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SORPTION ENHANCED REACTION PROCESS (SERP) FOR THE PRODUCTION OF HYDROGEN

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Abstract

This paper summarizes recent progress in developing the Sorption Enhanced reaction Process for hydrogen production. Details of single-step reaction experiments and fully cyclic process experiments are described. It is demonstrated that enhanced H2 product (higher purity, conversion) can be continuously produced during cyclic operation of the reactors. The reactor performance is improved by increasing the reactor temperature, steam/methane ratio, or purge amount, or by decreasing the reactor pressure. The data generated by the cyclic process unit is currently being used to generate an H2-SER process design for fuel cell applications.

Introduction

The goal of this work is to develop a novel, more cost-effective steam-methane reforming (SMR) process for the production of hydrogen. The overall SMR reaction is given by:

$$CH_4 + 2\ H_2O \Leftrightarrow CO_2 + 4\ H_2$$

The novel concept is called the Sorption Enhanced Reaction Process (SERP). The reactants, steam and methane, are fed at 450-550°C and 10-50 psig into a tubular reactor containing an admixture of reforming catalyst and an adsorbent for removing carbon dioxide from the reaction zone. A reactor effluent consisting of enriched hydrogen (~90%) is directly produced during this step. The primary impurity is methane with relatively low levels (ppm) of carbon oxides. Once the adsorbent is saturated with CO_2, it is regenerated in situ by using the principles of pressure swing adsorption (PSA) at the reaction temperature.

The potential benefits of producing H_2 by the SERP concept are:

1. reforming at a significantly lower temperature (400-500°C) than a conventional SMR process (800-1000°C), while achieving high conversion of methane to hydrogen
2. production of hydrogen at feed gas pressure (10-50 psig) and at relatively high purity directly from the reactor (e.g., 90% H_2, 10% CH_4, < 0.5% CO2, < 50 ppm CO on a dry basis)
3. significant reduction or even elimination of downstream hydrogen purification steps
4. reduction of CO in the SER reactor effluent to ppm levels - elimination of shift reactors
5. minimization of side reactions, e.g., coking
6. reduction of the excess steam used in conventional SMR.

Key program objectives for the cooperative APCI/DOE SER Project during the current year are listed below:

1. Demonstrate the H_2-SER process under cyclic operation and characterize performance with respect to important operation parameters
2. Refine H_2-SER designs and evaluate process economics
3. Scale-up production of the proprietary high temperature adsorbent with an external vendor

Experimental Systems

Most of the experimental equipment used to characterize the performance of various CO_2 adsorbents and for investigating the H_2-SER process steps has been described by Hufton et al. (1997; 1998; 1999) and Mayorga et al. (1997). Adsorbent screening is performed with a thermal gravimetric adsorption unit (for measurement of dry CO_2 working capacity), a binary desorption unit (to determine CO_2 capacity in steam environments), and a hydrothermal stability unit (to assess physical and chemical stability of adsorbents in steam/CO_2 mixtures at elevated temperatures). Single-step reaction experiments and adsorption breakthrough experiments have been carried out in an electrically-heated fixed bed tubular reactor (SER#1) system. This unit can be used to investigate individual steps of the process, rather than the fully cyclic operation of an industrial SER process unit.

This year we built and operated three new pieces of equipment. A major investment of both time and (APCI) capital was focussed on construction of a process test unit (SER#2) required to demonstrate the H_2-SER process under cyclic operation conditions. A schematic and photograph of this unit was given by Hufton et al. (1999), along with a detailed description of the system. Unlike the current SER#1 lab unit, the SER#2 system permits study of the full sequence of SER process steps, performed in repetitive fashion, in a pair of industrial-scale tubular reactors at relatively high feed/purge flow rates (feed G-rates up to 30 lbmole/hr-ft^2). These steps include high pressure reaction, countercurrent depressurization, countercurrent subatmospheric purge with steam or steam/H_2, and repressurization with steam or steam/H_2. Analytical equipment permits evaluation of effluent gas compositions, temperature, pressure, and flow rates, which ultimately can be used to evaluate the CH_4 conversion, H_2 product purity, and H_2 productivity with respect to important process variables.

