au alloy the recovery of Pd active sites was higher.

A process control system design was proposed to control CO conversion of the membrane reactor by manipulating the inlet steam flow rate. Two main illustrative cases were considered, namely the process regulation and servo mechanism. In both control structures, quite satisfactory process control was attained maintaining the CO conversion at levels higher than 95% so that the retentate stream could become suitable for high pressure CO_2 sequestration.

Throughout the performance enhancement and safety analysis, the preferred reaction conditions for the Pd/alloy based membrane reactor were determined with the aid of a non-isothermal membrane reactor model. Membrane reactor operating conditions were determined to achieve the target performance levels of 98% CO conversion and 95% H_2 recovery. Either the total reaction side pressure was determined to be at least 35 atm at a fixed permeate side pressure of 1 atm or the permeate side pressure has to equal or be lower than 0.6 atm (with vacuum) at a fixed total reaction side pressure of 30 atm, to attain the performance target levels of $X_{CO} = 98\%$ and $R_{H_2} = 95\%$, by using a feed temperature of 350°C, permeate pressure of 1 atm, $H_2O:CO$ ratio of 4.5 and 50% $p_{Bulk,max}$ for an adiabatic membrane reactor. In addition, Hazard and Operability (HAZOP) analysis was pursued to identify potential hazards as well as failure modes with goal to prevent potential risks to personnel, environment, equipment and/or process efficiency and performance. Detailed HAZOP worksheets were tabulated to be used as a reference source.

A two dimensional membrane reactor model was also developed and used to assess the total Pd/Au-based membrane reactor area and reactor dimensions for industrial conditions to achieve the performance target levels of $X_{CO} = 98\%$ and $R_{H_2} = 95\%$. Furthermore, a comprehensive economical analysis was performed for the Pd/Au-based membrane reactor integrated into an Integrated Gasification Combined Cycle (IGCC) plants (IGCC-MR). The static NPV analysis framework, based on “averages” or “best guesses” for the values of the pertinent NPV-model (inherently uncertain) inputs, suggested that the IGCC-MR technology option appeared to be attractive under the scenario of a 25 \$/ton tax imposed on CO_2 emissions starting in 2015. The IGCC-MR was predicted to provide a positive NPV of 0.3 B\$, in contrast to the negative NPV values of IGCC-PBR and SC-PC with CO_2 capture plants with the above regulatory action on carbon emissions was implemented. The expected total capital investment for the membrane reactor module consisting of 10 μm thick Pd-based membrane tubes (140320.6 ft^2) was estimated to be 1268 \$/ft² with a minimum and maximum value of 305 and 2250\$/ft², respectively.

PSA system was evaluated for the removal of sulfur compounds from the produced Syngas. After a series of computer simulations and experiments with zeolite 5A and Hisiv 3000 it was found that during the adsorption process a large amount of the CO_2 was lost making PSA unsuitable for this application which required CO_2 sequestration.

Experimental methods

Sample Preparation

Mainly, the supports used in this study were provided by Mott Metallurgical, Inc. Coupons consisted of 316 L PSS (porous stainless steel) with a 0.5 μm media grade (dimensions: 1 cm x 1 cm x 0.1 cm). The tubular membrane supports consisted of a porous Inconel alloy with a 0.1 μm media grade (dimensions: length - 6 cm, outer diameter - 1.25 cm, thickness - 0.16 cm). All supports were cleaned to remove impurities with an alkaline solution. The cleaned supports were oxidized at either 700°C or 800°C for 12 hours in order to form an oxide intermetallic diffusion barrier between the support metals and the H₂ selective Pd layer.

To block the larger pores of the support before plating the dense Pd layer, the support was attached to a vacuum and immersed in an Al₂O₃ slurry for 10 seconds. The slurry may have also been composed of Al(OH)₃ particles in some cases. The support was dried at 140°C for 12 hours. To seal the slurry within the pores of the support, the support was activated once under vacuum and plated with Pd for 10 minutes. A Pd/Ag barrier was deposited which further bridged the larger pores of the support and also functioned as an intermetallic diffusion barrier between the support metals and the hydrogen selective layer. After activating the support 3 times, Pd was plated for 30 minutes, Ag for 60 minutes, Pd for 60 minutes, Ag for 60 minutes and Pd for 60 minutes. The resulting Pd/Ag barrier layer was lightly sanded with 1200 grit SiC paper and cleaned before plating the dense Pd layer. The supports were sensitized and activated with Pd nuclei according to the procedure outlined previously. Prior to plating, the activated supports were dipped in 1 M HCl for 30 seconds and then DI water. Following the platings, the He permeance was measured and if the membrane had a He flow rate of less than 0.03 sccm at $\Delta P = 1$ bar, the membrane was deemed dense and characterized, otherwise the membrane was re-plated with Pd. In order to increase leak stability sequential annealing/polishing/replating steps were performed on many membranes.

Au plating was carried out with the galvanic displacement method (GDM), which was also considered as an electroless plating procedure. The reaction for the plating of Au by the displacement of Pd can be described by the following:

For the displacement reaction to take place spontaneously, a higher reduction potential (E₀) of Au complexing ions than that of Pd complexing ions in the plating bath is required. In the present study, a NaAuCl₄•2H₂O solution was used for the displacement bath,

Several factors could affect the displacement plating reaction including the reduction potential between support and the desired metal, metal concentration, bath pH, bath temperature, and surface roughness of the support.

Membrane Permeation Testing

The experimental shell and tube set-up for testing the hydrogen permeance and selectivity is shown in Figure 1. The permeation setup consisted of a Watlow ceramic tube furnace and a 316L SS shell casing. Hydrogen or helium flow to the membrane was controlled with a pressure regulator. A ballast volume of 500 ml was used to ease the transition between H₂ and He gases. The He sweep was a low pressure line on the tube side which prevented the membrane from oxidizing during start up/shut down conditions and flushed the permeate side of the membrane during the transition between H₂ to He atmospheres. The He sweep was not used during permeation experiments. Omega type K thermocouples monitored the temperature of the permeate flow inside the tube and the temperature between the shell casing and the furnace.

The same schematic test rig of Figure 1 was slightly modified for H₂S poisoning/a recovery experiment. The feed gas of H₂ or He was supplied from the gas cylinders with a pressure regulator (0 - 350 psig) to the reactor shell and a digital mass flow meter was used to measure the permeate flow rate at the inside of the membrane (tube side). A small portion (100 -

200 sccm) of the feed gas which entered the reactor shell was purged via the needle valve. A ballast volume of 4.4 liters before the module and a He sweep (purge) gas at a pressure of 1 bar in the tube side were used to ease the transition between H_2 and He. The He sweep gas was also used to prevent the testing membrane from oxidizing during the start-up/shut down operation of the testing, but not used during the permeation tests. The oven controlled the temperature of the reactor and a thermocouple inside the membrane recorded the temperature. H_2S/H_2 gas mixture feed of desired concentration feed were prepared by mixing H_2S/H_2 gas mixture of known concentration and pure H_2 through a home-made gas-mixer packed with stainless steel wool. The flow of H_2S/H_2 gas mixture of known concentration and the flow of the pure H_2 were controlled individually by digital mass flow controllers for desired feed flow and concentration of H_2S/H_2 gas mixture feed. A back pressure regulator (BPR, 0 - 200 psig) was installed at the outlet of the shell side, which controlled the feed pressure. In current work, a 5 ppmv H_2S/H_2 gas mixture cylinder was used for preparing 0.2 - 5 ppmv H_2S/H_2 gas mixtures. A gas chromatography (GC) system (SRI 8610C) equipped with a flame photometric detector (FPD) was used to determine the sulfur concentration of the mixed gas.

Figure 1. Schematic diagram of the apparatus used for membrane testing.

Figure 2 shows the annealing module for the H_2S exposure test of the coupon samples, which consisted of stainless steel tubes and Swagelok fittings. The prepared Pd and Pd/Au alloy coupons were placed on the stainless steel sample holder and inserted into the module inside the furnace. The furnace used was a BLUE M tube furnace, model TF55035A with a programmable PID temperature control (maximum temperature of the furnace was $1100^{\circ}C$). Pure helium was used to purge the housing during the heating stages and then the H_2S/H_2 gas mixture was switched to the system when the desired temperature was reached. 30 minutes before cooling, the module was switched to pure helium again and continued to be purged with helium until the system cooled down to the room temperature. The samples were poisoned with concentrations of H_2S varying from 0.2 - 50 ppm between the temperatures of $350 - 500^{\circ}C$ for 2 - 24 hours and recovered in H_2 for 48 hours at $500^{\circ}C$.

Figure 2. Schematic of the H₂S exposure test for the coupon samples.

PSA system description and construction

The PSA system constructed consisted of two separate stages. Figure 3 and Figure 4 are pictures of the system. Figure 3 shows a view from the front while Figure 4 shows the PLC. The PSA system is a two column system with five pneumatic valves per column. The valves redirect the gas flow to cause different conditions within the columns. The proposed PSA cycle is: pressurization, feed, blow down, evacuation, and purge. Adsorption occurs at high pressure, during the feed step. Desorption occurs at low pressure, during evacuation and purge.

Due to the test conditions, the system was completely heat-traced to maintain the temperature at 200°C. Special valves were selected to handle the temperature, pressure, and corrosive components, as well as the fast cycling rate that is expected during the experiments. A programmable logic controller (PLC) was used to control the experiments.

Figure 3. Front View of PSA System

Figure 4. PLC and Modules

Sample Characterization

Sample characterizations were carried out with the Amray 1610 Turbo scanning electron microscope (SEM) equipped with a Princeton Gamma-Tech Avalon energy dispersive X-ray light element detector and a RBA-1610 5MC type Robinson retractable backscattered electron detector for qualitative and quantitative analysis. The spatial resolution for SEM-EDS (energy dispersive spectroscopy) lay between 0.8 - 1.2 μm and the penetration depth was about 1 μm for the samples investigated. The phase identification analysis of coupons was performed with a Rigaku Geigerflex X-Ray diffractometer (XRD) equipped with a $\text{CuK}\alpha$ radiation source ($\lambda=1.54 \text{ \AA}$), and a curved crystal monochromator.

The near surface elemental analysis was performed with a Thermo Scientific K-alpha XPS at the HTML at ORNL. The instrument used an Al $\text{K}\alpha$ source operated at 200 W, with an analysis area of approximately 200 x 400 μm . The pass energy used for survey spectra and high energy resolution spectra were 25 and 50 eV, respectively. Advantage 4.38 software (Thermo Scientific) was used for the peak-fitting and quantitative analysis with a Smart-type background.

Results and Discussions

Performances of composite Pd membranes

Effect of preparation method on the H_2 permeance

All membranes prepared under grant DE-FC26-07NT43058, and listed in Table 1, for the study and the improving of permeance and long term stability were based on two methods: (1) the use of amorphous $Al(OH)_3$ or annealed α alumina particles as grading material and (2) the use of two or three annealing steps followed by mechanical polishing during the synthesis. Method 1 affects membrane permeance while method 2 affects membrane leak stability. The testing of membrane #032 (reported in Q7) cast light on the interesting feature that membranes prepared with $Al(OH)_3$ and annealed 2 or 3 times in He would lose permeance due to a certain sintering and densification of the $Al(OH)_3$ grading layer. To assess such mechanism membrane #030 was prepared with $Al(OH)_3$ but without any pre-annealing at 550°C and polishing step and when dense tested at 300°C in H_2 , annealed at 550°C in He and tested back at 300°C.

As can be seen in Figure 5, the hydrogen flux of the membrane 032 was altered significantly after the high temperature annealing treatment. The final H_2 flux at 300°C and a pressure gradient of 15 psi ($P_{High}=30$ psia & $P_{Low}=15$ psia), was ~ 34 scfh/ft². Since the intermetallic diffusion of the support metals (Ni, Cr and Fe) into the dense Pd layer could be associated with the deterioration of the H_2 flux of the membrane, a similar annealing treatment was also conducted under H_2 atmosphere (shown in Figure 6) in order to elucidate the effect of high annealing temperature of 550°C on the H_2 flux. As can be seen in Figure 6, monitoring H_2 flux at 550°C and then at 300°C resulted in no further flux decline indicating that the oxide layer formed at 800°C was an effective barrier with sufficient resistance against intermetallic diffusion. Monitoring the hydrogen flux before and after the annealing treatment under both He and H_2 atmospheres at 550°C (Figure 5 and Figure 6) suggested that the flux decline could be associated with the sintering and the phase transformations of the $Al(OH)_3$ grading layer.

Figure 5. H_2 characterization history for membrane 032 before and after annealing at 550°C/12h/He

Figure 6. H₂ characterization history for membrane 032 before and after annealing at 550°C/12h/H₂

Membranes #034, #035, #036, #049, #050 and #053 were also prepared to elucidate such phenomenon. Hence, to isolate the sintering and/or phase transformation effect of the as-received powder, the grading of the Inconel support tube for the synthesis of the membrane #034 was carried out using the heat treated powder, so that no further changes would take place during the high temperature pAP treatments. To support the above discussion and elucidate the effect of high temperature annealing on both the H₂ flux and the grading layer, α -Al₂O₃ particles were utilized as the grading layer for the synthesis of membrane #035. The permeation testing of the 8.7 μ m thick pure-Pd/Inconel membrane #034 and ~20 μ m thick pure-Pd/Inconel membrane #035 are shown in Figure 7 and Figure 8, respectively. The permeation testing for the membranes were conducted with an identical procedure to that of membranes #032 and #033, where an in-situ annealing at 550°C/He/12h was carried out before and after the H₂ characterization at 300°C. As expected, the H₂ fluxes for neither of the membranes were affected from the in-situ annealing treatment, suggesting the importance of the materials selection for the grading layer.

Figure 7. H₂ characterization history of membrane #034 in the temperature range of 300-550°C.

Figure 8. H₂ characterization history of membrane #035 in the temperature range of 300-550°C.

At 300°C, the stable H₂ permeances for the membranes #034 and #035 were ~12 scfh/ft²-psi^{0.5} (Pt=15 psia) and ~6 scfh/ft²-psi^{0.5} (Pt=15 psia), respectively. For the clarity of comparison, the impact of the high temperature annealing treatment on the hydrogen flux due to the subsequent changes in the grading layer for the Al(OH)₃ graded membranes #029 through #034 are summarized in Figure 9.

Figure 9. H₂ permeance comparison of membranes 029-034 at 300°C

Membrane #036, being fabricated with alumina particles showed a similar behavior as #034 and #035 i.e. no hydrogen permeance decline at 300°C after annealing at 550°C. However, membrane #037, being fabricated with Al(OH)₃ particles showed the same behavior as #032 i.e. a decreased in permeance at 450°C and 525°C due to the densification of the Al(OH)₃ grading layer. Data for both membrane #036 and #037 is not shown in this final due to their low selectivity values and the reader is referenced to Q9 report for more details. The same behavior was also seen for membrane #050 (see Q13 figure 6)

For this purpose, the hydrogen permeation testing of the 8.6 μm thick Pd/PSS₃₁₀ membrane #053 was conducted at 300°C, as shown in Figure 10.

Figure 10. H₂ characterization of the 8.6 μm thick pure-Pd/PSS₃₁₀ membrane #053 at 300°C

At 300°C, the hydrogen permeance of the 8.6 μm thick Pd/PSS₃₁₀ membrane #053 was as high as $\sim 29.5 \text{ scfh/ft}^2\text{-psi}^{0.5}$ ($\Delta P=15 \text{ psi}$ with $P_t=15 \text{ psi}$) and $\sim 33.9 \text{ scfh/ft}^2\text{-psi}^{0.5}$ ($\Delta P=105 \text{ psi}$ with $P_t=15 \text{ psi}$) based on the high-pressure Sieverts' Law data.

It should also be noted that the permeance of the membrane #053 (shown in Figure 10) was in good agreement with the highly permeable membranes #025 and #032 that were prepared using similar grading and plating techniques. Although the membrane #053 was highly selective over the initial 100 hours of testing, significant fluctuations in hydrogen flux were observed for the remainder of the testing as can be seen in Figure 10. The final leak test at the end of ~ 180 hours showed a significant leak that resulted in a H₂/He selectivity of <50 .

Tests on membrane #032 (see Figure 6) indicated that the loss in permeance seems not to be intermetallic diffusion, however, none of the membranes prepared and tested were cut and analyzed by SEM-EDX techniques to assess the any possible degree of Al(OH)₃ sintering and/or intermetallic diffusion. Further SEM studies will confirm the exact cause of permeance loss in membranes fabricated with Al(OH)₃ grading and annealing steps at 550°C.

Table 1. Composite Pd membranes prepared by Al(OH)₃ grading technique and intermediate annealing steps at 550°C

Mem#	Year	Area cm ²	Support	Alloy	Method	δ μm	T K	Permeance Scfh ft-2 psi0.5	Activation energy kJ mol ⁻¹	Selectivity	Test time h
025R	2007 Q2	20	Al(OH) ₃ /Inconel 800C	Pd	ESP / 400 rpm	4.2	573 623 673 723 773	25.8 35.8 41.8 48.3 stable 57.8 stable	13.9	547 554 190 34 41	Total 1000
027	2008 Q3-Q4	20	025R	Pd-Au _{4-5wt%}	ESP+GDM	6.2	573 623 673 723 773	16 20.2 23.4 25.2 → 23.4	11.7 (300-400C)	77000 100000 ↓100	1250
029	2008 Q4-Q5-Q6	20	Al (OH) 3/ Inconel 800C	Pd	ESP / 400 rpm Anneal at 550C / 3 times	7.6	573 623 673 723	9.5 13.3 17.0 19.6	16.3 300-450 But not real indication of the true one	∞ ∞ ∞ ∞ - ↓6000	200 200 2200 930 - 785
030	2008 Q5-Q8-Q9	20	Al (OH) 3/ Inconel 700C	Pd	ESP / 400 rpm Anneal at 550C / 3 times	7.85	673 723	18 22.1	19 300-450 But not real indication of the true one	10 000 10 000	700 453
031	2008 Q5-Q6-Q7	20.0	Al (OH) 3/ Inconel 800C	Pd	ESP / 400 rpm No intermediate annealings	7.0	573 623 673 723	8.8 10.7 14.5 16.8 stable	15.4 300-450	∞ - stable ↓4500	100 50 150 - 1000 821
032	2009 Q7	20	Al (OH) 3/ Inconel 800C	Pd	ESP/400 rpm No intermediate annealings	3-5	573 723	34.6 → 21.5 After annealing at 550°C 37.8 After annealing step 6 → 2		↓500	350 total
033	2009 Q9	20	Al (OH) 3/ Inconel 800C	Pd	ESP / Anneal at 550C / 2 times	8.7	573 723	After annealing at 550°C 12		↓10 000	

034	2009 Q9	20	Heat treated Al(OH)3 + Al2O3 particles/ Inconel 800C	Pd	ESP / Anneal at 550C / 3 times	8.7	573	12 stable After annealing at 550°C			
							723	22			
035	2009 Q9	20	Heat treated Al(OH)3 + Al2O3 particles/ Inconel 800C	Pd	ESP / Anneal at 550C / 3 times	20	573	5 stable After annealing at 550°C			
036	2009 Q10	20	Al2O3 particles/ Inconel 800C	Pd	ESP/mechanical polish	11.4	573	15.5 stable After annealing at 550°C		n. r.	Total 400
036R	2010 Q11	20	036	Pd-Au _{3-5wt%}	GDM+ESP	12	723	33.4			
							798	16 - 9.4			
							823	24.0		↓600	Total 900
										↓200	
037	2009 Q10	20	Al(OH)3 particles/ Inconel 800C (like 032)	Pd	ESP/mechanical polish	4.9	573	9			150
							723	12 ↓ 8.4			200
							798	11.3↓5.0			150
038	2009 Q10-Q11	20	Al2O3 particles/ PSS 600C	Pd	ESP/mechanical polish No pre-annealing	6	723	37.9		330	150
039	2010 Q11		Al2O3 particles / Inconel 700C	Pd	Like 038	7.3	723	33	11.6 300-525	↓335	165
040	2009 Q10-Q11	20	Al2O3 particles/ Inconel 800C	Pd	ESP + vacuum	12.3	573	12			
							723	20.1			
041	2010 Q11	20	Al2O3 particles/ PSS 550C	Pd	Like 038 + vacuum	8.6	723	20 ↓ 17.5 Decrease after 50 h at 550C			
042	2010 Q11	20	Al2O3 particles/ PSS 550C	Pd	Like 038	13.4	723	20			

043- 044- 045- 046- 048-	2010 Q12		PSS310		Stop synthesis						
049			Al ₂ O ₃ /PSS316 CEM			13.3	723	16.1		< 20	200
050			Al(OH) ₃ /PSS316 CEM			19- 25	723	↓11.5		1338	120
051			Al(OH) ₃ /PSS316 CEM		Stop synthesis						
052			Al ₂ O ₃ /PSS316 CEM		Stop synthesis						
053			Al(OH) ₃ /PSS310 Mott			8.6	573	29.5-33.9		<50	180

Hydrogen permeance and Hydrogen flux at high pressures

When comparing the hydrogen permeance at 450°C of membranes having undergone 2-3 annealing steps during preparation and characterization to membranes with no prepared with no annealing steps it is quite clear, from Table 1, that membranes with no annealing steps have a greater permeance. As written earlier, such low permeance may be due to a densification of the Al(OH)₃ layer or intermetallic diffusion. The phenomenon needs to be investigated by SEM EDX methods.

Hydrogen flux projections for all 025R, 027 and 029 membranes tested at 400°C are summarized as a function of pressure gradient at 400°C in Figure 11[a] and at 450°C in Figure 11[b].

Figure 11. Summary of H₂ flux data as a function of pressure gradient for membranes 025, 025R, 027 and 029 at [a] 400°C and [b] 450°C

In order to achieve DOE's 2010 flux targets, the main objective set for the synthesis of membranes #030 and #031 was high flux (i.e., 025R and 027) and selectivity stability (i.e., 029). The initial synthesis history plots for the membranes #030 and #031 are given in Q8 and Q7 respectively. As shown in Figure 12, the H₂ flux at ~442°C and at a ΔP of 102 psi ($P_{\text{High}}=117$ psia & $P_{\text{Low}}=15$ psia) was ~178 scfh/ft² for membrane #030 close to DOE 2010 target. High pressure measurement flux was not performed on #031.

Figure 12. High pressure H₂ flux data for membrane #030 at 442°C

Figure 13 shows the H₂ flux for the 3-5 μm Pd/Inconel membrane 032 at 442°C and at a ΔP of 100 psi ($P_{\text{High}}=115$ psia & $P_{\text{Low}}=15$ psia) which was as high as ~359 scfh/ft² and exceeded the DOE's 2010 and 2015 H₂ flux targets¹. The final H₂/He selectivity of the 3-5 μm thick pure-Pd/Inconel membrane 032 at the end of 350 hours of testing was ~450.

Figure 13. Summary of high-pressure H₂ flux test for membrane 032 at ~450°C (as of 12/05/2008)

¹For 2010 and 2015, the hydrogen flux targets are 200 and 300 scfh/ft², respectively, at a ΔP = 100 psi H₂ partial pressure and T = 300-600°C, with $P_{\text{Feed}} = 150$ psia & $P_{\text{Sweep}} = 50$ psia (Test Protocol v7 - 5/7/2008).

High pressure flux measurements were also performed on a 6 μm thick Pd/Inconel membrane #038 as shown in Figure 14[a], which resulted in an excellent hydrogen permeance of $\sim 37.9 \text{ scfh/ft}^2\text{-psi}^{0.5}$ ($P_{\text{Low}}=15 \text{ psia}$) at $\sim 450^\circ\text{C}$. The hydrogen flux of the 6 μm thick Pd/Inconel membrane #038 at $\sim 450^\circ\text{C}$ and at a ΔP of 104.5 psi ($P_{\text{High}}=119.5 \text{ psia}$ & $P_{\text{Low}}=15 \text{ psia}$) was $\sim 279.3 \text{ scfh/ft}^2$, which exceeded the DOE's 2010 H_2 flux targets and in close proximity to the 2015 targets. At the end of ~ 170 hours, the H_2/He selectivity at 450°C was >330 and stable, which was significantly high for a membrane prepared without the pre-annealing and/or surface polishing (pAP) treatments. Similarly, the leak growth at 525°C was minimal and the selectivity was ~ 250 .

Figure 14. Membrane #038: [a]. High pressure H_2 flux at $\sim 450^\circ\text{C}$ [b] Membrane #039: High pressure H_2 flux at $\sim 450^\circ\text{C}$

Figure 14[b] shows the high-pressure hydrogen flux of the 7.3 μm thick pure-Pd/Inconel membrane #039. Similar to membrane #038, the high-pressure flux of membrane #039 at $\sim 450^\circ\text{C}$ and at a ΔP of 103.3 psi ($P_{\text{High}}=118.3 \text{ psia}$ & $P_{\text{Low}}=15 \text{ psia}$) was $\sim 237.7 \text{ scfh/ft}^2$, which also exceeded the DOE's 2010 H_2 flux targets, was in close proximity to the 2015 targets.

Although no pre-annealing and/or surface polishing (pAP) treatments were conducted to enhance the selectivity stability, the changes in the H_2/He selectivity at 450°C were low. The helium leak at the end of ~ 165 hours of testing at 450°C was 0.15 sccm/psi ($P_{\text{Low}}=30 \text{ psia}$ & $P_{\text{Low}}=15 \text{ psia}$) for an untreated membrane (H_2/He ideal selectivity of ~ 335).

Figure 15 shows the high-pressure H_2 flux testing of the 12.3 μm thick Pd/PSS_{316L} membrane #040. Although no pre-annealing and/or surface polishing (pAP) treatments were conducted to enhance the selectivity stability, the changes in the H_2/He selectivity over the temperature range of $300\text{--}450^\circ\text{C}$ were low. The helium leak at the end of ~ 122 hours of testing at 450°C was as low as 0.21 sccm/psi ($P_{\text{Low}}=15 \text{ psia}$) for an untreated membrane (H_2/He ideal selectivity of $\sim 150\text{--}450$). As shown in Figure 15, the H_2 flux of the 12.3 μm thick Pd/PSS_{316L} membrane #040 at $\sim 450^\circ\text{C}$ and at a ΔP of 105 psi ($P_{\text{High}}=120 \text{ psia}$ & $P_{\text{Low}}=15 \text{ psia}$) was $\sim 151 \text{ scfh/ft}^2$, approaching the DOE's 2010 H_2 flux targets.

Figure 15. Membrane #040: Sieverts plot and [c]. High pressure H₂ flux at ~450°C

The high pressure testing of membrane #053, shown in Figure 16, showed that the hydrogen flux at a temperature as low as 300°C was 256 scfh/ft² ($\Delta P=105$ psi with $P_i=15$ psi), which noticeably exceeded DOE's 2010 hydrogen flux targets.

Figure 16. High pressure H₂ flux of the pure-Pd/PSS_{316L} membrane #053 at 300°C

Hence, it was possible to achieve high permeance composite membranes with fluxes exceeding 2010 and 2015 DOE targets with selectivities in the order of 300-500 without any annealing treatment at 550°C in He. Annealing steps certainly increased the leak stability, as shown here after, yet with a certain loss in permeance.

Long term selectivity stability at 450°C

Comparing membranes prepared by inter annealing steps at 550°C in He followed by polishing and membranes prepared without annealing steps it is quite clear that the selectivity stability of annealing membranes is significantly higher than membranes without annealing steps. This is clear by comparing the following long term stability studies and membranes on Table 1. This section compares membranes 029, 030 and 033 prepared with annealing steps and membranes 031 prepared with no annealing steps.

The long-term H₂ permeation and the selectivity stability testing of the membrane 029 has been completed after >175 days and is shown in Figure 17 and Figure 18, respectively.

Figure 17. H₂ characterization history for membrane 029

Figure 18. Long-term He leak growth and H₂/He selectivity comparison between membranes 027 and 029 in the temperature range of 300-450°C

At the end of ~3450 hours, as shown in Figure 17, the He leak at 400°C and at a ΔP of 35 psi ($P_{\text{High}}=50$ psia & $P_{\text{Low}}=15$ psia) was still undetectable, indicating the continuation of the excellent H₂/He selectivity stability.

As shown in Figure 19 and Figure 20, the long-term H₂ permeation testing of the 7.85 μm pure-Pd/Inconel membrane #030, was completed after testing over the temperature range of 300-450°C for a total of ~1400 hours (>58 days). The stable H₂ flux of ~35 scfh/ft² at ~450°C and at a ΔP of 15 psi ($P_{\text{High}}=30$ psia & $P_{\text{Low}}=15$ psia) with no He leak growth and the excellent H₂/He selectivity stability with an H₂/He ideal selectivity of ~10000 at ~450°C and at a ΔP of 35 psi ($P_{\text{High}}=50$ psia & $P_{\text{Low}}=15$ psia) was maintained for over 1200 hours.

Figure 19. H₂ characterization history for membrane #030

Figure 20. Long-term He leak growth and H₂/He selectivity stability of membrane #030 in the temperature range of 300-450°C.

The performance of the 7.85 μm pure-Pd/Inconel membrane #030 was another clear demonstration of the reproducibility of the selectivity stability results achieved with the membranes #029 and #031 by the 2-3 annealing steps at 550°C and polishing steps.

The long-term H₂ permeation and the selectivity stability testing of the membrane 031 has been completed after >90 days, as shown in Figure 21 and Figure 22, respectively.

Figure 21. Long-term H₂ characterization history for membrane 031

Figure 22. Long-term He leak growth and H₂/He selectivity stability of membrane 031 in the temperature range of 300-450°C.

Membrane #031 is the only membrane in this section prepared with annealing steps at 550°C in He and its final selectivity was in the order of 4000 which was high yet lower than the final selectivity of membranes 029, 030 and 033 here after.

Following the in-situ annealing at 550°C/He/12h and H₂ permeation testing at 300°C, the long-term characterization of the membrane #033 was continued at 450°C as shown in Figure 23[a]. As can be depicted in Figure 23[a], a stable H₂ permeance of ~12 scfh/ft²-psi^{0.5} (P_t=15 psia) at 450°C was retained even after a longer duration (72 hours) annealing of the membrane #033 at 550°C under H₂ atmosphere. Similar to the testing of the membrane #032, the H₂ flux was not affected by the high temperature annealing treatments indicating the stability of the oxide layer against intermetallic diffusion. After a total testing period of ~800 hours (Figure 23[b]) over the entire temperature range studied (300-550°C), the membrane #033 showed no significant leak growth and had a stable H₂/He selectivity of ~10000 at 450°C.

[a].

[b].

Figure 23. [a]. H₂ characterization history and [b]. He leak growth and H₂/He selectivity stability of membrane 033 in the temperature range of 300-550°C.

It should also be noted that the excellent selectivity stability of the 8.7 μm thick pure-Pd/Inconel membrane #033 was a further confirmation on the effectiveness of the high temperature pAP treatments in mitigating leak growth and enhancing the selectivity stability.

Membrane #036 was repaired to make membrane #036R. The membrane underwent a non-explained loss in hydrogen permeance at 450°C (see Figure 5 in Q11) and a very high increase in He leak due to annealing steps at 500 and 525°C. Different annealing atmospheres were studied in the annealing process of #036R and it was found that leaks grew at a much faster pace in pure hydrogen than in He (see Figure 6 in Q11) the fundamental reason behind this phenomenon is till not known and further testing, experiments are needed to conclude on the effect of gas atmosphere in the He leak growth kinetics.

As conclusion, annealing steps at 550°C certainly increased the selectivity stability of membranes though led to a significant decrease in permeance due to intermetallic diffusion or densification of the Al(OH)₃ grading layer.

Testing of Pd/PSS membranes under high pressure, mixed gas, and WGS conditions

High pressure H₂ testing of the Pd/PSS_{316L} membrane AA-12R

The synthesis and initial characterization details of the membranes utilized in the subsections of 5.2 are given in Table 3.

