Report Title:
Enhanced Hydrogen Production Integrated with CO₂ Separation in a Single-Stage Reactor

Type of Report: Semi Annual Technical Progress Report

Reporting Period Start Date: October 1, 2004
Reporting Period End Date: March 31, 2005

Authors: Dr. Himanshu Gupta, Mahesh Iyer, Bartev Sakadjian and Prof. Liang-Shih Fan

Report Issue date: April, 2005

DOE Contract No: DE-FC26-03NT41853

Name and Address of Submitting Organization:
Department of Chemical and Biomolecular Engineering
The Ohio State University
140 West 19th Avenue
Columbus OH 43210

Contact Information of Principal Investigator:
Professor Liang-Shih Fan
Phone: 614-688-3262
Fax: 614-292-3769
Email: fan.1@osu.edu
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Abstract

Hydrogen production by the water gas shift reaction (WGSR) is equilibrium limited due to thermodynamic constrains. However, this can be overcome by continuously removing the product CO₂, thereby driving the WGSR in the forward direction to enhance hydrogen production. This project aims at using a high reactivity, mesoporous calcium based sorbent (PCC-CaO) for removing CO₂ using reactive separation scheme. Preliminary results have shown that PCC-CaO dominates in its performance over naturally occurring limestone towards enhanced hydrogen production. However, maintenance of high reactivity of the sorbent over several reaction-regeneration cycles warrants effective regeneration methods. We have identified sub-atmospheric calcination (vacuum) as vital regeneration technique that helps preserve the sorbent morphology. Sub-atmospheric calcination studies reveal the significance of vacuum level, diluent gas flow rate, thermal properties of diluent gas, and sorbent loading on the kinetics of calcination and the morphology of the resultant CaO sorbent. Steam, which can be easily separated from CO₂, has been envisioned as a potential diluent gas due to its better thermal properties resulting in effective heat transfer. A novel multi-fixed bed reactor was designed which isolates the catalyst bed from the sorbent bed during the calcination step. This should prevent any potential catalyst deactivation due to oxidation by CO₂ during the regeneration phase.
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EXECUTIVE SUMMARY

Typically hydrogen is produced from fossil fuels by their reaction with air and/or steam to produce syngas or water gas which is a mixture of CO, H₂, H₂O and CO₂. However, increased hydrogen production involves the water gas shift reaction (WGSR) which shifts the CO in the system to H₂ by reacting with steam. However, WGSR is equilibrium limited due to thermodynamic constrains which favors H₂ production at low temperature. However, this limitation can be overcome by continuously removing the CO₂ by-product, thereby driving the WGSR forward and enhancing hydrogen production. This project aims at using a high reactivity, mesoporous calcium based sorbent developed at Ohio State University (PCC-CaO), for removing CO₂ using reactive separation scheme. Preliminary results on simultaneous WGSR and carbonation reactions have shown that PCC-CaO dominates in its performance over naturally occurring limestone. However, sustained sorbent performance over several calcination carbonation reaction (CCR) cycles warrants effective regeneration methods.

Detailed thermodynamic analyses reveal that for operation under atmospheric pressures corresponding to a CO₂ partial pressure of 1 atm. requires calcination temperatures above 890 °C. However, it has been amply demonstrated by our research group as well as other reports in the literature that the CO₂ capture capacity of most high temperature sorbents falls drastically with increasing number of CCR cycles. Besides, high temperature is well known to cause sorbent sintering, a major cause for loss in reactivity. However, by operating under sub-atmospheric conditions we can lower the calcination temperature well below 890 °C, as calculated by thermodynamic curves, thereby preventing the high temperature sintering effects. Thus, we have identified sub-atmospheric calcination (vacuum) as vital regeneration technique that can help preserve the sorbent morphology.

The calcination for the CCR process can be conducted either through temperature swing or pressure swing operations or their combination. For, pressure swing operation the objective is to reduce the CO₂ partial pressure in the calciner system. However, use of any other inert gas mixtures like N₂ or air to reduce the CO₂ partial pressure would mix with the CO₂ liberated from calcination and this would defeat the very basis of generating a pure sequestration ready CO₂ stream. One possible alternative is to use steam as a diluent gas which can be condensed downstream and thus steam-CO₂ separation can be achieved. Besides, steam can also provide the necessary heat for calcination.