The Cyclic Lifetime Unit (CLU) was built in the lab to enable evaluation of the long-term stability of the CO_2 adsorbent during repetitive cyclic exposure to SER reaction and regeneration conditions (i.e., 250 psig steam/N_2 followed by depressurization and purge with 10 psig N_2, all at 400-550C). The unit was automated and routinely operated 24 hours a day. The experimental approach was to place a sample of adsorbent into the unit, expose it to a sequence of reaction/regeneration steps (e.g., 1000 steps), remove the sample and compare its adsorption properties with fresh material.

The last piece of equipment was used to characterize the heat of adsorption of CO_2 on the CO_2 adsorbent at 400-500C. It consisted of an isolated vessel submerged in a temperature-controlled fluidized sand bath. Adsorbent was placed within the vessel, regenerated at 500C with N_2, evacuated, and then dosed with a known amount of CO_2. By isolating the CO_2-containing vessel and changing the temperature, one could monitor the change in CO_2 pressure via a pressure transducer. These P-T data were then analyzed to evaluate the heat of adsorption associated with the experimental CO_2 adsorption capacity.

Results and Discussion

H_2-SER Process Experiments

The process steps utilized in the H_2-SER process are listed in Table 1. An industrial system would utilize two or more reactors in parallel, each subjected to the process steps, but staggered in time so constant feed and product streams would be produced.

Table 1. H_2-SER Process Steps.

1. **Sorption-Reaction Step**: The reactor is initially presaturated with a mixture of steam and H_2 at the desired reaction temperature and pressure. Steam and methane at a prescribed ratio (e.g., 6:1) are fed to the reactor and an enriched H_2 product (~90% purity) is collected as the reactor effluent. The reaction step is continued up to the point when the H_2 purity in the product decreases to a preset level. The feed is then diverted to a second identical reactor.

2. **Depressurization Step**: The reactor is countercurrently depressurized. The effluent gas can be recycled as feed to another reactor or used as fuel.

3. **Purge Step**: The reactor is countercurrently purged with a mixture of 5-10% H_2 in steam to desorb the CO_2. The desorption pressure may range between 0.2 and 1.1 atmospheres. The desorbed gas consists of CH_4, CO_2, H_2 and H_2O and is used as fuel after removing H_2O via condensation.

4. **Pressurization**: The reactor is countercurrently pressurized to the reaction pressure with the steam / H_2 mixture. At this point, the regeneration of the reactor is complete and it is ready to undergo a new cycle.

Experiments with Ni-based catalyst

Hufton et al. (1999) presented experimental results which demonstrated the concept of H_2-SER in the single-step SER#1 test unit. These experiments were not cyclic, rather they focused on the reaction step of the process. The laboratory reactor was packed with a 1:1 (wgt) mixture of CO_2 adsorbent and Ni-based catalyst and heated to 450C. After reducing the catalyst with H_2, the reactor was saturated with a mixture of 20% H_2 / 80% steam, and then fed a feed gas of 14% methane in steam. Reactor performance was evaluated by measuring the effluent gas composition and flow rate during the experiment and using these data to calculate the CH_4 conversion and amount of H_2 produced. The reactor produced 0.8 mmole of H_2 product per g of solid at an average purity of 96% H_2, 4% CH_4, and less than 50 ppm CO + CO_2. The methane conversion to H_2 product reached 82%. The conversion and product purity were substantially higher than the thermodynamic limits for a catalyst-only reactor at these same conditions (28% conversion, 53% H_2, 34% CH_4, 13% CO/CO_2).

The next major task for development of the H_2-SER technology was to demonstrate the continuous production of H_2 under completely cyclic operating conditions. These tests were carried out this year with the SER#2 test unit. A 2:1 mixture of CO_2 adsorbent / Ni-based catalyst was packed into both reactors and subjected to the process steps of Table 1. The reaction feed gas was 6:1 steam/methane (S/C) and the reaction was carried out at 450C, 50 psig. At the specific conditions of the experiments, a product gas consisting of 71-75% H_2 was produced at a methane conversion of 33-37%. The amount of H_2 produced per unit mass of solid (adsorbent and catalyst) was only ~0.15 mmole/g. Although the H_2 production was enhanced in these experiments (equilibrium H_2 mole fraction is 53% and CH_4 conversion is 28% at these conditions), it was clear that the results were not nearly as good as expected from the single-step experiments.