The membrane AA-12R was comprehensively tested in H₂ at 450°C with the shell-side pressure varied from 0 - 325 psig and the tube-side pressure varied from 0 - 200 psig. The shell and tube-side pressure ranges for each series of experiments conducted both in the ascending and descending order of the pressure settings are reported in Table 2. Sieverts' law plots of the flux data collected from the experiment series 1-4 and 5-8 are presented in Figure 24 [a] and [b] respectively. The *n*-value for each series of measurements was also calculated by fitting to Eq. 1 using Newton's iterative method, and is reported on the trend-line labels in each figure. The *n*-value of 0.5 was used to plot the data in each figure so that a clearer comparison and discussion could be made.

Table 2. List of shell-side and tube-side H₂ pressure ranges for each series of experiments conducted.

Series #	Method	P _s (psig)	P _t (psig)
1	Fixed P _t (baseline)	22.0 - 331.2 (ascending)	14.3
2	Fixed P _s	324.9	14.7 - 198.2 (ascending)
3	Fixed P _s	214.6	190.7 - 14.5 (descending)
4	Fixed P _t	217.6 - 22.6 (descending)	14.3
5	Fixed P _t	27.2 - 324.9 (ascending)	60.3
6	Fixed P _t	118.7 - 321.9 (ascending)	104.4
7	Fixed P _t	168.5 - 322.8 (ascending)	149.9
8	Fixed P _t	213.9 - 324.9 (ascending)	195.5

Table 3. Characterization of all membranes studied in Section 5.2.

Membrane	Support: Supplier Type, Size	Grading: Technique, Thickness	Pd/Ag Thickness (μm)	Dense layer Pd (μm)	Initial H ₂ Testing time, Temperature	Total testing time, Max Temperature	PH ₂ (scfh/ft ² -psi ^{0.5}), Temperature	Initial selectivity (after initial H ₂ testing), Final selectivity
AA-5	Mott Inconel - 0.1 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 5.7 μm	2.7	9.7	130 h 300 - 450°C	1310 450°C	9.5 (300°C) 11.3 (350°C) 14.6 (400°C) 17.0 (450°C)	5200 2800
AA-6	Mott Inconel - 0.1 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 5.4 μm	2.4	10.3	250 h 300 - 450°C	850 h 450°C	12.7 (300°C) 15.5 (350°C) 19.0 (400°C) 22.0 (450°C)	7050 1100
AA-7	Mott Inconel - 0.1 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 2.7 μm	2.5	8.5	120 h 450°C	350 h 450°C	24.3 (450°C)	2100 25
AA-8	Mott Inconel - 0.1 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 1.2 μm	3.4	7.0	100 h 450°C	710 h 450°C	19.4 (350°C) 23.0 (400°C) 27.7 (450°C)	13,400 170
AA-12R*	Chand Eisenmann PSS _{316L} - 0.2 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 0.6 μm	0	12.1	150 h 450°C	150 h 450°C	31.4 (450°C)	3500 240
AA-21	Chand Eisenmann PSS _{316L} - 0.2 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 1.5 μm	4.8	15.7	360 h 350 - 450°C	860 h 450°C	12.3 (350°C) 14.7 (400°C) 20.3 (450°C)	1250 180
AA-24	Chand Eisenmann PSS _{316L} - 0.2 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 2.6 μm	6.2	7.4	650 400°C	800 400°C	24.0 (400°C)	4200 360
AA-25	Chand Eisenmann PSS _{316L} - 0.2 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 3.1 μm	9.1	12.2	190 450°C	190 450°C	15.5 (350°C) 24.0 (400°C) 32.7 (450°C)	12600 80
MA-79	Chand Eisenmann PSS _{316L} - 0.2 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 5 μm	12	10	1700 400°C	2450 400°C	19.9 (400°C)	1350 330
MA-86b	Chand Eisenmann PSS _{316L} - 0.2 μm 0.5" OD - 2.5" L	α -alumina with Pd-glue 2.4 μm	1.8	7.5	1000 400°C	2300 450°C	28.8 (400°C) 29.9 (450°C)	2100 20

R* - indicates polishing and re-plating steps were taken after previous testing

[a].

[b].

Figure 24. Sieverts' law plots of the high pressure H₂ experiments as well as the calculated n -values. [a]. Series 1-4. [b]. Series 1, 5-8.

$$F = C(P_s^n - P_t^n) \quad (1)$$

where F is the flux across the membrane in [scfh/ft²], C is the n -dependant permeance in [scfh/ft²-psi ^{n}], and n is the characteristic pressure dependence of the membrane.

Series 1 in Figure 24[a], which was the baseline case and the typical method of H₂ permeance measurement (a fixed P_t equaling the atmospheric pressure and an incrementally increased P_s), yielded a H₂ permeance of 37.5 scfh/ft²-psi^{0.5}, 17% higher than the H₂ permeance measured at low pressure ($P_s = 29.4$ & $P_t = 14.7$ psia). The elevation in permeance was due to the non-ideal behavior of the membrane; the support resistance and the increased concentration of H atoms in the membrane Pd-lattice, reflected by the n -value of 0.63. The flux across the support, grading, and Pd/Ag barrier layers was proportional to the ΔP across those layers for Knudsen diffusion and the $P_{\text{average}} \cdot \Delta P$ for viscous flow so the composite membrane should have an n -value differing from 0.5 depending on the contributions of mass-transfer resistance from those layers and from the dense Pd-layer. Viscous flow was more significant than

Knudsen flow in the support when the tube-side pressure was higher because the mass transfer resistance by viscous flow was reduced by a higher average pressure. The viscosity of a gas does increase with pressure, but for hydrogen in the pressure and temperature range used (450°C and P_{H_2} : 14.7 - 340 psia), the viscosity varied by less than 5% [1]. If there were significant mass transfer resistance in the support, grading, and Pd/Ag barrier layers, then the mass transfer resistance would be decreased at high pressure.

Series 2 and 3 (Figure 24[a]) were conducted by fixing the shell-side pressure and increasing (or decreasing) incrementally P_t . Both series resulted in a significantly higher H_2 permeance (up to 17% higher) of the membrane than the baseline case of Series 1 and significantly higher n -values. At 450°C and a H_2 pressure of 340 psia the approximate solubility of hydrogen atoms in the Pd lattice was 3.75 mol/L, corresponding to an H/Pd ratio of 0.033 mol_H/mol_{Pd} [2]. At H/Pd ratios of greater than 0.01, crucial assumptions in the derivation of Sieverts' law are no longer valid, causing the experimental n -values to diverge above 0.5 at high pressures.

Series 3 and 4 (Figure 24[a]) were conducted in the reverse order of Series 1 and 2 to verify that the order of measurements would not affect the results; indeed Series 1 and 4 matched to within 1.1% despite being measured in ascending and descending order respectively. Series 2 and 3 were not expected to overlap since the fixed shell-side pressures were not the same.

Series 5-8 (Figure 24[b]) were conducted with fixed $P_t > 14.7$ psia, such that the P_t for each series was higher than the previous; $P_{t,5} < P_{t,6} < \text{etc.}$ At each higher P_t , the H_2 permeance also increased, up to 49.9 scfh/ft²-psi^{0.5} ($P_t = 195.5$ psia), the calculated n -values, however, were all very close to 0.62, deviating by less than 4%. The H_2 permeance calculated from Series 8 was 56% higher than the H_2 permeance measured at low pressure indicating that there could be significant H_2 flux advantage gained by operating at an elevated tube-side pressure when the mass transfer resistance of the support is high. All the series conducted with a fixed P_t yielded low n -values (< 0.64), while the series conducted with a fixed P_s yielded high n -values (> 0.77). It is likely that over a large pressure range neither Sieverts' law nor the generalization of Sieverts' law given by Eq. 1 were adequate to fit the experimental data and a more complex model will have to be utilized to better account for the viscous and Knudsen flow contributions in the support, grading, and Pd/Ag layers, as well as the high solubility of hydrogen in the Pd lattice.

Mixed gas testing

In order to aiding in comprehension of the WGS-CMR results and properly model the WGS CMR, a series of mixed gas experiments were conducted at 350 - 450°C, 50 - 200 psig, with the mixtures listed in Table 4, and with feed space velocities of 750 - 40,000 h⁻¹ [0.2 - 21 scfh]. The mixed gas experiments were conducted with the membranes AA-5, AA-6, and AA-21, with the properties and initial characterizations listed in Table 3.

Table 4. Composition of gas mixtures used in this study.

	H ₂	He	CO ₂	CO	H ₂ O
Mixture A	80%	-	20%	-	-
Mixture B	61.7%	-	37.1%	1.2%	-
Mixture C	61.7%	38.3%	-	-	-
Mixture D	61.7%	-	38.3%	-	-
Mixture E	61.7%	-	-	-	38.3%

Four sets of experiments were conducted by varying the total feed flow rate at a fixed pressure, and utilizing the membrane AA-5, and mixtures A and B, to gain a preliminary understanding of the separation dynamics in our system. The results of those experiments in terms of permeate flux and H_2 recovery versus feed flow rate are shown in Figure 25 and Figure 26 for mixtures A and B respectively.

Figure 25. Permeate flux vs. total flow for Mixture A with membrane AA-5.

Figure 26. Permeate flux vs. total flow for Mixture B with membrane AA-5.

At low total flow rates, <5 scfh, the H₂ permeation was primarily limited by the driving force across the membrane. Permeation occurred until the partial pressure of hydrogen on the shell-side was very close to the tube-side pressure. As a consequence, at low total flow rates the hydrogen recovery was very high. At high total flow rates, >5 scfh the permeate flux reached an upper bound as it became limited by the permeance of the membrane. For Mixture A with a feed pressure of 70 psia the permeate flux appeared to reach an upper limit at approximately 60 scfh/ft², 24% below the expected flow based on partial pressure of hydrogen in the feed. At yet higher total flow rates, above 8 scfh, a sharp increase occurred in the permeate flux, approaching within 5% of the expected flux. At a feed pressure of 215 psia the permeate flux appeared to reach an upper limit at approximately 170 scfh/ft², 13% below the expected flux. At higher total flow rates, above 25 scfh, a similar sharp increase in permeate flux occurred,

approaching within 4% of the expected flux. For Mixture B the permeate flux reached upper limits of 32 and 90 scfh/ft² for low and high pressures respectively, 30 and 29% below the expected fluxes based on partial pressure of hydrogen in the feed.

The sharp increase in permeate flux observed for both experiments with Mixture A is unlikely to be caused by a transition to turbulent flow since the Reynolds number for the system is only ~200 for a total flow of 25 scfh. The sharp increase in permeate flux was not observed for either experiments with Mixture B, but it is possible that the total flow was not increased to high enough levels for it to be observed. In either case, the apparent limitation of permeate flux significantly below the expected flux was likely caused by a boundary layer effect around the membrane due to the laminar nature of the flow [3,4]. When H₂ is separated from the gas mixture by a membrane, the other components of the mixture (in this case CO and CO₂) become more concentrated near the membrane surface. The resulting concentration gradient from the membrane surface to the bulk gas results in diffusion of the non-permeable components away from the membrane surface, and diffusion of the H₂ in the bulk towards the membrane surface. The resulting steady-state concentration gradient acts as a resistance for H₂ flux, in series with the resistance of the membrane itself, and lowers the resulting H₂ flux. The resistance of the gas boundary layer is dependent on the flow rate of the bulk gas through the system (with higher flow rate resulting in lower gas phase resistance) and the diffusion coefficients of the gas components (with higher diffusion coefficients resulting in lower resistance).

In addition to the gas phase resistance, it was also likely that the presence of CO in Mixture B caused some decrease in the permeance by reversible binding to the surface [4-6]. The inhibition effects of CO, CO₂, and H₂O were further investigated with a series of experiments conducted with the membrane AA-6 (Table 3) and using the mixtures B, C, D, and E (specified in Table 4). The gas mixtures chosen all had the same mol fraction of H₂ present (62%) and therefore it was expected that differences in membrane flux would be due to the differences in physical or chemical properties of the other non-permeable species (He, CO₂, CO, and H₂O). The results from the experiments are shown in terms of F/F_0 where F was the measured H₂ flux and F_0 was the calculated flux of pure H₂ at a partial pressure of 116 psia (equivalent to the partial pressure of H₂ in the gas mixtures).

The flux vs. flow graphs in Figure 27 show the relationships between the permeating H₂ flux and the total flow of the mixed gases. Since the concentration of H₂ in each gas mixture is the same, discrepancies between them must be caused by particular properties of the additive gases or differing interactions between the additive gases and the Pd-membrane. The quantification of these effects will lead to a better understanding of the permeation inhibition caused by the additive gases.

At 350°C for total flow rates exceeding 15 scfh the permeating flux from Mixture B approached a maximum at approximately 146.0 scfh/ft², 97% of the flux at the equivalent partial pressure of pure H₂ (Figure 27[a]). The permeating flux from Mixture C approached a maximum at approximately 76% of the pure hydrogen flux, and that of Mixture D approached a maximum at approximately 65% of the pure hydrogen flux. At total flows of less than 5 scfh the permeate flux was limited by the partial pressure driving force across the membrane, at total flows of greater than 15 scfh the permeate flux was limited by the permeance of the membrane and at intermediate total flows a combination of both effects was present. The lower diffusivity of H₂-CO₂ compared to H₂-He caused the hydrogen flux of Mixture C to be lower than that of Mixture B due to more significant concentration polarization close to the membrane surface over the whole range of flow rates tested [3]. Literature suggests that CO₂ does not interact significantly with the palladium surface between 300-500°C [4-6] making permeation inhibition unlikely for Mixture C. Mixture D, containing 1.2% CO, showed an 11% lower flux than Mixture B. Since CO has a diffusion coefficient higher than CO₂, the 11% lower flux was not likely caused by concentration polarization but rather by CO inhibition [4,6].

Figure 27. Permeate flow vs. total flow membrane AA-6 with 4 gas mixtures [a]. 350°C, [b]. 400°C (membrane AA-21 used for Mixture E here only) and [c]. 450°C (Mixture B is shown in squares, Mixture C in diamonds, Mixture D in circles, and Mixture E in triangles).

At 400°C for total flow rates exceeding 15 scfh the permeating flux from Mixture B approached a maximum at approximately 153.9 scfh/ft², 99% of the flux at the equivalent partial pressure of pure H₂ (Figure 27[b]). The permeating fluxes from Mixture C and D approached maxima at approximately 78, and 74% of the pure hydrogen flux. At 400°C Mixture D showed only a 4% lower flux than Mixture C, most likely due to inhibition by CO. Mixture E showed a 32% lower flux than Mixture C at the highest feed rate, 10 scfh, most likely due to more significant inhibition by the high concentration of H₂O, which has also been previously reported in the literature [6].

Finally, at 450°C for total flow rates exceeding 15 scfh the permeating flux from Mixture B approached a maximum at approximately 198.1 scfh/ft², 99% of the flux at the equivalent partial pressure of pure H₂ (Figure 27[c]). The permeating fluxes from Mixtures C and D approached maxima at approximately 74 and 75% of the pure hydrogen flux, reflecting the same effects of mass transfer and membrane permeance limitations as at the other two temperatures. At 450°C Mixture D showed an approximately equal flux to Mixture C, indicating that CO inhibition was not occurring to a detectable extent at this temperature. The permeation inhibition by CO was significantly less at 400°C than 350°C, and undetectable at 450°C; this was in good agreement with the literature [4-6]. A maximum H₂ recovery of 92.6% was achieved for the dry syngas mixture (67% H₂, 1.2% CO, and 37% CO₂) at 450°C, 200 psig and 0.5 scfh due to the high shell-side pressure and high membrane permeance.

A Langmuir type competitive adsorption mechanism was assumed such that the fractional surface coverage by each species θ_x was given by equation (1).

$$\theta_x = \frac{(K_x P_x)^n}{1 + (K_x P_x)^n + \sum (K_y P_y)^m} \quad (1)$$

where K_x is the Langmuir adsorption equilibrium constant (LAEC) for the gas species x (in atm⁻¹), P_x is the partial pressure of each gas species, n is the pressure exponent for each gas species (1 for CO, CO₂ and H₂O, and 0.5 for H₂), and y represents each other gas species.

It was further assumed that the Pd surface was 'masked' by adsorbed species such that the effective membrane area was reduced proportionally to the fraction of surface coverage by non-permeable adsorbed species. The fraction of surface still available for permeation, therefore, was the fraction covered by adsorbed hydrogen, θ_H , plus the fraction of free surface sites, θ_* . The H₂ flux through the membrane considering adsorbed surface species, F_{H_2} , is given by equation (2)

$$F_{H_2} = F_{H_2,0}(\theta_{H_2} + \theta_*) = \frac{F_{H_2,0}(1 + \sqrt{K_{H_2} P_{H_2}})}{1 + \sqrt{K_{H_2} P_{H_2}} + K_{CO} P_{CO} + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O}} \quad (2)$$

where $F_{H_2,0}$ is the flux through the membrane under pure H₂ conditions. The LAEC for H₂ was estimated by $K_{H_2} = \exp(-\Delta G/RT)$ with $\Delta G = -54.1$ kJ/mol from Faglioni and Goddard [7]. The unknown LAEC's were calculated algebraically based on the limiting H₂ flux at high GHSV from the mixed gas experiments shown in Figure 27, and are listed in Table 5. Ideally a high enough feed rate should have been utilized so that the curves in the figure reached a clear asymptote, however, since that did not quite occur, the limiting flux was estimated by dividing the H₂ flux (at the highest feed rate) by the H₂ flux from the H₂/He mixture at that same feed rate and temperature.

Table 5. Langmuir adsorption equilibrium constant, K_x , for each gas species at each temperature tested (atm⁻¹). Note: steam has not yet been investigated at 350 and 450°C.

	350°C	400°C	450°C
CO	5.45	2.44	0.29
CO ₂	0.24	0.22	0.29
H ₂ O	NA	0.84	NA

The significance of the inhibition of each species at 400°C was CO > H₂O > CO₂. Since the H₂ flux from the steam mixture was much less than from the CO₂ containing mixture, it could be understood

that the steam bound to the Pd surface much more significantly than CO₂, which was confirmed by the calculation of the LAEC in Table 5. The LAEC for CO, however, was significantly greater than that of steam (about 4x), suggesting that if a mixed gas contained a greater percentage of CO (than 1.2%) the H₂ flux through the Pd membrane would drop considerably. Even though the surface interaction of the steam was greater than that for CO₂, a high H₂ flux and high H₂ recovery was still possible, even with high concentrations of steam in the mixed gas. At low flow conditions (1.3 scfh) H₂ recovery of 89% was achieved for over 18 hours. At high flow conditions (9.5 scfh), H₂ fluxes as high as 96 scfh/ft² (with 40% H₂ recovery) were achieved.

Gielens *et al.* [8] conducted experiments on a micro-sieve supported Pd-membrane prepared by sputter deposition, with H₂/CO₂ and H₂/H₂O mixtures at 350, 400, and 450°C and 1 atm (P_{tube} = 1 atm N₂ sweep). They found that (reversible) inhibition by H₂O was much greater than that of CO₂, but that coke was gradually being deposited by their H₂/CO₂ mixture to lower the membrane permeance over several hours. Li *et al.* [6] conducted mixed gas permeation experiments on PSS supported Pd-membranes with H₂/N₂, H₂/CO, and H₂/H₂O mixtures at 380°C and 3 atm (P_{tube} = 1 atm). At a composition of 1.8% additive in 98% H₂ at high feed rates (5500 sccm) they found almost no discernible inhibition by CO (when compared to N₂), but they observed a 16% lower H₂ flux for the H₂O mixture indicating much more significant inhibition (H₂O > CO). Hou and Hughes [4] conducted experiments with H₂/CO₂, H₂/CO, and H₂/H₂O at 275°C and 2 atm (P_{tube} = 1 atm). They concluded that the extent of inhibition by each species was ordered as H₂O > CO > CO₂. Even though the majority of the experiments conducted by Hou and Hughes [4] were at 275°C, they also tested the H₂/H₂O mixture (20% H₂O in H₂) from 275 - 350°C, observing that the inhibition by H₂O was much less at higher temperatures. Due to the discrepancy between these literature studies and our own findings, further experiments should be conducted with several equivalent H₂/CO and H₂/H₂O mixtures, and at temperatures of 350, 400, and 450°C. A complication in conducting these experiments will be the tendency of H₂/CO mixtures to form coke on the membrane surface. It is possible that if the temperature dependencies of CO and H₂O adsorption were significantly dissimilar, greater inhibition would occur from H₂O at lower temperatures (<380°C) and from CO at higher temperatures (>380°C).

WGS CMR testing

A series of four packed bed (PB) WGS reaction tests were conducted at a pressure of 212 psia and with a feed composition of 1.1:1 H₂O:CO to validate the equilibrium calculation for the WGS reaction as shown in Figure 28. Four WGS CMR experiments were also conducted at the same pressure, feed composition, and feed rate with the membrane AA-5 and the results of those experiments are also plotted in Figure 28. The initial characterization of AA-5 is given in Table 3. In all of the WGS CMR experiments a gradual decrease in H₂ recovery and CO conversion over time was observed as evidenced by Figure 29, and therefore those data points are labeled as 'pseudo-steady state' in Figure 28. The PB WGS data did not show similar drifting over time indicating that a true steady state was reached within the first 60 minutes of each experiment; in all cases experiments were continued for at least four hours.

Figure 28. CO conversion vs. temperature. ($P = 212$ psia, $H_2O/CO = 1.1$, $GHSV = 1600$ hr^{-1} . Packed bed reactor conversions shown in squares, catalytic membrane reactor {with AA-5} conversions shown in triangles, equilibrium conversion shown as a solid line.)

At 300°C the CO conversion value was only 55.1%, 37% below equilibrium for that temperature. The high-temperature shift catalyst, HiFUEL 210 Iron-Chrome High Temperature Shift Catalyst (purchased from Alfa Aesar), had optimal activity above approximately 400°C, and therefore had significantly less activity below that range. At 350, 400, and 450°C the CO conversion was within 1.6% of the expected equilibrium value. The carbon balances for the reactions were 94.6, 96.9, 100.1, and 100.6% respectively. Despite the gradual decrease in H_2 recovery and CO conversion, a higher value of CO conversion was achieved in all four CMR experiments than in the PB experiments due to the removal of H_2 from the system and the resultant shifting of the WGS equilibrium towards the products as per Le Chatelier's principle [9,10].

Figure 29 shows the CO conversion and H_2 recovery over time for a reaction carried out at 450°C with a steam to CO ratio of 1.1:1 and a GHSV of 1600 hr^{-1} . After 300 minutes the hydrogen recovery decreased by 8.7% from its initial value of 79% and the CO conversion decreased by 0.9% from its initial value of 92%. The permeance of the membrane was observed to incrementally decrease after each experiment as shown in Figure 30. The CMR was dismantled without attempting experiments at different feed and temperature conditions due to the decreased membrane permeance. The membrane was observed to have coke deposits embedded on the surface, mainly towards the inlet end of the reactor. The deposits were very thin and tightly bound to the surface. A picture of the membrane after use in the WGS experiments is shown in Figure 31.

The low H_2O/CO ratio of 1.1 allowed for carbon deposition on the membrane surface to gradually occur. The deposition of carbon reduced the membrane permeance over time by blocking the Pd-surface for H_2 permeation, and resulting in the slow reduction of H_2 recovery seen in Figure 29, as well as the incremental decreases in the Sieverts' law permeance shown in Figure 30. The carbon balances for the reaction experiments were all within 4% of unity, and any weight gain by the catalyst due to coking was undetectable, it is therefore unlikely that any significant amount of coke was deposited on the catalyst or that the catalytic activity was adversely affected. While it is generally known that the Fe/Cr-oxide catalyst is resistant to coke formation under WGS conditions [11], there is at least some literature evidence that the Pd-surface has a propensity towards coke formation in the presence of CO by equation 3 [12,13], and so these results were not a complete surprise. Since it is unlikely that the catalytic activity was decreased by coking, the gradual decline in CO conversion observed in all four CMR experiments was probably the result of lower H_2 recovery, and therefore a lesser shift in the WGS equilibrium.

Figure 29. CO conversion and H₂ recovery vs. Time. (T = 450°C, P = 212 psia, H₂O/CO = 1.0, and GHSV = 1600 hr⁻¹)

Figure 30. Sieverts' law permeance of the membrane at 450°C

Figure 31. Membrane appearance after use in WGS experiments.

A further set of WGS CMR experiments was conducted with the membrane AA-6 over the temperature range of 350 - 500°C and with a $\text{H}_2\text{O}/\text{CO}$ ratios of 1.6 and 2.6. Higher $\text{H}_2\text{O}/\text{CO}$ ratios were utilized in an attempt to avoid coke formation on the membrane surface. The results of all the experiments in terms of CO conversion and H_2 recovery versus temperature are shown in Figure 32[a] and [b] respectively. The results in Figure 32 are also overlaid with the equilibrium conversion at the experimental conditions and the 1-D simulation results from the WGS CMR model (described thoroughly in the 9th quarterly report, pp. 16 - 18, and in the literature [14]).

At the temperatures of 350 and 400°C, with $\text{H}_2\text{O}/\text{CO} = 1.6$, the CO conversion and the H_2 recovery decreased gradually over the testing period (pseudo-steady state behavior). Figure 33[a] shows the CO conversion and the H_2 recovery over time for the experiment performed at 400°C. The gradual decline observed was very similar to those seen in the experiments performed previously with a steam to CO ratio of approximately 1.1:1, indicating that similar coke formation was probably occurring. At the temperatures of 450 and 500°C the reactions reached a true steady state, with very little change after the first hour of testing. Figure 33[b] shows the CO conversion and the H_2 recovery over time for the experiment performed at 450°C. The coke formation reaction, equation 3, had an enthalpy of -125 kJ/mol, suggesting that the reaction should have a strong inverse dependence on temperature, which could explain why evidence of coking was seen at the lower temperatures only. At the highest steam to CO ratio of 2.6:1, no evidence of coke formation was observed.

[a].

[b].

Figure 32. CO conversion [a] and H₂ recovery [b] as a function of temperature for a constant CO feed rate of 7.95 mmol/min. (Membrane: AA-6; P = 212 psia; $\diamond$: H₂O/CO = 1.6, GHSV = 2,100 h⁻¹; $\square$: H₂O/CO = 2.6, GHSV = 2,900 h⁻¹).

Figure 33. CO conversion and H₂ Recovery vs. Time on Stream. [a]. T = 400°C, [b]. T = 450°C (P = 212 psia, H₂O/CO = 1.6, and GHSV = 2100 hr⁻¹)

Effects of H₂O/CO ratio

When comparing the CO conversion from Figure 28 and Figure 32[a] for a set temperature (such as 400 or 450°C), it was clear that a higher H₂O/CO ratio led to a higher CO conversion for all three sets of experiments, as expected and consistent with packed bed WGS reactor cases [15,16]. The H₂ recovery was dependent on the membrane permeance and the CO conversion, while the CO conversion increased as the H₂O/CO ratio increased. However, when the H₂O/CO ratio was too high (such as with excess steam), the dilution of H₂ caused the H₂ recovery to decrease, as seen when comparing the H₂ recoveries at the same temperatures in Figure 32[b]. The maximum H₂ recovery, observed at the H₂O/CO ratio 1.6 and 450°C, resulted from the high CO conversion in addition to minimal dilution by the steam. A lower H₂O/CO ratio was therefore preferable for the sake of H₂ recovery, but restrained by the deposition of coke which occurred at or below the H₂O/CO ratio of 1.6.

Effects of Temperature

Figure 32 shows the CO conversion profile as a function of temperature for experiments conducted with H₂O/CO ratios of 1.6 and 2.6. Maximum CO conversions of 97.3 and 98.2% were observed for H₂O/CO = 1.6 and 2.6 respectively, both at 450°C. At temperatures of 400°C and above the CO conversion in all experiments exceeded the equilibrium conversion; with greater advantage being gained under conditions where the equilibrium conversion was much lower, such as high temperatures and low H₂O/CO ratios. At 350°C the CO conversion was 68.4%, significantly less than the equilibrium conversion, indicating that the reaction was catalytically limited at that temperature; 350°C was below the optimal temperature range of the iron-chrome oxide catalyst.

Several factors influenced the relationship between the CO conversion and the temperature in the WGS CMR. At lower temperatures the equilibrium constant was higher but the reaction rate was lower, and the permeance of the Pd-membrane was lower. At higher temperatures the reaction rate was higher and the permeance of the Pd-membrane was also higher, but the equilibrium constant was lower. Since no sweep or vacuum was applied to the tube-side of the membrane, the driving force of H₂ across the membrane dropped to zero as the partial pressure of H₂ in the reaction side approached 1 atm, at which point the equilibrium expression still applied and limited the conversion to what could be called the dynamic equilibrium [17]. The presence of the opposing factors (catalytic rate, membrane permeance, and equilibrium constant) suggests the possibility of a maximum in the CO conversion at some intermediate temperature as was observed in Figure 32[a].

Figure 32[b] shows the H₂ recovery as a function of temperature for both sets of experiments conducted with H₂O/CO ratios of 1.6 and 2.6. The H₂ recovery increased with increasing temperature up to 500°C (with higher H₂ recovery corresponding to an H₂O/CO ratio of 1.6) because the permeance of the Pd-membrane increased with temperature. Since the H₂ recovery was dependent on the H₂ production via the WGS reaction, it was possible that there would be a temperature-dependent maximum in H₂ recovery as well, but not necessarily at the same temperature as the maximum in CO conversion; this intuitively expected result occurred in the simulation results only.

Basile et al. [9] performed a series of six WGS CMR experiments in the temperature range of 250-360°C and observed a temperature dependent maximum in the CO conversion of approximately 93% at 323°C with a H₂O/CO ratio of 0.96, a pressure of 15 psia, and GHSVs of 210 and 420 h⁻¹, utilizing a alumina supported 0.2 µm Pd membrane. The attributed the temperature dependent maximum to a 'compromise between' the kinetic reaction rate and the thermodynamic equilibrium of the reaction. Barbieri et al. [10] also observed a temperature dependent maximum in the CO conversion of approximately 92% at 300°C with a H₂O/CO ratio of 1:1, a pressure of 88 psia, and GHSVs of 2,070, 3,180, and 4,550 h⁻¹, utilizing a 60 µm unsupported Pd/Ag membrane. They conducted three WGS CMR experiments at each of 3 different GHSVs in the temperature range of 280-320°C and reported a maximum of 94% conversion at 300°C and 2,070 h⁻¹. Both Basile et al. [9] and Barbieri et al. [10] utilized a low-temperature shift copper-zinc oxide catalyst. Bi et al. [16] conducted a series of experiments at four different temperatures in the range of 325-400°C, with a H₂O/CO ratio of 3:1, a pressure of 176 psia, a GHSV of 6,300 h⁻¹, with a ceramic supported 1.4 µm Pd membrane, and utilizing a catalyst with much higher activity at intermediate temperatures. They reported a maximum CO conversion of 98.0% at 375°C, 1.3% higher than at 400°C, which they attributed to a balance between the H₂ permeance of the membrane increasing with temperature and the methane formation side-reaction at temperatures exceeding 375°C. Additionally, although Basile et al. [9] utilized an ultra-thin membrane with the low H₂/N₂ ideal selectivity of 8 which could have influenced their results, Barbieri et al. [10] employed a relatively thick membrane with a nearly infinite ideal selectivity and obtained a very similar maximum CO conversion temperature. The results of the three studies [9]; [10][16][10] in terms of CO conversion as a function of temperature are compared to our results in Figure 34.

Figure 34. CO conversion as a function of temperature for WGS CMR results from Figure 32 as well as results from the literature [9][10][16].

Based on the results presented in Figure 32 as well as those from the literature shown in Figure 34 it became apparent that the temperature of the maximum CO conversion was dependent on the optimal activity temperature of the catalyst and the GHSV of the feed, with a higher temperature being optimal for a higher feed flow rate. While the WGS reaction was traditionally conducted at low temperatures, with a low GHSV, to take advantage of the equilibrium constant and obtain a high CO conversion, the CMR allows for the use of a much higher temperature, to take advantage of the higher catalytic activity for greater throughput. Finally, it should be also pointed out that operating at a higher temperature would also be preferable in terms of energy efficiency in the IGCC process as the WGS operating temperature would be closer to the coal gasifier effluent temperature.

