

# DEVELOPMENT OF A CATALYST/SORBENT FOR METHANE REFORMING

## FINAL REPORT

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**ABSTRACT**

This project led to the further development of a combined catalyst and sorbent for improving the process technology required for converting  $\text{CH}_4$  and/or  $\text{CO}$  into  $\text{H}_2$  while simultaneously separating the  $\text{CO}_2$  byproduct all in a single step. The new material is in the form of core-in-shell pellets such that each pellet consists of a  $\text{CaO}$  core surrounded by an alumina-based shell capable of supporting a  $\text{Ni}$  catalyst. The  $\text{Ni}$  is capable of catalyzing the reactions of steam with  $\text{CH}_4$  or  $\text{CO}$  to produce  $\text{H}_2$  and  $\text{CO}_2$ , whereas the  $\text{CaO}$  is capable of absorbing the  $\text{CO}_2$  as it is produced. The absorption of  $\text{CO}_2$  eliminates the reaction inhibiting effects of  $\text{CO}_2$  and provides a means for recovering the  $\text{CO}_2$  in a useful form.

The present work showed that the lifecycle performance of the sorbent can be improved either by incorporating a specific amount of  $\text{MgO}$  in the material or by calcining  $\text{CaO}$  derived from limestone at  $1100^\circ\text{C}$  for an extended period. It also showed how to prepare a strong shell material with a large surface area required for supporting an active  $\text{Ni}$  catalyst. The method combines graded particles of  $\alpha$ -alumina with noncrystalline alumina having a large specific surface area together with a strength promoting additive followed by controlled calcination. Two different additives produced good results:  $3\text{ }\mu\text{m}$  limestone and lanthanum nitrate which were converted to their respective oxides upon calcination. The oxides partially reacted with the alumina to form aluminates which probably accounted for the strength enhancing properties of the additives. The use of lanthanum made it possible to calcine the shell material at a lower

temperature, which was less detrimental to the surface area, but still capable of producing a strong shell.

Core-in-shell pellets made with the improved shell materials and impregnated with a Ni catalyst were used for steam reforming  $\text{CH}_4$  at different temperatures and pressures. Under all conditions tested, the  $\text{CH}_4$  conversion was large ( $>80\%$ ) and nearly equal to the predicted thermodynamic equilibrium level as long as  $\text{CO}_2$  was being rapidly absorbed. Similar results were obtained with both shell material additives. Limited lifecycle tests of the pellets also produced similar results that were not affected by the choice of additive. However, during each lifecycle test the period during which  $\text{CO}_2$  was rapidly absorbed declined from cycle to cycle which directly affected the corresponding period when  $\text{CH}_4$  was reformed rapidly. Therefore, the results showed a continuing need for improving the lifecycle performance of the sorbent.

Core-in-shell pellets with the improved shell materials were also utilized for conducting the water gas shift reaction in a single step. Three different catalyst formulations were tested. The best results were achieved with a Ni catalyst, which proved capable of catalyzing the reaction whether  $\text{CO}_2$  was being absorbed or not. The calcined alumina shell material by itself also proved to be a very good catalyst for the reaction as long as  $\text{CO}_2$  was being fully absorbed by the core material. However, neither the alumina nor a third formulation containing  $\text{Fe}_2\text{O}_3$  were good catalysts for the reaction when  $\text{CO}_2$  was not absorbed by the core material. Furthermore, the  $\text{Fe}_2\text{O}_3$ -containing catalyst was not as good as the other two catalysts when  $\text{CO}_2$  was being absorbed.

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## EXECUTIVE SUMMARY

In the first phase of this innovative research project, it was shown how a new material can be made and used for greatly simplifying the complex, multistep, industrial process which is presently used for steam reforming methane to produce hydrogen. The new material combines a catalyst for the reforming reaction with a sorbent for the byproduct carbon dioxide. The sorbent occupies the core of a pellet contained within a porous protective shell that supports the catalyst. The material is easily prepared with a revolving drum pelletizer by first pelletizing powdered limestone to form the cores and then continuing the process to add a relatively thick coating of shell-forming material to each core. The latter is generally a mixture of powdered alumina and limestone which form a hard shell when the pellets are calcined. The shells are subsequently impregnated with a Ni catalyst. Preliminary testing showed that the new material is capable of steam reforming  $\text{CH}_4$  in a single step when utilized in a fixed bed reactor at  $600^\circ\text{C}$  and 1.0 atm.