Further investigation of the Ni-based catalyst in the non-cyclic laboratory unit (SER#1) showed that the fully reduced nickel catalyst can remove significant quantities of CO_2 from the reaction gas in addition to the CO_2 adsorbent. Therefore, the nickel catalyst contributes to the SER effect during the reaction experiments. Although the form of CO_2 on the catalyst was not determined, it cannot be effectively removed by purging with N_2. Hydrogen is required to remove the CO_2 as CH_4. Since this is not acceptable for the H_2-SER process, efforts were directed towards identification of an alternative catalyst material.

Single-step experiments with alternative catalyst

An alternative catalyst was found and tested in the SER#1 test unit. Catalyst-only experiments clearly revealed that it did not adsorb CO_2, nor did it induce an SER effect when exposed to steam and methane. Since the material appeared promising, an extensive series of experiments, with both the single step and cyclic test units, was initiated. The rest of the experiments described in this report will deal with mixtures of CO_2 adsorbent and the alternative catalyst.

Mixtures of CO_2 adsorbent and alternative catalyst, in weight ratios of 1:2, 1:1, and 2:1, were sequentially tested in the single-step SER#1 unit. The influence of reaction temperature, pressure, and feed gas S/C ratio were evaluated, and the results are presented in Table 2. The base case experiment was conducted at 450C, 55 psig, and with a 6:1 steam/methane feed gas. Effluent gas was collected until the average H_2 composition dropped to 85%. At that point, a total of 0.56 mmoles of H_2 / g of solid had been collected (referred to as the H_2 productivity), and the effective CH_4 conversion to H_2 product (defined as moles H_2 produced / 4 / moles CH_4 fed) was 54%. Both the CH_4 conversion and H_2 productivity declined sharply when the reaction pressure was increased to 155 psig or the feed gas S/C ratio was decreased to 3:1. Conversely, the CH_4 conversion and H_2 productivity both increased significantly when the temperature was raised to 500C. Thus, one can conclude that the reaction step performance is favored by higher temperature, higher S/C ratio, and lower pressure. These are the same effects which tend to increase the conversion of the overall reforming reaction.

Table 2. Results of Single-Step Reaction Experiments with 2:1 adsorbent / alternative catalyst.

Conditions	H_2 Purity (%)	CH_4 Conversion (%)	H_2 Productivity (mmole H_2/g solid)
6:1 S/C, 55 psig, 450C	85	54	0.56
6:1 S/C, **155 psig**, 450C	85	24	0.08
3:1 S/C, 55 psig, 450C	85	20	0.05
6:1 S/C, 55 psig, **500C**	85	59	0.78

The next set of single-step reaction experiments was designed to investigate the effect of adsorbent / catalyst ratio on reaction step performance. The data in Table 3 show that the amount of 80% H_2 product is consistent between all of the experiments if the productivity is normalized by the amount of adsorbent in the reactor. This indicates that the amount of adsorbent in the reactor is largely responsible for determine how much H_2 will be generated. It will therefore be beneficial to use a high adsorbent / catalyst ratio in the SER reactors (up to the point where catalytic limitations become important).

Table 3. Results of Single-Step Reaction Experiments with 1:2, 1:1, and 2:1 adsorbent / alternative catalyst.

Reactor Mixture	H_2 Purity (%)	H_2 Productivity (mmole H_2 / g solid)	H_2 Productivity (mmole H_2 / g adsorbent)
1 ads : 2 cat	80	0.33	1.0
1 ads : 1 cat	80	0.44	0.9
2 ads : 1 cat	80	0.75	1.1

Cyclic experiments with alternative catalyst

Thirty six cyclic H_2-SER process experiments were conducted in the SER#2 test unit using a reactor packed with 2:1 adsorbent / alternative catalyst mixture. The cycle steps of Table 1 were used except H_2 was omitted from steps 3 and 4. A typical experiment was carried out at 490C with 6:1 S/C feed gas at 50 psig, followed by regeneration with steam at 5 psia. In all of the runs, the average H_2 product purity was maintained at ~88% by adjusting the reaction and purge times. The effect of reaction pressure, temperature, feed S/C ratio, and purge amount on the cyclic steady-state H_2 productivity (defined at 88% H_2 for the rest of this report) was evaluated.