Effect of GHSV

A series of WGS CMR experiments were conducted with the simulated syngas mixture composed of: 22.7% CO, 22.0% H₂, 9.9% CO₂, and 45.4% H₂O, at 212 psia ($P_{low} = 14.7$ psia), and 350, 400, and 450°C, and GHSVs of 1100, 2100, 3400, 4500, and 5400 h⁻¹, utilizing the membrane AA-8. The initial characterization of AA-8 is given in Table 3. The feed gas used for the following experiments was chosen based on the composition of syngas produced in a GE Energy coal gasification plant [18]. The feed gas on a dry basis was composed of 41.6% CO, 40.3% H₂, and 18.1% CO₂ and prepared by Middlesex Gases & Technologies Inc.

A plot of CO conversion vs. GHSV for the experiments with temperatures of 400 and 450°C, overlaid with the 1-D simulation results, is shown in Figure 35[a]. A plot of H₂ recovery vs. GHSV for those same experiments is shown in Figure 35[b]. A plot of retentate gas composition on a dry basis vs. time for three of the experiments performed at 400°C with GHSVs of 1100, 3400, and 5400 hr⁻¹ is shown in Figure 35[c].

Figure 35. [a]. CO conversion vs. GHSV. [b]. H₂ recovery vs. GHSV. [c]. Retentate gas composition on a dry basis vs. time for three of the experiments performed with the membrane AA-8, at 400°C. (Feed composition: 22.7% CO, 22.0% H₂, 9.9% CO₂, 45.4% H₂O, T = 400 and 450°C, P = 212 psia, P_{low} = 14.7 psia, and H₂O/CO = 2)

For GHSVs below approximately 2200 h^{-1} the CO conversion results at 400°C appeared to reach a plateau, at higher GHSVs ($3400 - 5400 \text{ h}^{-1}$) the CO conversion decreased in a linear fashion. At 400°C and a GHSV of 1100 h^{-1} a CO conversion of 97.9% (15% in excess of equilibrium) was achieved with a hydrogen recovery of 87.5%. At 450°C the CO conversion appeared to reach a plateau at GHSVs below approximately 4500 h^{-1} , then declined at the highest GHSV (5400 h^{-1}). The maximum conversion achieved at 450°C was 97.0% (21% in excess of equilibrium) with a hydrogen recovery of 85.2% at a GHSV of 1100 h^{-1} . The H_2 recovery vs. GHSV data, Figure 35[b], displayed the same crossing as that observed in the CO conversion vs. GHSV data, Figure 35[a], but occurring at a slightly higher GHSV (approximately between $2100 - 3400 \text{ h}^{-1}$). Oddly however, at high GHSVs and 450°C the H_2 recovery did not appear to decrease linearly, instead it seemed to remain level at approximately 78% up to a GHSV of 5400 h^{-1} . The reason that the H_2 recovery did not follow the same trend as the CO conversion at 450°C is unclear.

The steady state behavior of the reactor was evident from the plot of retentate composition vs. time in Figure 35[c]. Measurements of the retentate composition, the retentate flow, and the permeate H_2 flow all varied by less than 5% over the course of 5 hours. The high mol fraction of CO_2 in the retentate stream, already at the elevated pressure of 212 psia makes the WGS CMR very attractive for the potential IGCC process with CO_2 sequestration. The ability of the WGS CMR to deliver a CO_2 enriched stream, already at elevated pressure has the potential to reduce the compression cost for sequestration by over 50% (2.4% net power savings over acid gas removal followed by compression) [18,19].

At GHSVs below approximately 1700 h^{-1} a higher conversion was achieved at the lower temperature (400°C) while at GHSVs above approximately 1700 h^{-1} , higher conversion was achieved at the higher temperature (450°C). The reason for the crossing of these two trends, between approximately $1100 - 2100 \text{ h}^{-1}$, was the balance of temperature dependent factors which influenced the CO conversion in the WGS CMR: kinetic reaction rate, H_2 permeance of the membrane, and the driving force of H_2 across the membrane. At a low GHSV the CO conversion was limited by the driving force of H_2 across the membrane. In this case, the equilibrium constant which was higher at 400°C allowed for a higher CO conversion. At a high GHSV the CO conversion was limited by both the kinetic reaction rate and the H_2 permeance of the membrane, both of which were higher at higher temperatures. Some qualitative discussion can be made about these factors based on the data presented. Since the CO conversions and H_2 recoveries were approximately constant at low GHSVs (below $\sim 1700 \text{ h}^{-1}$ at 400°C and below $\sim 4500 \text{ h}^{-1}$ at 450°C) the limiting factor was most likely the driving force of H_2 across the membrane; higher conversion being prevented by a minimal 14.7 psia of H_2 pressure in the reaction mixture. If vacuum was applied or a sweep gas admitted to the permeate side, further H_2 would be removed/recovered at low GHSVs and CO conversions of very close to 100% would be observed. It can be assumed that none of the experiments performed in Figure 35 were catalytically limited, since the CO conversion in all of the experiments exceeded the equilibrium conversion. The experiments performed at high GHSVs (above 1700 h^{-1} at 400°C and above 4500 h^{-1} at 450°C) were probably limited by the H_2 permeance of the membrane since they exceeded equilibrium conversion, but still had H_2 recoveries of significantly less than the ideal H_2 recoveries (89.3% at 400°C and 88.6% at 450°C) assuming a permeate side pressure of 14.7 psia and no sweep gas. From this discussion it is clear that the application of a membrane with higher permeance would allow for simultaneously higher throughput, greater CO conversion, and greater H_2 recovery in the WGS CMR.

The simulation results correlated well with the CO conversion results at all temperatures and GHSVs in Figure 35[a], differing by as greatly as 1.7% at 450°C and high GHSV. There was, however, a discrepancy of up to 20% with the two sets of H_2 recovery results in Figure 35[b]. The discrepancy between the simulation and experimental data was the greatest at high GHSVs but still significant, up to 4% at the lowest GHSVs. It is possible that some of the assumptions made in the development of the model need to be revisited and modified; specifically the assumption that there is no radial mass transfer limitation in the reaction zone. If a gas boundary layer (in which H_2 was depleted) around the membrane were present, and not accounted for in the model, the simulation would yield an artificially high hydrogen recovery and CO conversion. A resistance term should be factored into the model to account for the mass transfer resistance of such a boundary layer.

At a GHSV of 4500 h^{-1} an additional experiment was conducted at a temperature of 350°C . Further experiments at 350°C were not conducted due to the declining selectivity of the membrane. The results of the three experiments with a GHSV of 4500 h^{-1} as well as the results of the simulation for those same conditions are shown in Figure 36.

Figure 36. CO conversion vs. temperature. (Membrane: AA-8, Feed composition: 22.7% CO, 22.0% H₂, 9.9% CO₂, 45.4% H₂O, P = 212 psia, P_{low} = 14.7 psia, H₂O/CO = 2, and GHSV = 4500 hr⁻¹)

The CO conversion of 57.1% was significantly below the equilibrium conversion at 350°C due to low catalytic activity at that temperature. At 400 and 450°C, however, the conversion increased to 89.2 and 95.4%, 6.2 and 18.9% in excess of equilibrium conversion respectively. The simulation results correlated well with the experimental results at 400 and 450°C but deviated by as much as 14% at 350°C. The significant discrepancy at 350°C is unsurprising since the experimental conditions were outside of the optimal temperature range of the catalyst. The simulation results indicated the likelihood of a maximum CO conversion with regard to temperature at approximately 460°C. Although a maximum was not observed experimentally (as experiments in this series were not performed above 450°C).

Durability testing of Pd/PSS membranes under mixed gas and WGS conditions

Several long-term (>50 hours) mixed gas and WGS experiments were conducted to ascertain both the stability of the overall system in terms of CO conversion and H₂ recovery, and the stability of the supported Pd-membrane in terms of H₂ permeance and H₂/Inert selectivity. In most cases stable CO conversion and H₂ recovery were observed, indicating stable membrane permeance as evidenced, for example by the WGS reaction shown in Figure 37, and the H₂ permeance before and after the WGS reaction experiment in Figure 38.

Figure 37. 2nd WGS reaction test conducted with membrane MA-79 ($P_{\text{rxn}} = 220$ psia; $P_{\text{tube}} = 14.7$ psia; $T = 400^{\circ}\text{C}$; Feed: 18.5% CO, 55.5% H₂O, 17.9% H₂, 8.1% CO₂; GHSV = 2550 h⁻¹)

Figure 38. H₂ permeance and selectivity testing of the membrane MA-79, including two WGS reactions ($P = 220$ psia, $T = 400^{\circ}\text{C}$, GHSV = 2100 h⁻¹).

In several cases: AA-6 (10th quarterly report, pp. 10-13), AA-21 (14th quarterly report, pp. 9-12), and AA-24 (16th quarterly report, pp. 7-9), membranes which had a stable leak or relatively small leak growth over several hundred hours of initial testing in pure H₂, developed leaks at a much greater rate when subjected to either H₂/H₂O mixed gas conditions or WGS reaction conditions. The clearest example of this is shown with the case of a reaction experiment conducted with membrane AA-24 over 110 hours presented in Figure 39 in terms of CO conversion, H₂ recovery, CO measured in the permeate, and H₂/CO separation factor versus reaction time.

[a]

[b]

Figure 39. Reaction test conducted with membrane AA-24 [a]. CO conversion and H₂ recovery [b]. H₂/CO separation factor ($P_{\text{rxn}} = 65$ psia; $P_{\text{tube}} = 14.7$ psia; $T = 400^\circ\text{C}$; Feed: 18.5% CO, 55.5% H₂O, 17.9% H₂, and 8.1% CO₂; GHSV = 2700 h⁻¹)

The separation factor was estimated by equation 4, considering the feed composition and the retentate composition determined from GC measurements every 3 hours.

$$\text{Separation Factor} = \frac{(y_{\text{H}_2}/y_{\text{A}})}{(x_{\text{H}_2}/x_{\text{A}})} \quad (4)$$

where y_{H_2} is the mole fraction of H₂ in the permeate, y_{A} is the mole fraction of species A in the permeate, x_{H_2} is the mole fraction of H₂ in the feed, and x_{A} is the mole fraction of species A in the feed.

As mentioned in Table 3, the membrane AA-24 had a H₂/He ideal selectivity of 4200 before the reaction experiment and 360 as measured within 24 hours afterward. Although the CO conversion and H₂ recovery remained stable over the 110 hour testing period, the level of CO in the permeate stream was observed to continuously increase over time in an exponential fashion. Since the decline in H₂/CO

separation factor was continuous, the leak growth could not have been due to any particular event such as a loss of pressure or disruption of the H₂O feed pump (as had previously been a problematic) but must have been due to a diffuse process.

In some other experiments involving the membranes MA-79 and MA-86b, stable selectivity was observed for extended testing periods as shown in Figure 38 and Figure 40 for the two membranes respectively. In the case of MA-79, only a slight decrease in selectivity was observed over a 65 hour WGS experiment with simulated syngas, although a gradual decrease in H₂ recovery during that experiment suggested coke formation might have been occurring on the membrane surface. In the case of MA-86b, several 50 hour experiments were conducted with H₂/H₂O mixtures over which time the selectivity was observed to remain stable, as shown in Figure 40.

Figure 40. H₂ permeance and selectivity testing of the membrane MA-86b including three 50 hour H₂/H₂O mixed gas experiments (T = 400°C, P = 38, 66, and 66 psia, Feed: 10% H₂O, 20% H₂O, and 20% H₂O in H₂, GHSV = 2100 h⁻¹).

The leak growth rates of all the membranes tested first in pure H₂, then under WGS and mixed gas conditions are tabulated in Table 6. For the membranes AA-5, AA-6, and AA-8, only short term (<6 hours) experiments were conducted, and so an average rate of leak growth was calculated based on the multiple experiments; this cannot be considered representative of the individual experiments conducted with these membranes.

Table 6. Leak growth rates of membranes tested under mixed gas and WGS conditions.

	Leak growth rate in pure H ₂ [scfh/ft ² -h-psi]	Conditions, Temperature [°C]	Time tested under conditions [h]	Leak growth rate in mixed gas/reaction conditions [scfh/ft ² -h-psi]
AA-5*	1.67×10^{-6}	WGS, 400 - 450°C	24	7.48×10^{-6}
AA-6*	4.93×10^{-6}	WGS, 350 - 500°C	35	6.43×10^{-5}
AA-8*	2.24×10^{-6}	WGS, 350 - 450°C	72	1.47×10^{-4}
AA-21	3.86×10^{-6}	H ₂ /H ₂ O, 400°C	70	1.10×10^{-4}
AA-24	6.47×10^{-7}	WGS, 400°C	110	3.03×10^{-5}
MA-79†	3.25×10^{-7}	WGS, 400°C	65	2.11×10^{-6}
MA-86b‡	7.65×10^{-7}	H ₂ /H ₂ O, 400°C	190	2.09×10^{-6}

* used for short (<6 hours) experiments only, reported leak growth averaged for several experiments

† evidence of coke formation during WGS experiment was observed

‡ evidence of surface poisoning due to the newly installed pre-heater was observed

During pure H₂ testing all of the membranes exhibited leak growth rates on the same order of magnitude, and close to the range of leak growth rates reported in the literature [20]; [21]; 8.66×10^{-8} to 1.50×10^{-6} scfh/ft²-h-psi at 400°C in pure H₂. It has been shown that microstrain in the electroless deposited Pd-layer on the order of 100 MPa was irreversibly relaxed at temperatures in excess of 350 - 400°C due to crystallite growth in the Pd-layer [22]. However, Guazzone et al. [22] also concluded that the relaxation of microstrain did not lead to significant leak growth since the strain was not large enough to cause cracks in the Pd-layer, nor did its relaxation result in pinhole formation. There is somewhat of a consensus that the leak growth in Pd-membranes was mainly the result of pinhole formation which occurred due to sintering, and began at temperatures in excess of 450°C [20-23]. The exceptionally low rate of leak growth observed in all of the membranes tested was thus in line with the pinhole formation mechanism.

The leak growth rate observed in all of the membranes was greater during periods of H₂/H₂O mixed gas testing or WGS testing than during pure H₂ testing. In some cases (MA-79 and MA-86b) the growth rates differed by only a factor of 3 - 6, but in some other cases (AA-8 and AA-24) the difference was as great as a factor of 50 - 65. The accelerated leak growth led to the conclusion that the reactive conditions were adversely affecting the dense Pd-layer.

It was previously hypothesized that the steam in the feed mixture during reaction experiments might be the detrimental factor leading to selectivity decline by partially oxidizing the membrane surface; however this hypothesis was unsupported in the literature. Indeed, several studies have shown the opposite, that H₂O, which reversibly adsorbs on the Pd-surface, has ceased to effect the H₂ permeance within 30 minutes of returning to pure H₂, and did not result in a significant loss of selectivity in any cases [4,6,8].

It has been shown that carbon is soluble in palladium up to 13 at.% and can be introduced via CO exposure at high temperatures [6,12,24,25]. It has been further shown that dissolved carbon can result in an increase in the Pd-lattice constant of 2%, which could result in microstresses and/or morphology changes, leading to increased leak growth by cracks or pinhole formation [12,25]. It is possible that even though the thermodynamic activity of carbon was less than unity in many cases and therefore did not result in bulk coke formation, carbon could still have absorbed into the Pd-layer and/or the support PSS, resulting in changes to the bulk Pd. It seemed likely that if the dissolved carbon accelerated the leak growth by some mechanism, the effect would have been more significant during the testing of MA-79 since the activity of carbon was greater than unity (1.74), and not at all significant in the cases of H₂/H₂O mixed gas separation where no carbon species were present. However, as the data in Table 6 shows,

there was relatively insignificant leak growth during the 65 hour WGS reaction with MA-79, and highly accelerated leak growth during the 70 hours of H₂/H₂O separation with AA-21.

In some cases when platinum group metals have been exposed to reactive conditions, surface morphology changes were observed at temperatures significantly lower than the Tamman temperature, the temperature at which sintering and grain growth were expected [26]. It has been suggested that this phenomenon was the result of an increased diffusion rate of surface metal atoms due to the interaction of adsorbed gases. Kulprathipanja et al. [27] reported hillock formation on the order of 150 - 400 nm in Pd₆₅Cu₃₅ electroless plated coupons exposed to CO and CO₂ at 450°C, but not coupons exposed to H₂. They also reported massive leak growth in their 3.0 µm Pd₇₅Cu₂₅ membrane upon exposure to H₂/CO and H₂/CO₂ mixtures. Since they observed some segregation of the copper away from the surface of the coupons, they suggested that the roughening and leak growth were most likely due to a bcc to fcc phase change taking place near the surface. However, they did not hypothesize as to how CO or CO₂ could have caused this. Since most of the membranes were prepared by slightly different methods and tested under multiple sets of conditions, it was not possible to compare surface morphologies in order to justify or rule out this possibility.

In some cases such as the membrane AA-21, unusual surface defects were observed and investigated by microscopic analysis. Cross-sections of the membrane AA-21 appeared normal as can be seen in Figure 41[a] and no evidence of intermetallic diffusion was observed by EDS line scans. Upon examination of the surface of the membrane, a number of larger (50 - 200 µm in size) defects were observed as can be seen in Figure 41[b]. The defects, which were visible to the naked eye, numbered between 10 and 20 per cm². When the sample was tilted to 85° (off of the vertical) as in Figure 41[c], it was apparent that the defects were voids penetrating into the membrane surface. The edge of one of the membrane pieces was polished until it intersected one of the defects so that a cross-section of the defect could be seen, Figure 41[d]. From the cross-section, it was apparent that a section of the Pd-layer fractured off of the surface leaving a void behind, extending 5-10 µm into the membrane layer but not all the way to the support.

Figure 41. SEM images of the Pd/PSS_{316L} membrane AA-21 [a]. Cross-section at 1000x [b]. Surface at 100x [c]. Surface at 700x and an 85° angle [d]. Cross-section of a defect 700x (unmounted).

Large defects like these had not been previously observed on Pd/PSS membranes and it seemed plausible that they may have been the cause of the accelerated leak growth. Furthermore, it also seemed plausible that increased micro-stresses in the Pd-layer might have been the cause of the defects. It was more likely, however, that the defects were already present on the membrane surface from overly intensive polishing treatments before loading the membrane into the system. This did not, however, explain the He leak growth during the exposure of the membrane to steam; very few pinholes and no cracks were observed on the surface of the membrane, suggesting that the cause of the leak was indeed the defects. It is possible that the exposure of the membrane to high pressure H₂/H₂O mixture opened up leaks in the already present defects on the membrane, leading to the decline in the selectivity. Following the characterization of AA-21, extraordinary care was taken to ensure that no such defects existed on the other membranes' surfaces before testing (AA-24, MA-79, and MA-86b). Regardless, in the post-testing characterization of the membranes AA-24, MA-79, and MA-86b, no similar defects were observed (by light microscopy or by SEM).

An alternative explanation for the apparent increase in leak growth rates during the WGS and mixed gas conditions was that the leak growth rates of all the membranes gradually increased over time due to inadequate fabrication techniques. All of the membranes were prepared with some extent of surface polishing in between Pd-plating steps. It was at first supposed that this surface polishing resulted in a more uniform surface for further Pd-plating, but it has more recently been considered that the surface polishing may result in a poorer adhesion of the subsequent Pd-layers or small (<1 μm) gaps between the layers. If such flaws were incorporated into the membranes, their long-term stability would be lower. It was therefore possible that over time the rate of leak growth of all the membranes increased, and so a test conducted later in the membrane lifetime could have showed a higher rate of leak growth only because it was conducted later. In other words, if a membrane were to be fabricated by the same technique, tested under WGS conditions immediately, and then under pure H₂ for several hundred hours, it would show a

greater rate of leak growth during the pure H₂, second phase of testing. An example of leak growth which accelerated during pure H₂ testing the membrane AA-25, described in Table 3, and characterized in Figure 42.

Figure 42. H₂ testing history of the membrane AA-25.

Further long-term experiments will have to be conducted to explore the possible causes of He leak growth during reaction conditions. Membranes should be fabricated with minimal surface polishing in an attempt to achieve increased leak stability. Long-term WGS experiments should be conducted alongside 'control' membranes which have been prepared identically, but tested under pure H₂ only to determine if any morphology changes on the Pd-surface could have occurred due to the WGS mixture and/or an H₂/H₂O mixture. Finally, membranes should be tested for long-term under only one set of conditions, then characterized, so that there is no doubt as to what may have caused various changes such as defect formation, cracks, pinhole formation, surface morphology changes, and compositional changes such as dissolved carbon or intermetallic diffusion.

Pd-Au composite membrane fabrication and sulfur resistance of Pd-Au alloys

Pd-Au membrane fabrication and their testing in H₂S laden hydrogen

Four Pd-Au/Inconel membranes, designated as C-07, C-09, C-11, and C-12, were prepared by the displacement plating of Au. The 0.1 μm media grade Inconel supports were purchased from Mott Metallurgical Corp and had $\sim 3.9 \text{ in}^2$ effective area (0.5"ODx2.5"L). Prior to Pd plating, the supports were oxidized in air (700°C /12h) to form an intermetallic-diffusion barrier layer and graded with $\alpha\text{-Al}_2\text{O}_3$ (1 μm Al_2O_3 particles) to modify the pore size of the support. Consecutive Pd/Ag layers were deposited after the grading to act as an extra intermetallic-diffusion barrier layer. The pre-annealing steps (2 - 3 times) were conducted at 550°C in He for 12 hours followed by mechanical treatments with 600 and 800 grit SiC sand papers during the final runs of Pd depositions to minimize the He leak growth rate. The dense Pd membranes were characterized in pure H₂ over the temperature range of 350 - 450°C prior to Au deposition. Thin Au layers ($\sim 0.5 \mu\text{m}$) were deposited on top of the dense Pd layer by the galvanic displacement plating technique [28-31]. Higher Au content was achieved by increasing the number of Au layers deposited on top of the Pd layer, Thin Pd layers ($\sim 0.5 \mu\text{m}$) were deposited between Au layers for the following Au displacement platings. The compositions of the Pd-Au membranes are summarized in Table 7. The gravimetric thicknesses of the membranes were in the range of 14-19 μm with approximately 4-12 wt % Au. After annealing at 500°C in H₂ (for $\sim 48\text{h}$), the Pd-Au membranes were characterized in pure H₂ flow over the temperature range of 350 - 450°C followed by the sulfur-poisoning tests with 0.2-5 ppmv H₂S/H₂ gas mixtures in the permeation testing module.

Table 7. The PdAu/Inconel membranes tested.

Membrane	Thickness [μm]	Au wt%	Number of Au layers
C-07	14.1	5.4	1
C-09	18.8	4.2	1
C-11	17.7	8.5	2
C-12	17	12.3	3

Membranes C-07, C-09, C-11, and C-12 have been characterized in H₂ as both pure Pd membranes and Pd-Au membranes over the temperature range of 250-450°C. The characterization results including H₂ permeance, activation energy, and selectivity ($\alpha_{\text{H}_2/\text{He}}$) were summarized in Table 8. All of the Pd-Au membranes followed Sieverts' law. The steady state H₂ permeance values measured at 350°C were 19.8, 16.6, 11.1, and 9.6 scfh/ft²-psi^{0.5} for membrane C-07, C-09, C-11, and C-12, respectively.

In order to examine the effect of Au composition on H₂ permeance, comparison of H₂ permeances before (as pure-Pd membrane) and after Au deposition (as Pd-Au membrane) was made on all four membranes separately. Since the thickness and the mass transfer resistance of the porous supports was not the same on each membrane, those factors were taken into account for better comparison. The measured permeances of the pure-Pd membranes supported on Inconel (as listed in the 2nd column in Table 8) were compared with the calculated permeance of the pure-Pd foil with the same thickness (as listed in the 3rd column in Table 8). The difference (in percentage) between the measured H₂ permeance of Pd membranes and free standing Pd foils of the same thickness was assumed to be caused by the mass transfer resistance of the porous support. Based on the relative permeance of measured Pd membranes to Pd foil (as listed in the 3rd column in Table 8), the expected H₂ permeance of pure Pd membranes were then estimated with the new thickness after further Pd and Au deposition. Finally, the measured H₂ permeances of the Pd-Au membranes (as listed in the 4th column in Table 8) were then compared to the estimated H₂ permeances of the Pd membranes of the same thickness to reveal the effect of Au composition on H₂ permeances (as listed in the 5th column in Table 8).

In comparison to the pure-Pd membranes, the membranes C-07 and C-09, which showed higher permeances than the pure-Pd membranes, exhibited lower activation energies (10-13% lower). In the

contrast, the membranes C-11 and C-12, which exhibited lower permeances than the pure-Pd membranes, showed an increase of 5-15% in the activation energies. Finally, the ideal selectivities of the Pd-Au composite membranes were in a fairly good range of 900-4500 at the end of characterization times over 150 hours (as listed in the 6th column in Table 8).

Table 8. H₂ permeance, activation energy, and selectivity of PdAu/Inconel membranes C-07, C-09, C-11, and C-12.

C07	Pd (12.7 μm)		Pd-Au (14.1 μm ; 5.4 wt% Au)	(single Au layer)	
T (°C)	P_{H_2} (scfh/ft ² -psi ^{0.5})	% of Pd foil	P_{H_2} (scfh/ft ² -psi ^{0.5})	% Pd mem.	$\alpha_{\text{H}_2/\text{He}}$ (~340h)
450	27.2	86	25.4	103	($\Delta p=14.7$ psia; 450°C)
350	18.7	90	19.8	117	~1300
250	11.0	94	11.3	115	
	$E_a=14.3\text{kJ/mol}$		$E_a=12.9\text{kJ/mol}$	90	
C09	Pd(17.7 μm)		Pd/Au (18.8 μm ; 4.2 wt% Au)	(single Au layer)	
T(°C)	P_{H_2} (scfh/ft ² -psi ^{0.5})	% of Pd foil	P_{H_2} (scfh/ft ² -psi ^{0.5})	% Pd mem.	$\alpha_{\text{H}_2/\text{He}}$ (~200h)
450	23.7	104	22.9	103	($\Delta p=14.7$ psia; 450°C)
350	16.3	109	16.6	108	~4500
250	10.0	119	10.9	115	
	$E_a=13.5\text{kJ/mol}$		$E_a=11.7\text{kJ/mol}$	87	
C11	Pd(16.9 μm)		Pd/Au (17.7 μm ; 8.5 wt% Au)	(double Au layers)	
T(°C)	P_{H_2} (scfh/ft ² -psi ^{0.5})	% of Pd foil	P_{H_2} (scfh/ft ² -psi ^{0.5})	% Pd mem.	$\alpha_{\text{H}_2/\text{He}}$ (~150h)
450	18.1	76	16.3	94	($\Delta p=14.7$ psia; 350°C)
400	15.2	78	13.7	94	~4300
350	12.5	80	11.1	93	
	$E_a=13.8\text{kJ/mol}$		$E_a=14.3\text{kJ/mol}$	104	
C12	Pd(15.8 μm)		Pd/Au (17 μm ; 12.3 wt% Au)	(triple Au layers)	
T(°C)	P_{H_2} (scfh/ft ² -psi ^{0.5})	% of Pd foil	P_{H_2} (scfh/ft ² -psi ^{0.5})	% Pd mem.	$\alpha_{\text{H}_2/\text{He}}$ (~150h)
450	15.8	62	13.5	92	($\Delta p=14.7$ psia; 350°C)
400	14.1	67	11.5	87	~900
350	11.8	70	9.6	87	
	$E_a=11.0\text{kJ/mol}$		$E_a=12.7\text{kJ/mol}$	115	

The graphical representation of the permeance data listed in Table 8 reveals the effect of Au content on the Pd-Au alloy membrane performance better. The normalized permeances of the Pd-Au alloy membranes with respect to pure-Pd membranes are shown in Figure 43 as a function of Au composition at 350 and 450°C. The normalized permeance profile of the Pd-Au composite membrane has a peak at the Au content of 5 wt% as shown in Figure 43. However, the permeance of the Pd-Au membrane became lower than Pd membrane when Au composition was higher than ~8 wt%. The results were in good agreement with the previous experimental works in literature [32-34]. The addition of Au (up to 20wt%) into Pd increases the solubility of hydrogen while the diffusivity of hydrogen in Pd-Au alloy is decreased with increasing Au content [35,36]. As a result, improved H₂ permeance could be achieved by alloying a small amount of Au into Pd membranes.

Figure 43. Normalized H₂ permeance of the Pd-Au composite membranes as a function of Au composition.

Figure 44 shows the permeance history of membrane C-12 during the exposure to a 2 ppmv H₂S/H₂ gas mixture at 400°C and subsequent recovery in pure H₂ at 400°C and 500°C. The H₂S concentration at the outlet of the shell side (retentate side) during the H₂S exposure as well as recovery was also plotted in Figure 44. Upon the H₂S exposure, the H₂ permeance decreased immediately and reached a steady state value of 61% of the original value (before the H₂S exposure) at the end of 24 hours exposure, indicating that about 40% of the surface active sites for H₂ dissociation were blocked by sulfur.

After 24 h exposure to 2 ppmv H₂S, the inlet flow was switched to pure H₂ at the same temperature to recover the permeance. As shown in Figure 44, the permeance was recovered to a steady value of 90% of the original value over a period of ~24 h. The rate of permeance recovery (slope in the plot) decreased as the recovery time increased and reached a constant value asymptotically. Additional recovery at a higher temperature of 500°C resulted in a further permeance increase and H₂S desorption, indicating more H₂S desorption and permeance recovery occurred at the higher temperature. The results suggested that the H₂ permeance recovery was directly related to the H₂S desorption. Since the H₂S adsorption on metals was exothermic in nature, more permeance was recovered at higher temperatures due to more H₂S desorption. After the recovery at 500°C, the temperature was decreased to 400°C to compare the H₂ permeance before and after the H₂S exposure. Since the H₂ permeances of the Pd-12 wt % Au composite membrane (C-12) before and after exposure to 2 ppmv H₂S were identical, it is important to note that almost complete recovery (100%) of the H₂ permeance was possible at 500°C by using H₂ flow.

Figure 44. Poisoning and recovery of the membrane C-12 at 400°C with a 2 ppmv H₂S/H₂ gas mixture.

Similar H₂S and the recovery testing were also performed on membrane C-09 and C-11 with H₂S concentrations from 0.2 to 5 ppmv at 400°C. Figure 45 summarizes the percentage of remained permeance after the H₂S exposures as a function of H₂S concentration of the membranes C-09, C-11, and C-12 at 400°C. Note that each H₂S testing was performed for 24 h in the presence of H₂S followed by the full recovery at 500°C. As shown in Figure 45, the higher the H₂S concentration was, the more the H₂ permeance was lost (i.e. less permeance remained) of all of the Pd-Au composite membranes. Thus, more surface active sites were blocked due to the gas-solid phase adsorption equilibrium as the H₂S concentration was increased. In addition, the decrease of the permeance became smaller as evidenced the remained permeance tended to reach a constant value asymptotically at higher H₂S concentration. The asymptotical behavior of the remained permeance could be explained by the fact that the gas-solid phase adsorption between the Pd-Au alloy surface and the gaseous H₂S approached to the saturation equilibrium as the H₂S concentration was increased.

As shown in Figure 45, as the Au composition was increased, the permeance loss declined for the entire H₂S concentration range tested. The better sulfur tolerance of the Pd-Au composite membranes having higher Au compositions would be explained by the fact that the binding energy between H₂S and the Pd/Au decreases as the Au composition is increased [37]. Figure 45 also exhibits the remained permeance of the pure Pd and FCC Pd-Cu (5wt% Cu) membrane that has been tested in the presence of H₂S under the similar testing conditions [38]. The Pd-Au membranes with all of the Au compositions showed less permeance decline than the pure-Pd membrane. More importantly, the Pd-Au membranes showed better sulfur resistance than the FCC Pd/Cu membrane for the Au compositions above 8 wt%.