During the second phase of the project, which is the subject of this report, the sorbent and shell materials were further developed to improve the lifecycle performance of the materials. Initial testing had shown that the absorption capacity of CaO derived from limestone declined as the material was subjected to the cyclic process of  $\text{CO}_2$  absorption and regeneration. To reduce the rate of decline, other CaO precursors were considered. This led to the discovery a calcined mixture with 0.25 g MgO/g CaO was a more stable sorbent than CaO. Furthermore, the initial sorbent calcination conditions also affected the rate of decline. Therefore, a sorbent prepared by calcining limestone at  $1100^\circ\text{C}$  for 2 hr was more stable than one calcined at  $900^\circ\text{C}$  for 3 hr. Consequently, by the end of a 1200 cycle test, the absorption capacity of materials prepared by either method was 45% greater than that made by calcining limestone at  $900^\circ\text{C}$ .

The development of a strong, porous shell material with a large surface area for supporting an active Ni catalyst required combining several different grades and particle sizes of alumina in appropriate concentrations together with a small amount of limestone or other sintering promoter. Other variables included the calcination temperature and time. The particle mixture included a large fraction of  $\alpha$ -alumina to impart strength to the finished material and a smaller fraction of noncrystalline alumina with a large specific surface area to provide the necessary surface area. Although the inclusion of 10 wt% limestone (3  $\mu\text{m}$  size) in the mixture produced a shell material with the required compressive strength after calcination at  $1100^\circ\text{C}$ , similar results were achieved by the inclusion of lanthanum nitrate which formed  $\text{La}_2\text{O}_3$  when calcined. The  $\text{La}_2\text{O}_3$  proved advantageous because it provided a high compressive strength at a lower temperature which was less detrimental to the surface area.

To demonstrate the use of the improved shell material, core-in-shell pellets were prepared, some with Microna 3 limestone in the shell and others with lanthanum nitrate in the shell. In each case the bulk of the shell material consisted of the same mixture of  $\alpha$ -alumina and noncrystalline alumina. The resulting core-in-shell pellets were subsequently impregnated with a Ni catalyst and then tested in a fixed bed reactor to see how well they would perform while reforming methane under different operating conditions. Each test run was characterized by an initial period of operation when most of the  $\text{CO}_2$  produced was rapidly absorbed by the freshly regenerated sorbent followed by a period of slow  $\text{CO}_2$  absorption as the sorbent approached saturation. In a subsequent series of test runs conducted at different temperatures (550, 600, and

650°C) and pressures (1, 3, 5 and 10 atm), the results obtained with the two kinds of core-in-shell pellets were remarkably similar. In both cases the CH<sub>4</sub> conversion during the fast CO<sub>2</sub> absorption period was large (>80%) and nearly equal to the predicted thermodynamic equilibrium value for a given temperature and pressure. Furthermore, the conversion of CO was essentially 100% for any given temperature and pressure.

To further evaluate the performance of the core-in-shell pellets with the two different shell formulations, limited lifecycle tests were conducted by reforming CH<sub>4</sub> at 1.0 atm using a 3:1 mole ratio of steam to CH<sub>4</sub>. Pellets with each shell formulation were subjected to 10 cycles of CH<sub>4</sub> reforming and sorbent regeneration. Each cycle consisted of a prolonged period when CH<sub>4</sub> was reformed at 650°C followed by an extended period of sorbent regeneration at 850°C. During a large portion of the first period when most of the CO<sub>2</sub> generated was rapidly absorbed, CH<sub>4</sub> conversion remained at a high, constant level. However, as the number of cycles increased the time during which CO<sub>2</sub> was rapidly absorbed decreased which caused the conversion of CH<sub>4</sub> to drop off as well. Since similar changes were observed with both kinds of core-in-shell pellets, the change in the time of rapid CO conversion was most likely due to the decrease in absorption capacity of the CaO cores, which had been noted previously, rather than to any change in the shell material. Various physical tests conducted on the core-in-shell pellets before and after the lifecycle tests showed that pellets with the different shell formulations experienced similar changes in surface area and compressive strength.

