DOE/GO/10059--71

**Sorption Enhanced Reaction Process for Production of Hydrogen
DOE-Air Products Cooperative Agreement
Instrument # DE-FC36-95G010059**

PHASE I FINAL REPORT

July 1997

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Summary

Phase I of the Air Products/DOE Sorption Enhanced Reaction Project is complete, and the technical accomplishments are summarized in this report. The work was carried out to develop a more efficient process, termed the sorption enhanced reaction process (H_2 -SERP), for producing hydrogen via steam methane reforming.

An effective CO_2 adsorbent consisting of a mixed metal oxide promoted with potassium carbonate (K_2CO_3/HTC) has been developed which satisfies initial capacity, stability, and kinetic goals. In addition, the adsorbent is compatible with the H_2 -SER catalyst, and the carbonate phase is not leachable in a steam environment. Production of this material has been scaled up to the kg range. Future efforts will be focused on developing second-generation materials (new classes or modifications of K_2CO_3/HTC) exhibiting improved capacity, kinetics, or isotherm shape..

The H_2 -SERP concept has been experimentally demonstrated. It is clear that including a CO_2 adsorbent along with the SMR catalyst enhances the methane conversion to products and improves the hydrogen purity of the effluent gas. The best performance thus far has been obtained for a 1:3 adsorbent (K_2CO_3/HTC)/prereformer catalyst system operated at $450^\circ C$, 55 psig, and with a feed consisting of 11% CH_4 / 89% H_2O . For a 95% H_2 product, the methane conversion for the SERP system is 68%. The conversion and H_2 purity of a conventional catalyst-only system operated at these conditions are only 34% and 57%, respectively, based on thermodynamic calculations. Increasing the reactor temperature and steam/methane ratio improves the performance of the system. Future experiments are designed to extend the reaction step pressure range to 250 psig and to make efforts to quantify the desorption step. A second cyclic experimental unit based on two-bed operation is under design and will be used to answer questions that cannot be resolved with the current unit.

A process simulator has been developed and will be applied to the H_2 -SERP system. Economic analysis of a preliminary H_2 -SERP design suggests that it can produce H_2 at a significantly lower cost than conventional reforming at a production rate of 2.5 MM SCFD.

1. Introduction

Hydrogen is one of the most suitable energy sources from both technological and environmental perspectives for the next century, especially in the context of a sustainable global energy economy. In addition to providing a highly flexible way of storing and using electric energy, hydrogen makes it possible to diversify energy supply sources used in the transportation sector and to reduce the effects of pollution linked to the use of the fossil fuels. However, hydrogen is not a primary energy form and must be manufactured in processes requiring consumption of both primary energy and capital resources. The most common industrial process to produce high-purity (99.99+ mol %) hydrogen is to reform natural gas by a catalytic reaction with steam at a high temperature. In 1991, for example, conventional steam-methane reforming (SMR) contributed to approximately 2.4 billion standard cubic feet per day (SCFD) of hydrogen production in the United States, most of which was produced for the chemical and petroleum refining industry markets. By 1998, the growth of SMR-produced hydrogen in the U.S. is expected to reach 3.4 billion SCFD, with the increased demand attributed to hydrogen's use in reformulated gasolines required by the Clean Air Act. This growth trend is expected to increase well into the next century, when commercialization of advanced hydrogen use technologies, such as fuel cells, will create new markets for hydrogen in the utility, commercial, residential, transportation, and industrial sectors. Consequently, the development of advanced hydrogen production technologies, based largely upon natural gas as the source of energy and the primary raw material, will ensure that hydrogen is economically competitive and will serve as the transition to an eventual renewable-based hydrogen production infrastructure.

2. Background

The most common industrial process to produce high-purity (99.99+ mol %) hydrogen is to reform methane by reaction with steam followed by purification of hydrogen by pressure swing adsorption (PSA). The SMR reaction is typically carried out at a temperature of 800-1000°C and at a gas pressure of 200-300 psig over a nickel-based catalyst. The two key simultaneous reactions for this process are:

(a)	$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$	Reformation
(b)	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	Water gas shift

A typical SMR feed consists of a gaseous mixture of CH_4 and H_2O in the molar ratio of 1:3 at a temperature of 850°C and at a pressure of 250 psig. The reformer effluent would be 4.8% CH_4 , 12.0% CO , 9.4% CO_2 and 73.7% H_2 (mol %) on a dry basis. This effluent is then fed to a shift reactor containing an iron- or copper-based catalyst, and operating at $250\text{--}400^\circ\text{C}$, where reaction (b) predominates. The effluent from the shift reactor may have a composition of 3.0% CO , 16.7% CO_2 , 4.5% CH_4 and 75.8% H_2 (mol %) on a dry basis. The overall conversion of feed CH_4 , for this example, is 81.5%. The shift reactor effluent is cooled down to $30\text{--}40^\circ\text{C}$ in order to remove most of the water from the gas stream and is fed to a Pressure Swing Adsorber (PSA). This unit operates at the reformer exit pressure (typically 200-300 psig) and produces a high-purity gaseous H_2 product (99.99+ mol %) by selective adsorption of H_2O , CO_2 , CO and CH_4 from H_2 . Typical H_2 recovery from the PSA process is 75-85%. The PSA waste gas containing carbon oxides, methane, and hydrogen is used as a fuel for the SMR reactor.

Both the reformation (a) and the water gas shift [high (HTS) and low (LTS) temperature] (b) reactions are equilibrium-controlled reactions. The equilibrium conversion of CH_4 to CO and H_2 by reaction (a) is favored at a higher temperature, while the equilibrium conversion of CO to CO_2 and H_2 by reaction (b) is favored at a lower temperature. On the other hand, the kinetics of both reactions are faster at a higher temperature. The equilibrium constants (K_a and K_b) of reactions (a) and (b) at 850°C are, respectively, $514 (\text{atmosphere})^2$ and 1. The equilibrium constants are functions of temperature only.

Thus, at a temperature of 850°C, and assuming fugacity coefficients are unity, one may write:

$$\frac{(P^2)(Y_{CO})(Y_{H_2})^3}{(Y_{CH_4})(Y_{H_2O})} = 514 = K_a \quad \text{Reaction (a)} \quad (1)$$

$$\frac{(Y_{CO_2})(Y_{H_2})}{(Y_{CO})(Y_{H_2O})} = 1 = K_b \quad \text{Reaction (b)} \quad (2)$$

The above equations describe the relationship between the equilibrium gas phase mole fractions (Y_i) of component i in the reactor at a gas phase pressure of P (atmosphere).

The SMR reactor is operated at a relatively high temperature (800-1000°C) in order to drive reaction (a) more to the right (higher equilibrium conversion of CH_4 to CO and H_2), along with some conversion of CO to CO_2 and H_2 at that temperature. The subsequent shift reactor is run at a relatively lower temperature of 250-400°C, where the equilibrium constants for reactions (a) and (b) are, respectively, 6×10^{-5} (atmospheres)² and 12.3. Additionally, the catalyst employed in the shift reactors is kinetically inactive for reaction (a). Thus, reaction (b) dominates in that reactor, with negligible formation or conversion of CH_4 .

3. Objective

The goal of this work is to develop an even more efficient process for reforming steam and methane to hydrogen product than the conventional SMR process. The application of Sorption Enhanced Reaction (SER) technology to SMR has the potential to markedly reduce the cost of hydrogen through lower capital and energy requirements. The development of a more cost-effective route to hydrogen production based on natural gas as the primary energy source will accelerate the transition to a more hydrogen-based economy in the future.

4. SER Concept Description

The equilibrium gas phase compositions (mole fractions) of H₂ and CO in the SMR reactor can be expressed by combining the equilibrium constraints for reactions (a) and (b) as:

$$(Y_{H_2}) = \left[\frac{K_a \cdot K_b (Y_{CH_4})}{(Y_{CO_2})} \right]^{0.25} \left[\frac{Y_{H_2O}}{P} \right]^{0.50} \quad (3)$$

$$(Y_{CO}) = \left[(Y_{CO_2}) \right]^{0.75} \left[\frac{K_a (Y_{CH_4})}{(K_b)^3} \right]^{0.25} \left[\frac{1}{P Y_{H_2O}} \right]^{0.50} \quad (4)$$

The above two relationships clearly indicate that the composition of H₂ in the reaction product increases, and the composition of CO in the reaction product decreases as the composition of CO₂ in the reaction product decreases (for a given set of compositions for CH₄ and H₂O at a fixed reaction pressure and temperature). This is simply a mathematical consequence of LeChatelier's principle, which states that reaction (b), and indirectly reaction (a), are both pushed to products as CO₂ is removed from the system. The concept of SER proposes that the CO₂ concentration in the reaction zone be reduced by selectively removing CO₂ from the gas phase via sorption on a suitable sorbent (physisorption, chemisorption, bulk absorption or combinations). This will enhance the concentration of H₂ and reduce the concentration of CO in the reactor product gas. Regeneration steps are then required to reactivate the sorbent by desorbing CO₂.