In all of the cyclic experiments, more H_2 is produced from the feed methane than would be by a catalyst-alone reactor (predicted by reaction thermodynamics), and it is of higher purity. The major contaminant in the SER H_2 product is CH_4, with typically less than 0.5% CO_2 (and very often nondetectable, or less than 50 ppm) and typically non-detectable (< 50 ppm) levels of CO. For reference, a catalyst-only system would yield 67.5% H_2, 16.0% CO_2, 12,000 ppm CO, balance CH_4 for operation at 490C, 6:1 S/C, 10 psig.

The effects of reaction pressure and temperature on the normalized H_2 productivity (for ~88% average H_2 product) are illustrated in Figures 1 and 2 for 6:1 S/C feed gas. A fixed amount of purge gas was used. Decreasing the feed gas pressure and increasing the reactor temperature increases the cyclic steady-state H_2 productivity. These trends are consistent with the results obtained from single-step experiments. They are opposite the trends normally observed for conventional pressure swing adsorption (PSA) systems used for bulk separations, where generally decreasing the feed gas pressure and increasing the temperature yields lower adsorption capacity and bed productivity. The difference is believed to be due to the influence of the reforming reaction - lower pressure / higher temperature increase the amount of CO_2 formed in the equilibrium zone of the reactor, making it easier to remove a larger fraction of that CO_2 and hence drive the reforming reactions towards completion. Higher temperatures can also improve the efficiency of desorbing CO_2 from the adsorbent, which may also have a role in increasing the H_2 productivities in Figure 2.

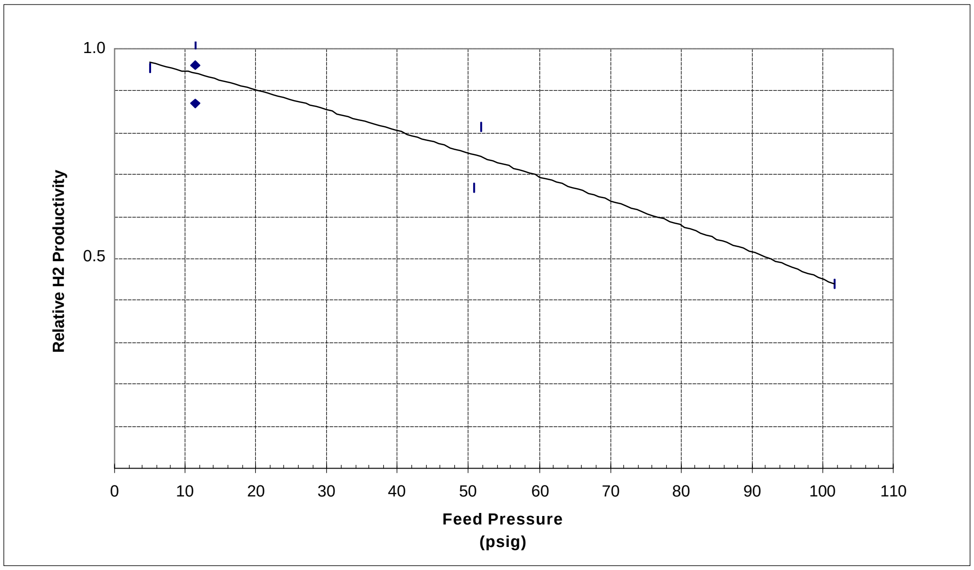

Figure 1. Effect of Feed Pressure on Cyclic H_2 Productivity for H_2 Product of 88% average Purity; 2:1 adsorbent / catalyst, 490C, 6:1 S/C feed.