Less permeance decline of the Pd-Au membrane with even higher Au compositions was reported in the literature. Way et al. [37] reported a ~ 40% permeance decline of a Pd₈₅Au₁₅ (~25 wt% Au) after exposure to 5 ppmv H₂S at 400°C, while McKinley [32] observed a 20% permeance decline of a 40 wt% Pd-Au membrane after exposure to 4 ppmv H₂S at 350°C. By combining the results from the literature and the current study, the remained permeance as a function of Au composition was plotted as shown in Figure 46 [a]. The remained permeance was increased as the Au composition was increased as shown in Figure 46 [a]. Even though the highest remained permeance was obtained from the Au content range of 0-10 wt% when relative permeance of the Pd-Au membranes with respect to the pure-Pd membrane permeance was taken into account (as shown in Figure 46[b] - H₂S effect was not included), the optimum Au composition to achieve the maximum performance in the presence of H₂S was determined to be in the range of 10 - 30 wt% (as shown in Figure 46 [c]- H₂S effect was included).

Figure 45. Comparison of the Remained permeances of the Pd-Au membranes (C-09, C-11, C-12) with the ones of the pure-Pd and FCC Pd/Cu membrane as a function of H_2S concentration at 400°C.

Figure 46. [a] Remained permeance in the presence of 5 ppmv H_2S at 400°C, [b] Normalized permeance of the Pd-Au membrane (w/o H_2S poisoning effect) and [c] Normalized permeance of the Pd-Au membrane combined with the H_2S tolerance as a function of Au composition (* from reference [37]; ** from reference [32]; *** from reference [32,34]).

A Pd-Au membrane, C-16R, was prepared by re-plating the Pd membrane C-16 after its characterization at elevated temperatures. The detailed synthesis history and characterization of the membrane C-16 can be found in the 14th DOE quarterly report.

A noticeable He leak developed on membrane C-16 after 130 h testing at temperatures up to 450°C. The membrane was then removed from the shell and tube reactor and mechanically treated with

600 and 800 grit sand papers. Following the mechanical treatment, Pd was deposited by applying maximum vacuum (~ 27 in) inside the tube. After 2×90 minutes plating, the membrane was mechanically treated with 800 grit SiC sand paper to smooth out the surface. Another run of Pd plating (2×90 min) was then performed on the membrane.

While the membrane was close to be dense, a thin layer ($\sim 0.5 \mu\text{m}$) of Au was deposited on the membrane by the galvanic displacement plating technique. After Au deposition, a thin Pd layer (25 min; max vacuum) was deposited. A 2nd Au layer was then deposited followed by another 25 minutes Pd plating with vacuum. The synthesis ended after a 3rd Au layer was deposited on top of the membrane, resulting in membrane C-16R having 12 μm thickness in total with approximately 16.7 wt% Au.

Membrane C-16R was prepared in order to study first the poisoning effect of H_2S on PdAu alloys. Before subjecting the membrane to any stream of hydrogen containing H_2S the membrane was first characterized in pure H_2 .

Before the H_2 characterization over the temperature range of 350-450°C, the 12.0 μm thick Pd-Au/Hastelloy membrane with the Pd/Ag intermetallic diffusion barrier was annealed at 500°C in He and H_2 for over 48 hours in order to form a Pd/Au alloy layer on top of the membrane. The resultant H_2 permeance history including the annealing stage is shown in Figure 47. A stable H_2 permeance at 500°C during the annealing stage was observed. This suggested that the formation of a Pd/Au alloy reached the equilibrium value at 500°C within the first few hours. Indeed, a previous coupon study regarding the isothermal formation of Pd/Au alloy has shown that the majority of the Pd/Au inter-diffusion and alloy formation occurred within the first 10-12 hours. Furthermore, the coupon study also indicated that Pd-Au inter-diffusion could occur and start to form Pd/Au alloy below 500°C. As a result, the membrane C-16R had most likely started to form PdAu alloy even during the temperature increasing period. Followed the annealing, the membrane C-16R was then characterized from 450 to 350°C, and a stable H_2 permeance was observed at all testing temperatures indicating the stable structure of the membrane C-16R.

Figure 47. H_2 characterization of the membrane C-16R.

The Sieverts plots taken during the permeation testing of the membrane C-16R are shown in Figure 48. The H_2 permeance of the membrane C-16R was 14.7 scfh/ft²-psi^{0.5} ($\Delta P=14.7$ psi with $P_{\text{tube}}=14.7$ psia) at 350°C, and increased to 20.9 scfh/ft²-psi^{0.5} as the temperature was increased to 450°C. The activation energy of the membrane C-16R (shown in Figure 48) was estimated to be 13.3 kJ/mol over the temperature range of 350-450°C.

Figure 48. Sieverts' plot of membrane C-16R at 350, 400 and 450°C.

The He leak of membrane C-16R was measured several times during the entire testing course of ~ 170 hours (as indicated in Figure 47). No measurable He leak was recorded even at the end of the testing, resulting in the ideal H_2/He selectivity of membrane C-16R remaining close to infinite throughout the entire testing course. The outstanding He leak stability of membrane C-16R could be attributed to that the membrane had been characterized at elevated temperatures followed by polished and re-plated before the characterization. Such steps functioned as a pre-annealing/polishing step that was designed for mitigating the He leak growth during the membrane synthesis.

Figure 49 shows the permeance history of the membrane C-16R during the exposure to a 5 ppmv $\text{H}_2\text{S}/\text{H}_2$ gas mixture at 400°C and subsequent recovery in pure H_2 at 400°C and 500°C. The H_2S concentration at the outlet of the shell side (retentate side) during the H_2S exposure as well as the recovery was also plotted in Figure 49. Upon the H_2S exposure, the H_2 permeance decreased immediately and reached a steady state value of 50% of the original value (before the H_2S exposure) at the end of 72 hours of exposure, indicating that about half of the surface active sites for H_2 dissociation were blocked by sulfur.

Figure 49. Poisoning and recovery of the membrane C-16R at 400°C with a 5 ppmv H₂S/H₂ gas mixture.

Before the recovery, Sieverts' testing was performed on the membrane C-16R in the 5 ppmv H₂S/H₂ gas mixture at 400, 350 and 450°C in order to examine whether the transport mechanism of H₂ being altered by the presence of H₂S. Figure 50 shows the resultant Sieverts' plot of the membrane C-16R taken in the presence of 5 ppmv H₂S. The good linearity of the data in the Sieverts' plot indicated that the membrane C-16R still followed Sieverts' law in the presence of 5 ppmv H₂S although much lower permeances were observed at all testing temperatures as expected. Obeying Sieverts' law in the presence of H₂S indicated that the H₂ permeating through the membrane remained diffusion-controlled rather than switching to surface adsorption-controlled. Peden *et al.* [39] reported that the H₂ transport mechanism would switch from diffusion-controlled to surface adsorption-controlled when the sulfur coverage on Pd surface was greater than a critical coverage of 0.4 mono layers (ML). The result suggested that the sulfur coverage on the Pd/Au surface was below the critical coverage under the testing condition. Previous studies indicated that each adsorbed sulfur could effectively block 4-13 active sites for H₂ dissociative adsorption [40,41]. Roughly 50% of the active sites blocked by sulfur suggested that the sulfur coverage on C-16R was 0.04 - 0.125 ML.

Activation energy for H₂ permeating would be altered on the sulfur-adsorbed Pd surface due to energy barrier for H₂ dissociation and diffusion created by the adsorbed sulfur [39-42]. However, the activation energy for H₂ permeation in the presence of H₂S could not be estimated on C-16R due to that the sulfur coverage was not the same at different temperatures. Indeed, the percentage of permeance decline increased as the temperature was decreased from 38% at 450°C to 62% at 350°C by comparing the permeance before and during the H₂S exposure (as shown in Figure 47 and Figure 50).

Figure 50. Sieverts' plot of membrane C-16R in 5 ppmv H₂S/H₂ gas mixture at 350 - 450°C.

After a cumulative 80 h exposure to 5 ppmv H₂S (including the Sieverts' testing), the inlet flow was switched to pure H₂ at 400°C to recover the permeance. As shown in Figure 49, the permeance was recovered to a steady value of 80% of the original value over a period of ~90 h along with the decrease of sulfur concentration at outlet of the retentate side. The rate of permeance recovery (slope in the plot) decreased as the recovery time increased and reached a constant value asymptotically. Additional recovery at a higher temperature of 500°C resulted in a further permeance increase and H₂S desorption, indicating more H₂S desorption and permeance recovery occurred at the higher temperature. The results suggested that the H₂ permeance recovery was directly related to the H₂S desorption. Since the H₂S adsorption on metals is exothermic, more permeance was recovered at higher temperatures due to more H₂S desorption. After the recovery at 500°C, the temperature was decreased to 400°C to compare the H₂ permeance before and after the H₂S exposure. Since the H₂ permeances of the membrane C-16R before and after the H₂S exposure/recovery test were identical, it is important to note that complete recovery (100%) of the H₂ permeance was possible at 500°C by using H₂ flow even after a long term H₂S exposure of ~80 hours. Figure 51 are the Sieverts' plot of the membrane C-16R before the H₂S exposure and after the recovery. The identical permeances at all testing temperatures as well as the activation energies before and after the H₂S test once again suggested the full restoration of membrane C-16R. A small He leak of 0.04 sccm ($\Delta P = 14.7$ psi with $P_{\text{tube}} = 14.7$ psia) during the recovery at 500°C (at elapsed time of ~310 h in Figure 49) was measured on C-16R, resulting in the selectivity of C-16R remaining over 10000.

Figure 51. Sieverts' plot of membrane C-16R at 350 - 450°C before and after exposure to a 5 ppmv H_2S/H_2 gas mixture.

As describe above, the sulfur resistance increased with the increasing Au content in the Pd/Au membrane which would be explained by the fact that the binding energy between H_2S and the Pd/Au decreased as the Au composition was increased. Figure 52 shows the relative permeance in 5 ppmv H_2S (with respect to the original permeance before H_2S exposure) as a function of Au composition at 400°C along with the results reported in the previous works [37,43]. The relative permeance increased almost linearly with the Au composition, and that of the membrane C-16R located quite precisely within the range of the previous works.

Figure 52. Relative permeance in the presence of 5 ppmv H_2S at 400°C as a function of Au composition (* from reference [37]; ** from reference [43]).

Fundamental study on the H₂S poisoning of Pd and Pd-Au alloys

Pure-Pd and the un-annealed Pd/Au bi-layer samples have been previously been studied in the 3rd quarterly report (Q3) with the following conclusions: both the EDX spectra and surface X-ray mapping showed the existence of elemental S indicating the formation of surface sulfides. On the other hand, the effect of poisoning and recovery treatments on the surface morphology for the Pd/Au alloy layer was not noticeable within the spatial resolution of the EDX. EDX and XRD not being particularly suited for the study of surfaces the following study here below was conducted to assess the poisoning and recoverability of Pd and Pd-Au samples with XPS, perfectly suited for the study of adsorbed species on the surface.

Porous stainless steel coupons (1.5 cm x 1 cm x 0.1 cm; 0.1 μ m media grade) purchased from Mott Metallurgical Corp were oxidized at 700 - 800°C for 12 hours and plated with approximately 8 - 10 μ m of Pd. Pd/Au samples were plated with an additional 0.5 μ m of Au. The Pd/Au samples were annealed for 24 hours in H₂ at 550°C to form the fcc alloy on the surface.

Pd reacts with H₂S and forms palladium sulfide (Pd₄S) in the WGS reaction temperature range of 350-500°C. As shown in Figure 53[a], the XRD patterns of un-poisoned Pd (annealed at 500°C in H₂ for 48 hours) and after the H₂S exposure indicated that the bulk Pd₄S formed after the exposure to a 50ppm H₂S/H₂ gas mixture for 24h at 400°C. The SEM pictures of Pd after the H₂S exposure also showed a significant deformation compared to the one after the annealing due to the formation of Pd₄S. According to our previous studies, Pd₄S formation was a function of exposure temperature, time, and H₂S concentration. After recovering in pure H₂ for 48 hours at 500°C, the disappearance of Pd₄S phase and sulfur composition was observed in the XRD patterns and EDS analysis (as shown in Figure 53[a], [d]), indicating the reversibility of the bulk sulfidation although the morphology was not restored to the original state. However, according to the permeation experiments, Pd membranes could not fully restore the permeance after H₂S exposure indicating that the existence of irreversible sulfide bonding between Pd and sulfur. No significant phase and morphology changes were observed on the Pd/Au alloy after the H₂S exposure (as shown in Figure 54) indicating no bulk sulfide formation. The significant permeance drop of C-16R during the H₂S exposure indicated the formation of a/some surface sulfides. To study the surface sulfur, surface sensitive instrument for chemical analysis, i.e. XPS, was utilized.

Survey scans of the samples indicated the existence of Pd, Au (on the Pd/Au samples), S, C, O, and small amount of Si on the surfaces. Carbon, oxygen, and silicon were adventitious and usually resulted from the contamination during the sample handling and storage. For more precise quantitative analysis, high resolution scans on the elements interested were performed. Figure 55 [a] shows the high resolution core level spectra of S 2p of the Pd samples pre-reacted with 10 ppm H₂S/H₂ for 24 hours at 350°C and after recovering in H₂ for 48 hours at 500°C. Two separate S-species were apparent from the data shown: the feature at ~162-165 eV was attributed to a sulfide and the feature at ~168 eV to a sulfate. Sulfide was the metal-sulfur bonding which was the major interest in the study since it caused the permeance decline while sulfate was the bonding between sulfur and oxygen on the surface usually came from environment. The well-defined doublet sulfide peaks observed on the sulfur pre-reacted sample indicates the single sulfide specie which was most likely palladium sulfide. After recovering, the intensity of the sulfide peak decreased dramatically suggesting the occurrence of the desulfurization of Pd. It should be noted that the recovery condition was the same for all the samples mentioned in the entire coupon study which was in H₂ at 500°C for 48 hours. The condition was chosen due to most of the full permeance restoration were observed on the Pd/Au membranes under such recovering condition. Figure 55[b] shows the high resolution core level spectra of S 2p of the Pd-Au alloy samples pre-reacted with 0.5 ppm H₂S/H₂ for 24 hours at 450°C and after recovering in H₂ for 48 hours at 500°C. Sulfide and sulfate species were also seen in the spectra. Smaller intensity of the sulfide peaks and less-defined peak shape suggested that less sulfur was adsorbed but likely more than one metal sulfide was formed during the H₂S exposure. The decrease of sulfide species was also seen on the Pd-Au sample after recovering indicating the desulfurization of Pd-Au.

Figure 53. [a] XRD patterns of un-poisoned, H₂S-poisoned, and H₂-recovered Pd, and SEM picture of [b] un-poisoned, [c] H₂S-poisoned, and [d] H₂-recovered Pd (The sulfur composition inserted in the pictures were detected by EDS).

Figure 54. [a] XRD patterns of un-poisoned, H₂S-poisoned, and H₂-recovered Pd/Au, and SEM picture of [b] un-poisoned, [c] H₂S-poisoned, and [d] H₂-recovered Pd/Au (The sulfur composition inserted in the pictures were detected by EDS).

Figure 55. High resolution core level spectra of S 2p of the sulfur pre-reacted and recovered [a] Pd and [b] Pd/Au sample.

As mentioned previously, since the major interest of the study was to quantify the sulfides, Peak fitting of the S 2p peaks was performed by using Advantage 4.38 software to differentiate and determine the quantity of sulfide from sulfate. An example of peak fitting was given in Figure 56.

Figure 56. Peak fitting for the S 2p peak.

Figure 57 shows the amount of sulfide formed on the Pd surface after the exposure to a 50 ppm H₂S/H₂ gas mixture for 24 hours as a function of temperature and after the recovery. The amount of sulfide formed during the poisoning decreased with increasing temperature, which was in good agreement with our previous data of XRD. This temperature dependence was due to the exothermic nature of the chemisorption of H₂S on Pd. After the recovery, almost identical and significant amount of sulfide remained on the surface of the samples that were poisoned at different temperatures suggesting that the remained sulfide were most likely irreversible under the recovery condition. Barbier et al.[43] have reported found that the amount of irreversible sulfur was independent of the concentration of H₂S in the feed, while the total amount of sulfur deposited increased with increasing H₂S content.

Figure 57. Ratio of sulfide on Pd after exposure to 50 ppm H₂S for 24 hours as a function of temperature and after the recovery

Figure 58 shows the amount of sulfide formed on the Pd/Au surface after the exposure to a 50 ppm $\text{H}_2\text{S}/\text{H}_2$ gas mixture for 24 hours as a function of temperature and after the recovery. No apparent temperature dependence of the sulfide formed after the poisoning was observed compared to Pd. This could be that much less sulfur was absorbed on the Pd/Au evidenced by the smaller and less-defined sulfide peaks as mentioned previously. However, the permeation data of the Pd/Au membrane in the presence of H_2S clearly exhibited the temperature dependence of the sulfur poisoning with more permeance decline at lower temperatures [44].

Although it was not significant, the amount of sulfide decreased after the recovery indicating the desorption of sulfur on the Pd/Au surface. The un-poisoned Pd/Au sample showed a roughly 5 at% sulfide on the surface, which was very close to the values after the recovery. It should be noted that the peak fitting of S 2p peaks for the Pd/Au samples was performed by assuming one sulfide species of “PdAu alloy sulfide”. This assumed that the surface composition of the Pd/Au alloy was uniform for the Pd/Au samples.

Figure 58. Ratio of sulfide on Pd/Au after exposure to 50 ppm H_2S for 24 hours as a function of temperature and after the recovery

The Pd and Pd/Au (8 - 11 wt% Au) coupon samples characterized in this study were prepared on the 0.1 μm media grade PSS or porous Hastelloy C-22 coupons (1cm x 1cm or 1cm x 1.5cm). The H_2S poisoning and the recovery of the Pd and Pd/Au coupons were conducted in the annealing module inside a BLUE M tube furnace. The detailed preparation of the coupons as well as the experimental setup and procedure can be found in the previous quarterly reports. The exposure conditions for the Pd and Pd/Au alloy coupons were with the H_2S concentrations of 0.2 - 55 ppm at 350 - 500°C for 2 - 24 hours. The recovery of the poisoned samples was performed at 500°C in H_2 for 48 hours.

The XPS instrument used for the surface chemical analysis was the Thermo Scientific K-alpha at the High Temperature Material Laboratory at Oak Ridge National Laboratory, Tennessee.

Figure 59[a-e] shows the XPS spectra for the Pd samples before and after the H_2S exposures under different conditions. The spectrum for the Pd sample before the H_2S exposure (Figure 59[a]) shows not only the Pd peaks, but also the carbon 1s peak, nitrogen 1s peak, oxygen 1s² and Auger KLL peak,

² O 1s peak overlaps with Pd 3p peak at ~530 eV, the presence of the O Auger KLL feature (shown at ~1000 eV) confirmed the presence of O 1s peak as well as oxygen.

sodium 1s and KL1 peak, and chlorine 2p peak. In addition, although not apparent, the S 2s and 2p peaks were also observed in the spectrum. The presence of sodium along with chlorine was most likely from hands (NaCl) during the sample handling. On the other hand, carbon, oxygen, nitrogen, and sulfur usually came from the environment due to the unavoidable adsorption of the gaseous contaminants during the sample storage.

Similar spectra compared to the un-poisoned one were observed for the samples after the exposures to H₂S under different conditions (See Figure 59 [b]-[e]). Although it was not obvious in the plot, the intensities of the sulfur 2s and 2p peaks increased after the poisoning even under the mildest exposure conditions. These conditions included 0.2 ppm H₂S/400°C/24 hours (See Figure 59 [b]), 50 ppm H₂S/400°C/2 hours (See Figure 59 [c]), and 50 ppm H₂S/500°C/24 hours (See Figure 59 [d]), where no Pd₄S phase was detected by the XRD and SEM after the poisoning. The spectrum of the Pd sample after the H₂S exposure under the condition that generated the highest extent of the sulfidation (i.e. 50 ppm H₂S/350°C/24 hours) showed the most intense sulfur 2s and 2p peaks as expected (See Figure 59 [e]). The relative atomic fractions of Pd and S on the Pd samples before and after the H₂S exposure under the different conditions are summarized in Table 9. It should be noted that the sulfur fraction was calculated based on the sulfur 2p and Pd 3d peak in the survey scans. Noticeable increases in sulfur atomic fraction were observed on the poisoned samples compared to the un-poisoned one even under the mildest exposure conditions. The results showed that sulfur had indeed adsorbed on the Pd surfaces following the exposure to the H₂S/H₂ mixture.

Figure 59. XPS survey spectra of [a] un-poisoned Pd, after exposing to [b] a 0.2 ppm H₂S/H₂ at 400°C for 24 hours, a 50 ppm H₂S/H₂ [c] at 400°C for 2 hours, [d] at 500°C, and [e] 350°C for 24 hours

Table 9. Composition of poisoned Pd samples

Sample conditions	Pd (at%)	S (at%)
Un-poisoned	90.5	9.5

0.2 ppm H ₂ S/400°C/24 hours	77.1	22.9
50 ppm H ₂ S/400°C/2 hours	79.6	20.4
50 ppm H ₂ S/500°C/24 hours	80.4	19.6
50 ppm H ₂ S/350°C/24 hours	62.2	37.8

High resolution (narrow) scans of the elements of interest, including Pd, S, C, and O, were performed on the poisoned Pd samples for more accurate quantitative analysis and the chemical status of the elements. The analysis of the high resolution sulfur peak was especially emphasized in the study since the quantity and the bonding status of sulfur was the major interest of the work. Figure 60 shows the high resolution core level spectrum of S 2p of the Pd sample exposed to the 50 ppm H₂S/H₂ mixture for 24 hours at 400°C. The peak fitting of the spectrum is also shown in Figure 60. Two separate S-species were apparent from the data shown: the feature at ~162 - 165 eV was attributed to a sulfide and the feature at ~168 eV to a sulfate. The presence of the sulfide species confirmed the bonding between Pd and sulfur, which caused the permeance decline of the membranes in the presence of H₂S. On the other hand, the presence of sulfate species (S bonded with oxygen) was most likely due to the adsorption of the environment contaminants and the partial oxidation of the sulfide on the surfaces during the storage.

As shown in Figure 60 the broad and non-descript shape of the sulfate peak indicated a number of sulfate bonding chemistries. The deconvolution of the sulfate peak, therefore, became extremely difficult due to the lack of knowledge of how many bonding chemistries that comprised the peak and their corresponding standard binding energies. In fact, the quantification of the amount was more important than the differentiation of the bonding chemistries of sulfate since the bonding chemistries of sulfate would not provide the information regarding the bonding chemistry between Pd and sulfur, which was more the concern in the study. As a result, only a set of sulfur double peak with S 2p_{3/2} at ~168.8 eV was used to fit the sulfate peaks to quantify the sulfate fraction. It should be noted that sulfur possessed a doublet peak structure in the 2p orbitals. For the peak fitting conditions used in the study for both the Pd and Pd/Au samples, the full-width, half-maximum (FWHM) values were constrained between 0.5 - 3.5 and the Lorentzian/Gaussian (L/G) ratio was constrained between 0 - 50%. The distance of the 2p orbital split was also 1.16 eV. All S 2p_{1/2} peaks were equal to half the area of the corresponding 2p_{3/2} peak, and the FWHM and L/G ratios of the doublets were kept equal.

Figure 60. High resolution XPS scan and peak fitting of the S 2p peak of the Pd sample after the H₂S exposure of 50 ppm at 400°C for 24 hours

On the other hand, the observed well-defined doublet sulfide peaks indicated a predominant Pd-sulfide species with the S 2p_{3/2} peak at ~163.2 eV (See Figure 60). However, a small shoulder at lower binding energies of ~162 eV indicated a small fraction of another Pd sulfide species since the only metal present on the sample surface was Pd.

In fact, the sulfide species of the lower binding energy (~162 eV) became more apparent under milder poisoning conditions where the bulk Pd₄S was not detected after the exposures (e.g. 500°C/24 hours/55 ppm H₂S). Figure 61 shows the high resolution spectra of S 2p of the Pd samples exposed to the 50 ppm H₂S/H₂ for 24 hours at 350 - 500°C. While the spectra of the Pd samples after the H₂S exposures at 350 - 450°C were similar with the predominant Pd sulfide species (S 2p_{3/2} at ~163.2 eV) appearing in the spectra, the spectrum after the exposure at 500°C shows the broad and non-descript sulfide peak with the summit of the peak shifting towards the lower binding energy. The less-defined sulfide peak indicated that more than one sulfide species was present on the samples' surface and none of them was predominant, which was due mainly to much smaller sulfide peak at 163.2 eV compared to other poisoning temperatures. In fact, the intensity of the sulfide peak at 500°C was much smaller compared to other spectra at lower temperatures, suggesting much smaller amount of sulfur presented on the sample. Similar broad and non-descript sulfide peaks with much smaller peak intensities and the shift of the peak summit toward the lower binding energy were also observed on the samples after the exposures under the conditions that did not generate the bulk Pd₄S formation, such as below 5 ppm H₂S at 400°C for 24 hours, or 2 hours exposure at 400°C with a 50 ppm H₂S/H₂ mixture. The results appeared to suggest that the sulfide of the lower binding energy (~162 eV) most likely resulted from the Pd-S bonding at the top surface, while the sulfide of higher binding energy (~163.2 eV) was caused by the Pd-S bonding in the sub-layers. Forbes et. al. [45] proposed a structural model for the sulfur-adsorbed on Pd (1 1 1) surface with one sulfur atom on the top surface and two sulfur atoms in the sub-layers exposing to 4 Pd atoms per unit cell. The model has been substantiated by the authors with the results of the atomic resolution scanning tunneling microscope (STM) and the low energy electron diffraction (LEED) analysis of the (7^{0.5}*7^{0.5})R19° sulfur over-layer lattices formed on the Pd (1 1 1) surface. The Pd-S bonding in the sub-layers was considered to be the precursor for the bulk sulfide. Since the bulk Pd₄S phase has been

confirmed by the XRD on the poisoned Pd samples which exhibited the sub-layers Pd-S bonding as mentioned in the previous quarterly report, the Pd-S bonding in the sub-layer (~ 163.2 eV) most likely resulted from the Pd_4S .

In addition, the binding energy of the sulfide S 2p peak was found to increase with increasing surface sulfur coverage on the Pd surface [46]. As shown in Figure 61, the results obtained agreed with the trend. It should be noted that after the exposure to milder conditions (e.g. $500^\circ\text{C}/24$ hours/55 ppm H_2S), the sulfur coverage was also smaller. The binding energy for the S 2p peak of PdS was reported to be 161.5 ± 0.3 eV [46]. As a result, the sulfide with the binding energy of ~ 162 eV was probably PdS. However, according to the thermodynamics, PdS is less stable compared to other possible sulfide such as Pd_3S or Pd_{16}S_7 and required much higher H_2S concentration to form. As a result, a further characterization is still needed to confirm the type of the Pd-S bonding formed on the Pd surface (at ~ 162 eV).

Figure 61. High resolution XPS scans of the S 2p peak of the Pd samples after the H_2S exposure of 50 ppm for 24 hours at $350 - 500^\circ\text{C}$

Figure 62 shows the high resolution core level spectra of Pd 3d orbitals of the Pd samples before and after the exposure to the 50 ppm $\text{H}_2\text{S}/\text{H}_2$ for 24 hours at $350 - 500^\circ\text{C}$. The position of the Pd $3d_{5/2}$ peak before poisoning was at 335.38 eV, while the binding energy of the Pd-Pd bonding was 335.1 eV. The slight peak shift to a higher binding energy was possibly due to the slight surface oxidation. The formation of PdO at 298K was confirmed in the literature [47]. The presence of the oxygen was also confirmed by the survey spectra (See Figure 59).

The shifts of the Pd 3d peaks to the higher binding energy after the poisoning were observed in Figure 62, especially at lower poisoning temperatures. When Pd and S form a bonding, the electrons in Pd transferred to sulfur due to the higher electron affinity of sulfur. This resulted in the binding energy shift to a lower value for sulfur compared to S-S bonding and to a higher value for Pd compared to Pd-Pd bonding. Along with the binding energy of sulfide observed (~ 163.2 eV, Figure 61), the shift of the Pd 3d peaks to the higher binding energy substantiated the Pd-S bonding. It should be noted that the S-S bonding had the binding energy of 164 eV for the S 2p peak.

As shown in Figure 62, the shift of the Pd 3d peak increased with the decreasing poisoning temperatures suggested the increase of the Pd-S bonding with decreasing temperature. Higher extents of the sulfur poisoning on the Pd samples at lower temperatures were confirmed in the XRD and SEM studies in our previous works. Chaplin et al. [48] has also reported that the shift of the Pd 3d peak increased with increasing sulfur fouling (poisoning) extent of the Pd-based catalysts. Similarly, the shifts of the Pd 3d peaks to the higher binding energy after poisoning under other conditions tested in the study

(i.e. 0.2 - 50 ppm H₂S for 2 - 24 hours at 400°C) were also observed with the only difference being the extent of the peaks shift. Once again, the higher extents of the peak shift due to more Pd-S bonding were observed on the samples under the conditions which caused the higher extent of sulfur poisoning.

Figure 62. High resolution XPS scans of the Pd 3d peak of the Pd samples after the H₂S exposure of 50 ppm for 24 hours at 350 - 500°C

Figure 63[a] shows the composition as a function of depth of the Pd sample exposed to the 50 ppm H₂S at 450°C for 24 hours. The depth was determined by using a known sputter rate (5 nm/min) calibrated with a standard SiO₂ film. The S 2p signal was deconvoluted into sulfide species and sulfate species. Due to the small signal strength, both sulfide and sulfate signals were multiplied by 5 in the plot. The carbon signal decreased largely with depth, which confirmed that the carbon was a surface contaminant and came from the environment. Both Pd and sulfide signals increased as the adventitious carbon was removed by the sputtering. While Pd increased to a constant value of approximately 70 at%, the sulfide increased initially to ~11 at% and then decreased to reach a plateau value of ~8 at%. The unchanged sulfide composition during the entire depth profile suggested sulfur bonded with Pd deep into the Pd layer. Indeed, bulk sulfide (Pd₄S) was confirmed on the sample after the H₂S exposure under the condition (XRD and SEM). On the other hand, the sulfate decreased at all sputter increments from ~4 at% initially to a constant value ~2 at%. This confirmed that the sulfate species was only present on the surface. The narrow scans of the S 2p at each sputter increment shown in Figure 63[b] substantiated that the sulfide phase was still present deep into the Pd layer while sulfates were only present on the surface. Finally, the plateau values for the adventitious carbon and sulfate signals reached after ~10 nm, might have been due to shadowing of the supporting Ar-ion beam because of high surface roughness of the porous coupon samples.

Figure 64[a] shows the composition as a function of depth of the Pd sample exposed to the 50 ppm H₂S at 500°C for 24 hours. Similarly, the S 2p signal was deconvoluted into a sulfide specie and a sulfate specie. Both sulfide and sulfate signals were multiplied by 10 in the plot due to the extremely small signal strength. While Pd increased to approximately 70 at%, the sulfide increased initially to ~4 at% as carbon was removed then decreased to ~2.5 at%. The sulfate decreased at all sputter increments from ~3 at% initially to < 1 at%. The narrow scans of the S 2p at each sputter increment are shown in Figure 64[b]. In addition to sulfate, sulfide also decreased with increasing supporting increments although the decreasing rate was smaller compared to the sulfate. The result suggested that the sulfide formed in the near surface area and did not penetrate too deep into the Pd layer.

Figure 63. [a] Composition as a function of depth of the Pd sample after the exposure to the 50 ppm H₂S at 450°C for 24 hours, and [b] corresponding narrow scans of the S 2 p peak at each sputtering increment

Figure 64. [a] Composition as a function of depth of the Pd sample after the exposure to the 50 ppm H₂S at 500°C for 24 hours, and [b] corresponding narrow scans of the S 2 p peak at each sputtering increment

In addition to the poisoning, the recovery of the poisoned Pd samples was also characterized to further understand the Pd-S interactions. Figure 65 compares the high resolution spectra of Pd 3d orbitals of the Pd sample after poisoning with 50 ppm H₂S/H₂ for 24 hours at 350°C and after the recovery at 500°C in H₂ for 48 hours. The spectrum of the un-poisoned sample was also included in Figure 65 as a reference. The spectrum of the Pd sample after poisoning showed a shift of the Pd peaks to a higher binding energy compared to the un-poisoned Pd due to the Pd-S bonding as discussed previously. After the recovery, the Pd peaks shifted back to almost the original positions before the poisoning indicating the reduction of most of the Pd-S bonding formed during the H₂S exposure. Similar shift of the Pd 3d peaks back to the original positions after the recovery was also observed on the Pd samples poisoned under other conditions tested in the study. However, it was insufficient to determine if there was still Pd-S bonding presented on the surface after the recovery based merely on the high resolution spectra of Pd 3d peaks.