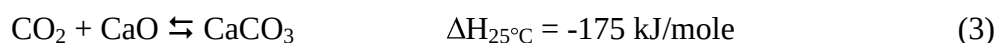
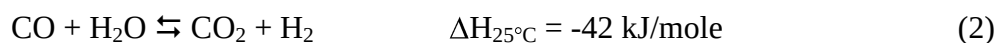
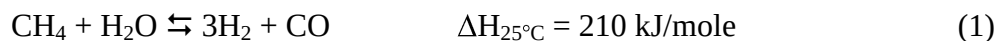
Finally core-in-shell pellets with three different catalyst formulations were tested for application to the water gas shift reaction to see whether a more durable and less costly catalyst could be found. One formulation was identical to the alumina and 10 wt% Microna 3 limestone formulation used for conducting CH<sub>4</sub> reforming except the Ni catalyst was omitted. A second formulation was identical to the first except that 10 wt% Fe<sub>2</sub>O<sub>3</sub> was included. The third formulation was similar to the Ni catalyst formulation used for CH<sub>4</sub> reforming except that it was made with a coarser limestone (-212/+63 µm) in 5 wt% concentration. Core-in-shell pellets with these formulations were subsequently tested in the fixed bed reactor supplied with steam and CO in a 3:1 mole ratio. These tests were conducted at 1.0 atm and at different temperatures ranging from 480 to 600°C. As anticipated the best results were achieved with the Ni catalyst. The CO conversions obtained with this catalyst closely approximated the thermodynamic equilibrium values whether CO<sub>2</sub> was completely absorbed or not absorbed at all.

The results obtained with the formulation composed of only alumina and limestone were almost the same as those achieved with the Ni catalyst during the period when virtually all of the CO<sub>2</sub> was absorbed. However, during the period when no CO<sub>2</sub> was absorbed, the CO conversion was much lower, although it did improve as the temperature was raised. Therefore, it appeared that while CO<sub>2</sub> was being rapidly removed from the reaction mixture, the alumina and/or the associated CaO served as a good catalyst for the water gas shift reaction, but once the sorbent was saturated, the CO<sub>2</sub> partial pressure increased to the point where it interfered with the kinetics of the catalyzed reaction. The results achieved with the formulation containing Fe<sub>2</sub>O<sub>3</sub> fell between the others.

## INTRODUCTION

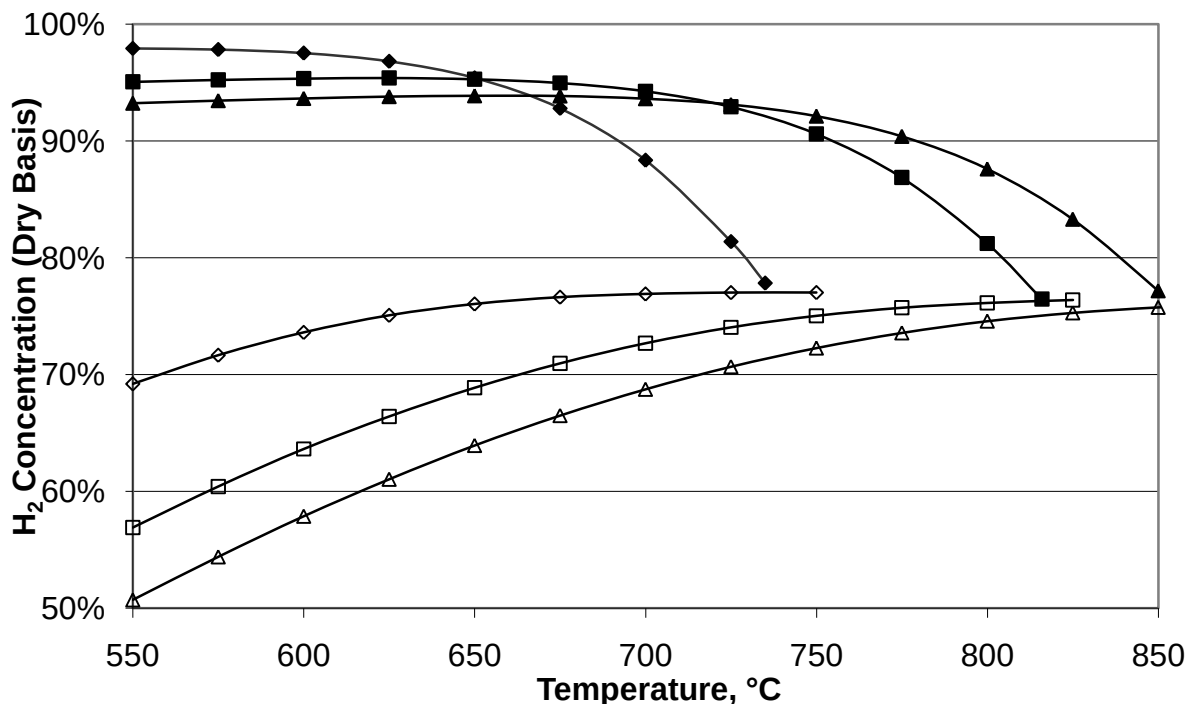
The purpose of this innovative research project was to develop a unique material that would facilitate the reaction of methane and/or carbon monoxide with steam while simultaneously separating the reaction products. The material would combine a catalyst for both the methane reforming and water gas shift reactions with a sorbent for carbon dioxide, the principal byproduct of these reactions. A reactor provided with the material would convert the product of a coal gasifier into nearly pure hydrogen in a single step, and thereby replace a complex, multistep reaction and product separation process. Therefore, the successful development of the material would provide a basis for a much more efficient and economical method of producing hydrogen from coal.