The H₂-SER concept allows the SMR reactions to be carried out at a significantly lower temperature while achieving substantial conversion of CH₄ to H₂. This level of conversion is reached by driving reactions (a) and (b) more to the right (due to simultaneous removal of CO₂ from the reaction zone) at a lower temperature, even though K_a is unfavorable at a lower temperature. This advantage, in conjunction with the possibility of significantly reducing CO

concentration in the reaction products, may offer several major operational and cost benefits over conventional SMR-HTS/LTS-PSA systems for H₂ production. They include:

- Significant cost advantage by replacing high temperature, expensive alloyed steel construction of the SMR reactor with less expensive stainless steel construction.
- Major simplification and improvement of the PSA purification of H₂ due to extensive reduction in the CO and CO₂ content of the SMR reactor effluent.
- Potential elimination of the shift reactor(s).
- Elimination or significant reduction of carbon formation in the reactor.
- Reduction of sensible heat losses and decrease in the size of heat exchange equipment.

A comparison of the operating characteristics of a conventional SMR process and the proposed H₂-SER process is shown in Table 1.

4.1. Description of Proposed H₂-SER Process

In the proposed H₂-SER process the reactants, steam and methane, are fed at 300-500°C and 50-250 psig into a reactor containing an admixture of reforming catalyst and an adsorbent for removing carbon dioxide. A reactor effluent consisting of essentially pure hydrogen (98+%) is produced during this step. Once the adsorbent is saturated with CO₂, it is regenerated in situ via the principles of pressure swing adsorption. The process is therefore cyclic, and each reactor must undergo repetitive reaction / regeneration steps. A continuous hydrogen-rich product can be obtained from the system if two or more beds are utilized. As one bed is reacting, the other(s) are regenerating.

The steps for the direct production of essentially pure H_2 by the cyclic H_2 -SERP are shown in Figure 1 and are described below:

1. *sorption-reaction step*: The reactor is initially presaturated with a portion of the product H_2 at the desired reaction temperature and pressure. Steam and methane at a prescribed ratio (e.g., 2:1) are fed to the reactor, and an essentially pure H_2 product (>98% 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 weakly adsorbing gas such as methane 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 either separated for recycle of the CH_4 purge gas or used as fuel.
4. *product purge step*: The weakly adsorbing purge gas (CH_4) is countercurrently displaced from the reactor with product H_2 . The displaced CH_4 is recycled as purge gas or used as fuel.
5. *product pressurization*: The reactor is countercurrently pressurized to the reaction pressure with pure H_2 . At this point, regeneration of the reactor is complete and it is ready to undergo a new cycle.

Steps 4 and 5 of the SERP concept, when the reactor is purged and pressurized to the reaction pressure with hydrogen product, is a critical step of the process. If any gas other than product gas is used, then the effluent stream will not consist of relatively high-purity hydrogen during the next reaction step. The use of hydrogen is counter-intuitive, though, since LeChatelier's

principle would suggest that its presence will oppose reaction (a). The presence of the CO₂ adsorbent and the inherent operation of a fixed bed yield the desirable effect of enhanced methane conversion and high product purity.

4.2. Batch Calculations

An initial estimate of the benefits of removing CO₂ from the SMR reaction zone can be generated with thermodynamic calculations for a batch system. The simultaneous reactions (a) and (b) described by Eqns 1 and 2 are considered at 450°C, 4.4 atm and an initial steam-methane molar ratio of 4:1. With only catalyst, a methane conversion (moles of CH₄ reacted per mole of CH₄ present at the start of the reaction) of only 21.1% can be achieved at these conditions. The final reaction product composition is 42.9% CH₄, 0.35% CO, 11.1% CO₂ and 45.6% H₂ on a dry basis.

On the other hand, when the same reactions are carried out in the presence of a sorbent that selectively removes CO₂ from the reaction zone (99.99% removal), the methane conversion increases by a factor of four to 83.4%. The reaction product composition in this case is 4.7% CH₄, 0.0005% CO, 0.0024% CO₂ and 95.3% H₂ on a dry basis. This demonstrates the remarkable increase in CH₄ conversion and H₂ purity that can be achieved with the SER concept.

Similar, if not better, conversion and hydrogen purity could be obtained with a continuous system by using an appropriately designed process scheme with a tubular reactor.

5. Description of Previous Work

The concepts based on LeChatelier's principle that (a) the conversion of reactants to products, and (b) the rate of forward reaction in an equilibrium-limited reaction can be increased by selectively removing some of the reaction products from the reaction zone are very well known [Gluud et al., 1931]. Numerous applications of this concept using fixed-bed, continuous countercurrent moving bed, and simulated countercurrent moving bed chromatographic reactors

have been published. The detailed review of the literature is given elsewhere [Carvill et al., 1996].

The process concepts combining chemical reaction and adsorptive separation of reaction products in a single unit operation with sorbent regeneration using pressure swing adsorption are generally called Periodic Separating Reactors [Vaporciyan and Kadlec, 1987, 1989] or Pressure Swing Reactors [Lee and Kadlec, 1989; Kirkby and Morgan, 1994]. Table 2 lists some of the key experimental studies reported in the literature under the general acronym of PSR.

Two investigations especially relevant to this program are described below:

(i) Han and Harrison [1994] experimentally demonstrated that high conversion of carbon monoxide to hydrogen (higher than that dictated by thermodynamic equilibrium) could be achieved in the absence of a catalyst by the water gas shift reaction $[\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2]$ when one of the reaction products (CO_2) was removed from the reaction zone by its reaction with calcium oxide $[\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3]$. They used dolomite (~55% CaO + 45% MgO) as the sorbent at a reaction temperature of 550°C and at a total gas pressure of 15 atmospheres. No process scheme for regeneration of dolomite was disclosed.

(ii) Brun-Tsekhovoi et al. [1986] used a specially treated form of dolomite containing active CaO and chemically inert MgO as sorbent in a continuous fluidized-bed reactor containing microspheres of nickel on alumina catalyst. Freshly regenerated particles of the sorbent were fed to the fluidized bed reactor in a direction countercurrent to reactant gas flow. Large sorbent particles were used so that they could travel under gravity through the fluidized catalyst particles towards the feed gas end of the bed. The size and density differences of the catalyst and the sorbent materials allowed complete separation between them at the gas inlet end. The sorbent particles were pneumatically carried to a thermal regenerator for desorption of CO_2 . A very significant enhancement of CH_4 conversion to H_2 (compared to that achieved by catalyst alone) at pressure levels of 10–100 atmospheres and at a reaction temperature of 627°C was reported. The product gas leaving the fluidized bed reactor contained 92–96% H_2 . A dust separator was

required to clean the H_2 product gas. The proposed process scheme also included a gas turbine to recover power from the hot effluent gas exiting the sorbent regenerator. The turbine generated power to drive the pneumatic compressor for transporting the exhausted sorbent to the regenerator at the reaction pressure and temperature.

The above two studies are important because they show the use of metal oxides as sorbents for the application of the sorption enhanced reaction (SER) principle to (a) steam-methane reforming (SMR) and (b) forward water-gas shift reaction. The emphasis of the present work is very different. It carries out simultaneous reaction-separation in a single unit operation in order to obtain high conversion of CH_4 to H_2 at a much lower temperature while producing high-purity H_2 at reaction pressure. This allows the use of stainless steel for reactor construction and eliminates or substantially reduces downstream H_2 purification requirements, both of which result in lower H_2 production costs.

6. Objectives of Phase I of Air Products/DOE H_2 -SER Project

Under the Cooperative Agreement with the DOE, Air Products has agreed to perform a 3-phase, 60-month technology development program consisting of experimental, engineering, and process development activities to establish commercial justification for a full-scale demonstration of an advanced SMR process based upon the concept of SER. The three phases of the program are as follows:

Phase I:	Concept Feasibility
Phase II:	Engineering Development
Phase III:	PDU Demonstration

Phase I efforts will be conducted over the first 24 months of the project and will focus on developing a suitable practical chemisorbent for CO_2 and on demonstrating the technical feasibility of the H_2 -SER process concept for SMR. A detailed Statement of Work corresponding to Phase I, Concept Feasibility, is presented below.

Objective : To demonstrate the feasibility of performing Steam Methane Reforming at a low temperature (300-600°C) with a suitable metal oxide chemisorbent for production of hydrogen and to develop base design data for engineering development and economic evaluation.

TASK I.1 Chemisorbent Selection and Preparation

- I.1.1 Evaluate available candidates for selective CO₂ chemisorption and select material for SMR.
- I.1.2 Produce a large surface area (>500 m²/g) pelletized sample of the selected chemisorbent material.
- I.1.3 Develop an activation/regeneration procedure for the supported chemisorbent.

TASK I.2 Demonstrate and Develop Process for SER-SMR

- I.2.1 Modify Air Products' lab apparatus for handling steam to perform steam-methane reforming reactions.
- I.2.2 Study reaction-chemisorption in a continuous reactor and evaluate effect of process variables on conversion of methane to hydrogen.
- I.2.3 Evaluate each step of the SER process separately (i.e., activation, reaction, purge, and regeneration) to identify preferred operating conditions.
- I.2.4 Test SER-SMR cyclic operation in a single reactor to demonstrate process viability.