Figure 65. High resolution XPS scans of the Pd 3d peak of the Pd samples before, after the H₂S exposure of 50 ppm for 24 hours at 350°C, and after recovery in H₂ at 500°C for 48 hours

Figure 66 displays the high resolution spectra of S 2p orbitals of the Pd sample after poisoning with 50 ppm H₂S/H₂ for 24 hours at 350°C and after the recovery at 500°C in H₂ for 48 hours. As shown in Figure 66, the significant decrease of the sulfide peak intensity after the recovery substantiated once again the reduction of the Pd-S bonding. In addition, the shape of the sulfide peak became broad and lost its apparent doublet peak feature. Since the well-defined sulfide peak most likely resulted from the Pd-S bonding in the sub-layers as mentioned earlier, the result suggested that most of the sulfide formed in the sub-layer were recovered to Pd after the recovery. Indeed, the disappearance of the Pd₄S phase was observed on the Pd sample after the recovery as discussed in the previous quarterly report. However, there was still noticeable amount of sulfur on the sample after the recovery. This indicated the recovery did not remove all the sulfur adsorbed on the Pd surface.

Figure 66. High resolution XPS scans of the S 2p peak of the Pd samples before, after the H₂S exposure of 50 ppm for 24 hours at 350°C, and after recovery in H₂ at 500°C for 48 hours

Figure 67 exhibits the high resolution spectra of S 2p orbitals of the Pd sample after poisoning in a 50 ppm H₂S/H₂ for 24 hours at 500°C and after the recovery. A decrease of the sulfide peak intensity after the recovery was observed in Figure 67 due to the reduction of the Pd-S bonding. However, the decrease was not as noticeable as the one observed in the case of poisoning at 350°C (See Figure 66) due to the fact that the sulfide formed was much less under the condition. Although the amount of the sulfide was smaller during the poisoning, there was still a noticeable amount of sulfide that remained on the surface after the recovery. This indicated that a certain amount of the sulfur was bonded with Pd with a high binding energy and it was difficult to remove those sulfur under the recovery condition.

Figure 67. High resolution XPS scans of the S 2p peak of the Pd samples before, after the H₂S exposure of 50 ppm for 24 hours at 500°C, and after recovery in H₂ at 500°C for 48 hours

Figure 68[a] shows the composition as a function of the depth of the Pd sample after the recovery that was previously exposed to the 50 ppm H₂S at 450°C for 24 hours. The sulfide and sulfate signals deconvoluted from the S 2p signal were increased by a factor of 10 in the plot due to the extremely small signal strength. Once again, the increase of Pd to approximately 75 at% due to the removal of the adventitious carbon signal was observed. Both the sulfide and the sulfate decreased with continued sputtering from ~ 2 at% to <1 at%. The narrow scans of the S 2p at each sputter increment shown in Figure 68[b] also confirmed the decrease of both sulfide and sulfate signals with increasing increments. Since the sample after poisoning showed the sulfide presence deep into the Pd layer as shown in Figure 63, the result suggested that most of the Pd-S bonding in the bulk was removed and only Pd-S bonding near the surface remained after the recovery.

Figure 68. [a] Composition as a function of depth of the Pd sample after the exposure to the 50 ppm H_2S at 450°C for 24 hours, and [b] corresponding narrow scans of the S 2 p peak at each sputtering increment

Figure 69 shows the sulfide fraction (relative to Pd) on the Pd samples after the poisoning with the 50 ppm H_2S for 24 hours and the recovery as a function of temperature. The sulfide and palladium contents were calculated from the high resolution XPS S 2 p peak (deconvoluted) and Pd 3d peak. It should be noted that the sulfide fraction estimated included both sulfide species (the S 2p peak at 163.2 eV and 162 eV, respectively as shown in Figure 60). The fraction of sulfide after the poisoning decreased with increasing temperature from roughly 32 at% at 350°C to ~ 13 at% at 500°C . Less sulfide formed at lower temperatures was due to the less stability of the sulfide at higher temperatures according to thermodynamics.

Figure 69 also shows that the sulfide fraction decreased to 7 - 10 at% after the recovery. A slightly higher sulfide fraction was observed on the sample that was previously poisoned at lower temperatures with more sulfide formed. Noticeable amounts of sulfide remained on the samples after the recovery indicated that a certain amount of the Pd-S bonding were irreversible under the recovery condition. Much more sulfide reduction was observed at $350 - 450^\circ\text{C}$ compared to 500°C . Since poisoning at $350 - 450^\circ\text{C}$ formed bulk sulfide while poisoning at 500°C most likely formed only the surface sulfide as evidenced by SEM, XRD, and XPS, the result suggested that most Pd-S bonding in the bulk was reduced to pure Pd-Pd bonding. On the other hand, the surface sulfide contained a higher percentage of irreversible Pd-S bonding. Indeed, surface sulfide was much more stable compared to bulk sulfide and could present under the conditions where bulk sulfide was not stable according to the thermodynamics. As a result, it was much more difficult to break the surface Pd-S bonding. In addition, the binding energy of sulfur to Pd increased as the sulfur coverage was decreased [49]. This caused the Pd-S bonding to be more difficult to break at low sulfur coverage.

Figure 69. Total Pd sulfide on the Pd surfaces after the poisoning and the recovery as a function of temperature. The poisoning was performed with the 50 ppm H₂S/H₂ mixture for 24 hours at 350 - 500°C and the recovery condition was fixed at 500°C in H₂ for 48 hours

Figure 70 shows the sulfide atomic fraction on the Pd samples after poisoning with the 50 ppm H₂S at 400°C and after the recovery as a function of time. After poisoning, the sulfide fraction appeared to increase asymptotically with increasing exposure time from ~ 7 at% after 2 hours exposure to a plateau value of ~ 28 at% after 24 hours exposure. This indicated that the amount of sulfide formed increased with increasing exposure time, and the sulfide formed near the surface reached the saturation value as the exposure time increased. After the recovery, significant reduction of the sulfide fraction on the samples was observed indicating the removal of sulfur. The amount of sulfide reduced after 4 - 24 hours exposures (the conditions that caused the bulk sulfide formation) was much more significant compared to that after 2 hours exposure which did not result in the formation of the bulk sulfide. Once again, this was due to the higher stability of the surface sulfide than bulk sulfide and the low surface coverage as mentioned earlier

Figure 70. Total Pd sulfide on the Pd surfaces after the poisoning and the recovery as a function of exposure time. The poisoning was performed with the 50 ppm H₂S/H₂ mixture for 2 - 24 hours at 400°C and the recovery condition was fixed at 500°C in H₂ for 48 hours

Figure 71 shows the sulfide atomic fraction on the Pd samples after poisoning with the 0.2 - 50 ppm H₂S at 400°C for 24 hours along with the sulfide fraction after the recovery. As expected, the sulfide fraction increased with increasing H₂S concentration. Approximately 9 at% sulfide presented on the surface with the 0.2 ppm H₂S exposure and increased to 28 at% with the 50 ppm H₂S exposure. A sudden increase was observed above 5 ppm H₂S exposure, which indicated the beginning of the bulk sulfide formation. A large increase in the intensity of the sulfide peak was also seen on the samples with the presence of bulk sulfide (See Figure 61). Once again, the reduction of the sulfide fraction on the samples was observed after the recovery. In addition, due to the higher stability of surface sulfide than bulk sulfide and the higher sulfur coverage, more significant reduction of sulfide under the conditions that formed the bulk sulfide (i.e. > 10 ppm H₂S) was observed. The noticeable amount of irreversible sulfide remained on the samples after the recovery confirmed that the irrecoverable permeance loss of the Pd membrane after the H₂S exposure was caused by the un-recovered sulfur in our previous work.

Figure 71. Total Pd sulfide on the Pd surfaces after the poisoning and the recovery as a function of H₂S concentration. The poisoning was performed with the 0.2 - 50 ppm H₂S/H₂ mixture for 24 hours at 400°C and the recovery condition was fixed at 500°C in H₂ for 48 hours

Figure 72 shows the XPS survey spectra for the Pd/Au samples before and after the 24 hours exposures with the 50 ppm H₂S/H₂ mixture at 350 - 500°C. The presences of palladium and gold (Au 4f, ~84 eV) on the samples were confirmed by the spectra before and after the H₂S exposures. In addition, carbon (C 1s), nitrogen (N 1s), oxygen (O 1s, O KLL), sodium (Na 1s, Na KL1), chlorine (Cl 2p) along with small amount of sulfur (S 2s and 2p) were also presented on the samples randomly. As mentioned previously, sodium, chlorine, carbon, oxygen, nitrogen most likely resulted from the sample handling and storage due to the contact with contaminants from the environment. Gaseous sulfur containing compounds from the environment could also be adsorbed on the sample surface during the sample storage as evidenced by the small S peak in the spectrum of the un-poisoned sample (See Figure 72).

The spectra of the samples after the poisoning showed a slight increase in intensity of the S peaks (See Figure 72), which indicated sulfur adsorption. The relative atomic fractions of the elements of interest, including Pd, Au, and S on the Pd/Au samples before and after the H₂S exposures were

summarized in Table 10. The elemental fractions were calculated based on the S 2p, Pd 3d, and the Au 4f peaks.

Figure 72. XPS survey spectra of the Pd/Au samples before and after the 24 hours exposures with the 50 ppm H₂S/H₂ mixture at 350 - 500°C

Table 10. The composition of the poisoned Pd/Au samples

Sample conditions	Pd (at%)	Au (at%)	S (at%)
Un-poisoned	78.1	14.8	7.1
50 ppm H ₂ S/350°C/24 hours	70.8	15.5	13.5
50 ppm H ₂ S/400°C/2 hours	66.8	15.5	17.7
50 ppm H ₂ S/450°C/24 hours	66.2	11.3	22.5
50 ppm H ₂ S/500°C/24 hours	61.5	17	21.5

Figure 73[a] and [b] respectively show the high resolution core level spectra of Pd 3d and Au 4f orbitals of the Pd/Au samples before and after the exposure to 55 ppm H₂S/H₂ for 24 hours at 350 - 500°C. The positions of the Pd 3d_{5/2} and Au 4f_{7/2} peaks before poisoning was at 335.2 and 83.6 eV. The slight position shifts of both Pd and Au peaks compared to the Pd-Pd and Au-Au bonding was due to the Pd/Au alloying and the slight oxidation as mentioned earlier.

In contrary to poisoned Pd (See Figure 62), the shifts of the Pd 3d and Au 4f peaks after the poisoning were negligible as shown in Figure 73 although the presence of the sulfide (i.e. Pd-S, Au-S, or Pd_xAu_y-S) on the Pd/Au samples was confirmed by the high resolution scans of the S 2p peak which will be described shortly. Usually, shifts of the metal bonding (Pd, Au) to higher binding energies when metal sulfide (Pd sulfide, Au sulfide) formed were observed [38,48,50,51] due to the electrons transfer from the metal to sulfur. The insignificant shifts of the Pd 3d and Au 4f peak observed was most likely due to the

extremely small sulfide formed. Chaplin et al. [6] reported that the shift of the Pd 3d peak increased with increasing sulfur poisoning extent of the Pd-based catalysts.

In addition, several researches [52,53] have shown that the Au 4f peak position of the Au₂S nanostructures was identical to that of metal Au. The lack of Au peak shifting observed on the Au₂S was due to the covalent characteristic of the Au-S bonding due to the small electron affinity between S and Au [52]. As a result, it was also possible that the negligible shift of the Pd and Au peaks observed on the poisoned Pd/Au samples resulted from the enhancement of the covalent characteristic of the sulfide bonding by Au alloying.

The negligible shifts in both Pd 3d and Au 4f peaks of the poisoned Pd/Au samples (See Figure 73) made the peak deconvolution with different bonding chemistries (including the Pd-S and Au-S) extremely difficult. In addition, a number of possible bonding including Pd-Pd, Pd-O, Pd-S, Pd-Au for the Pd peak and Au-Au, Au-S, Au-O, Au-Pd without the standards also increased the difficulty for the peak deconvolution.

Figure 73. High resolution XPS scans of [a] Pd 3d and [b] Au 4f peak of the Pd/Au samples after the H₂S exposure of 55 ppm for 24 hours at 350 - 500°C

Figure 74 shows the high resolution core level spectrum of S 2p of the Pd/Au sample exposed to the 50 ppm H₂S/H₂ for 24 hours at 350°C. The deconvolution of the peak is shown in Figure 74. Similar to the poisoned Pd (See Figure 60), both sulfide (at ~162 - 165 eV) and sulfate (at ~168 eV) were presented on the surface. As mentioned previously, while the sulfide species resulted from the metal-sulfur bonding (i.e. Pd-S, Au-S, or Pd_xAu_y-S), the sulfate species most likely resulted from the adsorption of the environmental contaminants and the partial oxidation of sulfide on the surface. In addition, Figure 74 also shows that the intensity of the peak was very small as evidenced by the rough (zigzag) outline of the peak. This indicated that the amount of sulfide formed on the Pd/Au surface was extremely small.

In contrast with the poisoned Pd (See Figure 60), Figure 74 also shows that the sulfide peak of the poisoned Pd/Au was broad. This indicated the sulfide peak was composed of a number of sulfide bonding chemistries. Indeed, in addition to the two possible Pd-S bonding chemistries (at ~162 and 163.2 eV) as mentioned earlier, Au-S (more than one), and Pd_xAu_y-S bonding chemistries also possibly existed on the sample. In order to ease the peak fitting, an assumption was made with only one predominant Pd and Au sulfide species and no alloy sulfide presented on the samples. Since no bulk sulfide formed on the Pd/Au samples, the Pd sulfide peak at 162 eV was chosen. Since Au has a higher electronic affinity than Pd (therefore, closer to the value of sulfur), the position of the Au sulfide peak was considered to be at higher binding energy than Pd sulfide. As a result, the predominant Au sulfide (Au₂S) peak at 162.6 eV reported in the literature [52-54] was chosen for the peak deconvolution in the study.

Figure 74. High resolution XPS scan of the S 2p peak and the peak fitting of the Pd/Au sample after the H₂S exposure of 50 ppm at 350°C for 24 hours

Figure 75[a] shows the composition as a function of depth of the Pd/Au sample exposed to the 50 ppm H₂S at 350°C for 48 hours. As mentioned previously, the depth was determined by using a known sputter rate calibrated with a standard SiO₂ film. The S 2p signal was deconvoluted into a sulfide species and a sulfate species. Both sulfide and sulfate signals were multiplied by 10 in the plot due to the extremely small signal strength. The significant decrease of the adventitious carbon fraction removed by the sputtering resulted in the increases in both Pd and Au fractions to ~75 and 7 at%, respectively. The total sulfide fraction decreased from ~2.3 at the surface to ~0.5 at% at the depth of 10 nm. The sulfate also decreased at all sputter increments from ~1.1 at% initially to ~0.2 at%. The narrow scans of the S 2p at each sputter increment are shown in Figure 75[b]. Both sulfate and sulfide decreased with increasing increments although the sulfate decreased much faster than the sulfide. The results confirmed that the sulfide formed on the Pd/Au sample during the H₂S exposure was essentially on the surface even with the H₂S concentration as high as 55 ppm at 350°C for as long as 48 hours. The results of the XRD and SEM characterization in our previous study [44] also suggested the lack of bulk sulfide formation on the Pd/Au samples under the similar testing conditions.

Figure 75. [a] Composition as a function of depth of the Pd/Au sample after the exposure to the 50 ppm H_2S at 350°C for 48 hours, and [b] corresponding narrow scans of the S 2p peak at each sputtering increment

Figure 76 shows the high resolution spectra of S 2p orbitals of the Pd/Au sample after poisoning with 50 ppm $\text{H}_2\text{S}/\text{H}_2$ for 24 hours at 350°C and after the recovery. A decrease of the sulfide peak intensity after the recovery was observed, indicating the reduction of sulfide on the sample. Since, the sulfide formed was much less on the Pd/Au sample, the decrease was less noticeable compared to the recovered Pd. As seen in Figure 76, both sulfide and sulfate peak were still visible after the recovery indicating the presence of the sulfur on the Pd/Au sample. However, the shift of the peak summit position suggested that the fractions of Au and Pd sulfide changed after the recovery.

Figure 76. High resolution XPS scans of the S 2p peak of the Pd/Au sample before, after the H_2S exposure of 50 ppm for 24 hours at 350°C , and after recovery in H_2 at 500°C for 48 hours

Figure 77 shows the total sulfide (i.e. Au-S+Pd-S) formed on the Pd/Au samples with 55 ppm H_2S for 24 hours as a function of temperature. The much smaller amount of sulfide formed on the Pd/Au sample compared to the Pd samples substantiated the better sulfur resistance of the Pd/Au than Pd. The

better sulfur resistance observed on the Pd/Au samples was most likely due to the reduction of thermal stability of the sulfide after alloying. Figure 77 also shows that the total sulfide formed on the Pd/Au samples increased with the decreasing temperature within 6 - 8 at%. Since the sulfide bonding was the major cause for the permeance loss in the presence of H₂S, the trend agreed with the observation that more permeance decline of the Pd/Au membranes was seen at lower poisoning temperatures [44]. Less thermal stability of the sulfide species at higher temperatures as well as the exothermal adsorption accounted for the phenomenon observed. The higher total sulfur observed at higher temperatures was mainly due to more sulfate presented on the surface possibly due to the more contaminants adsorption during the sample storage.

Figure 77. Total sulfide (Pd-S+Au-S) formed on the Pd/Au samples after poisoning with 55 ppm H₂S/H₂ mixture for 24 hours as a function of temperature

Figure 78 displays the atomic fractions of Au and Pd sulfide relative to the film composition (i.e. Pd+Au) after poisoning with the 50 ppm H₂S for 24 hours at 350 - 400°C and the recovery. The right y-axis in Figure 78 shows the percentage of the Au-S in the total sulfide after poisoning and after the recovery. Surprisingly, most of the sulfide species formed after the poisoning was the Au sulfide (80 - 97%). Since the Au fraction on the Pd/Au samples was within 11.3 - 17 at % (as shown in Table 10), the result that most sulfide formed was Au sulfide suggested that the Au-S bonding was more preferential than the Pd-S bonding.

Due to the fact that the sulfide (bulk) formed with more noble metals (e.g. Au) generally was less stable and required higher H₂S concentrations to form compared to the less noble metals such as Pd, one would expect more preferential bonding between Pd and sulfur than Au and sulfur. However, the thermodynamics (i.e. the Gibbs' free energy for formation) for forming bulk sulfide and surface sulfide was significantly different. In addition, the adsorption characteristics between sulfur and metals also altered the surface metal-sulfur bonding largely from bulk metal sulfide bonding, resulting in different sulfide species formed on the surface and in the bulk. As a result, the prediction for the preference of the surface sulfide formation by the bulk sulfide thermodynamics was insufficient. In fact, Pomerantz [38] reported similar contradictions between the thermodynamic predictions and the experimental observations of the surface sulfide species formed on the sulfur poisoned Pd/Cu alloys. The author also attributed the contradiction to the difference between the bulk sulfide and surface sulfide thermodynamics. In any case, the preferential bonding between Au and S possibly resulted in the less permeance decline of the Pd/Au membranes

compared to the Pd membranes observed in the presence of H_2S since the Pd-S bonding was largely reduced, resulting in more Pd sites for the H_2 dissociation.

In addition, Figure 78 also shows that while the amount of the Pd sulfide formed after the poisoning decreased with increasing temperature from ~ 2 at% at 350°C to ~ 0.5 at% at 500°C , the amount of the Au sulfide were nearly identical of approximately 6 at% in the entire testing temperature range. The decrease of the Pd sulfide formation with increasing temperature agreed with the observation on the pure Pd samples discussed previously (as shown in Figure 69). On the other hand, the identical amount of the Au sulfide formed at different temperatures suggested that the adsorption of sulfur on the Au sites forming surface Au-S bonding reached the saturation capacity.

Figure 78. The Pd sulfide (Pd-S) and the Au sulfide (Au-S) formed and the percentage of Au-S in total sulfide on the Pd/Au surfaces as a function of temperature after the poisoning and the recovery. The poisoning was performed with the 55 ppm $\text{H}_2\text{S}/\text{H}_2$ mixture for 24 hours at $350 - 500^\circ\text{C}$ and the recovery condition was fixed at 500°C in H_2 for 48 hours. (M in the left y-axis is Pd or Au)

In fact, the amount of the Au sulfide formed was found to be identical while increasing the H_2S exposure time as shown in Figure 79, which shows the Au and Pd sulfide fractions after poisoning with the 50 ppm H_2S at 350°C for 2 - 48 hours. As seen in Figure 79, while Pd sulfide increased with increasing time from ~ 1 at% after 2 hours to ~ 2 at % after 48 hours, the Au sulfide remain roughly 5.2 at % for as long as 48 hours. The increase of the Pd sulfide with increasing time was consistent with the results of the Pd samples (See Figure 70). No change of the Au sulfide with increasing exposure time suggested that once the surface Au-S bonding formed and reached saturation, insignificant Au-S bonding would further formed. The results provided the possible reason why Pd/Au alloys showed the better resistance for bulk sulfide formation under the testing conditions. The preferential Au-S bonding largely reduced the Pd-S bonding below the bulk Pd sulfide region, while the Au-S bonding itself showed the resistance to incorporate into the bulk layer.

As also observed in Figure 78, in spite of the scatter of the data points, the result appeared to show that more Pd-sulfide was reduced compared to the Au sulfide after the recovery. In fact, the change of the Au-sulfide after the recovery was nearly negligible. The preferential Au-S bonding on the surface also suggested the more energetically stable of the Au-S bonding compared to the Pd-S bonding. As a

result, the Pd-S bonding would be much easier to be broken compared to the Au-S bonding. The breaking of the Pd-S bonding resulted in the permeance restoration of the Pd/Au membranes observed after the recovery. Due to the increase of the Pd-S binding energy at low sulfur coverage [49], it was difficult to break all the Pd-S bonding and restore all the permeance loss as observed on the Pd membranes in our previous study. In the case of Pd/Au alloy, however, the nearly irreversible Au-S bonding remained the relative high overall sulfur coverage on the surface, which potentially decreased the Pd-S binding energy even when the Pd-S fraction became very small. As a result, the Pd-S bonding could possibly be reduced completely during the recovery causing the near 100% permeance recovery of the Pd/Au membranes as described in the previous quarterly report. Finally, due to the high sulfur affinity, the metal samples always adsorb sulfur from the environments resulting in a slight sulfur fraction on the sample as mentioned previously (as shown in Table 9. and Table 10). The presence of adventitious sulfur potentially increased the error while quantifying the sulfur on the Pd/Au samples caused by the poisoning and the recovery since the sulfur amount was extremely small.

Figure 79. The Pd sulfide (Pd-S) and the Au sulfide (Au-S) formed on the Pd/Au surfaces as a function of time after poisoning with the 55 ppm $\text{H}_2\text{S}/\text{H}_2$ mixture at 350°C for 2 - 48 hours. (M in the left y-axis is Pd or Au).

Water Gas Shift reactor modelling, safety analysis and economic analysis

Approach for the Process Intensification for the Pd-Based Membrane Reactors

Dynamic Membrane Reactor Model with the Process Control Framework

A systematic process dynamic modeling framework was developed in order to analyze and characterize the transient behavior of a Pd/alloy-based (Pd/Au or Pd/Cu) WGS membrane reactor. Furthermore, simple process control ideas are proposed aiming at enhancing process system performance by inducing the desirable dynamic characteristics in the response of the controlled process during start-up as well as in the presence of unexpected adverse disturbances (process upset episodes) or operationally favorable set-point changes that reflect new hydrogen production requirements. The process control system design study for the membrane reactor was detailed in the 10th quarterly progress report, pp 14-35 and in the process control paper [55].

Indeed, a simple PI feedback control system was considered in order to meet membrane reactor performance requirements such as one casted in terms of the overall CO conversion level of the WGS reaction by controlling the CO fraction (dry basis) at the reactor exit.

In particular:

- The controlled output variable considered in the present study was the fraction of CO at the exit of the shell side which in turn dictates the overall CO conversion. The set point can be chosen depending on the desired CO conversion level. The set point was 2.32% and 1.2% for the servo and regulator problems respectively, which would be discussed next in greater detail.
- The manipulated input variable considered was the steam molar flow rate at the reactor entrance/inlet.

In order to meet the primary control objectives, the PI controller generated an actuating signal and determined an input variable profile by processing the error between the measured output variable and its set-point value in the following fashion:

$$Error = f_{CO}^{Dry}|_{exit} - f_{CO}^{Set Point}$$
$$F_{H_2O}(t)|_{y=0} = F_{H_2O}(t=0)|_{y=0} + K_c \cdot Error + \frac{K_c}{\tau_I} \int_0^t Error \cdot dt$$

An appropriate set of values for the integral time constant τ_I and the proportional gain K_c in Eq 0 had to be determined (controller tuning problem). A direct and transparent approach has been utilized in the estimation of the proper set of values for the adjustable controller parameters. These were explicitly determined on the basis of a set of desirable dynamic characteristics of the controlled process response such as speed, smoothness and robustness in the presence of disturbances subject to process economics and energy efficiency constraints.

A bench scale water-gas shift membrane reactor was chosen as an illustration case for the process control system design. Two illustrative cases namely, regulator problem to keep the CO conversion level at the desired level in case of an unexpected pressure drop and servo-mechanism problem to enhance the CO conversion levels were examined by using the dynamic membrane reactor model [55].

The most important reaction parameter which has a direct and strong effect on the membrane reactor performance was determined as reaction pressure. Thus, reaction side pressure was used as key parameter for the regulator control problem. In addition, only 30% of the permeance of a 10 μ m Pd foil was used to calculate the H₂ flux, in order to quantitatively capture the adverse effect of mechanisms such as poisoning into account.

Non-isothermal one dimensional membrane reactor model and process safety analysis

A steady state non-isothermal membrane reactor model was used for both membrane reactor performance enhancement and to address process safety and risk assessment. A one-dimensional reactor model represented a quite useful tool for a quick, yet reliable, assessment of the overall membrane reactor performance as well as a computationally attractive option for screening the design space and thus identifying viable designs that would merit further examination through the development of higher dimensional membrane reactor models [56,57]. The details of the one dimensional models could be found in 13th quarterly report, pp 17-30.

A comprehensive and practical model-based investigation and characterization of key process parameters and operating conditions that could potentially induce certain process hazards in Pd-based membrane reactor systems used for hydrogen production was developed. The standard principles of Hazard and Operability (HAZOP) analysis [58,59] were followed to identify incidents where process safety could be compromised. A guide word such as "MORE, LESS or NO" is normally assigned to one of the selected variables and deviations in all other process variables were identified and monitored [60,61]. Within the above context, issues related to root causes identification, scenario development, consequences characterization on the basis of adverse deviations of the total feed flow rate and temperature, H₂O:CO ratio, catalyst loading, reaction and permeate side pressures and feed purity from normal operating conditions are discussed with the aid of the proposed membrane reactor modeling framework and detailed simulation studies [62].

Multi-component gas diffusion through the defects

In particular, selectivity of Pd-based membranes is critically linked to final application area of the H₂ product, extra purity H₂ to be used in PEM fuel cell applications or medium grade purity H₂ (>94%) to be used in electricity generation through power plant applications. In light of the above considerations, a systematic membrane reactor modeling framework that explicitly takes into account the multi-component gas diffusion through the defects in the membrane was developed (12th quarterly progress report, pp 10, and 13-14). Within the proposed framework, the detailed mass balance equations of an isothermal steady state mathematical model for Pd-based membrane reactors were coupled with the equations of a multi-component gas diffusion model through the defects of the membrane. In particular, the proposed multi component gas diffusion model through the membrane defects was structurally realized through the Dusty Gas Model (DGM) [63] and has the capacity to quantitatively characterize the H₂ purity of the permeate flow. The permeation of H₂ is described by two transport mechanisms; the diffusion in the porous parts of the Pd layer (defects) and the solution diffusion in the dense Pd layer.

Two-dimensional membrane reactor modeling and membrane reactor integration options into IGCC power plants

Even though the one-dimensional (1D) model provides useful information for quick estimations of membrane reactor performance, it is very limited to predict the behavior of large-scale membrane reactors, particularly for the estimation of hydrogen recovery and membrane area. Thus, the mass and momentum balance equations in the radial and axial coordinates were simulated to characterize the membrane reactor performance at isothermal and steady state conditions. In addition, axial dispersion and radial convection was neglected, the ideal selectivity of the membrane was assumed to be infinite and neither vacuum nor sweep was used in the permeate side. The detailed partial differential equations and related definitions of all of the terms are given the 15th quarterly progress report, pp 26-34 and pp 43-46.

The basic three configuration possibilities of membrane reactors integrated into coal gasification plants were investigated in order to identify the ones with enhanced performance prospects based on production target levels. Three illustrative configuration examples were examined: 1) membrane separation unit ($P_{\text{tube}}=15$ psia) to remove the H₂ content of the syngas first and then conversion of CO in a membrane reactor that follows ($P_{\text{tube}}=7.5$ psia); 2) a membrane reactor operating at a high permeate side pressure to reduce the compression costs of H₂ ($P_{\text{tube}}=150$ psia) followed by second membrane reactor to remove the remaining H₂ ($P_{\text{tube}}=7.5$ psia); 3) a combined-membrane reactor representing a single reactor unit whose first 70% of its spatial domain is filled with catalyst and the remaining part is used merely for H₂

separation purposes ($P_{\text{tube}}=7.5$ psia) in order to utilize both the membrane and catalyst under maximum efficiency.

Net Present Value analysis and Monte Carlo Techniques

The DOE/NETL report [18] was used as the cost basis for the economics calculations. The detailed block flow diagrams of the GEE IGCC plant with CO₂ capture reported in DOE/NETL report [18] were compared with the target flow diagram of a Pd-based membrane reactor embedded into the IGCC plant (IGCC-MR). The detailed flow diagram of the IGCC-MR after the requisite modifications is shown in Figure 80. The gray colored units were specific for the IGCC plant with traditional packed bed reactors (IGCC-PBR) and the blue colored units are designated for the IGCC plant with a membrane reactor module embedded.

The feed specifications, reaction conditions and permeation properties used in the isothermal membrane reactor model are listed in Table 11. The 2D membrane reactor model (details of the 2D model were given in the 15th quarterly progress report, pp 25-35, DOE Award No: DE-FC26-07NT43058) which runs for industrial scale conditions was evaluated under the feed specifications, reaction conditions and permeation properties given in Table 11. The dimensions, total feed flow rates and exit flow rates of the single membrane tube and also the whole water gas shift membrane reactor, which also conforms to the industrial scale IGCC plant load specifications, are listed in Table 12.

The Net Present Value (NPV) method was used to evaluate the project value of the membrane reactor technology. The NPV of a series of future cash flows is their present value minus the initial investment required to obtain the future cash flows (Equation (4)). The NPV of an investment quantifies the increase in wealth that one realizes if the investment on the project is made, and mathematically represented by the following formula [64]:

$$PV = \sum_{t=1}^N \frac{C_t}{(1+r_t)^t} = \frac{C_1}{1+r_1} + \frac{C_2}{(1+r_2)^2} + \frac{C_3}{(1+r_3)^3} + \dots \quad (1)$$

$$(2)$$

$$(3)$$

$$NPV = C_o + PV \quad (4)$$

Table 11. Feed specifications, reaction conditions and permeation properties

Total inlet flow rate to the MR [mol/s]	9575.2 (8191 w/o CO ₂ comp.)
Feed composition [%]	CO: 23 - CO ₂ :9 - H ₂ :22 - H ₂ O: 46
Reaction temperature [°C]	450
Reaction side pressure [psia]	735
Permeate side pressure [psia]	14.7
Permeance [ft ³ / [ft ² .h.psi ^{0.5}]	33.4
Bulk catalyst density [lb/ft ³]	61.9

Table 12. Industrial scale membrane reactor specifications used for cost analysis

Single membrane tube		Water gas shift membrane reactor module	
Pd thickness [μm]	10.00	No of membrane tubes	8584
O.D. of the membrane, r_1 [ft]	0.17	Total Pd Area [ft^2]	140320.6
I.D. of the shell casing, r_2 [ft]	0.25	Total Pd weight [ctw]	7099377
Length of the membrane, L [ft]	31.24	Total V_{annulus} [ft^3]	7306.5
Membrane Area [ft^2]	16.35	Total $F_{\text{CO}_2, \text{exit}}$ [Mlb/year]	9410.7
V_{annulus} [ft^3]	0.85	Total W_{catalyst} [lb]	339069.7
$F_{\text{total, in}}$ [lbmol/hr]	8.85	# of bundle MR in series	8
$F_{\text{CO}_2, \text{exit}}$ [lbmol/hr]	2.84		
W_{catalyst} [lb]	39.50		

Indeed, the effect of uncertain parameters on the value of the project was included into the NPV model with a simple method called “Monte Carlo (MC) simulation”. Monte Carlo simulation uses distributions of uncertain inputs to find a distribution of uncertain performance or equivalently a range and frequency of various performance outcomes (in our case an NPV distribution profile).