The method would make it possible to conduct all three of the following reactions within the same material provided CaO is used as a sorbent for CO<sub>2</sub>:



Since reactions 1 and 2 are limited by thermodynamic equilibrium, the absorption of CO<sub>2</sub> by CaO in reaction 3 drives reaction 2 towards completion which in turn increases the driving force for reaction 1. Because reaction 1 is endothermic, the equilibrium conversion of CH<sub>4</sub> by this reaction is favored by higher temperature. On the other hand, since reactions 2 and 3 are exothermic, the equilibrium conversion of CO by reaction 2 and the equilibrium conversion of CO<sub>2</sub> by reaction 3 are favored by lower temperatures.

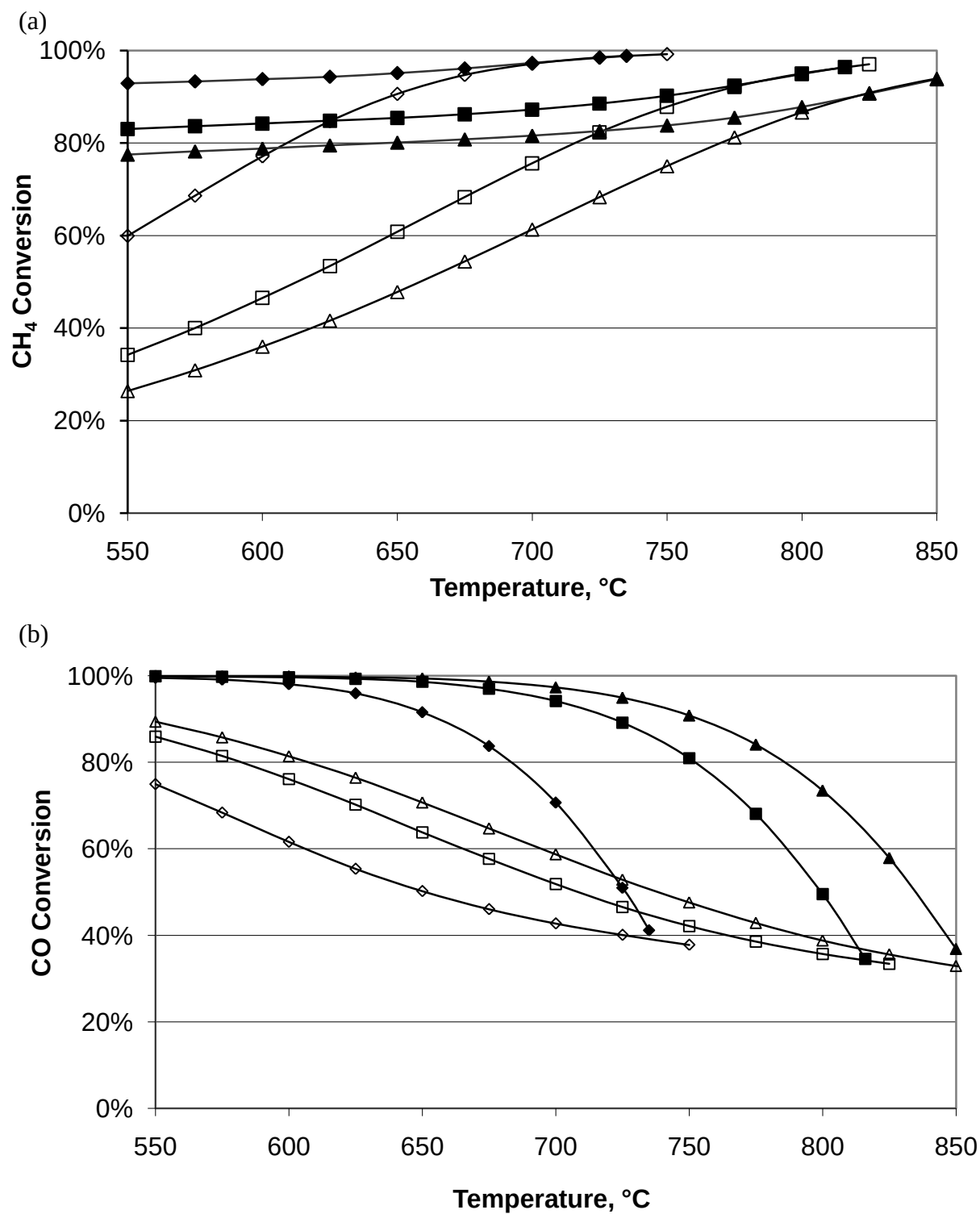
A detailed thermodynamic analysis of the reaction system is revealing. For a system supplied initially with 1.0 mole CH<sub>4</sub> and 3.0 moles H<sub>2</sub>O in chemical equilibrium, it was possible