Sub-atmospheric calcination studies reveal the significance of vacuum level, diluent gas flow rate, thermal properties of diluent gas, and sorbent loading on the kinetics of calcination and the morphology of the resultant CaO sorbent. Higher sorbent loading leads to heaping resulting in slower calcination kinetics due to poor heat transfer effects. This results in poor sorbent morphology that loses reactivity over subsequent cycles. Diluent gas flows during calcination augments the necessary convective heat transfer rate which is directly related to the diluent gas flow rate. This results in improved calcination kinetics and sorbent morphology. Diluent gas thermal properties like thermal conductivity and specific heat capacity play a significant role on the heat transfer rates during calcination. This was evident by investigating the effects of various inert gases like Ar, N₂ and He which are not easily separable from CO₂ after calcination.
However, steam has been identified as a potential diluent which has better thermal properties and can be easily separated from CO₂.

Preliminary simultaneous WGSR and carbonation experiments demonstrated a loss in the reactivity of the sorbent-catalyst system during the second reaction cycle. This is because the sorbent was regenerated in-situ and the CO₂ evolved during the calcination caused the WGS catalyst deactivation. This corroborates with similar observations reported in the literature. Hence, a novel multi-fixed bed reactor was designed which isolates the catalyst bed from the sorbent bed during the calcination step. This should prevent the catalyst deactivation due to oxidation by CO₂ during the regeneration phase. This setup enables us to demonstrate the effect of CO₂ on catalyst activity. However, under actual operating mode, as shown in the Project Vision outlined in the Annual Technical Progress report (September 2004), the sorbent particles will be injected upstream of the WGS catalyst bed. This is an entrained flow system whereby the particles flow through the catalyst bed enhancing hydrogen production and capturing CO₂. The reacted sorbent particles are subsequently separated from the gas mixture, calcined in a separate rotary calcined and subsequently injected for carbonation. Thus, the contact between CO₂ resulting during calcination and WGS catalyst would not occur under commercial scale operation as envisioned for a coal-gasification plant.
INTRODUCTION

The major processes for hydrogen production from fossil fuels include steam methane reforming (SMR), gasification of coal, catalytic cracking of natural gas to form H₂ and carbon, steam reforming of hydrocarbons, and partial oxidation of hydrocarbons (Rosen and Scott, 1998; Rosen, 1996). All these processes lead to formation of water gas, a mixture of CO, CO₂, H₂O and H₂. The Water Gas Shift Reaction (WGSR) is used to further hydrogen production. However, WGSR is equilibrium limited and is less favored towards hydrogen production with increasing temperatures due to thermodynamic constrains. While catalysts aid in achieving this equilibrium, they cannot alter the thermodynamic limitations to provide a higher hydrogen yield.

\[
\text{WGSR: } \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -40.6 \text{ kJ/mol} \quad (1)
\]

An effective technique to shift the reaction for enhanced hydrogen generation has been to remove hydrogen from the reaction mixture. However, membranes cannot completely remove hydrogen from the mixture. Another option for driving the WGS reaction forward is to remove CO₂ from the reaction mixture by reacting it with CaO. The carbonation reaction can be written as:

\[
\text{Carbonation Reaction: } \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \quad (\Delta H = -178 \text{ kJ/mol}) \quad (2)
\]

Thermodynamic analyses reveal the suitable reaction temperature ranges at which the CO₂ concentration can be lowered down to ppm levels by carbonation reaction (2). Thus, one can maximize production of hydrogen from coal. By conducting the WGSR such that CO is the limiting reactant, we can ensure complete utilization of the fuel as well. Besides these advantages, CO₂ is simultaneously removed from the gas mixture in the form of CaCO₃, thereby improving the purity of the hydrogen stream (the other contaminant being only water). The spent sorbent can then be calcined separately to yield a pure sequestration ready CO₂ stream, which is then amenable for compression and liquefaction before its transportation to sequestration sites. Calcination reaction, reverse of the carbonation reaction can be written as:

\[
\text{Calcination Reaction: } \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (\Delta H = +178 \text{ kJ/mol}) \quad (3)
\]

The resulting CaO sorbent is recycled to capture CO₂ in the next cycle. This cyclical CCR process can be continued as long as the sorbent provides a satisfactory CO₂ capture. However, for the sorbent to sustain its activity over multiple CCR cycles it needs to be calcined efficiently. High temperature causes sorbent sintering. This is especially crucial if calcination is carried out
at ambient pressure because thermodynamic analyses predict high temperature (>890°C) for CaCO₃ calcination. This analysis forms another basis for studying sub-atmospheric or vacuum calcination procedures.