TASK I.3 Economic and Engineering Analysis

Initiate first-pass economic and engineering evaluation.

TASK I.4 Reporting and Management

All activities associated with managing the project, reports, review meetings, and technical publications will be performed under this task, and the corresponding tasks in Phases II and III. All status, milestone schedule, and cost management reports will be submitted to DOE in accordance with the Cooperative Agreement.

7. Description of Phase I Work

For clarity, the description of the work will be presented in three separate sections corresponding to Tasks I.1-3 above.

7.1. TASK I.1 Chemisorbent Selection and Preparation

7.1.1. Sorbent Requirements

The CO₂ sorbents need to meet three critical property requirements in order to be used in the H₂ SER process: (1) minimal stable working capacity of 0.30 mmole CO₂/g under process conditions (i.e., 10 atmospheres of steam at 350-450°C); (2) adequate stability under hydrothermal conditions; and (3) acceptable sorption kinetics. In addition to these property requirements, the adsorbents need to be economically viable and scaleable to commercial quantities.

7.1.2. Thermodynamic Calculations

A variety of thermodynamic calculations were carried out over the course of this work. Calculations were done to estimate the equilibrium properties of the SMR reaction. In other calculations, the thermodynamic properties of metal oxide/metal carbonate systems were screened and used as an experimental guide. All calculations were done using HSC Chemistry for Windows by Outokumpu Research. Examples of these calculations are shown below:

Operating Environment. Thermodynamic calculations were carried out in order to estimate the equilibrium concentrations of reactants and products present within the reaction zone, assuming a 2:1 H₂O to CH₄ feed ratio and a total pressure of 18 atm (250 psig). Given these conditions, the equilibrium conversion of methane at 350-400°C is 2.95-4.94%. The equilibrium H₂O/CO₂ ratio over the temperature range of 300-600°C is shown in Figure 2. These data suggest that in order to drive the conversion of the SMR reaction, the adsorbent must be able to scavenge CO₂ from a gaseous environment containing a $\approx$ 50-fold molar excess of H₂O to CO₂ at 350-400°C.

Adsorbent Thermochemistry. Before laboratory work was begun, thermodynamic calculations were carried out for a variety of metal oxide/carbonate/hydroxide systems in order to develop a basic understanding of which systems had the thermodynamic potential to reversibly sorb CO₂ under the operating conditions of interest. This approach is better suited for the evaluation of bulk or stoichiometric reactions. Its utility is limited for the evaluation of surface phenomena such as physi-sorption or surface chemi-sorption. Also, this approach gives no information about the kinetics involved in these reactions. Recognizing these limitations, a number of metal oxide systems were evaluated, with particular emphasis given to the following general reactions:

These thermodynamic studies focused on identifying metal oxides for which $K_{eq}(\text{rxn iii.}) \cong 1$ and $K_{eq}(\text{rxn iv.}) \ll 1$ in the 350-400°C temperature range. These calculations were valuable in identifying materials and classes of materials as potential CO₂ adsorbents.

7.1.3. Experimental Testing Equipment

Potential CO₂ adsorbents were subjected to a battery of screening tests, using equipment such as the thermogravimetric analyzer (TGA), the Binary Desorption Unit (BDU) and the Hydrothermal Stability Testing Unit (HSTU). The TGA used for these analyses was a TA-2950 manufactured by TA Instruments. The BDU and HSTU were designed and built in-house specifically for this program. Descriptions of the screening tests for these three pieces of equipment are provided below.

7.1.3.1. Thermogravimetric Analysis (TGA)

The TA 2950 TGA can evaluate 25-500-mg samples in the temperature range of ambient to 1000°C under atmospheric pressures of dry or humid CO₂, N₂ or He. The TGA was equipped with a manufacturer-supplied "gas switching accessory" and an "auto-sampler". The gas switching accessory allowed samples to be alternatively exposed to CO₂ and N₂, or other gases,

in an unattended mode. The auto-sampler made it possible to run as many as 16 samples in a consecutive manner, with no operator intervention required between runs. The TGA was modified in-house to enable the feed gases to be diverted through a water bubbler tube if desired, in order to saturate the feed stream with room-temperature water vapor for testing purposes.

Capacity under Dry Gas Conditions. The first screening criterion of all potential adsorbents was the evaluation of their capacity under dry CO₂/N₂ cycling conditions. The references in this report to "capacity" or "reversible capacity" are a quantification of the amount of CO₂ taken up during the second exposure to CO₂ of a 2-3 cycle CO₂/N₂ test at a given temperature. Typically, the sample is activated at or near the testing temperature for 120 minutes, after which it is re-equilibrated to the testing temperature (if different than the activation temperature), then exposed alternately to 60 minutes of 500 Torr CO₂/N₂ at 140 sccm, and 60 minutes of pure N₂ at 100 sccm for a total of 2-3 cycles. Depending on the nature of the adsorbent and its preparation and activation conditions, the 2nd uptake can be substantially different from the 1st uptake. However, there is usually only a minimal difference between the 2nd and 3rd uptake or even the 2nd and 10th uptake. For this reason, the 2nd uptake is quoted in this report as the "reversible" capacity, and is used for comparing different materials.

Capacity under Low Humidity Conditions. A standard screening test was developed in order to gauge the effect of low humidity levels on the CO₂ capacity of selected adsorbents. To accomplish this, the TGA was equipped with a water bubbler in order to saturate the feed stream with water vapor. The standard screening test consisted of exposing an activated adsorbent to three sequential sets of cycling conditions as follows: (1) 0.7 atm CO₂/1.0 atm N₂, (2) 20 Torr H₂O/1.0 atm N₂ and (3) 0.7 atm CO₂-20 Torr H₂O/1.0 atm N₂. Each set of conditions typically consisted of five identical cycles. The final capacity under the 1st, 2nd and 3rd set of conditions was taken as CO₂ capacity under dry conditions, the water capacity, and the CO₂ capacity under humid conditions. The effect of 20 Torr of water on CO₂ capacity is gauged by comparing the capacity determined under the 1st and 3rd series of measurements. The screening method proved to be a good litmus test for sorbent viability. Surprisingly, measurements under low-humidity

conditions were a good qualitative indicator of how the adsorbent behaved under high-humidity steam conditions, as described in the next section.

7.1.3.2. Binary Desorption Unit (BDU)

Characterization of Binary Adsorptive Properties. The CO₂/H₂O Binary Desorption Unit (BDU) was used as a screening tool to evaluate the binary adsorptive behavior of CO₂ and H₂O on various experimental adsorbents at elevated temperatures (300-500°C) and pressures (<140 psig). A simplified schematic diagram of this unit is shown in Figure 3. This test was designed to evaluate the performance of experimental adsorbents under simulated process conditions of 10 atmospheres of steam, and 0.1-1.5 atm of CO₂ at 300-500°C. This test required 10-15 g of formed adsorbent. Therefore, only selected materials were evaluated by the BDU, which met previous performance criteria as measured by the TGA.

The four general steps for the operation of the BDU were: (1) activation, (2) adsorption, (3) bypass purge and (4) desorption. Initially the system was brought to the testing temperature and purged with N₂ in order to activate the sample and establish an inert atmosphere. Once this was achieved, the adsorbent was subjected to a pre-determined gaseous mixture of CO₂ and H₂O under constant conditions until equilibrium was established as indicated by RGA analysis of the effluent gas stream. In the 3rd step, N₂ was passed through the sample bypass line to remove physi-sorbed CO₂ and water between the sample tube and the analytical train. In the final step, CO₂ and water were desorbed from the sample with a N₂ purge. The purge was typically continued overnight (16 hours), during which data points were collected every 6 seconds.

The adsorption and bypass purge steps were carried out under a total pressure of 10 atm. The activation and desorption steps were done at ambient pressure. The total flow rate during the activation, bypass purge, and desorption steps was 300 sccm; 700 sccm was used for the adsorption step. The total amounts of desorbed CO₂ and H₂O were quantitated for each run during the desorption step. The amount of gas desorbed after 240 minutes of purge was the value quoted in this report. All measurements were corrected for void volume.

Catalyst-Adsorbent Compatibility Tests. The BDU was also used to conduct catalyst-adsorbent compatibility tests. For these tests the sample was reduced with a nonflammable H_2/N_2 mixture for 12-24 hours at 350-400°C. The sample consisted of either the adsorbent alone, the catalyst alone, or a 50/50 (by weight) mixture of adsorbent and catalyst. In a second step, the sample was aged with a gaseous mixture of steam and CO_2 for 72 hours at a total pressure of 10 atmospheres. As a final step, zero air was passed over the sample for 6-8 hours, prior to exposing it to ambient conditions.

Materials were monitored for their chemical and physical stability, as well as for their performance properties, in order to gauge the extent of degradation. The chemical and physical properties of the adsorbent and catalyst, such as composition, surface area and structure, were individually analyzed before and after testing.

7.1.3.3. Hydrothermal Stability Testing Unit (HSTU)

The HSTU was used to evaluate the stability of adsorbents at high temperature under a static environment comprising CO_2 (1 atm) and H_2O vapor (10-15 atm). The physical and performance properties of the adsorbents were analyzed before and after testing to evaluate their hydrothermal stability.