**Figure 1.** Equilibrium H<sub>2</sub> concentrations on a dry basis for a system supplied with 1.0 mole CH<sub>4</sub> and 3.0 moles steam. The closed symbols are with CO<sub>2</sub> absorption and the open symbols are without CO<sub>2</sub> absorption at 1 atm (◇), 5 atm (□) and 10 atm (△).

to calculate the resulting H<sub>2</sub> concentrations (Figure 1). It is apparent that the H<sub>2</sub> concentration would be strongly dependent on both the system temperature and pressure and whether or not CaO is present to absorb the CO<sub>2</sub>. From such an analysis it can be seen that a much larger H<sub>2</sub> concentration can be obtained over a wide range of temperature and pressure by having CaO present to absorb CO<sub>2</sub>. The thermodynamic analysis also provided a picture of the CH<sub>4</sub> and CO conversions that can be achieved under equilibrium conditions (Figure 2). In most cases these conversions would be much greater when CaO is present.

Although these thermodynamic principles had been recognized by others<sup>1-3</sup> for a long time, no attempt had been made to conduct all three reactions within the same material until the initial phase of the present project was undertaken.<sup>4-5</sup> Instead it had been shown that the three



**Figure 2.** Equilibrium conversions of (a) CH<sub>4</sub> and (b) CO for a system supplied with 1 mole CH<sub>4</sub> and 3 moles H<sub>2</sub>O. The closed symbols are with CO<sub>2</sub> absorption and the open symbols are without CO<sub>2</sub> absorption at 1 atm (◇), 5 atm (□) and 10 atm (△).

reactions could be carried out simultaneously in a reactor packed with a mixture composed of discrete catalyst particles and discrete sorbent particles.<sup>1-3</sup> Although this approach could be used with a fixed bed reactor, it would probably not prove satisfactory with either moving bed or fluidized bed reactors.

The initial development of a material that combined a Ni catalyst and sorbent for methane reforming in a single pellet was carried out in the first phase of this project.<sup>4-5</sup> The pellet was composed of a sorbent core surrounded by a porous shell of alumina. Similar core-in-shell pellets had been developed previously for desulfurizing hot coal gas and consisted of a core derived from limestone encased in a porous but strong shell of alumina.<sup>6-9</sup> Since the CaO cores were weak and tended to decrepitate, the pellets had been strengthened with alumina shells for greater durability. Fortuitously, the alumina shells also provided a means for supporting a nickel catalyst, which was subsequently demonstrated.<sup>4-5</sup> Initially the shells were made largely of  $\alpha$ -alumina having a relatively low surface area. Although the material was highly resistant to crushing, it displayed only modest catalytic activity. By replacing a portion of the  $\alpha$ -alumina with a higher surface area amorphous alumina, the activity of the Ni catalyst was increased substantially but with some decline in pellet strength. Addition of limestone particles to the shell material increased its strength. A preliminary study showed that the surface area and compressive strength of the shell material was controlled by the relative concentrations and particle sizes of the  $\alpha$ -alumina, high surface area alumina, and limestone particles plus the calcination temperature and time used for sintering the shell material.<sup>4-5</sup>