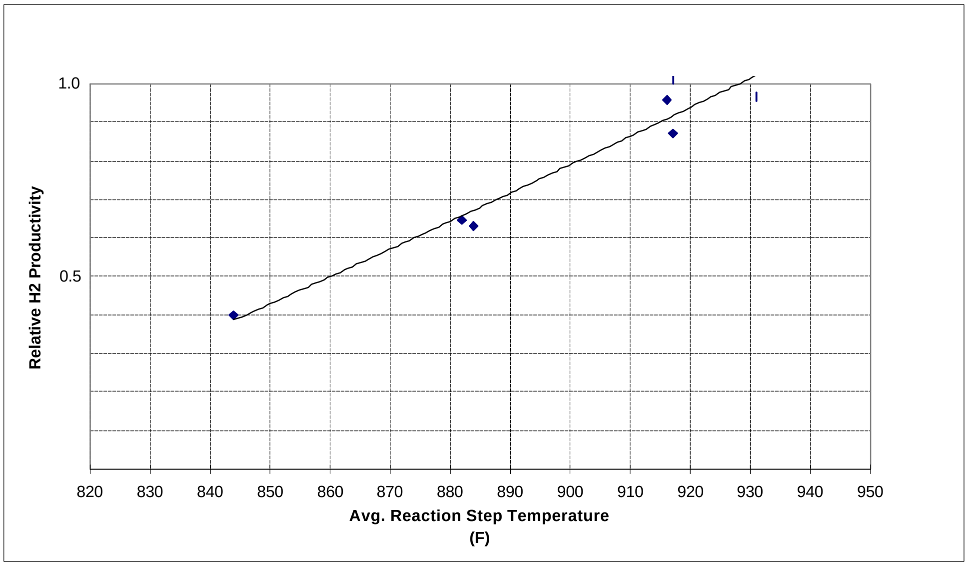

Figure 2. **Effect of Feed Temperature on Cyclic H_2 Productivity for H_2 Product of 88% average Purity; 2:1 adsorbent / catalyst, 6:1 S/C feed, 10 psig.**

Increasing the S/C ratio of the reaction step feed gas improves the H_2 productivity, as evidenced by the 4:1 and 6:1 S/C data in Figure 3 (plotted on a relative basis). This is also consistent with the results of the SER#1 single-step reaction experiments (Figure 1).

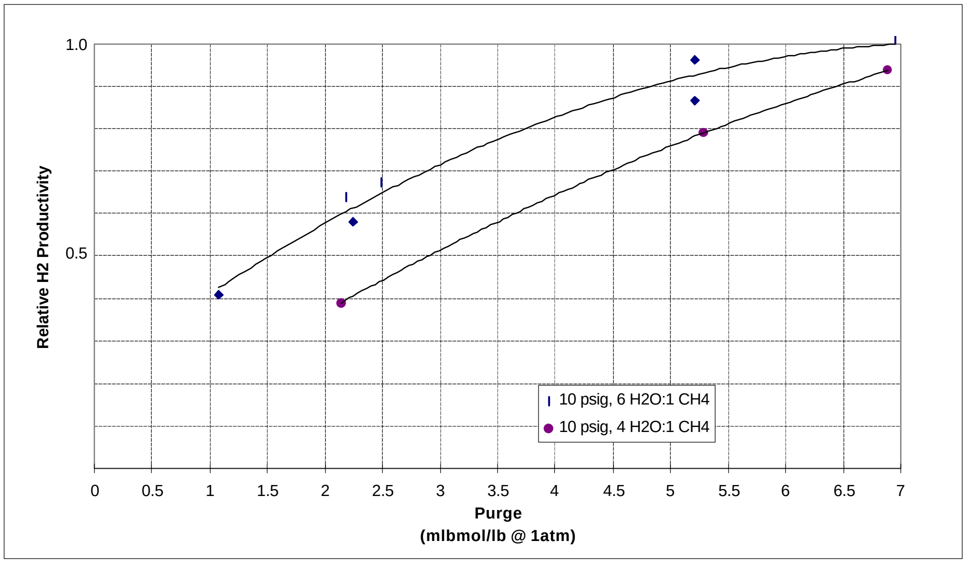

Figure 3. **Effect of Purge Amount on Cyclic H_2 Productivity for H_2 Product of 88% average Purity; 2:1 adsorbent / catalyst, 10 psig, 490C.**

Figure 3 also shows that increasing the amount of purge gas can substantially increase the H_2 productivity for a given S/C ratio. Increasing the amount of purge removes more CO_2 from the adsorbent and cleans the product-end of the reactor more thoroughly, so it is not surprising that this improves reactor performance. The benefit of increasing the purge amount declines as higher purge amounts are approached.