**Sub-atmospheric (vacuum) calcination**

It has been suggested in literature that CaO procured from the calcination of limestone under vacuum has a higher reactivity. Beruto and Searcy (1976) observed that, under air calcination at 650 - 800 °C, sharp edges of calcite powder were replaced by rounded surfaces and neck areas indicating severe sintering. The resulting CaO structure was highly crystalline as well. In contrast, the sharp edges of calcite were retained in the CaO obtained under vacuum. However, the CaO did not possess a high degree of crystallinity. The latter also showed high reactivity towards hydration. Dash et al., (2000) also observed a metastable-nanocrystalline calcia under vacuum and stable microcrystalline when calcined in helium. Beruto et al., (1980) estimated the surface area and pore volume of limestone based CaO to be about 78-89 m²/g and 0.269 ml/g respectively. However, this calcination occurred at 550°C under very high vacuum levels (aided by diffusion pumps) and the calcination took about a week to complete. While it is beneficial to observe a high SA and PV in the resulting CaO sorbent, such a calcination procedure is both time consuming and very expensive. A practical calcination technique that optimizes kinetics and sorbent morphology while attaining CO₂ separation goals needs to be developed.

Ingram and Marrier (1963) reported that the rate of reaction varies linearly with the difference between equilibrium partial pressure and the partial pressure of CO₂ surrounding the solid. This further supports the need for sub-atmospheric calcination that continuously removes CO₂ as it is formed around the calcining CaCO₃ particles. Experimentally, Kelley & Anderson (1935) demonstrated the onset of calcination at 640 °C, which would be the lower temperature bound for the CCR process under consideration.

This report describes the ongoing investigation which depicts the role of calcination temperature, level of vacuum, thermal properties of diluent gas, effect of diluent flow, on the kinetics of calcination and the morphology of the resultant CaO sorbent.
**EXPERIMENTAL**

**Calciner Design Details**

Figure 1 illustrates further details of the calciner system, for which a detailed description is provided in the previous Annual Report (September 2004). This diagram shows the 3-D layout of the reactor tube and the electric furnace surrounding it. It also illustrates the choice of the diluent gas among helium, nitrogen and argon that have been used in the experiments, whose results are described in this report in later sections.

![Figure 1: 3-D schematic diagram of the calciner reactor setup.](image)

**Multi-Fixed Bed Reactor Design**

*Rationale for novel reactor design*

We had performed simultaneous water gas shift and carbonation reactions in a fixed bed reactor using a catalyst-sorbent mixture. High temperature shift (HTS) catalyst (iron oxide supported on chromium oxide) was obtained from Süd-Chemie, Inc. OSU patented Precipitated calcium carbonate (PCC) and hydrated-lime from naturally occurring limestone (Linwood Hydrate, LH) were used as the precursors for the carbonation sorbents. The details of the investigation have been reported in the Annual Technical Progress report (September 2004). During the
experiments, after the sorbent bed had achieved the initial breakthrough, the bed was regenerated by calcining the CaCO₃ formed in flowing N₂ at 700 °C. This regeneration was performed *in-situ* by heating the fixed bed containing sorbent-catalyst mixture concurrently. Subsequently, the catalyst-sorbent bed was subjected to a second WGSR-carbonation reaction cycle. However, the sorbent-catalyst bed depicted poor performance in the 2nd reaction cycle and the system was not even able to reach the sorbent-free (equilibrium) CO conversion of 81%. As a part of another study, the individual sorbents (without catalyst) had been subjected to numerous carbonation-calcination reaction cycles in a 10% CO₂ stream at 700 °C (Iyer et al, 2004). The sorbents depicted satisfactory performance without losing substantial reactivity over consecutive cycles as observed in this specific case. Thus, loss in this reactivity can be attributed to the loss in the catalyst activity after the 1st regeneration cycle. This is because the catalyst was subjected to CO₂, an oxidizing atmosphere, during the calcination phase. Thus, the deactivated catalyst was not able to catalyze the WGSR in the subsequent 2nd reaction phase resulting in poor CO conversion in the 2nd cycle.