The adsorbents to be tested were placed in an alumina or quartz vessel, then into the Parr pressure bomb along with a pre-determined quantity of distilled water. The bomb was closed and CO_2 was expanded into the vessel to a given total pressure. The bomb was heated to the testing temperature (300-500°C) and held isothermally for the duration of the test (1-30 days). Once the test was completed, the vessel was cooled and excess pressure was vented before the container was re-opened to remove the adsorbent for analysis.

7.1.3.4. Synthesis

The furnace was used to prepare many single-component metal oxides and mixed metal oxides, either as free powders or deposited on inert supports. Mixed metal oxides were typically prepared from decomposition of their metal hydroxide, acetate, oxalate or carbonate precursors.

The metal oxides or metal carbonates deposited on supports usually involved the decomposition of deposited acetate precursors. Solid-solid reactions or solid-state dispersion reactions were carried out by heating a well-ground mixture of the solids at high temperature (400-800°C) for 6-24 hours.

A large number of small-scale (<100 mg) screening reactions were carried out in TGA ceramic pans (volume = 500 μ L). This typically involved solid-solid decomposition reactions, such as mixed metal acetates, or decomposition of metal nitrates deposited on alumina or silica. These "TGA-pan reactions" were particularly convenient when a series of screening experiments was required to evaluate the effect of concentration, reactant ratio, decomposition temperature, etc. Also, the TGA allowed easy atmospheric control, which was useful for the preparation of several metal oxycarbonate species requiring synthesis/decomposition under high-temperature CO₂ atmospheric conditions.

7.1.3.5. Impregnation of Porous Supports

A large number of the adsorbents were prepared by the impregnation of porous pre-formed supports, such as alumina beads, silica beads or granules, zeolitic pellets, Celite® beads or hydrotalcite beads or pellets. With the exception of some of the zeolitic materials, all of the impregnation reactions were conducted in open air bench-top conditions. Some of the more hydrophilic supports, such as the high-surface-area aluminas, silicas and zeolites, were activated at 200-500°C and stored under dry, inert conditions prior to impregnation. The general impregnation procedure, conducted on sample sizes ranging from 3 to 1000 g, consisted of adding a solution to the porous support to the point of incipient wetness. The wet beads or pellets were typically allowed to stand for 1 hour, and the sample was agitated occasionally to ensure that all of the gas within the pores of the support was displaced by solution. Any excess solution was decanted, and the beads/pellets were oven dried at 120°C overnight. At this point, many of the supported materials were activated in the reaction furnace at 300-500°C, either to remove waters of hydration, or to decompose the deposited precursor, such as in the case of impregnation reactions involving metal organic salts.

7.1.4. Results

7.1.4.1. Classes of Adsorbents

A large number of potential CO₂ adsorbents, comprising different families of materials, were evaluated over the course of this work. The materials screened as adsorbents included metal oxides, mixed metal oxides, oxide clays such as sepiolite, metal oxides supported on silicas, aluminas and a variety of zeolites. Several of the metal oxides were also promoted with alkali metal carbonate solution to further enhance their CO₂ adsorptive properties.

One of the most promising materials identified during the Phase I research was an adsorbent prepared from the thermal decomposition of a potassium carbonate-promoted hydrotalcite precursor, referred to as K₂CO₃/HTC. This material was determined to meet our preliminary requirements of satisfactory capacity, hydrothermal stability, and sorption kinetics. Further testing also established that this adsorbent was compatible with the commercial SMR catalyst, with regard to chemical stability and performance properties. These tests and results are described below.

7.1.4.2. Hydrotalcites

Background. Layered Double Hydroxides (LDHs) constitute a large class of layered inorganic compounds of the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n} \cdot zH_2O$, where M^{II} is a divalent cation (e.g., Mg⁺², Mn⁺², Fe⁺², Co⁺², Ni⁺², Cu⁺², Zn⁺² or Ca⁺²); M^{III} is a trivalent cation (e.g., Al⁺³, Cr⁺³, Mn⁺³, Fe⁺³, Co⁺³, Ni⁺³ or La⁺³); and Aⁿ⁻ is a gallery anion (CO₃⁻², OH⁻, Cl⁻, SO₄⁻²). The LDH structure consists of Mg(OH)₂-like sheets, separated by galleries of hydrated Aⁿ⁻ ions. When heated LDHs undergo dehydration (<250°C) and are known to give rise to materials with very high *internal* surface areas (>500 m²/g), depending on the extent of dehydration and the nature of the pillaring anion, Aⁿ⁻. LDHs have the potential to act as high-surface-area solid bases.

Thermal Stability. As a class, LDH materials have limited thermal stability, which brings into question their viability as high-temperature CO₂ adsorbents. The onset of thermal decomposition generally occurs at ≈ 200 -300°C. LDHs undergo several weight losses upon heating: the first weight loss is due to the reversible loss of interlayer H₂O molecules. At slightly higher temperature decomposition occurs, which is attributed to the conversion of the metal hydroxide layers to their constituent mixed metal oxides:

Hydrotalcite (HTC) materials, which are Mg-Al based layered double hydroxides, are known to give rise to particularly active mixed metal oxides upon thermal decomposition at 300-500°C. It is precisely for this reason that HTCs are often studied as catalyst precursor materials. During the course of the present investigation, it became apparent that these properties, in conjunction with their basic oxide nature, made them attractive precursors for high-temperature CO₂ adsorbents.

Powder Samples. A powdered sample of Sorb Plus® was procured from Alcoa for adsorption studies. Sorb Plus® is a hydrotalcite-containing material with an overall Mg/Al ratio of 3.4-3.6, slightly more Mg-rich than the mineral hydrotalcite [Mg₆Al₂(OH)₁₆][CO₃]•4H₂O, indicating the presence of MgO and/or MgCO₃. The Sorb Plus® was tested as-received and after treatment with 0.5, 2.0 and 5.0 M K₂CO₃ solutions. After impregnation and drying (120°C), the materials were activated at 400°C. Capacities as high as 0.78 mmole/g were recorded at 400°C under dry gas conditions on the TGA for Sorb Plus® treated with carbonate solution. This was considerably higher than our initial target of 0.30 mmole/g required under process levels of steam and CO₂.

Several samples of LaRoche hydrotalcite powder (LR-HTC) were also screened for use as CO₂ adsorbents. According to LaRoche, this product was a pure hydrotalcite, with a Mg/Al ratio of

3.7. The LR-HTC was tested as received, and after promotion with varying concentrations of K_2CO_3 solution. The materials were activated at 400°C after impregnation and drying at 120°C.

Formed Samples. Two formed samples of HTC were acquired from Alcoa: Sorb-Plus GP® (1/16 in. granular beads) and Alcoa HTC (1/16 and 1/8 in. extruded pellets). The former material was regarded as "experimental," and the latter, "semi-commercial". Each support was impregnated with several concentrations of carbonate solution and activated as before. Capacities as high as 0.64 mmole/g were recorded for the formed materials impregnated with 2.0 M carbonate solution. A summary of the powder and formed HTCs is given in Table 3. The materials with the best CO_2 capacity typically had 20-35 wt % K_2CO_3 . Impregnation with 2.0 M carbonate solution generally yielded the highest capacity adsorbents for the formed HTCs.

XRD Analysis. Four samples of LaRoche HTC materials were submitted for XRD analysis: (1) as-received; (2) calcined at 500°C; (3) treated with 0.5 M K_2CO_3 and dried at 120°C; and (4) treated with 0.5 M K_2CO_3 , dried at 120°C and activated at 500°C. The resulting XRD patterns represented sequential "snapshots" of the material in a typical preparation. The as-received powder contained a crystalline phase which was not identified. This phase was converted to poorly crystalline MgO and Al_2O_3 after calcination at 500°C. By treating this mixture of metal oxides with K_2CO_3 and drying at 120°C, the sample was converted to hydrotalcite, which then reverted back to the mixture of metal oxides after activation at 500°C. A separate series of hot-stage XRD analyses was run at 25, 200, 300 and 400°C, which confirmed that the hydrotalcite phase had greatly diminished at 200°C and was absent at 300°C. The active phase for CO_2 adsorption is therefore the metal oxide mixture, not the hydrotalcite phase. The MgO present in the active product had very low crystallinity, and hence high surface area, which may account for its very favorable CO_2 adsorptive properties.

Cyclic Stability under Dry Gas. A sample prepared from the treatment of Sorb Plus-GP with 2.0 M K_2CO_3 was subjected to 60 CO_2/N_2 cycles to determine its thermal and cyclic stability. The TGA data from this dry gas stability test are shown in Figure 4.

The working capacity of the sample decreased by 10% between the 2nd and 20th cycles from 0.50 to 0.45 mmole/g at 400°C. The capacity remained constant at 0.45 mmole/g from the 20th to the 60th cycle. This positive result paved the way for similar cyclic tests in the presence of steam, as described below.