In summary, the above data shows that the H_2-SER process concept works under cyclic conditions to yield relatively high purity (~88%) H_2 product containing very low CO_2 and CO levels. The H_2 productivity of the SER reactor can be increased by increasing the reaction temperature, S/C feed ratio or purge amount, or by decreasing the reaction pressure. These trends are consistent with the results of single step reaction experiments carried out in the SER#1 unit.

Process Design and Economic Evaluation

Hufton et al. (1999) compared the economics of a conventional H_2 production process with first pass H_2-SER process designs and noted that product cost savings of 15-30% were possible depending on plant size and H_2 purity requirements. The SER design was based on previous single-step reaction experiments and a number of engineering assumptions. The H_2 purity, conversion, and H_2 productivity used to generate the process design were 95%, 72%, and 1.1 mmole H_2/g solid, respectively. Cyclic performance parameters were not available, and the SER#2 test unit was built primarily to test these assumptions.

Now that cyclic process data are available, it is logical to revise the old process designs with the new input parameters. Although the cyclic data show that the SER concept is working, the performance is not nearly as good as assumed in the earlier designs. Typical H_2 purity, conversion, and H_2 productivity values obtained from the SER#2 tests are 88%, ~55-65%, and ~0.2 - 0.3 mmole/g solid.

The impact of these new parameters on the SER process was determined by generating H_2-SER process designs for the production of high purity (99.5%), high pressure (200-800 psig) H_2 product. Production levels of 0.2 and 22 MM SCFD H_2 were investigated. Since high purity H_2 was desired (and therefore a PSA separation unit was needed), it was assumed that the H_2-SER reaction step was carried out at 250 psig, with a 3:1 S:C feed gas. The economics of the first-pass, revised process design were found to be noncompetitive with conventional technology.

The major difficulty in developing a cost effective H_2-SER process for high pressure, high purity applications is due to some of the inherent characteristics of the SER process. Although the H_2-SER unit can directly produce higher purity H_2 than a conventional catalyst-only reactor, it is not high enough to satisfy high purity customers (99.9+%). Thus, a PSA unit is required to purify the SER effluent gas. The PSA adds a ~15% recovery loss to the process, and also requires that the feed gas be at an elevated pressure. More importantly, the requirement for high pressure product gas requires either operation of the SER unit at high pressure (where performance is poor) or use of a relatively expensive compressor to pressurize SER effluent gas produced at low pressure. Either approach adds cost to the system. It is also possible to improve the SER performance by increasing the S/C ratio of the feed gas and increasing the amount of purge gas (steam) during regeneration. Both of these require the use of more steam, which increases the operating cost for the process (especially large plants) and decreases the thermodynamic efficiency.

Thus, the best application for SER would be one where the SER effluent gas could be used directly (i.e., ~90% H2 purity is acceptable), the product pressure can be low (~10 psig), and steam costs are not necessarily a major cost item (smaller scale production units). These characteristics are consistent with fuel cell applications. In this case, the H_2 product gas is used at relatively low pressure, impure H_2 (50-90%) is acceptable as long as the CO level is kept low (<10 ppm), and the applications are typically small capacity (~0.1-0.2 MM SCFD)). Our future development efforts will be focused on this application.

CO_2 Adsorbent Development

Long range supply of the promoted K_2CO_3/hydrotalcite CO_2 adsorbent relies on the manufacture of the activated adsorbent by an external vendor. We have been working with two separate vendors of the HTC support to help develop an approach for producing an acceptable adsorbent. We interacted closely with our primary vendor to help solve a number of problems associated with extruding the promoted adsorbent. Eventually they were able to produce 160 lbs of the promoted extrudate using a 4" pilot extruder. This material showed a lower CO_2 capacity than the lab-generated material, although the steam stability, crush strength, and aging profile were acceptable. The vendor is not concerned with scaling the production up to a 6" commercial extruder, which would be capable of supplying projected commercial volumes.