These observations of catalyst deactivation are similar to those by Harrison and co-workers who report a single-step sorption-enhanced process to produce hydrogen from methane (Balasubramanian et al., 1999; Lopez-Ortiz and Harrison, 2001). They used the traditional concept of SMR with WGS using Ni-based catalyst to produce hydrogen, coupled with the novel scheme of *in-situ* continuous CO₂ capture using a calcium-based dolomite sorbent. However, they regenerated the dolomite sorbent in streams of N₂, 4%O₂ in N₂ and pure CO₂. They had to use high regeneration temperatures of 800-950 °C, especially while using pure CO₂. Exposure of the reforming catalyst to an oxidizing atmosphere (*viz*. O₂/N₂ or CO₂) while regenerating the sorbent used to oxidize their Ni catalysts to NiO. Hence, their deactivated catalyst had to be reduced back to Ni before every cycle using hydrogen. This is evident from the fact that it took about 20 minutes for the H₂ concentration maximize.

Another alternative would be to separate the sorbent-catalyst mixture after every reaction phase such that only the sorbent is subjected to the regeneration conditions while the catalyst remain unaffected. In addition, calcination in a pure CO₂ stream will result in higher operating temperatures due to the thermodynamic limitations of the calcination reaction in presence of the
CO₂ product. Higher temperatures and the presence of CO₂ during calcination would cause both the sorbent to sinter and the catalyst to deactivate. Hence, there is a need for a reactor design that prevents the catalyst from deactivation due to exposure to CO₂ product during calcination.

*Envisaged novel Multi-Fixed Bed Reactor*

The schematic illustration of the novel multi-fixed bed reactor is shown in Figure 2 below. The reactor consists of alternating fixed beds of HTS catalyst followed by CaO sorbent. During the reaction phase, the water gas reactant mixture, consisting of predominantly CO and H₂O enters one end of the reactor. Simultaneous WGSR and carbonation reactions occur, leading to enhanced hydrogen production. Finally, product gas, rich in hydrogen, leaves the other end of the reactor. Subsequently, in the regeneration phase, the two ends of the reactor are sealed and a diluent gas flow is introduced in between each of the three catalyst beds. Thus, there are three ports for introducing the diluent gas. In addition, vacuum will be introduced in between each of the sorbent beds as shown in the figure. These vacuum ports are strategically placed such that the applied vacuum will draw out the flowing diluent gas enabling calcination of the reacted sorbent. Besides, the CO₂ formed during the calcination process should flow out through these vacuum ports preventing the contact between the catalyst bed and CO₂. Besides, the use of sub-atmospheric calcination should lower the calcination temperature. Thus, we envision the sustenance of the catalyst activity and the sorbent reactivity. Nitrogen will be used as the diluent gas during initial testing phase. Future alternatives include the use of steam or steam/CO₂ mixtures.

This setup enables us to demonstrate the effect of CO₂ on catalyst activity. However, under actual operating mode, as shown in the Project Vision outlined in the Annual Technical Progress report (September 2004), the sorbent particles will be injected upstream of the WGS catalyst bed. This is an entrained flow system whereby the particles flow through the catalyst bed enhancing hydrogen production and capturing CO₂. The reacted sorbent particles are subsequently separated from the gas mixture, calcined in a separate rotary calcined and subsequently injected for carbonation. Thus, the contact between CO₂ resulting during calcination and WGS catalyst would not occur under commercial scale operation as envisioned for a coal-gasification plant. However, it is not feasible to demonstrate this under laboratory scale of operation.
Figure 2. Schematic of novel multi-fixed-bed reactor for investigating the effect of CO$_2$ during regeneration on the catalyst performance.
RESULTS AND DISCUSSION

Thermodynamics of sub-atmospheric Calcination

The thermodynamics of calcination, evaluated by HSC chemistry software, is represented in the form of equilibrium partial pressure of CO$_2$ as a function of temperature, as shown in Figure 3.