Monte Carlo simulation generates thousands of possible “futures” (or “future states”) by assigning random values to each input (sampled from a meaningful distribution through which the corresponding uncertainty is quantified), runs all these futures simultaneously through the NPV model (also known as uncertainty propagation through the NPV model), and finally generates the induced distribution of possible performance (project value) outcomes in the form of an NPV distribution profile while graphically summarizing all pertinent statistics [65]. The software XLSim [66] was used for the Monte Carlo simulations conducted in the present study. The detailed discussion about the NPV model development and also the Monte Carlo simulation technique could be found in the 16th quarterly report, 32-46.

Figure 80. Schematic flow diagram of a Pd-based membrane reactor module integrated into an IGCC plant (IGCC-MR)

Results and Discussion

The three companies GE, Shell and ConocoPhillips [67], all perceived as the three major players with respect to future IGCC projects [67] were considered to select a preferred membrane reactor composition. The membrane reactor was assumed to be placed after gas cleaning steps (sulfur containing gases and mercury).

The gasifier selection criteria for the application of Pd-based membrane reactor were CO conversion and hydrogen recovery levels as well as the concentrations of the impurities in the feed stream. ConocoPhillips E-Gas™ was not considered due to the CO₂ capture limitation because of the relatively high methane content in the syngas that would not be converted to CO₂ during the shift reaction. Since the GEE gasifier had the highest steam to CO mole ratio, the highest CO conversion of 98% and hydrogen recovery of 91% were obtained with GEE case. In addition to the high performance level, the low concentrations of impurities (H₂S, COS, etc.) makes the GEE gasifier attractive for the Pd-based membrane reactor applications. Thus, the gasifier type was chosen as the GE Energy gasifier for the economic analysis efforts as stated in the 14th quarterly progress report, p 22.

Dynamic modeling and control framework for performance assessment of Pd/alloy-based membrane reactors

In the specific underlying scenario considered for the regulator problem, it was assumed that while the process system was operating at a nominal steady state, the total pressure dropped from 15 to 10 atm unexpectedly staying at 10 atm for the rest of the process operation (disturbance step-change). The steam flow rate was determined as the manipulated variable to regulate the system to return to the original state. The effect of the controller action on the H₂ partial pressure in the reaction side is shown in Figure 81. The undesired effect of the unexpected system pressure drop was eliminated by the controller with a 5 seconds delay as shown in Figure 81. The simulations results indicated that the CO conversion level of the membrane reactor could be kept at 95% even in the presence of a strong disturbance such as system pressure drop.

Figure 81. Partial pressure profiles of H₂ in the reaction side/Regulator case: $K_c = 0.002/\tau_l = 0.8$ s.

In the servo-mechanism control, it was shown that the dry basis CO fraction of 2.32% at the reactor exit could be reduced even further (to 1.2%) under the action of a PI servo-mechanism controller in order to meet more stringent production requirements. Since the system was not disturbed, the controller manipulates the inlet steam flow rate in a smooth manner which was reflected with the H_2 partial pressure trend shown in Figure 82. The proper application of a servo-mechanism controller by manipulating the inlet steam flow rate could certainly induce the membrane reactor to attain an improved CO conversion level of 98%.

Figure 82. Partial pressure profiles of H_2 in the reaction side/Servo-mechanism: $K_c = 0.003/\tau_f = 2$ s

As a final reflection, even though the CO fraction at the reaction side exit (and thus conversion) was successfully controlled in both the regulator and servo-mechanism cases, H_2 recovery was reduced due to the decreased driving force for H_2 permeation. The same process control scenarios were repeated by using a membrane having permeance value equal to 100% of a $10\mu m$ Pd foil and compared with the above results in Table 13. The production rate and recovery of H_2 could be certainly improved by using a Pd-based membrane with higher permeance. Not only the H_2 recovery was improved but also the controller used less steam as the permeance increased.

Moreover, it should be pointed out that the purpose of the simple process control framework developed for the WGS MR was to show the feasibility of maintaining not only a high H_2 production rate but also high levels of CO conversion in the presence of external disturbances and set-point changes given hard process economics and energy efficiency constraints. Thus, a 20-30% decrease in H_2 recovery at the end of the process control action might be deemed acceptable until corrective action is taken and the total system pressure is restored to its original value within the shortest possible time for example. Furthermore, advanced multivariate control configurations and algorithms could potentially further enhance the quality of control by addressing the above challenges through a more sophisticated structure at the expense of higher costs and complexity in implementation, controller tuning and maintenance.

Notice also that the controller action led to an increase in the H_2O : CO ratio from 2 to 3.8 and 5.8 in the regulator and servo-mechanism cases respectively. Even though the heating cost of steam is certainly not negligible, there are other benefits that could be potentially realized

through the use of excess steam. The increased steam flow rate could definitely shift the WGS reaction towards the product side and thus increase reaction yields together with the removal of H_2 . Moreover, if temperature control is not highly effective in the case of a non-isothermal membrane reactor, the high latent heat of steam could help decrease the temperature rise in the reaction side due to the exothermic WGS reaction. Moreover, the Pd-based membrane should be protected from a possible formation of hot spots, and intermetallic diffusion and leak formation could become problematic at temperatures higher than 550°C due to decreased permeation and selectivity [68]. The temperature profile of the membrane reactor could be thus maintained under almost isothermal conditions by proper adjustment of the pre-heater temperature and by using the benefit of excess steam to eliminate a potential temperature rise due to the exothermic reaction. Furthermore, the deactivation of catalyst and/or the membrane by coke formation could be prevented by using excess steam.

Table 13. Process control results summary

Permeance coefficient	Control type	$f_{\text{CO,exit}}$	X_{CO}	R_{H_2}	H_2O/CO
30%	Regulator	2.32	95	56	3.8
	Servo	1.2	97.6	63.4	5.8
100%	Regulator	1.8	97	82	3.2
	Servo	1	98.3	89.8	4.3

Process safety aspects in water-gas-shift membrane reactors (WGSMR)

Throughout the conduct of the process safety analysis, only the Pd-based WGS membrane reactor unit was evaluated using HAZOP analysis. In particular, a non-isothermal model-based membrane reactor performance assessment was performed by analyzing the particular effects on process operation and performance of the feed temperature, feed flow rate, bulk catalyst density, the $H_2O:CO$ mole ratio, reaction side total pressure, membrane area and permeate side pressure on the CO conversion, H_2 recovery and reaction side temperature profile. Root causes, consequences and precautionary measures associated with any deviations in the operating conditions from the desirable ones were identified and evaluated in order to ensure process safety while maintaining performance target levels at $X_{\text{CO}} = 98\%$ CO conversion and $R_{\text{H}_2} = 95\%$ hydrogen recovery. At the same time, the objective to keep the maximum temperature in the reaction side below the safety limit of 500°C was pursued.

Effect of feed temperature

The reaction conditions for the Pd-based membrane reactor were identified to achieve the target levels of 98% CO conversion and 95% H_2 recovery. The limiting reaction side temperature to protect the Pd-based membrane integrity was set as 550°C . The characterization of the optimum feed temperature was performed by considering both the efficiency of the process and integrity of the Pd-based membrane. On one hand, the feed temperature should be higher than the threshold temperature of the WGS catalyst and the reaction rate should be high enough to achieve the performance target levels. The feed temperature of the membrane reactor was estimated to be approximately $300\text{--}350^\circ\text{C}$ for the WGSMR by using the contour plots for the effect of feed temperature on CO conversion, H_2 recovery and maximum reaction temperature shown in Figure 83.

Figure 83. Contour plots of [a] $T_{\text{Rxn.Max}}$ [b] R_{H_2} and [c] X_{CO} as a function of inlet feed flow rate and feed temperature at $P_{\text{Total,Rxn}} = 15 \text{ atm}$, $P_{\text{Tube}} = 1 \text{ atm}$, $\text{H}_2\text{O}:\text{CO} = 2$ and 100% $p_{\text{Bulk,max}}$.

Since the reaction and permeation rates are varying in different sections of the WGSMR, the safety analysis was performed by fractionating the whole reactor and defining inlet and outlet streams as shown in Figure 84. The CO concentration would be the highest in zone 1 and lowest in zone 3 of Figure 84. Similarly, the H_2 concentration would decrease from zone 1 through zone 3 due to the H_2 depletion by permeation. Thus, the highest amount of energy released by the reaction would be observed in zone 1 Figure 84; zone 2 and zone 3 would sequentially follow based on the overall amount of the heat release. The considerations and recommendations for the effect of changes in the feed temperature are summarized in an HAZOP worksheet shown in Table 14.

Figure 84. Hazard detection nodes and zones on the schematic diagram of a membrane reactor

Effect of feed flow rate

The Damköhler number (Da), which is the ratio of the maximum reaction rate at the reactor inlet to the space velocity, was used as a parameter to characterize and assess the consequences of the changes in the total feed flow rate as shown in Figure 85. The feed flow rate should be enough to achieve a Da number higher than 0.6 to maintain the CO conversion and H₂ recovery levels at 97 and 88%, respectively. However, the feed flow rate should not be too low either ($Da \gg 1$). If the feed flow rate decreased drastically, the membrane reactor would not be operated at the maximum capacity and insufficient H₂ would be produced. Operating at around $Da = 2$ would provide time to act to prevent hazards with the aid of a broader feed flow rate range (up to 5 times higher and lower of the original feed flow rate) and also to maintain the membrane reactor performance at the target levels. Moreover, the HAZOP worksheet for the effect of feed flow rate was assessed by assuming membrane reactor operation with $Da = 2$ as given in Table 15.

Figure 85. The effect of feed flow rate on [a] $T_{Rxn,Max}$ [b] R_{H_2} and X_{CO} at $T_{Feed} = 350^\circ C$, $P_{Total,Rxn} = 15 \text{ atm}$, $P_{Tube} = 1 \text{ atm}$, $H_2O:CO = 2$ and 100% $p_{Bulk,max}$.

Effect of bulk catalyst density

Hot spot formation on the membrane surface due to the fast forward reaction could damage the Pd membrane and also sinter the catalyst. Diluting the catalyst mass with an inert packing would not only help to prevent the formation of hazardous hot spots but also would reduce the cost of the membrane reactor. Moreover, the performance indicators, X_{CO} and R_{H_2} ,

were not significantly affected at the feed flow rates considered for ρ_{Bulk} values higher than 50% of the $\rho_{\text{Bulk,max}}$ as shown in Figure 86. Thus, packing the non-isothermal membrane reactor with 50% of the maximum bulk catalyst density was selected.

Figure 86. Contour plots of [a] $T_{\text{Rxn.Max}}$ [b] R_{H_2} and [c] X_{CO} as a function of inlet feed flow rate and bulk catalyst density at $T_{\text{Feed}} = 350^\circ\text{C}$, $P_{\text{Total,Rxn}} = 15 \text{ atm}$, $P_{\text{Tube}} = 1 \text{ atm}$, $\text{H}_2\text{O}:\text{CO} = 2$.

Effect of $\text{H}_2\text{O}:\text{CO}$ mole ratio

Another key performance parameter affecting the membrane reactor performance as significant as the total system pressure was determined as the steam content of the feed stream. An effective way of reducing the reaction side temperature would be feeding excess steam to make use of the high sensible heat of steam. Even though the heating cost of steam would be high, the utilization of excess steam to prevent high temperature zones for the safety of the operation of the Pd-Based membrane reactor is more crucial. Moreover, the increased steam flow rate would shift the WGS reaction to the products side and increase reaction yield along with the removal of H_2 . The simulation based results indicated that the $\text{H}_2\text{O}:\text{CO}$ mole ratio needs to be kept higher than 2 (around 4 for the adiabatic membrane reactor as shown in Figure 87, which is

the maximum level) to prevent hot spot formation or excessive reaction side temperature together with the utilization of effective heat exchangers to maintain the isothermal operation.

Figure 87. Contour plots of [a] $T_{\text{Rxn,Max}}$ [b] R_{H_2} and [c] X_{CO} as a function of inlet feed flow rate and the mole ratio of $\text{H}_2\text{O}:\text{CO}$ at $T_{\text{Feed}} = 350^\circ\text{C}$, $P_{\text{Total,Rxn}} = 15 \text{ atm}$, $P_{\text{Tube}} = 1 \text{ atm}$, $50\% \rho_{\text{Bulk,max}}$.

Effect of reaction side total pressure

Since the temperature rise in the reaction zone could be eliminated by using excess steam, other parameters such as reaction and permeate side pressure could be in principle used to enhanced H_2 recovery levels while inducing a temperature profile in compliance with process safety limits/standards. Unlike the traditional packed bed reactors, the reaction side pressure could have a dramatic effect on the performance of a Pd-based water gas shift membrane reactor. Low levels of hydrogen recovery and production rate of pure H_2 could be enhanced by increasing the reaction side total pressure thus increasing the driving force for H_2 permeation. The performance target levels of $X_{\text{CO}} = 98\%$ and $R_{\text{H}_2} = 95\%$ were attained at a reaction side pressure of 35 atm and higher by using $\text{H}_2\text{O}:\text{CO} = 4.5$ as depicted in Figure 88 [b] and [c] for an adiabatic WGS MR.

Since the operation of membrane reactors at high pressure is inevitable, relief systems should be used to avoid over-pressure incidences and alarm systems needed to be set up to warn the employees in the case of an adverse pressure increase. When the process fluid was expensive and/or toxic, leakages through a safety valve were not deemed acceptable [69]. The syngas contains high amounts of poisonous carbon monoxide and explosive H_2 which required usage of either a rupture disk or enclosed safety relief valves which sent the released syngas to a containment vessel instead of disposal to the process environment. In the case of actuation of the pressure relief systems, the discharged syngas should be collected and re-directed to the gas turbine without converting carbon monoxide. If the pressure rise in the membrane reactor was too rapid and the safety valves did not respond as desired then rupture disks had to be placed at the membrane reactor entrance and exit (zone 1 and 3, in Figure 84) instead.

The combination of a rupture disk-rupture disk-safety relief valve in series (RRS) system could be installed at the latter locations. A weep hole in the space between the disk and safety relief valve could prevent pressure buildup in the interspace if there was a pinhole on the disk [69]. Sparing of the relief equipment would provide on-line maintenance of the RRS system by switching and also the process would not need to be shut down for replacement (AIChE report 1993a). Rupture disks are temperature sensitive devices. The rupture disk must operate at pre-specified temperature and pressure levels preventing it from bursting. In addition, a heat-removing device might be needed in the safety relief valve to protect the valve from the hot reaction gas coming from the membrane reactor [70]. The reaction side total pressure related HAZOP worksheet is also prepared as given in Table 16.

Impurities in the feed stream

Chen and Ma [71] showed that after exposure of a pure palladium membrane to a 54.8 ppm H_2S/H_2 mixture, no permeance recovery was possible due to the irreversible formation of bulk Pd_4S . As a result, the replacement of the poisoned pure palladium membrane is necessary to maintain high productivity levels of the process. Pd-Alloy membranes, particularly Pd-Au and Pd-Cu, have the advantages of permeance recovery and selectivity stability of the Pd-based membrane after poisoning [71,72]. Membrane reactors, in which Pd-Au and Pd-Cu membranes are utilized, should be regenerated with H_2 after exposure to H_2S to increase the permeance of the membrane. The HAZOP worksheet summary of results related to the case of impurities in the membrane reactor feed stream can be found in Table 18.

The sulfur containing gases may not be the only impurities in the feed stream of the membrane reactor. The effect of other trace impurities, such as As, P, Sb, Zn, Cl, Hg, Cd and Se [73], on the Pd/alloy-based membranes is still unknown and has to be investigated for industrial scale applications.

Figure 88. Contour plots of [a] $T_{Rxn,Max}$ [b] R_{H_2} and [c] X_{CO} as a function of inlet feed flow rate and the reaction side total pressure at $T_{Feed} = 350^{\circ}C$, $P_{Tube} = 1$ atm, $H_2O:CO = 4.5$ and 50% $\rho_{Bulk,max}$.

Effect of permeate side pressure

The main goal was to mitigate the occurrence of any hazardous conditions in cases of high reaction side pressures while maintaining high performance target levels of $X_{CO} = 98\%$ and $R_{H_2} = 95\%$. In particular, the reaction side pressure was kept at a moderately low pressure of 30 atm and the permeate side pressure was changed to fall within the range of 0.1-1 atm with the application of vacuum. As shown in Figure 89 [b] and [c], the original performance target levels of $X_{CO} = 98\%$ and $R_{H_2} = 95\%$ were achieved at a permeate side H_2 pressure and reaction side total pressure of 0.55 atm and 30 atm respectively. The pertinent discussion and recommendations in the case of unexpected deviations in the permeate side pressure are summarized in Table 17.

Figure 89. Contour plots of [a] $T_{\text{Rxn.Max}}$ [b] R_{H_2} and [c] X_{CO} as a function of inlet feed flow rate and the permeate side pressure at $T_{\text{Feed}} = 350^{\circ}\text{C}$, $P_{\text{Total,Rxn}} = 30$ atm, $\text{H}_2\text{O}:\text{CO} = 4.5$ and 50% $p_{\text{Bulk,max}}$.

Table 14. HAZOP worksheet - Parameter: feed temperature

GW	Causes	Consequences	Prevention & Repair
More ($T_{Rxn,Max} > T_{Upper}^*$)	High steam temperature at node 2 High syngas temperature at node 1 Low feed flow rate at node 3 Malfunction of the reactor heating system	Hot spots Decreased permeance & selectivity (due to Intermetallic diffusion) Catalyst sintering Increased pressure due to increased temperature if pressure relief equipment fails simultaneously	High temperature alarms on node 3 and zone 1 Fast temperature control before node 1 and 2 (in heat exchangers for syngas cooling and steam heating) Maintain/check valves and pipelines Increase feed flow rate with a valve on node 4 Membrane replacement in case of intermetallic diffusion Isolation valves and chemical isolation at nodes 3, 4 and 5 together with flame sensors Inert feed at operating temperature and backup line for the syngas feed at inadequate temperature Refer to HAZOP worksheet for reaction side pressure
Less ($T_{Rxn,Max} < T_{Lower}^*$)	Low steam temperature at node 2 Low syngas temperature at node 1 High feed flow rate at node 3 Malfunction of the reactor heating system	Decreased CO conversion and H ₂ recovery Defects/cracks on the membrane surface and decreased selectivity (due to H ₂ embrittlement for pure Pd membranes)	Low temperature alarm on node 3 and zone 1 Fast temperature control before node 1 and 2 Maintain/check valves and pipelines Membrane replacement/repair in case of embrittlement Inert feed at operating temperature and backup line for the syngas feed at inadequate temperature

* T_{Upper} = 500°C which equals the maximum temperature limit in the reaction side, T_{Lower} = 300°C which equals the threshold temperature of the catalyst to maintain high CO conversion levels also to prevent H₂ embrittlement in Pure Pd membranes.

Table 15. HAZOP worksheet - Parameter: feed flow rate

GW	Causes	Consequences		Prevention & Repair
More ($\uparrow F_{\text{Feed}}^*$)	Malfunction of the flow control instruments on nodes 1, 2 & 3 Inappropriate adjustment and/or failure of the valves and pressure regulators on node 4 Leaks on the pipeline on node 4 before the pressure regulator	Da<2	Insignificant changes in T_{Rxn} , CO conversion and H_2 recovery Increased H_2 production rates	Regular maintenance and inspection of the control instrument, valves and pressure regulators Fast responsive temperature recorders and controllers
		Da<<2	Decreased T_{Rxn} due to reduced ΔH_{Rxn} Decreased CO conversion and H_2 recovery Increased H_2 production rates	Backup lines before and after the reactor, on node 3 and 4 Fast responsive temperature recorders and controllers A recycle switch from node 4 to node 3 in case of very low CO conversion Monitor H_2 production rate and permeate/retentate compositions
Less ($\downarrow F_{\text{Feed}}^*$)	(same causes with More and) Partial plugging of the lines before node 3 or on node 4 Partial clogging of the reactor by coke in the catalytic bed Leaks on the feed line before node 3	Da>2	Insignificant changes	Regular maintenance and inspection of the control instrument, valves and pressure regulators Fast responsive temperature recorders and controllers
		Da>>2	Membrane damage & catalyst deactivation in case of coke formation Pressure increase in the feed line due to plugging Pressure decrease due to leaks	Enclosed safety relief valves on node 3 and 4 Poisonous gas detectors on both reaction and permeate sides in case of leak Maintenance of the filter systems before node 3 Monitor H_2 production rate and permeate composition Regeneration / substitution of the membrane and/or catalyst
No ($F_{\text{Feed}}=0$)	(same causes with More and) Complete plugging of the lines before node 3 or on node 4 Complete clogging of the reactor by coke in the catalytic bed	Decreased T_{Rxn} as low as feed temperature No CO conversion and H_2 recovery Oxidation of the membrane in case of backflow		Extra feed line between node 1 and 3 Inert feed line to protect the membrane until repair Check valve on node 4 and 5 to prevent back flow Regeneration / substitution of the membrane in case of oxidation

* $\uparrow$: Increased , $\downarrow$: Decreased

Table 16. HAZOP worksheet - Parameter: reaction side total pressure

GW	Causes	Consequences	Prevention & Repair
More ($\uparrow P_{\text{Total,Rxn}}^*$)	Malfunction of the compressor and back pressure regulators, plugging or closing of the valves as well as connections at the membrane reactor exit Coke formation in the pipelines and/or in the reactor	Increased $T_{\text{Rxn}}^{\ddagger}$ Increased CO conversion and H_2 recovery Increased H_2 production rates Runaway reactions Membrane reactor failure by explosion due to excessive pressure	Increase steam flow rate or decrease mixed gas flow rate at node 2 in case of a minor causes, such as misuse of control equipment or initial stage of coke formation Monitor H_2 production rate and permeate composition Depressuring into a containment vessel to be fed to the gas turbine directly The combination of a rupture disk-rupture disk-safety relief valve (RSS) system in series in zone 1 and 3 Use a spare RSS system in parallel with interlocked valves
Less ($\downarrow P_{\text{Total,Rxn}}^*$)	Failure of the compressor and back pressure regulators, plugging or closing of the valves and connections at the zones before the membrane entrance Leakage and defects on the membrane and pipeline	Decreased CO conversion and H_2 recovery Decreased $T_{\text{Rxn}}^{\ddagger}$ Decreased H_2 production rates Decreased H_2 purity	Regular maintenance and inspection of the compressor, back pressure regulators, valves and pipelines Monitor H_2 production rate and permeate composition Repair/substitution of the membrane in case of low selectivity

* $\uparrow$: Increased , $\downarrow$: Decreased

$\ddagger$ Refer to Table 14 for changes in the reaction side temperature

Table 17. HAZOP worksheet - Parameter: permeate side pressure

GW	Causes	Consequences	Prevention & Repair
More ($\uparrow P_{\text{Tube}}^*$)	Blocked outlet of the membrane tube Failure of the vacuum pump	Decreased CO conversion and H ₂ recovery Decreased $T_{\text{Rxn}}^{\ddagger}$ Decreased H ₂ production rates Decreased H ₂ purity	Monitor H ₂ production rate and permeate composition Regular maintenance and inspection of the vacuum pump, connection points between the membrane tubes and the pipeline for the following units and valves Membrane tube and H ₂ pipeline designed for partial or full vacuum condition
Less ($\downarrow P_{\text{Tube}}^*$)	Malfunction of the vacuum pump Misuse of a manual/auto valve at the exit of the membrane tube exit (if any)	Increased CO conversion and H ₂ recovery Increased $T_{\text{Rxn}}^{\ddagger}$ Increased H ₂ production rates Increased H ₂ purity	Same with $\uparrow P_{\text{Tube}}$ and Vacuum relief valve actuates at the low pressure limit and to admit inert He into the tube side

* $\uparrow$: Increased , $\downarrow$: Decreased

$\ddagger$ Refer to Table 14 for changes in the reaction side temperature

Table 18. HAZOP worksheet - Parameter: impurities

GW	Causes	Consequences	Prevention & Repair
As well as (impurities such as H ₂ S)	Error and/or malfunction of the gas cleaning units before the membrane reactor	Poisoning of the membrane For pure Pd membranes: decreased and even demolished selectivity and permeance For Pd/alloy membranes, particularly Pd/Au and Pd/Cu: decreased but recoverable permeance Catalyst poisoning Corrosion in the membrane reactor equipment Decreased CO conversion and H₂ recovery Decreased T_{Rxn}[‡] Decreased H₂ production rates Decreased H₂ purity	Regular maintenance and inspection of the gas cleaning unit before the membrane reactor Monitor H₂ production rate and permeate composition Gas composition analyzer before the membrane reactor inlet Substitution of the pure Pd membrane and catalyst Regeneration of the Pd/Au or Pd/Cu membrane Poisonous gas detectors outside the membrane reactor module sensitive to both CO, H₂ and sulfur containing gases for the health safety Automatically activated inert purge system with remote control

‡ Refer to Table 14 for changes in the reaction side temperature

Pd-based membrane reactor model including multi-component gas diffusion through the defects (Dusty Gas Model)

A good match was obtained between the CO concentrations calculated by the use of membrane reactor simulation with the DGM and the ones determined experimentally (the long term water-gas shift membrane reactor experiments performed with the membrane AA-24, in 16th quarterly progress report, p 8) as shown in Figure 91. Even the membranes with comparatively low selectivity values ($\alpha_{H_2/He} = \sim 130$ and $D_{knudsen, effective} \times \rho_{defect} = 0.07 \text{ m}^2/\text{s}$) was shown to have the potential to be used for the electricity production in power plant application with an H_2 purity of 96% as shown in Figure 90. More importantly, both H_2 purity of 99.99% and flux target of 250 scfh/m² specified by the DOE could be easily achieved by using a Pd-based membrane having $\sim 34 \text{ ft}^3/[\text{ft}^2\text{-h-psi}^{0.5}]$ H_2 permeance and ~ 8000 ideal H_2/He selectivity, prepared through the current membrane synthesis technology developed in the CIMS laboratory, WPI.

Figure 90. H_2 purity levels of the Pd-based membranes in the ideal selectivity range of ~ 130 -7700

Figure 91. CO concentration levels in the permeate flow of the Pd-based membranes in the selectivity range of ~ 130 -7700

Two-dimensional membrane reactor modeling and membrane reactor integration options into IGCC power plants

A comprehensive first principle-based two dimensional (2D) membrane reactor modeling framework has been developed to take into account the radial concentration gradients and pressure drop of the Pd-based membrane reactor. The main objective of the 2D model was to reliably address the problem of possibly overestimating the H_2 recovery levels and the calculated membrane areas, which were less than the actual required ones as calculated through the traditional simple one-dimensional (1D) model. In particular, promising simulations results were found to be in satisfactory agreement with experimental results involving a lab-scale ($0.5''OD_M \times 1''OD_S \times 2.5''L$) membrane reactor within the GHSV range of ~ 1000 - 6000 h^{-1} .

In light of the above, the same model was utilized to characterize the performance of industrial scale membrane reactors. The permeation characteristics of a Pd-based membrane with the same permeance of a $10 \mu\text{m}$ thick Pd foil were utilized for the large-scale membrane reactor model. A slurry-feed coal-derived syngas at a total feed flow rate of 10 kmol/s was assumed to be processed at 735 psia reaction side pressure and 450°C within a bundle reactor.

The total membrane area with $Re < 1000$ was found to be 4.5 times of the one with $Re > 1000$, thus membrane reactor working at $Re > 1000$ needs to be preferred to reduce the Pd cost. Considering the advantages of operation at $Re > 1000$ such as reduced concentration gradient in the radial direction as shown in Figure 92, distribution of heat release by reaction along the length of the reactor, together with reduced membrane area to achieve $X_{CO} = 97\%$ and $R_{H_2} = 92\%$, the three basic configuration options were evaluated by using membrane reactors operating at $Re > 1000$.

Figure 92. [a] H_2 partial pressure in the reaction side and [b] X_{CO} & R_{H_2} profiles along the length of the reactor at $Re > 1000$; [c] H_2 partial pressure in the reaction side and [d] X_{CO} & R_{H_2} profiles along the length of the reactor at $Re < 1000$ at $T = 450^\circ\text{C}$, $P_{shell} = 735 \text{ psia}$, $P_{tube} = 15 \text{ psia}$.

In the first scenario, membrane separation followed by membrane reactor was evaluated. Since the syngas feed contained significant amount of H_2 (22%), H_2 separation took place at the first step operating at a permeate side pressure of 15 psia to provide sufficient driving force for H_2 permeation. The unprocessed CO coming from the first step was converted to H_2 and the produced H_2 together with the remaining H_2 from the first step was separated in the second membrane reactor. The permeate side pressure was decreased by using a vacuum pump to remove as much H_2 as possible at the last step. The permeated extra purity H_2 was compressed to 150 psia to be used for other processes such as hydrogenation/dehydrogenation reactions.

The model predictions in terms of H_2 partial pressure in the reaction side together with the CO conversion and H_2 recovery profiles were shown in Figure 93. While Figure 93 [a]&[b] represents the first membrane separation, Figure 93 [c]&[d] represents the membrane reactor in the second step. In Figure 93 [a], the partial pressure of H_2 for all locations in the radial direction was decreased along the length of the reactor due to the depletion of H_2 by permeation. The final H_2 recovery of 89.8% was achieved at the first step as shown in Figure 93 [b]. Since the extent of produced H_2 at the reactor inlet was higher than the amount of permeated H_2 , the increased H_2 partial pressure profiles at the reactor inlet in Figure 93 [c] were decreased gradually. The CO conversion and H_2 recovery levels of the membrane reactor were determined as 98.4 and 91.2%, respectively, as shown in Figure 93 [d]. In overall, the whole system could achieve overall CO conversion of 98.4% and H_2 recovery of 95.1%.

Figure 93 [a] H_2 partial pressure in the reaction side and [b] X_{CO} & R_{H_2} profiles along the length of the membrane at the first step [c] H_2 partial pressure in the reaction side and [d] X_{CO} & R_{H_2} profiles along the length of the membrane reactor at second step at $T = 450^\circ C$, $P_{shell} = 735$ psia.

In the second scenario, two membrane reactors in series operating at different permeate side pressures were considered. The permeate side pressure of the first membrane reactor was kept at a high pressure of 150 psia to reduce the compression costs of the permeated H_2 . Since the permeation in the first reactor will be terminated when the reaction side H_2 partial pressure equals the permeate side pressure of 150 psia, there will be still a significant amount of H_2 in the retentate. Thus, a second membrane reactor operating at a low permeate pressure of 7.5 psia was placed in order to react/remove the remaining CO/ H_2 .