It was further shown that the pellet shells could be impregnated with nickel by first soaking the calcined pellets in either an aqueous or organic solution of nickel nitrate followed by calcination at 600°C to decompose the salt into NiO.<sup>4-5</sup> The oxide was then reduced with

hydrogen to elemental nickel. The resulting catalyst was capable of reforming methane or propane when either reactant was mixed with steam in a 1:3 mole ratio of carbon to steam, and the mixture was passed over the catalyst at 600°C and 1.0 atm. In addition, the conversion of methane or propane was enhanced significantly by the absorption of CO<sub>2</sub>. Furthermore, it was shown that the catalyst/sorbent could be regenerated and reused several times without serious degradation of its catalytic properties or absorption capacity. However, it remained to be seen whether the catalytic activity and sorbent capacity could be maintained over a large number of cycles without serious degradation. Undoubtedly, additional work would be required to improve the lifecycle performance of the catalyst and sorbent and to improve the physical strength and durability of the material. Also the material needed to be tested at higher pressures and over a wider range of operating conditions to demonstrate a broader range of possible applications.

Although the primary emphasis of the second phase of this project was placed on developing a material for steam reforming methane, its potential usefulness for converting carbon monoxide into hydrogen by means of the water gas shift reaction was also evaluated.

To achieve these goals during the second phase of the project the investigation was organized into the following four tasks:

1. Improvement of the Ca-based sorbent core material to extend the lifecycle performance of the sorbent without excessive loss of CO<sub>2</sub> absorption capacity.
2. Improvement of the porous shell material and supported Ni catalyst to create strong core-in-shell pellets that have a high activity for reforming CH<sub>4</sub>.
3. Preparation and testing of core-in-shell pellets that utilize the improved core and shell formulations. This task included a performance evaluation of the more promising

formulations over a relatively wide range of operating conditions and extended time in service.

4. Evaluation of the combined catalyst and sorbent for the water gas shift reaction.

## EXPERIMENTAL METHODS

### Materials

A list of the solid materials used for preparing the sorbent core and surrounded shell formulations is presented in Table 1. The cores were generally made of limestone or in a few cases of dolomite. Limestone was obtained from two sources. Columbia River Carbonates in Washington State supplied limestone with upwards of 97%  $\text{CaCO}_3$  in two different sizes. One of these designated as Microna 3 had a mean particle size of 3.2  $\mu\text{m}$  and another designated as Microna 10 had a mean particle size of 11  $\mu\text{m}$ . Coarser limestone with 97%  $\text{CaCO}_3$  was supplied by Martin Marietta Aggregates from its quarry near Ames, Iowa. This material was

Table 1. Properties of materials used for preparing sorbent and shell materials.

| Material                           | I.D.             | Particle size<br>$\mu\text{m}$ | Surface area<br>$\text{m}^2/\text{g}$ | Supplier                   |
|------------------------------------|------------------|--------------------------------|---------------------------------------|----------------------------|
| $\text{Al}_2\text{O}_3^{\text{a}}$ | CP-7             | 6/7 <sup>b</sup>               | 250                                   | Alcoa                      |
| $\text{Al}_2\text{O}_3^{\text{a}}$ | DD-290           | 8/9.8 <sup>b</sup>             | 275                                   | Engelhard                  |
| $\alpha\text{-Al}_2\text{O}_3$     | T-64 (-325 mesh) | 8.65 <sup>b</sup>              | <1                                    | Almatis                    |
| $\alpha\text{-Al}_2\text{O}_3$     | A-16SG           | 0.48 <sup>b</sup>              | 8.2                                   | Almatis                    |
| Dolomite                           | Ohio             | -212/+63                       |                                       | Graymont Dolime            |
| Limestone                          | Microna 3        | 3.2 <sup>b</sup>               |                                       | Columbia River Carbonates  |
| Limestone                          | Microna 10       | 11 <sup>b</sup>                |                                       | Columbia River Carbonates  |
| Limestone                          | Iowa             | -212/+63                       |                                       | Martin Marietta Aggregates |

<sup>a</sup>Amorphous

<sup>b</sup>Median size

ground and screened to a size of -212/+63  $\mu\text{m}$ . Dolomitic limestone, or dolomite, was supplied by Graymont Dolime (OH) in Ohio. This material was also ground and screened to a size of -212/+63  $\mu\text{m}$ .

The pellet shells were largely composed of alumina. Two forms of  $\alpha\text{-Al}_2\text{O}_3$  were employed including T-64 tabular with a median particle diameter of 8.65  $\mu\text{m}$  and A-16SG powder with a median particle diameter of 0.48  $\mu\text{m}$ . In addition, an activated noncrystalline alumina hydrate powder was employed, and it had to be obtained from two different sources. Initially the powder was supplied by Alcoa as CP-7. Later the powder was supplied by Engelhard as DD-290. While the properties of the two materials were said to be very similar by the suppliers, the properties did differ slightly with respect to particle size and surface area.