![Equilibrium Partial Pressure of CO$_2$ as obtained by thermodynamics (0-1 atm)](image)

This figure indicates that carbonation is favored under process conditions above the curve and calcination occurs at conditions below the equilibrium curve. For example, the Gibbs free energy of calcination is negative for temperatures above 890°C for a partial pressure of CO$_2$ (P$_{CO2}$) of 1 bar. It has been amply demonstrated that the ultimate CO$_2$ capture capacity (W) of most sorbents employed at high temperature monotonically falls with increasing number of CCR cycles (Abanades and Alvarez, 2003; Iyer et al., 2004). While numerous studies have been conducted on the carbonation reaction to detail the sorbent reactivity, kinetics, mechanism and its mathematical modeling, sufficient emphasis has not been placed on the calcination process, as it relates to this CO$_2$ separation process. Current calciner designs primarily involve the combustion
of fuel with air inside the rotating tube to supply the sensible heat and heat of calcination directly. The exiting gases, still dominated by nitrogen, are enriched in CO$_2$, which is released from the calcining limestone. However, this design is not amenable to generating a pure CO$_2$ stream. It is thus imperative that the calcination designs and methods be optimized to maintain the sorbent structure to maximize reactivity, in a way that the purity of the eventual CO$_2$ stream is not compromised.

**Calcination Configurations**

![Calcination Configurations Diagram](image)

Figure 4: (a) Direct fired Calcination Configuration. (b) Indirect fired Calciner Configurations

This CCR scheme can be carried out in two modes of operation *viz.* temperature and pressure swing and any combination thereof. Calcination can be induced by either increasing the temperature of the carbonated product or by reducing the P$_{CO_2}$ in the calciner such that the
process conditions fall below the thermodynamic equilibrium curve. Figure 4 shows various configurations of the calciner operation which detail the mode of heat input to the calciner.

The usage of air in Figure 4(a) represents direct calcination, which is representative of the commercial calcination process mentioned earlier. However, a similar reactor design can be implemented in the CCR scheme if pure oxygen is used in place of air. The fuel would then form only CO₂ and H₂O due to its combustion. The released CO₂ from reacted product and the CO₂ from the fuel combustion can now be further purified by a simple condensation and removal of steam. Depending on the fuel used for the direct calcination, other trace gases such as SOx and NOx may be emitted, necessitating further control technologies. In particular, make-up calcium would be necessary to replace the sorbent consumed by SO₂ in the calciner (Iyer et al., 2004).

Alternatively, in the absence of pure oxygen, the heat of calcination can be supplied indirectly as shown in Figure 4(b). The addition of heat will induce calcination, which leads to CO₂ buildup in the calciner. However, the flow of CO₂ out of the reactor is possible only if the P_{CO₂} becomes greater than 1 bar. Thermodynamically, P_{CO₂} becomes greater than 1 bar only above 890°C. It is well known that high temperatures cause sorbent sintering, which reduces its porosity, thereby leading to a drastic reduction in reactivity. Pressure swing mode of operation enables lowering of the calcination temperature to circumvent the sintering problem. A lower P_{CO₂}, required by pressure swing operation, is achieved by either dilution of evolved CO₂ or by an overall reduction in pressure of the calciner. For example, a reduction in P_{CO₂} below 0.0358 bar would lower the calcination temperature to below 700°C. Lowering P_{CO₂} can be accomplished by flowing diluent gas through the calciner. However, only steam is an acceptable diluent gas since any other gas such as air, nitrogen, etc. will mix with the evolved CO₂ defeating the overall objective of isolating a pure CO₂ stream. The reduction in overall calciner pressure, while maintaining 100% pure CO₂, can be achieved using a vacuum pump which removes CO₂ as it evolves from calcination.