Hydrothermal Stability Testing in Parr Bomb. The static hydrothermal stability of K₂CO₃/Alcoa HTC extrudate was monitored by exposing the promoted pellets to 10 atmospheres of steam and 1 atmosphere of CO₂ at 400°C for 30 days in the Hydrothermal Stability Testing Unit (HSTU). Samples were removed for capacity, surface area and XRD analyses after 1, 7 and 30 days. A summary of the data is shown in Table 4.

TGA measurements showed an unexpected increase in capacity during the first week of steam testing, before they held constant at ≈ 0.65 mmole from the 7th day to the 30th day. The surface area dropped from 89 to 5 m²/g over the same time period, suggesting that capacity did not depend on surface area. The XRD analysis showed that MgO, MgAl₂O₄ and K₂CO₃ were formed by exposure to static steam conditions. Evaluation of the adsorption properties of these components individually and in various combinations did not reveal higher capacities.

BDU Testing in 10 Atmospheres of H₂O. A variety of selected adsorbents were screened on the BDU to characterize their binary adsorptive properties under simulated process levels of CO₂ and steam at 300-500°C. These tests clearly differentiated the promoted HTC as having the highest capacity of all previously tested adsorbents under simulated process conditions. The reversible capacity of the K₂CO₃/HTC was 0.52 mmole/g under the target operating conditions of 0.30 atm CO₂ and 10 atm H₂O at 400°C. The capacities were measured by quantifying the total desorbed CO₂ after saturating the sample with CO₂ and H₂O as described in the Experimental section. It was particularly interesting that the promoted HTC had approximately the same capacity under steam conditions as it did under dry conditions.

Isotherm data were collected on the BDU for the promoted HTC by taking measurements as a function of CO₂ partial pressure and temperature. These data, presented in Figure 5, show that the capacity increased with decreasing temperature as expected, since CO₂ adsorption is exothermic. The measured capacity at 0.30 atm of CO₂, for example, increased by 50%, from 0.52 to 0.75 mmole/g, as the temperature was lowered from 400 to 300°C. K₂CO₃/HTC was also evaluated for its longer term cyclic stability under simulated process conditions. During these tests, the sorbent was alternately exposed to 10 atm H₂O-0.30 atm CO₂ (adsorption step) and N₂ (desorption step). The CO₂ capacity was measured during each desorption step. Cyclic data for K₂CO₃/HTC at 400°C are shown in Figure 6. The promoted HTC had a stable working capacity of 0.45 mmole/g, which is 50% above the target value of 0.30 mmole/g.

Sorption/Desorption Kinetics. Carbon dioxide sorption column dynamics were conducted to evaluate the kinetics of CO₂ sorption. These experiments were carried out in a slightly modified version of the process test unit, which is described in detail in the Task I.2 section of this report. A sample of 159 g of K₂CO₃/HTC was packed into a 213-cm-long stainless steel column. The column was maintained at 400°C and 1 atm during all experiments. The breakthrough experiments were conducted by flowing a feed mixture containing 65.7% CO₂ in N₂ at 1 atm and 400°C after thoroughly activating the sample at 400°C in nitrogen. The effluent CO₂ compositions were monitored as functions of time by a CO₂ infrared detector, and the flow rates were measured with an electronic flow meter. Both signals were directly fed to a computer acquisition system every 2 seconds. The adsorption run continued until complete breakthrough of CO₂ was observed. The column was then regenerated by flowing CO₂-free nitrogen at 400°C. The concentration of CO₂ and the flow rate of the effluent were continuously monitored during regeneration using the same analytical devices in order to study the desorption characteristics of CO₂. The length of the mass transfer zone (LMTZ) was calculated from the breakthrough data using a standard method (Sircar and Kumar, 1983).

A plot of the length of the CO₂ mass transfer zone (LMTZ) versus the feed gas flow rate through the column (G rate) is shown in Figure 7. The mass transfer zone represents the length of column over which the CO₂ composition varies from the feed composition to essentially zero. Sharp mass transfer zones are preferred in order to maximize the efficiency of the adsorption process. A MTZ length of only 28 cm was estimated for a typical industrial G rate of 5g mole/hr/cm². This is a relatively small value, which indicates that the K₂CO₃/HTC material exhibits relatively fast CO₂ sorption kinetics.

Desorption experiments were carried out by purging the sorption columns (presaturated with pure CO₂ at 1.0 atmosphere and 400°C) with pure nitrogen at different flow rates. Figure 8 represents the desorption curves at two different flow rates. They show the specific amounts of CO₂ removed from the column as functions of the total amount of purge gas effluent. The desorption characteristics are independent of purge gas flow rate, which shows that the process is local equilibrium controlled. The solid line in Figure 8 is the calculated CO₂ desorption profile by local equilibrium theory (Sircar and Golden, 1996).

7.1.4.3. Sorbent/Catalyst Compatibility Tests

Compatibility tests were conducted using a physical admixture of promoted HTC adsorbent and a commercial SMR pre-reformer catalyst on the BDU. A 15-g sorbent-catalyst mixture (50/50 by weight) contained in an 8-in. column was exposed to 1000 sccm of 3.5% H₂/N₂ at 400°C for 24 hours to reduce the catalyst. Next, the mixture was exposed to 700 sccm of steam and CO₂ (pH₂O = 10.0 atm, pCO₂ = 0.30 atm) for 72 hours at 400°C on the BDU.

After steaming, the sorbent and catalyst pellets were separated. The sorbent was analyzed to have a capacity in dry gas of 0.57 mmole CO₂/g at 350°C, indicating a 10% improvement over the as-prepared sorbent (before steaming), suggesting that the catalyst does not have a negative impact on sorbent performance.

The activity of samples of the as-received and steamed pre-reformer catalyst was analyzed using a laboratory SMR unit. The operating conditions for both samples were: H_2O to CH_4 feed of 1.6; $\text{GHSV}(\text{CH}_4) = 12,000 \text{ hr}^{-1}$; and reduction for 2 hours at 450°C using 50% H_2 , 50% N_2 blend. The catalyst activity was gauged by the methane conversion and the hydrogen production. Measurements were recorded at 500, 650 and 800°C , and the conversion was evaluated based on H_2 production. The data from this experiment, summarized in Table 5, show that the SMR catalyst maintained its activity after being steamed at high temperature in the presence of the promoted HTC adsorbent. This experiment established that neither the adsorbent nor the catalyst suffered a performance loss as a result of a 72-hour exposure of an admixture of the two materials to simulated process conditions.

7.1.4.4. Materials Scaleup for Engineering Evaluation

To date the promoted HTC has been prepared in quantities as large as 800g (1 liter) per batch, totaling 10 kg. The batch size is limited by the amount of material that can be activated in the laboratory reaction furnace in a given run. Approximately 5 kg of this material have been made available for engineering process studies.

7.2. TASK I.2 Demonstrate and Develop Process for SER-SMR

The goals of this work were to (1) experimentally demonstrate the concept of H_2 -SERP, i.e., observe enhanced conversion of methane during an SER reaction step; (2) investigate the effect of various operating parameters on process performance; (3) characterize the efficiency of the regeneration steps; and (4) evaluate the cyclic performance of the process. The last step was not addressed in this work because of limitations of the experimental system. Instead, a second unit will be constructed that will be operated cyclically with two reactor beds. Details of this system will be given in the Future Work section of this report. All of the results presented in this report were obtained in the single-step process test unit, which is described below.

7.2.1. Experimental

A bench-scale apparatus for testing the SER concept was constructed with Air Products funds in 1993 to study a different reaction system, the reverse water gas shift reaction for the production

of CO. This basic unit was modified to run the steam methane reforming reactions for H₂-SER. These changes were required to accommodate the production and handling of steam, to permit composition analysis of the steam methane reforming components, and to address specific safety issues associated with the SMR system.

Figure 9 is a schematic diagram of the modified process test unit. It consists of a single reactor vessel (1.5 in. internal diameter and 70 in. long) enclosed in a tube furnace. The reactor was fitted with inlet and outlet lines for introducing feed gas (mixtures of CH₄ and H₂O), purge gas (H₂ or N₂) and pressurization gas (H₂), as well as removing depressurization and purge effluent gases. Steam was generated by vaporizing a constant flow of water in a vaporizer. It was then mixed with a constant flow of methane (controlled by a mass flow controller) and directed to the reactor. The purge gas flow rates were set with either flow controllers (H₂) or inlet pressure (N₂). All inlet gases were preheated to the reaction temperature with external heat tape. Back-pressure regulators were used to maintain constant reactor pressures during the reaction and regeneration steps. Condensers were placed ahead of the back-pressure regulators to cool the gas and remove any excess water. A five-point thermocouple inserted in the center of the reactor measured the temperature profile along the length of the reactor during all steps of the process. Reactor pressure was monitored with two high-temperature electronic pressure transducers positioned at each end of the reactor. Effluent gas flow rates were measured with either a wet test meter (>700 cc/min) or an electronic volumetric flow meter. The mole fractions of CH₄, CO, CO₂, and H₂ in the effluent gas were monitored continuously using a gas chromatograph-mass spectrometer (GC-MS).