In a few cases either lanthanum nitrate [ $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ] or magnesium nitrate [ $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] purchased from Sigma Aldrich were added to the cores. The magnesium nitrate was a reagent grade material. Due to the indeterminate nature of the hydrate in the lanthanum nitrate, a stock solution was prepared. The molarity of the stock solution was then determined gravimetrically by heating samples of a known volume of the stock solution in air to at least 900°C for 12 hr or more to convert the lanthanum nitrate to lanthanum oxide,  $\text{La}_2\text{O}_3$ , which could be weighed.

In some cases the shell material was also impregnated with the lanthanum nitrate or with other reagent grade salts including  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , which were obtained from Fisher Scientific. To prepare the Ni catalyst, the pellet shells were impregnated with a solution of nickel nitrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ]. The reagent was reported to have a purity of 99.999% by the supplier Sigma Aldrich. In one case ferric oxide ( $\text{Fe}_2\text{O}_3$ ) was employed as a

catalyst. The material was reported to have a purity of 99.6 wt% by the supplier, J. T. Baker Chemical Co.

The gas used for reaction testing of the catalyst/sorbent pellets included research grade CH<sub>4</sub> having a purity of 99.995% obtained from Air Liquide. Hydrogen (99.5% pure) from Air Products was used for reduction of the Ni catalyst prior to reaction testing of the core-in-shell pellets. Argon having a purity of 99.999% was obtained from Linweld to pressurize the reaction system prior to reaction testing.

For determining the absorption characteristics of the sorbent formulations, the sorbents were treated with a gas mixture consisting of 25 vol.% CO<sub>2</sub> and 75 vol.% N<sub>2</sub> produced by combining the two gases in controlled flow rates. The individual gases were technical grade with a purity of 99.5% according to the supplier. The sorbents were regenerated by passing the N<sub>2</sub> alone over the sorbent.

### **Sorbent Preparation for Characterization**

Sorbents in the form of CaO were prepared from limestone or other potential precursors in powder form by initially calcining about 6 g of the material spread in a thin layer in a quartz boat. The boat was heated in a horizontal tube oven from room temperature to 900°C over 2 hr, and then it was held at this temperature for a specified time, usually 3 hr. The calcined material was then cooled to room temperature over another 2 hr period. Some materials were calcined at 1100°C for a specified time, either 2 or 5 hr, after being heated from room temperature over a 3 hr period. The calcined material was then cooled to room temperature over a 2 hr period. All initial calcinations were conducted under a stream of air. In a few cases absorption tests were performed on an uncalcined material in which case the material was noted as “uncalcined.”

For some studies, magnesium nitrate or lanthanum nitrate was added to Microna 3 limestone in an amount designed to provide an appropriate concentration of either oxide in the calcined sorbent. This limestone was conservatively assumed to contain 97 wt%  $\text{CaCO}_3$ . The nitrate salt was dissolved in tetrahydrofuran (THF) and an appropriate amount of this solution was added to the Microna 3 to form a thick paste when mixed in a mortar. After mixing, the THF was evaporated, and the resulting powder was dried in the mortar at  $120^\circ\text{C}$  for at least 5 hr. The powder was then reground in the mortar and calcined at the appropriate temperatures using the temperature ramping procedures described above. Some sorbent tests were performed using Microna 3 limestone, which had been calcined prior to adding one of the nitrates. The procedure was the same as the preceding one except that the Microna 3 limestone was calcined in flowing air at  $750^\circ\text{C}$  for 5 hr before adding the nitrate. All samples were stored in a desiccator between the time of preparation and the time of characterization.

### **Sorbent Characterization Methods**

The absorption capacity and the effect of multiple absorption and desorption cycles on the life of the sorbent were determined with a thermogravimetric analysis (TGA) system which utilized a Cahn 2000 electrobalance. The sorbent was tested as a powder contained in a small ceramic, cylindrical cup, which had a diameter of 6 mm and height of 6 mm. The cup was half filled with sorbent material, which typically provided a sample mass of 20-40 mg. However, the mass would vary depending on the density of the material. For calcium acetate only 11.2 mg would half fill the cup. For testing, the sample was suspended in a vertical quartz tubular reactor having an inside diameter of 25 mm and was subjected to a series of absorption and desorption cycles conducted isothermally at  $750^\circ\text{C}$  and at 1.0 atm. During an absorption step a gas stream composed of 25 vol.%  $\text{CO}_2$  and 75 vol.%  $\text{N}_2$  was supplied to the reactor at a rate of

3.72 mmol/min for 20 min. This was followed by a desorption step in which only N<sub>2</sub> was supplied for 30 min at a flow rate of 2.79 mmol/min. The two steps constituted a complete cycle. While these conditions did not produce the high concentration of CO<sub>2</sub> required for an industrial application, they were well suited for experimentally conducting a large number of absorption and regeneration cycles because they did not require varying the temperature throughout each cycle which would have been very time consuming overall.