**Scale-up of Calcination**

Extensive work has been carried out during this period on the calcination of limestone. The effect of temperature, sorbent type and level of vacuum (absolute pressure) inside the calciner on
the calcination of limestone sorbent was studied previously by our research group. The earlier experiments were carried out on 0.5-2 g samples in the 700-800°C temperature range. However, it is important to study the calcination kinetics and physical properties of the resulting CaO sorbents on larger samples in view of scale-up considerations. We have observed that heaping of CaCO₃ during its calcination causes sintering of the sorbent particles due to the CO₂ evolved due to the calcination of the surrounding calcium carbonate particles. Heaping also induces additional heat transfer resistances due to masking of the underlying sorbent by the exposed layers. The heat transfer limitations are greater and generally slow the kinetics of calcination as the only way to convey heat to the CaCO₃ is through radiation and conduction through the ceramic tube. Thus a higher calcination temperature (T=800 and 880 °C) is required when relatively larger quantity of sorbent is calcined.

![Figure 5: Effect of sorbent loading on the calcination kinetics.](image)

We have established that heaping yields a lower surface area CaO sorbent, perhaps due to CO₂ aided sintering and the higher temperature of calcination. Figure 5 shows the effect of sorbent loading on the kinetics of the calcination of naturally occurring limestone, which we termed as
Linwood Carbonate (LC). This sample was procured from Linwood Mining & Minerals Company (5401 Victoria Avenue, Davenport, IA 52807-2991). Figure 4 amply illustrates that a larger sorbent loading requires more time to calcine. While 2g sample required about 700s for 80% extent of calcination, a 15g sample required approximately three times longer residence time. The effect of heaping on heat transfer is also clearly delineated in Figure 5. We can see that it takes about 5600 seconds for the last 20% conversion when a batch of 15g sample is being calcined. This is due to the fact that the heating rate necessary for calcination of the sorbent trapped in the middle layers is not adequate enough.

**Effect of Diluent Flow rate**

![Figure 6: Effect of Diluent Flowrate (0-1000ml/min of He) - Calcination of 10g LC, 28”Hg vacuum and T=880 °C](image)

It can be observed from the Figure 6 that the calcination time required for larger samples under pure vacuum conditions is too long. However, the addition of heat to the calcining sorbent through convective means should accelerate calcination. This is accomplished through the use of a pre-heated diluent gas flow over the calcining sorbent. Figure 6 shows the effect of flow rate of
diluent helium gas on the calcination behavior. Figure 5 indicates that in the absence of diluent flow, we achieve only 78% calcination in 2000s. In contrast a steady diluent flow of 120 ml/min attains ~93% in 2000s. As the diluent flow is increased to 500 ml/min, 90% calcination occurs within 1200s. It is also useful to note that an increase in diluent flow to 1000 ml/min does not decrease the heat transfer resistance significantly.

**Effect of Diluent Type**

Calcination experiments were conducted in the presence of different diluent gas types. This is to establish qualitatively the influence of thermal properties (thermal conductivity, heat capacity) of the diluent gas on the heat transfer properties, and thereby its influence on the calcination rate. For example, at 1000K the thermal conductivity of He (0.354 W/m.K) is higher than that of N₂ (0.0647 W/m.K), which could lead to a difference in the calcination rate (Perry and Chilton, 1998). Figure 7 indicates the influence of helium, nitrogen and argon on the calcination of 10g samples of Linwood carbonate. It can be observed from Figure 7 that helium indeed causes a faster calcination.

![Figure 7: Choice of Diluent Gas (He/N2/Ar) - Calcination of 10g LC at 28”Hg vacuum T=880 ºC.](image)

Figure 7: Choice of Diluent Gas (He/N2/Ar) - Calcination of 10g LC at 28”Hg vacuum T=880 ºC.
In a commercial operation, we cannot use these particular gases because the gas mixture exiting the calciner will consist of CO$_2$, which is evolved from the calcination process and these diluent gases, thereby defeating the overall purpose of isolating a pure CO$_2$ stream. However, these experiments lay a foundation for the use of higher thermal conductivity gases such as steam (0.0978 W/m.K). Steam has the added advantage of ease of separation from steam/CO$_2$ mixtures by its removal by condensation.