Most of the CO content of the feed was converted into H₂ in the first membrane reactor so the H₂ partial pressure was increased at the first 10% of the reactor, then decreased due to removal by H₂ permeation as shown in Figure 94 [a]. In Figure 94 [b], the H₂ recovery was only 42.1% at the first membrane reactor due to the low driving force for H₂ permeation proportional to the $\Delta P^{0.5} = 15 \text{ psi}^{0.5}$. The feed of the second membrane, which was the retentate of the first reactor, contained only 3.9% CO. Thus, the second membrane reactor behaved more or less like a membrane separation unit as shown in Figure 94 [c] with decreasing trends of H₂ partial pressure along the length of the reactor. The CO and H₂ contents of the retentate stream of the second reactor were reduced to 0.3 and 1.8%, respectively, by achieving $X_{\text{CO}} = 92.8\%$ and $R_{\text{H}_2} = 94.3\%$ as depicted in Figure 94 [d]. The overall CO conversion and H₂ recovery of the whole system were 99.6 and 95%, respectively.

Figure 94. [a] H₂ partial pressure in the reaction side and [b] X_{CO} & R_{H_2} profiles along the length of the membrane reactor at the first step [c] H₂ partial pressure in the reaction side and [d] X_{CO} & R_{H_2} profiles along the length of the membrane reactor at second step at $T = 450^\circ\text{C}$, $P_{\text{shell}} = 735 \text{ psia}$.

A closer look to the CO conversion profile in Figure 92 [d] revealed that only 3% of the total 97% conversion was converted in the last 40% of the reactor. Thus, one single membrane reactor whose first 70% works as a membrane reactor and the following 30% as a membrane separation unit was evaluated in the third option. The first 70% of the membrane reactor was filled with catalyst and the remaining part was assumed to be filled with inert packing.

The intense increase in the H₂ partial pressure at the reactor inlet was not observed in the combined membrane reactor due to the reduced catalyst weight as shown in Figure 95 [a]. Instead of the fast reaction rate at the inlet, the extent of reaction was distributed along the length of catalytic section of the membrane reactor. Both the catalytic bed and the membrane area was used more effectively by achieving $X_{\text{CO}} = 98.7\%$ and $R_{\text{H}_2} = 95.3\%$ in the combined membrane reactor unit as shown in Figure 95 [b].

Figure 95. [a] H₂ partial pressure in the reaction side and [b] X_{CO} & R_{H₂} profiles along the length of the combined membrane reactor at T = 450°C, P_{shell} = 735 psia.

The second configuration option with membrane reactors in series could be used to reduce the compression costs related with H₂ compression. Whereas, the third combined option is beneficial to reduce the required membrane area and it is a tailored version of membrane reactor which consists of reaction followed by separation. These two options could be used together as a combined membrane reactors in series to enhance the membrane reactor performance. More importantly, the membrane reactors in series option could also provide a flexible design possibility by providing a flexible plant capacity factor.

Economic assessment of the integration option of Pd-based membrane reactors into IGCC power plants

Economic analysis framework

The detailed cost estimation list of the Pd-based membrane reactor module with the dimensions determined based on the two dimensional membrane reactor module is given in Table 19. The total capital investment for the membrane reactor module was estimated to be \$1266/ft² which was slightly over the DOE cost target of \$1000/ft².

The highest O&M cost was associated with the IGCC-MR case as shown in Figure 96 [a]. The membrane life time was assumed to be 3 years and the annual membrane replacement cost was estimated as ~7.8 M\$ (Total cost of membrane tubes/ membrane life time = 23.65/3). As expected, the lowest O&M cost belonged to the pulverized coal power plants due to the extensive operational experience accumulated over the years. The reduction in the number of units for CO₂ separation and also the efficiency gains of the membrane reactor integration into the IGCC plant brings advantages in terms of total plant cost. In addition, it should be pointed out that the compression cost of H₂ from 1 atm to 30 atm to be used in the Advanced F-Class Gas turbine was included into the cost analysis (the feed to the gas turbine in all other cases does not need to be compressed). For a comparison of the membrane reactor integration option into IGCC plants with baseline IGCC and supercritical pulverized coal plants in the absence of a CO₂ tax, the size of the IGCC-MR w/o CO₂ compression plant was smaller than the size of the IGCC-MR with a CO₂ capture plant. In such a case it would be of course unrealistic to expect a lower plant cost for IGCC-MR than in the IGCC baseline and SC-PC cases and the NPV-results conform to such an expectation as shown in Figure 96[b]. The lower plant costs of SC-PC and IGCC baseline without any CO₂ capture and sequestration effort were within the expected levels. The higher plant cost in the IGCC-PBR case was mostly due to the plant size increase to compensate for the power requirement for CO₂ compression and to fulfill the net power output requirement of 550 MWe. The captured CO₂ leaving the second stage Selexol unit was at 23.7 psia and 51°C and was compressed to 2214.7 psia at constant temperature. The auxiliary load for the corresponding compression was estimated as 102.5 MWe. Similar to the IGCC-PBR case, the cost of the SC-PC

case with CO₂ capture was almost double the cost of the case without CO₂ capture because of the CO₂ capture unit (Econamine) and compression costs.

Figure 96. [a] Operational and maintenance costs [b] total plants cost of the following coal-fired power plant cases:

- IGCC: Baseline IGCC plant without CO₂ capture
- IGCC-MR: IGCC plant with membrane reactor with CO₂ capture
- IGCC-MR w/o CO₂ comp.: IGCC plant with membrane reactor without CO₂ capture
- IGCC-PBR: IGCC plant with traditional shift reactors with CO₂ capture
- SC-PC: Supercritical pulverized coal plant without CO₂ capture
- SC-PC w CO₂ cap.: Supercritical pulverized coal plant with CO₂ capture

Table 19. Estimation of capital investment cost for the Pd-based membrane reactor module

I. Direct Costs			
A. Equipment + installation + instrumentation + piping + electrical + insulation ...			
1. Purchased equipment	Reactor	HTS catalyst	Pd Membrane
	\$10,555.2	\$1,100,152.7	Pd Cost \$22,381,587.6
			Support [316L SS] \$1,267,870.2
			Total \$23,649,457.8
Total membrane module	\$24,760,165.8		
2. Installation (%55 of A1.)	\$13,618,091.2		
3. Instrumentation and controls, installed (%30 of A1.)	\$7,428,049.7		
4. Piping, installed (%80 of A1.)	\$19,808,132.6		
5. Electrical, installed (%40 of A1.)	\$9,904,066.3		
Equipment total	\$50,768,895.1	MR total	\$75,518,505.6
II. Indirect Costs			
A. Engineering and supervision (%30 of direct cost)	\$22,655,551.7		
B. Construction expense and supervision (30% of direct cost)	\$22,655,551.7		
C. Contingency (%15 of Fixed-capital investment)	\$21,322,872.2		
sub-total	\$66,633,975.5		
III. Fixed-capital investment = direct + indirect costs	\$142,152,481.2		
IV. Working capital (IV = (III+IV)*0.2)	\$35,538,120.3		
V. Total capital investment = III + IV	\$177,690,601.4		
Membrane module cost Summary			
1. Direct costs [\$ /ft ² Pd]	\$538.2		
3. Fixed capital investment [\$ /ft ² Pd]	\$1,013.1		
4. Total capital investment [\$ /ft ² Pd]	\$1,266.3		

While the IGCC-PBR with double stage Selexol unit and SC-PC with Econamine units were assumed to achieve 92% and 90% CO₂ separation levels [18], respectively, the IGCC plant with an embedded Pd-based membrane reactor was assumed to achieve 98% CO₂ capture level. Even though there is no theoretical limit of the CO₂ separation level that can be attained with the Pd-based membrane reactor, only 98% was used in order not to overestimate the membrane reactor profitability. The parameters used in the NPV analysis are listed in Table 20.

Table 20. Economic parameters

Plant life [years]	40			
Tax rate	40%			
Depreciation (annual)	30%			
Insurance and property tax rate	1.78%			
CO ₂ tax (\$/ t CO ₂ , 2015)	25			
CO ₂ tax growth rate	2%			
CO ₂ transportation & sequestration cost (\$/t CO ₂)	5			
Nominal discount rate [%]	w/o CO ₂ cap.	IGCC-MR: 9	IGCC: 8	SC-PC: 6
	w CO ₂ cap.	IGCC-MR: 9	IGCC: 8	SC-PC: 8
Inflation rate [%]	2.50%			
Electricity selling price [cents/kWh]	8.38			
Hydrogen selling price [\$/GJ]	7.5			
Plant capacity factor [%]	85.00%			
Pd price [\$/g]	14.3			
Support price for lab scale membrane [\$ for 4 in ²]	55			
Membrane life time [years]	3			

For a scenario assuming no regulatory action on carbon emissions, the NPV of the IGCC-MR case was compared to the IGCC baseline and supercritical pulverized coal plant cases because there is no need to capture CO₂. When the introduction of CO₂ taxes materializes and taxes are high enough to impel power plant owners to install the requisite equipment to capture CO₂, IGCC with traditional shift reactors along with the double stage Selexol unit as well as the supercritical pulverized coal plant with an Econamine unit ought to be directly compared to the IGCC-MR technology option. The SC-PC was shown to be the best option with the lowest NPV/Cost as in Figure 97 [a] and the highest NPV with revenue as shown in Figure 97 [b] if any enforcement of CO₂ emission control rule is not considered. For the current values of the economic inputs of the NPV model, the IGCC-PBR and SC-PC with CO₂ capture options generate negative NPV values if a CO₂ tax of \$25/ton CO₂ was applied after 2015 as shown in Figure 97 [b]. In addition, the size of the power-plants needs to be increased to make the project more profitable in the case of CO₂ capture/sequestration as can easily be seen from the drastic difference in the NPV values with and without CO₂ tax imposition in Figure 97 [b].

Figure 97. [a] -NPV/Cost and [b] NPV with revenue results of the power plants in case of no CO₂ tax (without capture) and with CO₂ tax (with capture)

Economic assessment under uncertainty: Integration of Monte Carlo methods into the NPV framework of analysis

The most significant uncertain inputs to the NPV model are the following:

1. Plant capacity factor
2. Pd price
3. Support price
4. Membrane lifetime
5. Initial CO₂ tax
6. The CO₂ tax starting year
7. CO₂ tax growth rate
8. Electricity selling price
9. H₂ selling price
10. Nominal discount rate
11. Inflation rate

Since all of the H₂ produced in the IGCC-MR case was assumed to be used for electricity production, the H₂ selling price was not included into the Monte Carlo simulation. Plant capacity factor plays one of the most important role in the uncertainty analysis. The IGCC plant with Pd-based membrane reactor option has never been demonstrated at commercial scale. Thus, the lack of operational experience introduces significant technology risk and uncertainty in the plant capacity factor. Similar concerns arise in both the IGCC-PBR and SC-PC with CO₂ capture cases, since none of them has ever been demonstrated at commercial scale.

For the sake of simplicity and also to elucidate barriers to investment on this new technology option, only two uncertain inputs, namely the electricity selling price and plant capacity factor were considered. CO₂ taxes were ignored and only electricity selling price was used as an uncertain input for the SC-PC case since extensive operational experience over the years for this particular technology could safely lead to a fixed plant capacity factor of 85%. The triangular distribution for the plant capacity factor with a maximum of 85%, minimum of 60% and a most

likely value of 75% was used for the IGCC baseline and IGCC-MR cases. Historical data for electricity selling price across all sectors since 1996 were resampled as the distribution: max: 9.94 ¢/kWh, min: 6.64 ¢/kWh, average: 8.38 ¢/kWh.

An immediate result of a MC simulation is the calculation of the expected NPV (ENPV) from the corresponding distribution profile in the presence of uncertainty. ENPV is simply the average of all the NPV realizations associated with each of the thousands of simulated possibilities and represents the average value of the project [65]. The ENPV values of the latter MC simulation together with the single estimate NPV based on averages are listed in Table 21. The flaw of average is manifested by the difference between ENPV of -0.12 B\$ and single projection NPV of 0.3 B\$ of the IGCC-MR. The risk in the capacity factor due to the lack of operational experience may cause the membrane reactor technology option to lose money.

Table 21. The MC simulation results with capacity factor and electricity selling price as uncertainties under no CO₂ capture/ no CO₂ tax condition

	IGCC-MR	IGCC-Baseline	SC-PC
Average [ENPV]	-1.16E+08	5.98E+08	2.18E+09
Max	7.40E+08	1.57E+09	3.04E+09
Min	-9.10E+08	-3.01E+08	1.30E+09
Single projection NPV*	3E+08	1.08E+09	2.22E+09

The NPV distribution profiles when the uncertainty drivers were capacity factor and electricity price is shown in Figure 98. The interpretation of Figure 98 is as follows: The y axis is the cumulative probability of achieving the corresponding NPV value on the x axis. This shows the percentage of times that profit was less than or equal to the amount shown on the horizontal axis. The likelihood of losing money may be determined by locating 0 on the horizontal axis, then going up to the curve to determine the percent of trials that are less than 0, about 66% for IGCC-MR and 2% for IGCC baseline. For instance, there was a 40% chance of losing 0.19 B\$ and more for the IGCC-MR case due to the risk in unknown total plant operation time (capacity factor). There was no change of losing money for the SC-PC case and the lowest NPV would be 1.3B\$ with an electricity selling price of 6.64 ¢/kWh and capacity factor of 85%. In summary, the trends in Figure 98 showed why investors hesitate to decide on the option of membrane reactor integration into IGCC plants under the current conditions.

Figure 98. The NPV distributions with capacity factor and electricity selling price as uncertainties under no CO₂ capture/ no CO₂ tax condition

The inclusion of all uncertain inputs into the Monte Carlo simulator

Initial analysis was performed to determine the membrane reactor module cost distribution itself under uncertain Pd price, support price and membrane life time. The MC simulation results for the uncertainty analysis of the membrane reactor module are shown in Figure 99 in terms of fixed capital investment and total capital investment (fixed capital investment + working capital) per ft² of the whole module. The expected total capital investment of 1268 \$/ft² listed in Table 22 was slightly higher than the 2015 target of 1000 \$/ft².

Table 22. The MC simulation results for the Pd-based membrane reactor module

	Fixed-capital investment	Total capital investment
Average	1014.7	1268.4
Max	1799.7	2249.7
Min	243.58	304.48

The uncertainty analysis under current conditions without any regulatory action on carbon emissions was conducted by comparatively assessing the economic performance results of the IGCC baseline, IGCC-MR without CO₂ compression and sequestration and SC-PC baseline. The plant capacity factor, nominal discount rate, inflation rate for all cases and Pd price, support price and membrane lifetime for the IGCC-MR case specifically were considered as the uncertain inputs. Following that, the uncertainty factor of the CO₂ taxes was included and the IGCC-MR was compared with the IGCC-PBR and SC-PC with capture. The detailed distributions of the uncertain inputs are listed in Table 23.

Figure 99. The membrane reactor module cost distribution in the presence of uncertainty

Table 23. Distributions of uncertain inputs

	w/o CO ₂ Tax/Capture			w CO ₂ Tax/Capture		
	Min	Most Likely	Max	Min	Most Likely	Max
Initial CO ₂ tax [\$/ tonne CO ₂]	-			0	25	50
CO ₂ tax growth rate [%]	-			2	5	8
Nominal discount rate [%]						
IGCC Baseline	6	7	9	-		
IGCC-MR	6	7	9	6	7	9
IGCC-PBR	-			6	7	9
SC-PC	6			-		
SC-PC w capture	-			6	7	9
Inflation rate [%]	2010-2011 Historical data, U.S. Dep. of Lab. Bureau					
Electricity selling price [cents/kWh]	2010-2011 Historical data, U.S. Energy Inf. Adm.					
Plant capacity factor [%]						
IGCC Baseline	60	80	85	-		
IGCC-MR	60	80	85	60	80	85
IGCC-PBR	-			60	80	85
SC-PC	85			-		
SC-PC w capture	-			60	80	85
Pd price [\$/g]	1979-2011 Historical data, www.kitco.com					
Support price [\$ for 4 in ²]	30	50	70			
Membrane life time [years]	1	3	5			

The NPV distributions including the effect of uncertain inputs with and without regulatory action on carbon emissions are shown in Figure 100 [a] and [b] respectively. In case of no CO₂ tax enforcement; while the IGCC-MR and IGCC baseline plants have a chance of 44 and 13 % losing money, the SC-PC option appears clearly as the most appealing one generating positive NPV outcomes as shown in Figure 100 [a]. However, the IGCC-MR potential should not be underestimated because of the negative NPV zone. The IGCC-MR could still produce a 54% positive NPV result which could be further enhanced by the improvements in the membrane reactor technology. More importantly, IGCC-MR case had the lowest 60% capacity factor which can be substantially improved by building operational experience given successful policy stimulation efforts for the deployment of a few demonstration plants at near-commercial scale undertaken by appropriate private sector-government partnerships.

Assuming CO₂ emission taxes in the future; the NPV/Cost distributions of the IGCC-MR plant were compared with the IGCC-BPR and SC-PC with capture plants. A meaningful distribution of the electricity selling price in such a regulatory environment poses certain challenges, but since all of the plants were assumed to produce the same net amount of electricity (550 MWe) the NPV/Cost without revenues was used for comparison purposes. The plant with a NPV/Cost distribution closer to the origin is preferable in this case. In Figure 100 [b], the IGCC-MR exhibits clearly a more attractive NPV/Cost distribution profile compared the IGCC-PBR and SC-PC with CO₂ capture plants. The latter result shows the high potential of the Pd-based membrane reactor technology option integrated into IGCC power plants should regulatory action on carbon emissions is introduced.

Figure 100. The NPV distribution results by considering multiple uncertain inputs without [a] and [b] with regulatory action on CO₂ emission

Sulfur compounds removal by PSA

Adsorbents, isotherms and adsorption kinetics

The main goal of the PSA system was to remove the sulfur compounds H_2S and COS from the feed SynGas. The other components that are present in the industrial setting include: H_2 , CO , CO_2 , and H_2O .

The first task performed by ARI was: adsorbent preparation, adsorbent selection, and isotherms and diffusivities measurements. Four adsorbents have been selected, obtained, and pretreated. All preliminary property measurements are reported in Table 24. Equilibrium isotherms were measured at 200 and 230°C in the apparatus shown in Figure 101.

Table 24. Summary of Adsorbent Properties

No.	Adsorbent Name	Density (g/cm^3)			Overall Void Fraction	Intraparticle Void Fraction	Specific Pore Volume (cm^3/g)	Sauter Mean Particle Size (mm)
		Solid	Bulk	Particle				
1	Zeolite 5A	2.707	0.787	1.019	0.709	0.624	0.612	0.91
2	Zeolite 13X	2.614	0.740	0.980	0.717	0.625	0.638	0.95
3	NaY	2.575	0.555	0.829	0.785	0.678	0.818	2.39
4	Hisiv 3000	2.388	0.709	1.071	0.703	0.551	0.515	2.80

Figure 101. Schematic diagram of volumetric equilibrium apparatus

The adsorbate loading was determined by measuring the shift in pressure of the gas phase. Equilibrium isotherm data were fitted using the Langmuir equation (1), in which q_i^* is the adsorbate loading at equilibrium pressure P and A and B are empirically determined Langmuir coefficients.

$$q^* = AP / (1 + BP) \quad (1)$$

Note that in the cases for which there was curvature in the isotherm data, the Langmuir equation was used. However, in no case was the actual saturation capacity observed experimentally. Hence, the extrapolated value listed in Table 25 is not very robust. Table 25 and Table 26 summarize the isotherm fits, providing the isotherm parameters in conventional units

(millimoles adsorbed per gram of adsorbent versus equilibrium pressure in psia). Plots of the component isotherms, each confined to a single adsorbent, are shown in former Quaterly reports Q4 to Q5.

Table 25. Adsorbent Isotherm Parameters at 200°C

Adsorbent	Gas	Langmuir Parameters		Saturation Capacity	α
		A	B	A/B	A_{ads} / A_{5A}
		mmol/g psia	Psia ⁻¹	mmol/g	--
Zeolite 5A	CO ₂	0.034917	0.003200	10.91	100.0%
	COS	0.056472	0.000000	-	100.0%
	H ₂ S	0.139598	0.002697	51.76	100.0%
Zeolite 13X	CO ₂	0.038075	0.016233	2.35	109.0%
	COS	0.048243	0.008352	5.78	85.4%
	H ₂ S	0.255812	0.153225	1.67	183.2%
NaY	CO ₂	0.024852	0.007279	3.41	71.2%
	COS	0.027321	0.000000	-	48.4%
	H ₂ S	0.062656	0.048481	1.29	44.9%
Hisiv 3000	CO ₂	0.008819	0.018367	0.48	25.3%
	COS	0.019304	0.012327	1.57	34.2%
	H ₂ S	0.045323	0.117574	0.39	32.5%

Table 26. Adsorbent Isotherm Parameters at 230°C

Adsorbent	Gas	Langmuir Parameters		Saturation Capacity	α
		A	B	A/B	A_{ads} / A_{5A}
		mmol/g psia	Psia ⁻¹	mmol/g	--
Zeolite 5A	CO ₂	0.027868	0.013334	2.09	100.0%
	COS	0.038124	0.002168	17.58	100.0%
	H ₂ S	0.081397	0.012698	6.41	100.0%
Zeolite 13X	CO ₂	0.018013	0.009820	1.83	64.6%
	COS	0.021508	0.001817	11.84	56.4%
	H ₂ S	0.073219	0.045858	1.60	90.0%
NaY	CO ₂	0.015317	0.006024	4.23	55.0%
	COS	0.016987	0.000000	-	44.6%
	H ₂ S	0.023919	0.000000	-	29.4%
Hisiv 3000	CO ₂	0.003958	0.003990	0.99	14.2%
	COS	0.008006	0.002575	3.11	21.0%
	H ₂ S	0.018135	0.062338	0.29	22.3%

The water vapor isotherms were conducted with all four adsorbents at 200 and 230°C by using the apparatus shown in Figure 101.

Figure 102 and Figure 103 show the capacity of the various adsorbents versus partial pressure for water at 200 and 230°C. NaY exhibited the highest capacity for water followed by 5A and 13X. The capacity for Hisiv 3000 was significantly lower than that for the other adsorbents.

One item of concern was the apparent cellular modifications that occurred when the dry zeolites were exposed to water at elevated temperatures. A capacity loss was observed during early tests where the zeolites were initially exposed to water at the high temperature, 200°C and above. For subsequent tests, including the results shown in this report, the adsorbents were pretreated by exposing them to humid air, 10% RH at room temperature, until equilibrium occurred at those conditions.

Figure 102. Water isotherms with dual mode fits at 200°C

Figure 103. Water isotherms with dual mode fit sat 230°C

Table 24 summarizes the isotherm fits using the Dual Mode equation, where:

$$q^* = [AP / (1 + BP)] + CP \quad (2)$$

Table 27. Adsorbent Isotherm Parameters for Water

Adsorbent	Temperature	Dual Mode Parameter (units of psia vs. g/g)		
		A	B	C
Zeolite 5A	200	0.12601	0.8854	0.000501
	230	0.04984	0.4644	0.000696
Zeolite 13X	200	0.09472	0.6895	0.000620
	230	0.03569	0.3722	0.001041
Hisiv 3000	200	0.00340	0.7142	0.000278
	230	0.00167	0.2879	0.000265
NaY	200	0.04974	0.2630	0.000696
	230	0.02154	0.1637	0.001031

One major of concern, was how the water in the system was handled. Figure 104 and Figure 105 below show the comparison of the isotherms for H₂O, CO₂, and H₂S for 5A and Hisiv 3000. H₂ and CO are not included since the capacity of the adsorbents for these components is low enough to be irrelevant for this discussion. As can be seen, the 5A has a very high capacity for water. In order to remove the H₂S, the water will also end up being removed. It is probable that some of the CO₂ will also be removed. The H₂ and CO will pass though the column and will exit as a high pressure product. A portion of the CO₂ will also be retained in the high pressure product.

Figure 104. 5A Isotherms at 200°C

In the case of the Hisiv 3000, the capacity for water is significantly lower than for 5A. It should be possible to remove all of the H₂S while retaining the majority of the water present in the system. Similarly, the CO₂ present will end up being split between the high pressure product and the H₂S waste stream.

Figure 105. Hisiv3000 Isotherms at 200°C

Transient uptake tests were intended to elucidate both short-time and long-time diffusion behavior. The most basic comparison is based on the time to reach equilibrium for a gas at a given initial condition for each adsorbent. Values for CO₂, COS, and H₂S are listed in Table 28 and Table 29 for data at 200 and 230°C, respectively. All data available as of 6/24/08 have been included. Three values are listed for each adsorbent, viz., the times to reach P_{final} (i.e., equilibrium or F=1.0), F=0.99, and F=0.90, respectively. Where F, fractional uptake, is defined as:

$$F = (q_t - q_0)/(q_\infty - q_0) \quad \text{where } q_\infty = q^* \quad (3)$$

Table 28. Diffusivity parameters for isotherms at 200°C

Adsorbent	Gas	Pinitial (psia)	Pfinal (psia)	Time to Pfinal F = 1.00 (min)	Time to F = 0.99 (min)	Time to F = 0.90 (min)
Zeolite 5A	CO2	4.2717	2.0359	15.6	6.25	1.7
	COS	2.8763	1.5682	13.4	3.75	1.4
	H2S	3.9755	0.8065	19.0	18.3	3.9
Zeolite 13X	CO2	4.0878	0.8448	62.4	44.1	1.04
	COS	4.0824	1.0955	28	17.5	2.5
	H2S	4.0992	0.1259	14.7	2.4	0.2
NaY	CO2	6.1497	3.8339	78.6	67.5	8.5
	COS	5.0169	3.1187	9	4.1	0.5
	H2S	4.6414	2.3480	14.2	6	0.6
Hisiv 3000	CO2	6.4593	4.9984	12	9.5	<0.1
	COS	4.9698	3.3482	12	2.5	<0.1
	H2S	4.5957	2.3348	17	15.5	1.9

Table 29. Diffusivity parameters for isotherms at 230°C

Adsorbent	Gas	P _{initial} (psia)	P _{final} (psia)	Time to P _{final} F = 1.00 (min)	Time to F = 0.99 (min)	Time to F = 0.90 (min)
Zeolite 5A	CO ₂	4.5473	2.2150	14.2	12.6	< 0.1
	COS	3.4404	1.8768	0.37	< 0.1	< 0.1
	H ₂ S	3.3290	1.2310	3.683	2.9	0.1
Zeolite 13X	CO ₂	4.6377	2.6083	16.1	16	2.0
	COS	3.1360	2.0124	< 0.1	< 0.1	< 0.1
	H ₂ S	3.1430	0.6221	8.5	4.8	0.4
NaY	CO ₂	3.7383	2.3037	47.5	46.7	14
	COS	3.5471	2.2773	0.98	0.86	< 0.1
	H ₂ S	4.2410	2.3302	9.7	6.5	0.8
Hisiv 3000	CO ₂	3.8945	3.1375	37.0	29.9	8.1
	COS	3.7715	2.8762	6.4	4.9	0.2
	H ₂ S	4.4601	2.7070	18.2	12.2	1.2

Preliminary computer simulations

In order to determine the best flow rates for a given set of step times for the PSA experiments, a series of computer simulations were conducted. Two different cycles were used. Cycle Type A, as listed in Table 30 used the following schematic represented in Figure 106.

Table 30. Simulation Conditions

Condition #	Feed Composition (%)					Cycle Type
	He (H ₂) + N ₂ (CO)	CO ₂	H ₂ O	COS	H ₂ S	
1	51	30	18.9	0	0.1	A
2	50.49	29.7	18.81	0	1.0	
3	51	30	18.9	0.05	0.05	
4	51	30	18.9	0	0.1	B
5	50.49	29.7	18.81	0	1.0	
6	51	30	18.9	0.05	0.05	
7	62.9	37.0	0	0	0.1	A

Figure 106. Cycle Type A Schematic

The possibility of recycling a portion of the by-product gas has also been explored; Cycle Type B, as listed in Table 30 and Figure 107, which shows the cycle with recycling.

Figure 107. Cycle Type B Schematic

In both cases: $P_H = 200$ psia, $P_M =$ atmospheric pressure and $P_L = 2$ psia. The system temperature was set at 200°C and the mass of adsorbent was 269.8 g / bed . Table 30 outlines the different conditions tested, while Table 31 shows the results of the simulations.

Table 31. Simulation Results

Condition #	Adsorbent	H ₂ Product Composition (%)					Flow Rate (sl/min)		H ₂ Recovery (%)
		He (H ₂) + N ₂ (CO)	CO ₂	H ₂ O	COS	H ₂ S	Fresh Feed	Total Feed	
1	Hisiv 3000	63.76	25.78	10.46	n/a	0.0018	2.193	= fresh feed	53.19
2		71.28	21.79	6.93	n/a	0.0015	1.554		29.26
3		88.33	9.72	1.94	0.0030	0	0.950		3.90
1	5A	91.61	8.39	8.39	n/a	0.0014	3.837	= fresh feed	86.20
2		97.24	2.76	0	n/a	0.0015	2.924		80.16
3		95.15	4.85	0	0.0012	0.0002	3.289		83.16
4		91.62	8.39	0	n/a	0.0013	3.525	3.837	93.86
5		97.26	2.74	0	n/a	0.0014	2.606	2.924	90.60
6		95.16	4.84	0	0.0012	0.0002	2.975	3.289	92.24
7		90.39	9.61	n/a	n/a	0.0016	3.837	= fresh feed	87.87

For the simulations, the times for each step were set then the optimal flow rate was determined in order to achieve the best hydrogen recovery. As can be seen above, the hydrogen recovery for Hisiv 3000 was at best 53.2% in the case with 1000 ppm H₂S in the feed and no COS. With higher a higher H₂S concentration 1% (10,000 ppm) that dropped to 29.3%. When COS was added the recovery was less than 4%.

The recovery of hydrogen for 5A was drastically better and didn't change nearly as much with the varying feed compositions. It ranged from 80.2 to 86.2% regardless of the feed. If the PSA system is modified to recycle the blowdown gas, then the recovery increases to more than 90%. However as previously mentioned almost all the water was removed from the feed.

PSA first results with sulphur free dry SynGas: the need for recycling

Figure 119 shows the configuration of the PSA system for this first test while Figure 106 shows the cycle used with no recycle at first. A series of PSA tests were conducted with 5A to confirm the results of the computer simulations. The tests conducted were based upon a single simulation case. With a feed composition of 62.9% He (H₂) + N₂ (CO), 37% CO₂, and 1000 ppm H₂S, the resulting helium product predicted was 90.39 % He (H₂) + N₂ (CO), 9.61% CO₂, and 16 ppm H₂S with a helium recovery of 87.87%.

Figure 108. PSA System Configuration

Table 35 summarizes the PSA first test results. For these tests, the goal was to have the CO_2 in the product stream equal the amount of CO_2 predicted by the simulation mentioned above (9.61%). During the laboratory experiments, helium is being substituted for hydrogen and nitrogen is being substituted for carbon monoxide. For all of the tests the following conditions were applied:

System high pressure = 200 psia

System low pressure = 1 atm absolute or 2 psia

System temperature = 200°C

Feed Composition $\approx$ 61.73% He (H_2), 1.23% N_2 (CO), and 37.04% CO_2

Table 32. PSA Test Results

Test #	Feed Flow rate (sl/min)	Helium Product Composition (mol %)			Product flow rate (sl/min)	Helium Recovery (%)	Step Times (sec)				
		He (H ₂)	N ₂ (CO)	CO ₂			Feed	BD	Evac	Purge	Press
1	4.63	96.02	1.56	2.12	2.24	74.5	410	20	100	270	20
2	4.63	89.37	1.51	9.13	2.78	70.6	500	20	190	270	20
3	4.22	88.89	1.59	9.52	2.22	75.3	495	20	285	170	20
4	8.34	89.22	1.51	9.27	4.53	77.8	238	20	138	60	20
5	8.30	88.50	1.46	9.50	4.42	77.2	209	20	138	31	20

The following plots show results of the test 5. During testing, certain parameters need to be maintained at certain conditions while others are just observed, The data contained in the following figures was collected when the PSA system appeared to be near or at steady-state.

According to the PSA test results, the computer simulations over-estimated the recovery of helium. After changing various system parameters, it became apparent that the largest loss of helium occurred during the blowdown step. Figure 122 shows the composition and flow rate profiles of the by-product stream during the cycle. Note the high flow rate coupled with the relatively high helium concentration, this causes a significant loss of helium during the blowdown step.