We have also engaged a second vendor in case the first fails to deliver [commercially or technically]. This vendor produced formed adsorbent in the lab in both extrudate and tablet forms. The lab tablets have similar crush strength and steam stability as benchmark extrudates and adequate CO_2 adsorption capacity. The pilot sample was not as successful, however, and was deficient in CO_2 capacity & crush strength after steaming. The second vendor now believes it was due to a change in the recipe where the hydrotalcite tablets were exposed to K_2CO_3 for an extended period of time, affecting the products more than expected. Two new samples have been recently received and are being evaluated in our lab (one of which has > 2X the targeted CO_2 capacity).

A critical requirement for the CO_2 adsorbent is that it remain stable over many adsorption-desorption cycles. Adsorbent stability was tested by repetitively exposing the adsorbent in the CLU to 34:1 steam:CO_2 at 250 psig for 20 mins followed by 5 mins of N_2 purge at atmospheric pressure. The testing was done at 450C. The adsorbent was periodically removed from the test apparatus and the equilibrium CO_2 capacity was determined at 450C and 0.7 atm CO2. The results, illustrated in Figure 4, show that the adsorbent was indeed stable, and maintained an equilibrium CO_2 capacity of 0.3-0.45 mmol/g over nearly 6000 cycles.

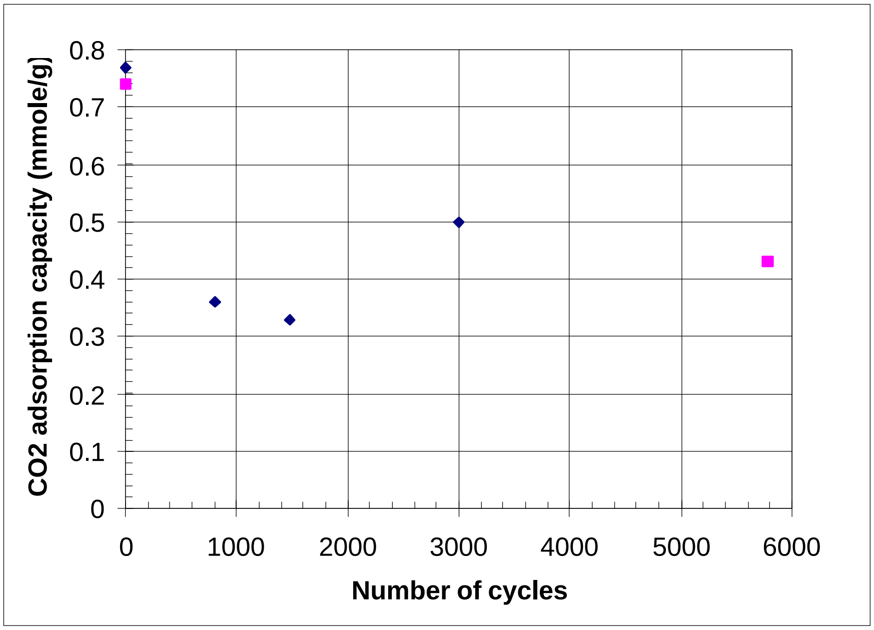

Figure 4. CO_2 Adsorption Capacity Measured after Repetitive Cycling in Steam.

Future Work

Future efforts will be directed towards the development of an H_2-SER process to satisfy the requirements of fuel cell applications. Process designs will be generated based on the cyclic process data from SER#$_2$ and evaluated against conventional technologies.

We are also planning some experiments to gain more fundamental knowledge regarding the interplay of adsorption and reaction in the SER process. We would like to determine the root cause of the immediate appearance of methane in the H_2 product gas (even though reaction kinetics and mass transfer kinetics have been determined to be very fast). Greater insight may lead to modifications which could potentially improve the SER process performance.

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