**Calibration and Testing of Hydrogen Analyzer**

The state of the art hydrogen analyzer (model H2A-528) with a 0-100% operating range was finally procured from Applied Analytics, Inc (after seven months of delay in delivery). The analyzer works on a patented principle by comparison of specific heat, density, diffusion and thermal conductivity in one compact solid state sensor. In contrast, most of other hydrogen analyzers available are based on only thermal conductivity measurements. Hence, this analyzer (model H2A-528) has a unique optical bench and is expected to function satisfactorily in the presence of other gases that might interfere with the measurements including carbon monoxide (CO) and other hydrocarbons. In our system, CO is the major source of interference. Hence, it was necessary to check the effect of CO on the analyzer calibration.

As the company had several problems in fabricating the equipment as per our requirement and delayed shipping the instrument for several months. Hence, the analyzer calibration with interfacing of the LCD display with the output voltage (4-20 mA) was performed in-house. In addition, the testing for CO interference was also performed. The analyzer was first calibrated to “0%” by using a 100% N$_2$ stream. It was then adjusted to “100 %” by using a pure H$_2$ stream. The “zero” and the “span” knobs had to be adjusted to synchronize the output current, the LCD display readout and the actual hydrogen concentration. The analyzer was then tested for calibration for varying H$_2$ concentrations from 0-100% by mixing pure H$_2$ with diluent N$_2$. The calibration plot with N$_2$ as the diluent is shown in Figure 8. The observed readings were obtained from the analyzer display while the theoretical H$_2$ concentrations were obtained by calculating the H$_2$ and N$_2$ flow rates. The plot shows a linear calibration curve with significant accuracy between the observed and expected values. The calibration was then subsequently repeated for varying H$_2$ concentrations from 0-100% by mixing pure H$_2$ with diluent CO. The details are
illustrated in Figure 9. The plot clearly shows that there is no effect of CO on the analyzer operation and the two plots are identical, considering experimental errors.

![Figure 8](image8.png)

Figure 8. Calibration of H₂ analyzer for varying H₂ concentrations (0-100%) in N₂.

![Figure 9](image9.png)

Figure 9. Calibration of H₂ analyzer for varying H₂ concentrations (0-100%) in CO.

**CONCLUSIONS**

Sub-atmospheric (vacuum) calcination studies reveal the significance of vacuum level, diluent gas flow rate, thermal properties of diluent gas, and sorbent loading on the kinetics of calcination and the morphology of the resultant CaO sorbent. Higher sorbent loading leads to heaping
resulting in slower calcination kinetics due to poor heat transfer effects. This results in poor sorbent morphology that loses reactivity over subsequent cycles. Diluent gas flows during calcination augments the necessary convective heat transfer rate which is directly related to the diluent gas flow rate. This results in improved calcination kinetics and sorbent morphology. Diluent gas thermal properties like thermal conductivity and specific heat capacity play a significant role on the heat transfer rates during calcination. This was evident by investigating the effects of various inert gases like Ar, N₂ and He which are not easily separable from CO₂ after calcination. However, steam has been identified as a potential diluent which has better thermal properties and can be easily separated from CO₂.

A novel multi-fixed bed reactor was designed which isolates the catalyst bed from the sorbent bed during the calcination step. This should prevent the catalyst deactivation due to oxidation by CO₂ during the regeneration phase. In addition, the hydrogen analyzer (model H2A-528) procured from Applied Analytics, Inc. showed no evidence of CO interference while measuring H₂ concentrations, a major problem with many analyzers, leading to accuracy in data measurement.

**Current Status of the Project**

A new multi-fixed bed reactor design that isolates the sorbent from the catalyst, and prevents the exposure of CO₂ to the catalyst has been completed and will be fabricated. In addition, the fabrication of the high-temperature high-pressure Magnetic Suspension Balance (HTHP-MSB) from VTI Corporation, FL, USA is nearing completion. The German made balance from Rubotherm has been incorporated in the equipment. In addition, the mass flow controllers from Brooks Instruments (model 5850E), which had been calibrated and tested last year have been also integrated into the HTHP-MSB. The control display with essential automation needs to be integrated before the unit is available for testing. Recent photographs of the unit are illustrated in Figure 12.
Figure 10. Photographs of the high-temperature high-pressure Magnetic Suspension Balance from VTI Corporation, FL, USA.

Conference Presentations
This project has resulted in following conference papers/presentation during the reporting period.


REFERENCES