For safety purposes, the entire experimental apparatus was installed within a ventilated enclosure, and system power was interlocked to the ventilation gas velocity. If ventilation was lost, the system could not be operated. Flammable gas and CO alarms were positioned within the system, and high-temperature and -pressure alarms were present at the reactor. The unit was controlled via a PLC, and emergency valve sequences were programmed to activate when alarm conditions were reached. High-temperature portions of the system at the reactor flanges were

enclosed with an aluminum housing and continuously purged with nitrogen. This prevented any potential flammable gas leak from igniting. Standard safety devices such as relief valves, rupture disks, and excess flow valves were used at appropriate locations throughout the system.

The catalyst used in this work contained Ni/NiO, which can form a carcinogenic dust. A separate ventilated enclosure (the Reactor Charging Unit, or RCU) was constructed to charge and unload the reactor. Gloves were attached to the walls of the device to facilitate the safe transfer of catalyst material.

The process test unit was developed to investigate single steps of the H₂-SER process, and not the fully cyclic operation that an industrial unit would utilize. Reaction temperatures and pressures of 350-450°C and 10-250 psig were possible, although problems with steam condensation were encountered at system pressures greater than 60 psig. All of the reaction runs described here were carried out at 50-55 psig. During a run, the feed or purge gas flow rates were set to known values and held constant. The reactor temperature (5 points) and pressure (inlet and outlet) were continuously monitored and recorded every minute. The effluent gas flow rate and gas phase composition were evaluated throughout the entire run and were updated once every two minutes. The relatively long time between analyses was a consequence of the time required by the GC/MS for resolution of the component peaks. This two-minute analysis time made it necessary to run the reaction step at relatively low feed flow rates (~500 cc/min) in order to obtain a sufficient number of data points during the run. An industrial unit would generally run at higher feed gas velocities.

7.2.2. Experimental Procedure.

The reactor was packed in the RCU with roughly 2 kg of a mixture of commercial prereforming catalyst (~1/8-in. pellets) and the K₂CO₃/HTC sorbent (1/8-in. extrudates). The reactor was placed in the process test unit and heated under N₂ flow to 450°C at roughly 1°C/min. The catalyst was then reduced under controlled H₂/N₂ flow, as suggested by the manufacturer. Following reduction, the reactor temperature was set to the desired operating temperature of 350-

450 °C and left at that level throughout all subsequent runs. The reactor was regenerated overnight in a flow of N₂ to remove water from the adsorbent.

The first set of runs was performed to determine the amount of H₂ present within the reactor at a given temperature and pressure. Contributions from hydrogen in the void gas spaces, dead volumes, and adsorbed phases were considered. The reactor was equilibrated with H₂ to the desired pressure, and then the gas was vented through a flow meter until the reactor was at ambient pressure. By analyzing the flow rate-time data, it was possible to evaluate how much H₂ was originally present in the column.

A reaction step was initiated by purging and pressurizing a previously regenerated column with hydrogen. The reaction started when the methane/steam feed gas was introduced into the column. The reactor temperature, pressure, and effluent gas composition and flow rate were monitored continuously during the run. Once the CO₂ capacity of the adsorbent was saturated, the column was depressurized and purged overnight with N₂. All regeneration steps were carried out in a flow direction that was opposite that of the feed step, i.e., in a countercurrent direction. The N₂ purge step prepared the column for the next reaction step, which typically was carried out one to three days later.

When all experiments with a particular catalyst/adsorbent system were complete, the reactor temperature was reduced to ~30-100 °C, and the catalyst was oxidized with a controlled flow of air in N₂. Once oxidized, the reactor was transferred to the RCU and unloaded.

7.2.3. Characterization of Process Performance

The H₂-SER reaction steps were characterized by evaluating the effective CH₄ conversion, the reactor productivity to H₂, and the average H₂ purity of the reactor effluent. These parameters were evaluated from the fixed CH₄ feed rate, the amount of solid packed in the reactor, and integration of the product of the effluent H₂ mole fraction and flow rate. The conversion is actually a combination of the conversion and the recovery and is evaluated as the *net* amount of

product hydrogen (the total amount of hydrogen out of the reactor minus the amount needed to initially pressurize the reactor) divided by the total amount of methane fed to the reactor. The average hydrogen mole fraction in the product stream was determined by assuming that all of the gas exiting the reactor was collected and mixed. The reactor productivity was determined as the net amount of product hydrogen divided by the total solid loaded in the reactor. All of these parameters could be evaluated throughout the reaction step, yielding curves for conversion, purity, and productivity as a function of reaction step time (or cumulative amount of reaction step effluent).

7.2.4. Results

Reactor Characteristics Runs were carried out with a reactor packed with 1:1 K_2CO_3 /HTC/catalyst and 1:3 K_2CO_3 /HTC/catalyst, for which the ratio is based on mass. The total void volume of these reactors was measured with He at room temperature and is listed in Table 6. The bulk density of the solid was calculated and is also listed in the table. Increasing the catalyst fraction increases the bulk density of the mixture, since the catalyst is much denser than the adsorbent.

H₂ Sorption Experiments Experiments were conducted to determine the amount of H₂ in the reactor at a given temperature and pressure by the procedure outlined above. Comparison of these values with those obtained for helium, which is assumed to be nonadsorbed, indicated that roughly 20% more hydrogen was present. In both cases the amount of gas varied linearly with the total system pressure. The Henry's Law constant, which is a proportionality constant between the excess amount of hydrogen in the reactor and the hydrogen pressure, was evaluated and is listed for each temperature and reactor system in Table 7. The constants were very small, indicating that only a very small amount of H₂ was in excess of the void gas amount. Generally, for reaction steps carried out at 55 psig, the results indicate that the amount of H₂ initially present in the bed (void & adsorbed) was roughly 0.07 to 0.09 mmole/g solid.

Base Case Experiment The first reaction experiment was performed with a 1:1 mixture of K_2CO_3 /HTC/commercial prereformer catalyst. The reactor was set to 350°C, filled with pure H₂

to 55 psig and fed 300 cc/min of gas containing 33.3% methane/66.6% steam. Figures 10 and 11 illustrate the effluent gas flow rate and composition as a function of time and total cumulative effluent, respectively. Both sets of data are on a dry basis, i.e., water was not included in the flow rate or composition measurements. The dry gas flow rate was clearly above the feed flow rate of CH_4 , indicating that more non-water gas species were being produced in the reactor. Figure 11 indicates that the additional species was H_2 . The mole fraction of hydrogen in the effluent gas was initially high as H_2 from the void space of the reactor was removed. The cross-hatched portion of this curve corresponded to the initial amount of H_2 in the column, calculated from the above desorption experiments. The H_2 mole fraction then dropped and varied from 40 to 60%. The only other species in the effluent gas was methane; carbon oxides were not detected during this particular experiment. The conversion, productivity, and average H_2 purity are plotted versus the amount of methane fed to the reactor in Figure 12. The conversion plateaued at around 24%, where the average H_2 purity was 55-60%. The productivity continually climbed throughout the run as H_2 was being produced, and reached 0.6 mmole/g at the end of the run. Since the reaction step was not run to complete CO_2 saturation, the three curves did not fall at the end of the step, as would be expected for a very long reaction step. The H_2 -SER unit yielded a CH_4 conversion of 24% and an average H_2 product purity of ~60%. These values were both higher than expected from a catalyst-only reactor operating at equilibrium (5.1% CH_4 conversion, 17% H_2 purity). Thus, this experiment clearly demonstrates that the inclusion of a CO_2 adsorbent in the reactor substantially improves the conversion of reactants and product purity of the effluent gas. The SERP concept was demonstrated.

Effect of Temperature, Steam/Methane Ratio, and Ads/Cat Ratio Further experiments were conducted to assess the effect of temperature, steam/methane ratio of the feed gas, and adsorbent/catalyst ratio on system performance. Increasing the temperature from 350 to 450°C for the 1:1 ads/cat system improved the CH_4 conversion and H_2 product purity. This behavior is illustrated in Figure 13. The general effect of this change was to increase the CO_2 mole fraction in the gas that was passed to the adsorbent. This allowed the adsorbent to remove a larger

fraction of the total available CO_2 , and thus improved the performance of the reaction step. Since increasing the steam/methane ratio resulted in a similar effect, it was not surprising that the same experimental observations were made (Figure 14). Thus, higher temperatures and higher steam/methane ratios were found to be desirable.

A plot of the effluent mole fraction for runs with the 1:1 and 1:3 ads/cat systems is presented in Figure 15. Decreasing the adsorbent/catalyst ratio, i.e., going to a catalyst-rich system, did not appreciably change the effluent gas composition history when plotted versus H_2 out/g of *adsorbent*. Thus, there was no effect on H_2 product purity. However, the overall productivity of the reactor fell, since the total amount of CO_2 adsorbent in the reactor was reduced. Note that these results were obtained with relatively low feed gas velocities. Differences in the effluent composition curves may still be apparent at industrial flow rates, where the kinetic activity of the catalyst is more vigorously challenged.