Figure 109. Concentration and Flow Profiles of the By-Product at Steady-State for Test 5

In order to increase the recovery, it will be necessary to recycle the blowdown gas back in with the feed gas. Hence the PSA system was run with 5A recycle in order to obtain the highest possible recovery. Figure 119 shows configuration of the PSA system with recycle while Figure 107 shows the cycle used.

Figure 110. PSA System Configuration

A series of PSA tests were conducted with 5A to determine whether recycling the gas produced during blowdown would increase the recovery of hydrogen. Through the course of testing, modifications were made to the system, as well as the cycle, to improve performance. The results with the best equipment configuration and the cycle with reduced helium losses are included in Table 35 below. Table 35 summarizes the PSA test results. For these tests, the goal was to have the CO₂ in the product stream equal to the amount of CO₂ predicted by the simulations (9.61%). During the laboratory experiments, helium is being substituted for hydrogen and nitrogen is being substituted for carbon monoxide. For all of the tests the following conditions were applied:

System high pressure = 200 psia

System low pressure = 1 atm absolute or 2 psia

System temperature = 200°C

Feed Composition ≈ 61.73% He (H₂), 1.23% N₂ (CO), and 37.04% CO₂

Table 33. PSA Test Results

Test #	Feed Flow rate (sl/min)	Helium in Feed (%)	Heavy Product flow rate (sl/min)	Helium in Heavy Product (%)	Helium Recovery (%)	Step Times (sec)				
						Feed	BD	Evac	Purge	Press
1	8.47	62.14	2.44	3.09	99.986	111.1	12	84	0.1	15
2	4.24	62.30	1.22	2.96	99.986	232.1	12	205	0.1	15
3	12.59	62.34	2.47	3.21	99.990	67.1	12	40	0.1	15

Since varying the feed step time didn't adversely affect the recovery of the helium, it was decided that we would try to run the system as quickly as possible. An additional test was started, but not completed, at a higher flow rate than Test 3 listed in the table, but the gas booster being used in the system was unable to process the recycle gas quickly enough. The maximum feed flow rate was approximately 12.6 sl/min for the system.

Compared to previous tests, the purge step time was significantly reduced. For the three component tests (He, N₂, CO₂), the only purge occurring was that which leaked through the "closed" metering valve due to pressure drop. In order to increase the recovery of helium, the purge step time was basically reduced to zero to prevent those losses.

Figure 111 through Figure 113 show the compositions and flow rates of the gas being measured by the mass spectrometer. The "light product" was the helium rich product which was produced continuously during the cycle. Whereas the "heavy product" was the waste gas produced during the evacuation step.

When sampling the gas of interest was directed through a flow meter and then onward to the mass spectrometer. One change to the system was the addition of a buffer bag to collect the evacuation gas so that the average composition of the heavy product could be measured instead of trying to measure it in real time. In order to collect the flow rate data for the recovery calculations, the heavy product flow was redirected through a wet test meter and wasn't being measured by the mass spectrometer. For example, this occurred at about minute 14 on Figure 111, the increase in nitrogen between 14 and 16 minutes was due to back flow of room air into the mass spectrometer.

Figure 111. Concentration and flow profiles at steady-state for Test 1

Figure 112. Concentration and flow profiles at steady-state for Test 2

Figure 113. Concentration and flow profiles at steady-state for Test 3

PSA first results with sulfur free wet SynGas

Since the performance for the new cycle with recycle was good, the next step was to add H₂O to the feed mixture and examine recovery while maintaining the required product purity. The PSA system was modified to handle water. After water tests H₂S and COS were added to the feed mixture. Figure 114 shows the configuration of the PSA system with recycle and water handling capabilities. The introduction of water to the system presented a series of challenges. As in many cases, the generation of an accurate and consistent feed gas can be more difficult in the lab than in industry. In the laboratory, the feed gas is a blended mixture of the individual pure components from their typical states at room temperature and in some cases atmospheric pressure.

For the dry system, each pure gas component was fed from a high pressure gas cylinder and was metered by a mass flow controller. The composition and flow rate were measured directly using a mass spectrometer and wet test meter.

For the humid system, however, the water was pumped as a liquid, and its flow rate was monitored. Subsequently, it was vaporized and added to the mixture at pressure (200 psia) and high temperature (~200°C). Several trials were required to generate the water vapor at reasonably stable rate. The current configuration can be seen in Figure 115.

Figure 114. PSA System Configuration

Figure 115. Current feed system configuration

As mentioned above, the liquid water was drawn from a reservoir by an electronic metering pump and then mixed with helium (hydrogen substitute) at about 200 psia. That mixture was heated to vaporize the water. A humidity probe was used to measure the composition of the two-component mixture. After the humidity measurement, nitrogen and carbon dioxide were added to the mixture since carbon dioxide could interfere with the performance of the humidity probe.

The other major challenge for the PSA system was the recycle system. The gas recovered during the blowdown step needed to be recycled in order to obtain a high enough recovery of the helium (hydrogen) being processed. The gas was recovered at atmospheric pressure and needed to be boosted to high pressure in order to mix in with the feed stream.

The blow down gas was found to have a dry composition of about 50% helium and 50% carbon dioxide with a small amount of nitrogen via a mass spectrometer. That particular instrument did not measure the water content. The gas actually contained a significant amount of water. In order to successfully recycle the gas, the water content needed to be reduced to about 7%RH at room temperature or else the water would condense within the gas booster at high pressure and cause a mechanical failure of the gas booster. Figure 116 summarizes what occurs during the recycle phase of the system.

Figure 116. Flow path of recycle gas

Tests have been conducted with the humid feed. With the addition of water, the feed composition was $\approx 50\%$ He (H_2), 1% N₂ (CO), 30% CO₂, and 19% H₂O. Due to issues with both the stability of the feed composition and mechanical problems with the gas booster, only two tests were preliminary completed.

As with the dry tests, the helium-rich product CO₂ concentration target was 9.6% . During operation, the helium-rich product flow rate and the step times could be adjusted until the helium rich product tank pressure and its composition were stable. Then flow and composition data were measured and collected for both the helium-rich product as well as the waste gas produced during the evacuation step. Table 34 summarizes the results for two consecutive test days with conditions that were approaching steady-state.

Table 34. Humid PSA Test Results

Test #	Dry Feed Flow rate (sl/min)	Helium in Dry Feed (%)	Light Product flow rate (sl/min)	Helium in Light Product (%)	LP Helium Recovery (%)	Heavy Product flow rate (sl/min)	Helium in Heavy Product (%)	HP Helium Recovery (%)	Helium Discrepancy (%)
1	6.11	61.75	4.05	88.58	95.14	2.00	4.29	97.72	3.28
2	3.06	61.94	1.92	88.75	89.82	1.02	3.97	97.86	8.04

Notes: LP = "Light Product" = Helium-rich product

HP = "Heavy Product" = waste product

Helium Discrepancy is defined below.

The LP helium recovery was based upon the amount of helium measured in the light product gas as compared to the feed gas. The HP helium recovery was based on the helium measurement for the waste product as compared to the feed gas. The helium discrepancy number is the calculation:

$$[(\text{He in feed} - \text{He in LP}) - \text{He in HP}] / \text{He in feed}$$
 where all units are in (g/min).

An overall dry basis mass balance discrepancy was also calculated for these tests. This calculation is:

$$[\text{Total gas in} - (\text{LP} + \text{HP})] / \text{Total gas in}$$
 where all units are in (g/min).

For Test 1, that value was -1.10% , whereas for Test 2 = -0.95% . Figure 117 and Figure 118 below show the light product composition versus time for Tests 1 and 2 near steady-state conditions.

Figure 117. Light Product Composition Versus Time for Humid Test 1

Figure 118. Light Product Composition Versus Time for Humid Test 2

PSA first results with H₂S laden wet SynGas

Figure 119 shows the configuration of the PSA system used when testing with H₂S and COS added to the feed mixture. Recycle was used for these experiments.

Figure 119. PSA System Configuration

The feed composition for the dry PSA tests was $\approx 61.73\%$ He (H_2), 1.23% N_2 (CO), and 37.04% CO_2 , where helium is being substituted for hydrogen and nitrogen for carbon monoxide. Once water was added to that blend, the target mixture of the components was $\approx 50\%$ He (H_2), 1% N_2 (CO), 30% CO_2 , and 19% H_2O . For the H_2S tests, the ratios of the four other components remained the same, but H_2S was added to the blend and ranged between ≈ 200 and $\approx 10,000$ ppm.

For all the H_2S tests, the following conditions were applied:

System high pressure = 200 psia

System low pressure = 1 atm absolute or 2 psia

System temperature = $200^\circ C$

Blow down time = 12.3 seconds

Purge time = 0.1 seconds

Pressurization time = 14.5 seconds

Table 35 summarizes the dry PSA test results.

Table 35. H₂S PSA Test Results

Test #	Light Product Composition					LP flow	Dry Feed flow	Ave H ₂ O flow	He recovery %		Cycles	Step Times In seconds				
	He	CO ₂	N ₂	H ₂ O	H ₂ S				sl/min			Based on LP	Based on HP	#	Evac	Feed
	%			ppm												
H ₂ S feed concentration nominally 200 ppm																
428a	88.06	10.15	1.83	0.0	0.0	6.19	9.20	1.73	95.74	97.28	78	31.5	58.4			
428b	86.70	11.54	1.75	0.0	0.0	6.34	9.20	1.58	96.40	97.50	45	35	61.9			
429a	84.69	13.51	1.79	0.0	0.0	6.42	9.31	2.17	95.34	97.69	64	40	66.9			
429b	83.27	15.02	1.70	0.0	0.0	6.65	9.31	1.88	97.09	97.82	69	45	71.9			
430a	78.54	19.85	1.59	0.0	0.0	7.24	9.38	2.24	97.44	98.33	67	60	86.9			
503a	74.97	23.43	1.55	0.0	0.0	7.59	9.32	1.92	98.76	99.10	56	75	101.9			
504a	71.87	26.60	1.47	0.0	0.0	7.80	9.14	1.57	100.14	98.94	90	90	116.9			
H ₂ S feed concentration nominally 1000 ppm																
505a	76.91	21.45	1.58	0.0	0.0	7.18	9.12	2.17	98.44	98.22	88	60	86.9			
506a	71.89	26.57	1.49	0.0	0.4	7.73	9.11	2.04	99.10	98.93	77	90	116.9			
507a	71.94	26.52	1.48	0.0	0.4	7.72	9.11	1.95	97.96	98.84	51	90	116.9			
510a	72.64	25.86	1.46	0.0	0.7	7.78	9.29	2.13	98.21	98.81	119	75	101.9			
511a	75.52	22.91	1.52	0.0	0.5	7.39	9.28	1.88	97.53	98.52	124	60	86.9			
512a	79.46	18.80	1.69	0.0	0.3	7.14	9.48	1.90	96.92	98.16	216	45	71.9			
513a	79.57	18.77	1.60	0.0	0.2	7.02	9.36	1.96	96.72	98.10	145	45	71.9			
517a	83.56	14.64	1.79	0.0	0.0	6.52	9.25	2.22	94.16	98.94†	174	30	56.9			
521a	71.39	27.12	1.46	0.0	2.7	8.36	9.32	2.35	103.94	98.81	451‡	75	101.9			
H ₂ S feed concentration nominally 4800 ppm																
602a	89.28	9.08	1.64	0.0	0.9	5.79	9.22	1.88	90.77	96.93	306	45	71.9			
603a	83.98	14.44	1.58	0.0	5.7	6.25	9.28	2.15	91.58	98.01	143	60	86.9			
H ₂ S feed concentration nominally 9,500 ppm																
604a	95.65	2.66	1.69	0.0	0.5	5.16	9.13	2.09	87.68	*	139	45	71.9			
608a	88.14	9.93	1.92	0.0	1.4	5.70	9.32	2.07	87.76	97.03	97	45	71.9			

† Estimated heavy product concentration

‡ Cycles over four days

* Recovery based on heavy product not obtained because of Mass Spectrometer error.

Notes: LP = "Light Product" = Helium-rich product

HP = "Heavy Product" = waste product

The LP helium recovery was based upon the amount of helium measured in the "light product" gas as compared to the feed gas. The HP helium recovery was based on the helium measurement for the waste product ("heavy product") as compared to the feed gas. Since the amount of helium in the "light product" was very close to amount of helium in the feed gas, it was believed that the recovery numbers based on the "heavy product" are more accurate.

For the PSA tests, it appeared that as long as the H_2S concentration in the feed gas was below 1000 ppm, the PSA system could easily remove the H_2S from the gas while maintaining 98+% recovery of the helium (H_2). As the H_2S concentration increased, difficulties arose.

It was decided to remove the H_2S , in the recycle loop, to prevent corrosion and to avoid problems with toxicity. It is possible that a commercial system could recycle H_2S -laden gas and not be limited by those concerns. Thereby, the commercial system could be simpler and possibly cheaper, than if compelled to remove H_2S as it was done.

The blowdown gas in the system needed to be recycled in order to maintain the high helium recovery. However, once the H_2S mole fraction of that gas stream was too high, most likely several percent, the H_2S neutralization portion of the recycle became overwhelmed. Looking at Figure 119, there are two parts of the recycle system which contain adsorbents. The H_2S removal bed contains a chemisorbent which reacts to remove the H_2S , where the desiccant bed adsorbs most of the water. At the lower concentrations, the H_2S removal bed has the capacity to neutralize all of the H_2S without issues. At about 10,000 ppm however, the H_2S removal bed was producing SO_2 , which was then recycled back to the system.

Our understanding is that it would be best to remove the H_2S using the PSA system, and not to capture it in the recycle unit. However, depending on the amount of H_2S in the feed, some portion of the CO_2 will also be rejected and in all cases, the water was completely rejected. The lower the H_2S concentration in the feed, the more CO_2 that can be allowed to remain in the light product before the H_2S concentration in the light product reaches the <1 or <20 ppm target threshold. Figure 120 shows a comparison of the light product compositions versus the feed concentration for a group of tests for which the evacuation times were all 45 seconds. The discrepancy between the test with a feed concentration of 9800 and 9500 is probably due to the fact that the chemisorbent bed was reloaded between the two experiments.

Another direct comparison that has been made is the difference between the temperature maximum and minimum for the three thermocouple located within the adsorbent beds. Figure 121 shows a typical temperature profile plot for both column for several cycles. Figure 122 shows the differences for the group of tests for which the evacuation times were equal while the H_2S feed concentration varied.

There was concern that with the higher H_2S concentration in the feed, that there was a chance that elemental sulfur would form. While emptying the water knock-out in the recycle system, a yellow, powdery, somewhat sticky substance was found. After further investigation, it appears that the substance is sulfur and not adsorbent dust. The water knock-out is kept at room temperature. The melting point of sulfur is 115.21°C . This would prevent the formation of solid sulfur within the column, but once the sulfur reaches cooler parts of the system, it freezes and falls out of the gas mixture. This would also be exacerbated at higher concentration of H_2S in the feed. The "light product" composition was measured and a peak was observed at the atomic mass of 1 showing that hydrogen is being produced in the system.

Adsorption research was stopped at this due to the large amount of CO_2 lost during the process and the difficulties in handling H_2S and COS. In conclusion it appeared that PSA is not suitable for the elimination of sulfur compounds from the SynGas.

Figure 120. Comparison of Tests with 45 second Evacuation Times

Figure 121. Typical Thermocouple Profile

Figure 122. Delta T Comparisons

Conclusions

- High pressure hydrogen flux measurement for the membrane 029 was close to the DOE-NETLs 2010 targets. A hydrogen flux of ~ 166 scfh/ft² was measured at $\sim 405^\circ\text{C}$ and at a ΔP of 101 psi ($P_{\text{High}}=116$ psia & $P_{\text{Low}}=15$ psia), which. 2010 flux targets were reported as 200 scfh/ft² at a $\Delta P = 100$ psi H₂ partial pressure and $T = 300\text{-}600^\circ\text{C}$, with $P_{\text{Feed}}= 150$ psia & $P_{\text{Sweep}}= 50$ psia (Test Protocol v7 - 5/7/2008). The long-term H₂ permeation and the selectivity stability testing of membrane 029 has been completed after >175 days (~ 4270 hours). For the extended testing period of 3550 hours and over the temperature range of $400\text{-}450^\circ\text{C}$, the He leak of the membrane 029 was not detectable, indicating an essentially infinite H₂/He selectivity that remained stable, The final He leak at 450°C and at a ΔP of 35 psi ($P_{\text{High}}=50$ psia & $P_{\text{Low}}=15$ psia) was as low as 0.016 scfh/ft² (<0.1 sccm), which corresponded to a H₂/He selectivity of ~ 6000 (4200 hours).
- Similar high selectivity stability results and high permeance were reproduced with membranes #030, #031 and #033 indicating that 2-3 annealing at 550°C in He + polishing steps is an effective technique to mitigate He leak development at 450°C and a suitable technique for industrial membrane preparation.
- High permeances were obtained on membranes prepared on Al(OH)₃ graded supports (#025, #032, #036, #038, #039 and #053).
- The 12.7 μm Pd/PSS_{316L} repaired membrane AA-12R was tested in H₂ with a shell-side pressure of up to 325 psia and a tube-side pressure of up to 200 psia. A maximum flux of 550.4 scfh/ft² ($P_{\text{high}} = 323.7$ & $P_{\text{low}} = 14.7$ psia) was measured.
- WGS conversions of up to 98.2% (5.2% in excess of equilibrium) were achieved for a temperature of 450°C , a pressure of 212 psia, a steam to CO ratio of 2.6:1, and a GHSV of 2900 hr⁻¹ for over 1 000 indicating the high stability of composite membranes prepared at CIMS in WGS conditions.
- WGS conversions as high as 97.9% (15% in excess of equilibrium) were achieved with a simulated syngas feed, a pressure of 212 psia ($P_{\text{low}} = 14.7$ psia), a temperature of 400°C and a GHSV of 1100 hr⁻¹. Similar experiments were performed with GHSV's of 1100, 2100, 3400, 4500, and 5400 hr⁻¹ where conversions in excess of the equilibrium conversion were observed in all cases.
- In most cases with H₂O/CO ratios of less than or equal to 1.6, evidence of coke formation on the membrane surface was observed, resulting in a gradual decline of CO conversion and H₂ recovery of up to 2 and 7% respectively over 5 hours.
- For each series of experiments with a set steam to CO ratio, a maximum in conversion versus temperature was present in the range of $400\text{-}500^\circ\text{C}$. Similar maxima have been reported in the literature and are most likely caused by the opposing influences of the catalytic activity, the membrane permeance, and the equilibrium constant.
- A feedback controller with proportional and integral action (PI controller) was considered and implemented to the water-gas shift membrane reactor. The controlled and manipulated variables were chosen as the CO fraction at the shell exit and the

steam molar flow rate at the inlet, respectively. The objective of the controller was to keep the overall CO conversion (>95%) at the desired value (set-point) in the presence of disturbances.

- Two control strategies namely regulatory control where an unexpected membrane reactor total pressure drop occurred and servo mechanism control where the set level of CO conversion was increased to 98%. In both cases, quite satisfactory process control was attained maintaining CO conversion at levels higher than 95% so that the retentate stream could become suitable for high pressure CO₂ sequestration.
- The absence of adequate control of the reactor temperature as well as the purity of the feed which may cause hot spots and decline in permeance and selectivity were identified and classified as critical for the operation of the WGS membrane reactor.
- Utilization of excess steam together with the application of vacuum on the permeate side were found to be the most effective method of reducing the temperature rise in the reaction zone without decreasing the overall CO conversion and H₂ recovery.
- Since the main advantage of the Pd/alloy based membrane reactor technology is the high-quality H₂ separation driven by the H₂ partial pressure difference between the reaction and permeate sides, operation at high reaction side pressure is inevitable. Therefore, high pressure reactor operation represents a process safety challenge.
- Under safe operation zone, the total reaction side pressure was determined to be at least 35 atm at a fixed permeate side pressure of 1 atm to attain the target performance levels. Alternatively, the permeate side pressure has to equal or be lower than 0.6 atm (with vacuum) at a fixed total reaction side pressure of 30 atm, to attain the performance target levels of $X_{CO} = 98\%$ and $R_{H_2} = 95\%$, by using a feed temperature of 350°C, permeate pressure of 1 atm, H₂O:CO ratio of 4.5 and 50% $\rho_{Bulk,max}$ for an adiabatic membrane reactor.
- The purity levels of the separated H₂ by using membranes having various selectivity values were successfully assessed through the use of a membrane reactor model including multi-component gas diffusion through the defects. The simulation results supported with the experimental findings showed that H₂ purity of 99.99% and flux target of 250 scfh/m² specified by the DOE could be easily achieved by using a Pd-based membrane having $\sim 34 \text{ ft}^3/[\text{ft}^2\text{-h-psi}^{0.5}]$ H₂ permeance and ~ 8000 ideal H₂/He selectivity, prepared through the current membrane synthesis technology developed in the CIMS laboratory, WPI.
- The single estimate/projection NPV results showed that the IGCC-MR was an economically attractive technology option generating a positive NPV in a scenario with a 25 \$/tonne CO₂ tax starting in 2015. The negative NPV values of IGCC-PBR and SC-PC with CO₂ capture plants would possibly preclude these options from investment consideration in the presence of regulatory action on carbon emissions.
- The average total product cost of an industrial scale water-gas shift membrane reactor module was determined as 1268 US\$/ft² in the presence uncertainties in Pd, support prices and membrane life time.

- The uncertainty in nine key inputs of the NPV/Cost model was considered for IGCC-MR, IGCC-PBR and SC-PC with capture options producing the same amount of net power output, 550 MWe. A comparatively more attractive NPV/Cost distribution profile obtained in the IGCC-MR case assessed against the ones in the IGCC-PBR and SC-PC cases in the presence of regulatory action on CO₂ emissions makes the Pd-based membrane reactor technology option integrated into an IGCC power plant a promising investment choice.
- Four Pd-Au membranes, C-07(14.1 μm, 5.4 wt% Au), C-09(18.8 μm, 4.2 wt% Au), C-11(17.7 μm, 8.5 wt% Au), and C-12(17.0 μm, 12.3 wt% Au), were synthesized utilizing the media grade 0.1 μm Inconel supports purchased from Mott Metallurgical. At 350°C, the measured H₂ permeances were 19.8, 16.6, 11.1, and 9.6 scfh/ft²-psi^{0.5} (ΔP=14.7 psi & P_t=14.7 psia) for the membranes C-07, C-09, C-11, and C-12, respectively.
- Among the four Pd-Au/Inconel membranes with the Au content range of 4-12 wt%; the maximum H₂ permeance was obtained from a Pd-5 wt% Au membrane.
- The H₂S poisoning tests of the Pd-Au/Inconel membranes showed that the sulfur resistance of the Pd-Au membranes increased as the Au composition increased. Over a long term H₂S test (~80 hours) at 400°C in the presence of 5ppm H₂S, the H₂ permeance of the membrane C-16R remained over 50% of the original H₂ permeance, and the permeance loss was totally recoverable. The optimum Au composition in terms of H₂ permeance by taking both sulfur resistance and relative permeance with respect to pure-Pd membrane into account was within 10 – 30 wt%. The permeance loss in Pd-Au alloys was recoverable.
- However, the XPS analysis indicated that there is still some irreversibly formed surface sulfide on the Pd surface. No bulk sulfide formation but only a small amount of surface sulfide formed on the Pd/Au alloy after the poisoning was observed, and the amount of sulfide reduced to the value of the un-poisoned sample after recovery.
- The sulfide fraction was much smaller on the Pd/Au alloy surface compared to Pd, indicating much less sulfide formation on the Pd/Au surfaces. Depth profile analysis confirmed that only surface sulfide formed on the Pd/Au surface.
- Adsorption research was stopped at this due to the large amount of CO₂ lost during the process and the difficulties in handling H₂S and COS. In conclusion it appeared that PSA is not suitable for the elimination of sulfur compounds from the SynGas.

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Appendix A : Models' Equations

A.1. Unsteady state (dynamic) mass and energy balance equations:

The mole balance equation for H₂:

$$\frac{df_{H_2}|_{y+\Delta y}}{dt} = \frac{1}{C_{Total}^{Shell} \cdot v_{shell}} \left[f_{H_2}|_y \cdot F_{Total}^{Shell}|_y - f_{H_2}|_{y+\Delta y} \cdot F_{Total}^{Shell}|_{y+\Delta y} + r_{H_2}|_{y+\Delta y} \cdot \Delta w - \frac{Q \cdot A_m}{l} \cdot \Delta P_{H_2}^{0.5} \right] \text{ Eq. 1}$$

Notice that the mole balance equations for CO, CO₂ and H₂O in the shell side and H₂ in the tube side can be written in a structurally similar manner as the Equation 4 above.

The energy balance equation in the reaction side:

$$\frac{dT}{dt} = \frac{Q - W_s - \sum F_i|_y (H_i|_{y+\Delta y} - H_i|_y) + (-\Delta H_{Rxn}|_{y+\Delta y})(r_i|_{y+\Delta y})}{\sum N_i|_{y+\Delta y} \cdot C_{pi}|_{y+\Delta y}} \text{ Eq. 2}$$

Adiabatic reactor and no shaft work $Q \& W_s = 0$

A.2. Equations for the adiabatic/isothermal 1D steady state model

Mole and Energy Balances:

$$\frac{dF_{H_2}}{dz} = \rho_{Bulk} \cdot A_c \cdot L \cdot r_{H_2} - A_m \cdot J_{H_2} \text{ Eq. 1}$$

$$\frac{dF_i}{dz} = \rho_{Bulk} \cdot A_c \cdot L \cdot r_i \text{ Eq. 2}$$

$$\frac{dF_i}{dz} = \rho_{Bulk} \cdot A_c \cdot L \cdot r_i - A_m \cdot J_i \text{ if Selectivity} \neq \infty \text{ Eq. 3}$$

$$\frac{dT}{dz} = \frac{(-r_{CO}) \cdot (-\Delta H_{Rxn})}{\sum F_i \cdot C_{pi}} \text{ Added to the adiabatic model Eq. 4}$$

$$J_{H_2} = \frac{Q}{l} \cdot (P_{H_2,shell}^{0.5} - P_{H_2,tube}^{0.5}) \text{ by Sievert's Law Eq. 5}$$

$$\text{Fixed Flux Ratio (FR)} = J_{H_2}/J_i \text{ Eq. 6}$$

$$\text{Separation Factor (S}_F\text{)} = [X_{H_2}/X_{(CO+CO_2+H_2O)}]_{Permeate} / [X_{H_2}/X_{(CO+CO_2+H_2O)}]_{Retentate} \text{ Eq. 7}$$

$$\text{CO Conversion} = 100 \times \frac{F_{CO}^{shell}|_{inlet} - F_{CO}^{shell}|_y}{F_{CO}^{shell}|_{inlet}} \text{ Eq. 8}$$

$$\text{CO Conversion} = 100 \times \frac{F_{CO}^{shell}|_{inlet} - F_{CO}^{tube}|_y - F_{CO}^{shell}|_y}{F_{CO}^{shell}|_{inlet}} \text{ if Selectivity} \neq \infty \text{ Eq. 9}$$

$$H_2 Recovery = \frac{F_{H_2}^{tube}|_y}{F_{H_2}^{tube}|_y + F_{H_2}^{shell}|_y} \quad \text{Eq. 10}$$

A.3. Equations for the isothermal 2D steady state model

Mass and momentum balance equations:

$$\frac{\partial(u.C_i)}{\partial y} - \frac{D_{ef,i}}{u} \left[\frac{\partial^2(u.C_i)}{\partial r^2} + \frac{1}{r} \frac{\partial(u.C_i)}{\partial r} \right] + \rho_{bulk,cat} R_i = 0 \quad (1)$$

$$\frac{dP}{dy} = \frac{f \cdot G \cdot \mu_{mix,g} \cdot (1 - \varepsilon)^2}{\rho_{mix,g} \cdot d_p^2 \cdot \varepsilon^3} \quad (2)$$

$$f = 150 + 1.75 \frac{Re}{(1 - \varepsilon)} \quad (3)$$

Boundary conditions:

$$u.C_i = u^0 C_i^0 @ y=0, \text{ reactor inlet} \quad (4)$$

$$\partial(u.C_i)/\partial r = 0 @ r = r_{shell}, \text{ on the shell casing} \quad (5)$$

@ $r = r_{tube}$, on the membrane:

$$\partial(u.C_i)/\partial r = 0 \quad (6)$$

$$\frac{d_p}{Peclet} \frac{\partial(u.C_{H_2})}{\partial r} = J_{H_2} \quad (7)$$

$$J_{H_2} = \frac{Q_o e^{-E_a/(R.T)}}{l} (P_{H_2,shell}^{0.5} - P_{H_2,tube}^{0.5}) \quad (8)$$

Dimensionless constants:

$$Peclet = 8.8 \left[2 - \left(1 - \frac{2 \cdot d_p}{ID_S - OD_M} \right)^2 \right] \text{ if } Re > 1000^3 \quad (9)$$

$$\frac{1}{Peclet} = \frac{0.4}{(Re.Sc)^{0.8}} + \frac{0.09}{\{1 + 10/(Re.Sc)\}} \text{ if } Re < 1000^4 \quad (10)$$

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3 From Faclo, D.M; Paola, D.D.; Marelli, L. and Nardella,P; Chem. Eng. J.; 128; (2007) 115-125.

4 From Wen, C. Y.; Fan, L. T.; Models for Flow Systems and Chemical Reactors; Dekker: New York, 1975.

$$Reynolds (Re) = \frac{d_p \cdot u \cdot \rho_{mix,g}}{\mu_{mix,g}} \quad (11)$$

$$Schmidt (Sc) = \frac{\mu_{mix,g}}{\rho_{mix,g} \cdot D_{i,mix,g}} \quad (12)$$

$$D_{ef,i} = \frac{1 - Y_i}{\sum_{j \neq i} Y_j / D_{ef,ij}}^5 \quad (13)$$

The density, viscosity of the gas mixture and diffusion coefficients for binary gas systems was calculated with the same methods detailed in the quarterly report 12, pp 25-26.

Isothermal power consumption of compressor/vacuum pump:

$$Power_{comp/vac} = \frac{1}{0.6} \cdot P_{intake} \cdot \vartheta_{mix,intake} \cdot \log \left(\frac{P_{discharge}}{P_{intake}} \right) \cdot F_{intake} \cdot MW_{mix,intake} \quad (14)$$

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⁵ From Adams, T. A. and Barton, P. I.; International Journal of Hydrogen Energy; 34, Issue 21, (2009), Pages 8877-8891.

Nomenclature

C	: concentration (mol/m^3)
D	: diffusion coefficient (m^2/s)
d_p	: particle diameter (μm)
E	: activation energy (J/mol)
F	: molar flow rate (mol/s)
G	: mass specific gas flow rate ($\text{kg}/[\text{m}^2.\text{s}]$)
ID	: inside diameter (m)
J	: flux ($\text{mol} / [\text{m}^2. \text{s}]$)
l	: Pd thickness of the membrane (μm)
MW	: molecular weight
No_{tubes}	: number of membrane tubes
NP	: net power (MWh)
OD	: outside diameter (m)
P	: pressure (Pa)
r	: radius (m)
R	: reaction rate ($\text{mol} / [\text{kg cat. s}]$)
Re	: Reynolds number
R_{H_2}	: hydrogen recovery (%)
Q_o	: permeability constant of the membrane ($\text{mol H}_2.\mu\text{m}/ [\text{m}^2. \text{s. atm}^{0.5}]$)
T	: temperature (K)
X_{CO}	: CO conversion (%)
y	: spatial coordinate (m)
Y	: mole fraction
z	: dimensionless spatial coordinate (y/L)

Greek symbols

ϵ	: void fraction of the catalytic bed
μ	: viscosity (Pa.s)
ϑ	: specific volume (m^3/kg)
ρ	: density (kg/m^3) ($\rho_{\text{Bulk, cat}}$: weight of catalyst/ annular reactor volume)

Subscripts

comp	: compressor
g	: gas

i/j : i/j^{th} species
 ef : effective
 mix : mixture
 M : membrane
 S : shell casing
 Shell : shell side of the membrane module where reaction is taking place (Reaction side)
 Tube : tube side of the membrane module where permeated H_2 is flowing through (Permeate side)
 vac : vacuum pump