Best Reaction Step Performance to Date Figure 16 illustrates the gas phase composition of the reactor effluent stream during the most attractive experiment conducted to date. The run was carried out with a reactor packed with a 1:3 mixture of adsorbent $\text{K}_2\text{CO}_3/\text{HTC}/\text{prereformer}$ catalyst at 450°C , 55 psig, and with a feed consisting of 11% methane and 89% steam. Again, the initial shaded area represents the amount of H_2 that was initially used to pressurize the reactor. This amount was lower than previous runs, since a mixture of 20% $\text{H}_2/80\%$ H_2O was used to pressurize in this run. Thus, the voids contained only one fifth of the usual H_2 amount. This mode of operation is feasible from an industrial point of view since H_2O is very easily removed from H_2 . From the illustration, it is clear that production of high purity hydrogen continued after this initial amount of H_2 had exited the reactor. The effluent gas consisted predominantly of H_2 , with only a small amount of CH_4 . Carbon dioxide was not detected by the GC/MS until the latter part of the experiment. Carbon monoxide was also very low, and could not be detected with our analytical system. If the reaction step was terminated when the average H_2 product purity was 95%, then the methane conversion was found to be 68%. Again, this was substantially higher than the equilibrium conversion of 34% and the product purity of 57%

expected for a catalyst-only system (thermodynamic calculations). The SERP reactor product purity during this run was approaching the range where further separation may be unnecessary for some applications, which would impart a very large economic advantage over conventional processes.

Desorption Characteristics of the System The CO₂ desorption characteristics of the K₂CO₃/HTC/prereformer catalyst system are currently under investigation. It is clear from TGA analysis and the kinetic breakthrough experiments that CO₂ is reversibly sorbed on the K₂CO₃/HTC material at 350-450°C. This is also evident from the process experiments, since reproducible effluent compositions are obtained for repetitive reaction steps. This would only be possible if the CO₂ was effectively removed from the sorbent during the N₂ purge step.

Carbon Analysis of Used Solid A sample of the used catalyst and adsorbent from the 1:1 reactor was submitted, along with fresh solids, for carbon analysis. No carbon accumulation was found on the used samples.

Novel Reactor Design A novel reactor system for carrying out SERP-SMR concept has been designed (Figure 17). A suitable reactor/adsorber system must (1) accommodate both the reaction medium (i.e., multiple packed columns (or tubes) containing a mixture of sorbent and catalyst pellets) and the heat transfer system; (2) approximately maintain isothermal conditions (300-500°C) across equilibrated sections of the reactor; and (3) supply heat to the mobile adsorption-reaction transfer zones in the packed columns. During the reaction-sorption step of the SERP-SMR process, a reaction mass transfer zone (RMTZ) travels along the bed from the feed end to the product end, and energy must be supplied for the net endothermic reaction and adsorption process. Heat must also be supplied to the reactor during the endothermic desorption step (depressurization and purge). The device must also keep the packed column in intimate but indirect contact with the heat transfer fluid. Traditional methods of heat exchange based on the transfer of sensible heat are impractical for SERP-SMR, since an infinite flow rate of heat transfer fluid is required to obtain nearly isothermal conditions along the column length. A novel shell and tube reactor system has been developed to meet these requirements. A reactant gas

mixture or desorbed gases flow through the tubes, which contain the admixture of catalyst and adsorbent. A recycled heat transfer fluid (HTF) vapor undergoes condensation on the shell-side of the tubes to provide heat during the reaction/sorption step. Since the HTF always remains at its condensing temperature, the reactor tubes remain nearly isothermal. Also, since condensation occurs only where the bed temperature drops (at the RMTZ), heat is transferred into the section of the packed column only where it is required. A vendor of the heat transfer fluid has been consulted with this application and is eager to help in development of the system. The upper temperature limit for application of these fluids is around 400°C, and operation at higher temperatures will require some form of fluid reclamation. Thus, the most attractive SERP operation at 450°C will be at the edge of heat transfer fluid technology.

Process Simulator for H₂-SER An existing adsorption process simulator has been modified to include reaction terms so that it may be used to model the performance of the SER process. Current efforts are focused on refining the reaction rate expression and adsorption isotherm data in order to match the simulator predictions with experimental reaction step data.

7.3. TASK I.3 Economic and Engineering Analysis

A preliminary process flow diagram was prepared for the H₂-SER process using the condensing vapor reactor system (Figure 18). Heat and mass balances and equipment sizes were evaluated based on the engineering assumptions listed in Table 8. An economic analysis of the design was performed by the Air Products H₂ business area, which showed that the H₂-SER process can lower H₂ production costs by roughly 20 to 30% compared with conventional SMR (2.5 MM SCFD H₂ product). This estimate will be revised as new experimental process data become available.

8. Future Plans

8.1. CO₂ Sorbent Development

Additional materials research and development work will be carried out to prepare a second-generation, high-temperature CO₂ adsorbent for the SER process. The emphasis of the materials research for future adsorbents will be dictated by the performance results of adsorbents currently being evaluated by the SER engineering process studies. The SER process may benefit from improved adsorbent properties such as increased capacity, improved kinetics, or modified CO₂ adsorption isotherm shape.

Our plan is to investigate several options for improved adsorbents, including the optimization of the promoted HTC materials, as well as the preparation and characterization of materials believed to be the most active component of the activated HTC adsorbents. The adsorption isotherm characteristics of materials will be evaluated in greater detail using the TGA that was recently modified to enable these studies. Plans are also being made to prepare the promoted HTC on the 50-lb scale in order to supply material for the H₂-SER cyclic engineering unit.

8.2. Process Development

The short-term objective of process experiments will be to continue to explore the effects of various experimental parameters on process performance. An important variable of interest is the reaction pressure. Operation at a pressure higher than 55 psig is desirable in order to minimize compression costs. Straightforward experimental modifications will be carried out to increase the maximum reaction pressure of the experimental system to 250 psig.

Process experiments conducted to date have been concerned with quantification of the reaction step only. The adsorbent is obviously regenerable, since repetitive experiments with the same reactor packing yield similar enhancements in CH₄ conversion. It is not clear, though, how much purge gas is needed to effectively remove enough of the adsorbed CO₂ from the reactor.

Insight into this question will be obtained by adding a more sensitive CO₂ detector to the reactor effluent and carefully quantifying the desorption steps.

The above question cannot be fully answered even with the additional desorption experiments, since it is not clear what the effect of residual adsorbed CO₂ has on the reaction step output. This question can only be answered definitively by conducting fully cyclic experiments with two or more beds at cyclic steady state. We plan on constructing such a system; in fact, it is currently in the design stage. The unit will be fully automated and will include all of the necessary hardware to repetitively perform the entire H₂-SERP process. The unit will contain two reactors of industrially relevant size (1-2 in. ID and 10-20 ft long). The proposed heat transfer system will be utilized to resolve unanswered questions regarding the heat transfer fluid. The unit will also allow for the investigation of specific reaction step feed rates (or G-rates, lbmole/hr-ft²) that are of industrial magnitude and are roughly forty times greater than those used in the current experimental system.

8.3. Design/Economics

Finally, as new information regarding the process or CO₂ adsorbent is developed (e.g., effect of higher G-rates, purge requirements, improved adsorbent CO₂ capacities, etc.), the preliminary H₂-SERP design will be revised and economic assessments will be refined. Parameters for the process simulator will be obtained from comparisons with lab-scale reactor data. The simulator will then be used to help design the industrial units.

9. Patent Information

Several patent applications for the SER process and process integrations have been filed with the United States Patent Office by Air Products and Chemicals, Inc. [Anand et al., 1995; Hufton et al., 1996a, 1996b; Nataraj et al., 1996]. Anand et al. and Nataraj et al. both deal at least in part with the H₂-SER process. Nataraj et al. also describes the K₂CO₃/HTC adsorbent and how it fits within the H₂-SERP concept. A second materials-oriented patent application (Mayorga et al., 1996) encompasses modified aluminas as SER adsorbents.

10. Acknowledgments

The authors would like to thank Joe Zenon and Jeff Brzozowski for performing most of the experiments and analysis described in this report. Thanks also to Shankar Nataraj for the preliminary H₂-SER design, Robert Moore for carrying out the economic analysis, and Grant Fox for developing the SER process simulator.

11. References

- Anand, M., Sircar, S., and Carvill, B.T., "Processes for Operating Equilibrium Controlled Reactions," U.S. Patent Pending (1995).
- Brun-Tsekhovoi, A. R., Zadorin, A. N., Katsobashvili, Ya. R., and Kourdyumov, S. S., "The Process of Catalytic Steam-Reforming of Hydrocarbons in the Presence of Carbon Dioxide Acceptor," *Hydrogen Energy Process VII, Proceedings of the World Hydrogen Energy Conference*, Pergamon Press, 2, 885 (1986).
- Carvill, B.T., Hufton, J.R., Anand, M., and Sircar, S., "Sorption Enhanced Reaction Process," *AIChE J.*, **42**, 2765 (1996)
- Gluud, W., Keller, K., Schonfelder, R. and Klempt, W., "Production of Hydrogen," U.S. Patent 1,816,523 (1931).
- Goto, S., Tagawa, T., and Omiya, T., "Dehydrogenation of Cyclohexane in a PSA Reactor Using Hydrogen Occlusion Alloy," *Chem. Eng. Essays (Japan)*, **19**(6) 978 (1993).
- Han, C., and Harrison, D. P., "Simultaneous Shift Reaction and Carbon Dioxide Separation for the Direct Production of Hydrogen," *Chem. Eng. Sci.*, **49**, 5875 (1994).
- Hufton, J.R., Sircar, S., Baade, W.F., Abrardo, J.M., and Anand, M., "Integrated Steam Methane Reforming Process for Producing Carbon Monoxide," U.S. Patent Pending (1996a).
- Hufton, J.R., Sircar, S., Baade, W.F., Abrardo, J.M., and Anand, M., "Integrated Steam Methane Reforming Process for Producing Carbon Monoxide and Hydrogen," U.S. Patent Pending (1996b).
- Mayorga, S. G., Golden, T. C., Gaffney, T. R., Brzozowski, J. R., and Taylor, F. W., "Carbon Dioxide Pressure Swing Adsorption Process Using Modified Alumina Adsorbents," U. S. Patent Pending (1996).

Nataraj, S.N., Carvill, B.T., Hufton, J.R., Mayorga, S.M., Gaffney, T.R., and Brzozowski, J.R., "Process for Operating Equilibrium Controlled Reactions," U.S. Patent Pending (1996).

Sircar, S., and Golden, T.C., "Isothermal and Isobaric Desorption of CO₂ by Purge," *I&E.C. Research* **34**, 2881 (1996).

Sircar, S., and Kumar, R., "Adiabatic Adsorption of Bulk Binary Gas Mixtures: Analysis by Constant Pattern Model," *I&EC Proc. Des. Dev.*, **22**, 271 (1983).

Vaporciyan, G.G., and Kadlec, R.H., "Periodic Separating Reactors: Experiments and Theory," *AIChE J.*, **35**, 831 (1989).

12. Tables

Table 1. H₂-SERP vs Conventional SMR for H₂ Production

	<u>Conventional</u>	<u>SER Goals</u>
Operating Temperature	800-1000°C	300-500°C
CH ₄ to H ₂ Conversion	80-85%	90+%
Reaction Product Composition (Dry Basis)	73.7% H ₂ +9.4% CO ₂ + 12.0% CO+4.8% CH ₄	98+% H ₂
Product Pressure	200-400 psig	200-400 psig

Table 2. Experimental Evaluation of PSR Systems

Authors	Process Steps	Reaction	Sorbent	Products
Vaporciyan and Kadlec, 1989	Feed, delay, exhaust	$2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$ feed diluted with N_2	5A Zeolite for CO_2	CO_2 distributed in both reaction effluent and desorption gas. Dilute CO_2 in both products.
Goto, Tagawa and Omiya, 1993	Feed, helium purge (or evacuate)	$\text{C}_6\text{H}_{12} \rightleftharpoons \text{C}_6\text{H}_6 + 3\text{H}_2$ feed diluted with helium	CaNi ₅ for H_2	H_2 product obtained in mixture with helium as desorbed product. C_6H_6 product obtained as reactor effluent partly mixed with helium.
Han and Harrison, 1994	No process, feed only.	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ feed (CO_2 , CO , H_2 and H_2O mixture) diluted with N_2 .	Dolomite for CO_2	Dilute H_2 in N_2 obtained during feed step.

Table 3. Summary of Carbonate Promoted Hydrotalcites

Sample	[K ₂ CO ₃] (M)	wt % K ₂ CO ₃	Mg/Al	CO ₂ cap. at 300°C (mmole/g)	CO ₂ cap. at 400°C (mmole/g)	CO ₂ cap. at 500°C (mmole/g)
Sorb Plus®	0	0	2.25	0.18	0.20	0.20
K ₂ CO ₃ /Sorb Plus®	0.5	30.9	2.27	0.32	0.78	0.75
K ₂ CO ₃ /Sorb Plus®	2.0	67.3	2.21	0.20	0.35	0.33
K ₂ CO ₃ /Sorb Plus®	5.0	88.0	2.20	0.07	0.25	0.19
LR-HTC	0	0	2.09	0.31	0.31	0.32
K ₂ CO ₃ /LR-HTC	0.1	9.8	2.01	0.33	0.39	0.43
K ₂ CO ₃ /LR-HTC	0.5	32.7	2.08	0.39	0.67	0.82
K ₂ CO ₃ /LR-HTC	2.0	70.4	2.15	0.21	0.35	0.43
K ₂ CO ₃ /LR-HTC	5.0	86.6	2.14	0.09	0.15	0.18
K ₂ CO ₃ /Sorb Plus-GP®	0.5	0	4.11	0.30	0.31	0.33
K ₂ CO ₃ /Sorb Plus-GP®	2.0	20.1	4.02	0.23	0.53	0.64
K ₂ CO ₃ /Sorb Plus-GP®	5.0	28.9	4.18	0.19	0.44	0.54
K ₂ CO ₃ /HTC extr., 1/8"	0.5	5.7	3.00	-	0.28	0.31
K ₂ CO ₃ /HTC extr., 1/8"	2.0	23.4	3.00	-	0.39	0.56
K ₂ CO ₃ /HTC extr., 1/8"	5.0	37.7	3.05	-	0.28	0.41

Table 4. Hydrothermal Stability Testing of Promoted Hydrotalcite at 400°C

Days exposed to Steam/CO ₂ @ 400°C	Capacity at 400°C (mmole/g)	Surface Area (m ² /g)	Component Analysis by XRD
0	0.37	89	K ₂ CO ₃ , HTC, MgO
1	0.42	28	MgO, MgAl ₂ O ₄ , K ₂ CO ₃
7	0.67	21	MgO, MgAl ₂ O ₄ , K ₂ CO ₃
30	0.63	5	MgO, MgAl ₂ O ₄ , K ₂ CO ₃

Table 5. Activity of SMR Catalyst

Sample	Temperature (°C)	% Approach to Equil. Conversion Based on H ₂
catalyst before steam/CO ₂	500	73.1
“	650	78.9
“	800	89.5
catalyst after steam/CO ₂	500	81.5
“	650	89.4
“	800	93.8

Table 6. Reactor Characteristics

Ads/Cat Ratio	Bed Porosity	Bulk Density (lb/ft³)
1:1	0.68	70.6
1:3	0.69	76.7

Table 7. Henry's Constants for H₂ on Ads/Cat Mixture

Ads/Cat Ratio	T (°C)	Henry's Constant (mmole/g/atm)
1:1	350	0.0022
	400	0.0036
	450	0.0035
1:3	450	0.0025

Table 8. Assumptions for Preliminary Design of H₂-SER System

-
- 2.5 MM SCFD H₂ production,
99.99% purity
 - 80% H₂ recovery
 - Reactor temperature of 700°F
 - 2.5 steam/methane in feed
 - Water not coadsorbed on adsorbent
 - Reactor size = 2x mass transfer zone
length (RMTZ)
 - RMTZ determined by heat transfer
requirements
 - 100°F heat transfer driving force for
HTF fluid / reactor internals
 - Furnace fuel needs provided by SER
blowdown / purge streams
 - CH₄ purge amount determined by
furnace fuel requirements
 - PSA required for H₂ cleanup
-

13. Figures

Figure 1
Schematic Illustration of H₂-SER Process Steps

Figure 2
Equilibrium Methane Conversion and Steam to CO_2 Ratio for SMR Reaction

Figure 3
Binary Desorption Unit

Figure 4
TGA Cycling of K_2CO_3 /Sorp Plus GP
Under Dry CO_2/N_2 Conditions

Figure 5
Isotherm Data for K₂CO₃/HTC

Figure 6
Cyclic Stability of K₂CO₃/HTC at 400°C
under Simulated Process Levels of CO₂ and Steam

Figure 7
Length of Mass Transfer Zone for
CO₂ Adsorption on K₂CO₃/HTC @ 400°C

Figure 8
Desorption Curves for CO₂-K₂CO₃/HTC at 400°C

Figure 9
Schematic of H₂-SER Test Apparatus

Figure 10
Effluent Flow Rate During Base Case Experiment

Figure 11
Effluent Gas Composition During Base Case Experiment

Figure 12
Reaction Step Parameters for Base Case Experiment

Figure 13
Comparison of Reaction Step Parameters for Different Reaction Temperatures; 1:1
ads/cat; 50-60 psig; 500 cc/min, 4:1 H₂O/CH₄

Figure 14
Comparison of Reaction Step Run Data for Different $\text{H}_2\text{O}/\text{CH}_4$ Feed Ratios; 1:1
ads/cat; 50-60 psig; 350°C

Figure 15
Reaction Step Effluent Composition for 1:1 and 1:3 K_2CO_3 /HTC/
prereformer catalyst ratios; 450°C, 55 psig, 4:1 H_2O/CH_4

Figure 16
Reaction Step Effluent Composition for Best Run; 1:3 K₂CO₃/HTC/
catalyst, 450°C, 55 psig, 8:1 steam/methane

Figure 17
Shell and Tube Reactor System for H_2 -SER

Figure 18
Preliminary H₂-SER Process Flow Diagram