Scanning electron microscope (SEM) images of the sorbent were collected by using a JEOL 840A SEM. Images were collected using an accelerating voltage of 20 kV and secondary electron imaging. The fresh sorbent samples were imaged after initial calcination at 900°C for 3 hr and tested sorbent samples were imaged following recarbonation of the samples after the 30<sup>th</sup> cycle.

The pore volume distribution of selected samples of sorbent material was determined with a Micromeritics ASAP 2020 instrument. The BJH method of desorption analysis was employed in which nitrogen was adsorbed at -196°C. This method required a larger sample of material than could be treated with the TGA system. Therefore, samples of sorbent material were treated in a heated, horizontal tubular reactor that could accommodate a quartz boat holding about 8 g of material. The samples were treated isothermally at 750°C by a cyclic process consisting of a 20 min. absorption step followed by a 30 min. desorption step. A gas mixture consisting of 25 vol.% CO<sub>2</sub> and 75 vol.% N<sub>2</sub> was supplied at a rate of 9.24 mmol/min for absorption while only nitrogen was supplied at a rate of 6.93 mmol/min for desorption. The process was interrupted periodically to remove a 0.5 g sample of material for analysis. This was timed so that the sample was collected 5 min. before the end of a desorption step.

### Shell Material Preparation for Characterization

The shell material formulation was composed largely of alumina together with a small amount of an additive such as limestone. Akiti et al.<sup>9</sup> had found previously that a 3:2 mass ratio of T-64  $\alpha$ -alumina to A-16SG  $\alpha$ -alumina was optimum. For the present study, half of the T-64  $\alpha$ -alumina was replaced with either DD-290 or CP-7 amorphous alumina to provide a larger surface area for supporting a nickel catalyst. This resulted in a specific mixture of alumina particles consisting of 30 wt% CP-7 or DD-290, 30 wt% T-64, and 40 wt% A-16SG that was employed throughout the present study. According to Engelhard, the supplier of DD-290, this material was equivalent to CP-7. For part of the study this mixture was combined with either limestone or another additive. If limestone was used, the proportions were such that the overall mixture contained either 5 or 10 wt% limestone which provided a Ca:Al atomic ratio of 0.026 or 0.055. These values are based on the assumption that the limestone contained 97 wt%  $\text{CaCO}_3$ . The same atomic ratios were employed when calcium was replaced with lanthanum, zinc or barium. This procedure resulted in the equivalent concentrations of the various oxides reported in Table 2.

**Table 2.** Equivalent concentrations of different oxides in two-component mixtures with  $\text{Al}_2\text{O}_3$ .

| Limestone<br>Conc., wt% | Ca:Al<br>Atomic Ratio | Equivalent Oxide Concentration, wt% |                         |      |     |
|-------------------------|-----------------------|-------------------------------------|-------------------------|------|-----|
|                         |                       | CaO                                 | $\text{La}_2\text{O}_3$ | BaO  | ZnO |
| 3                       | 0.015                 | 1.6                                 | 4.6                     | 4.3  | 2.3 |
| 5                       | 0.026                 | 2.7                                 | 7.7                     | 7.2  | 3.9 |
| 10                      | 0.055                 | 5.7                                 | 14.9                    | 14.2 | 8.1 |

The majority of the samples in this study were prepared for testing as cylindrical tablets having a diameter of 6 mm and thickness of 6 mm. A 20 g batch of tablets was prepared by first weighing out appropriate amounts of alumina and limestone and mixing the powders. The dry mixture was then combined with 5 to 7 ml of a 5 wt% lignin in deionized water solution to prepare a viscous, well-mixed suspension, which was poured into a plastic mold coated with a mold releasing agent. The tablets were allowed to dry overnight at atmospheric conditions prior to removal from the mold. This method produced about 45 tablets per batch.

In some cases limestone was replaced with calcium, lanthanum, zinc or barium nitrate. In these cases 20 g of the alumina mixture was weighed and an appropriate amount of the nitrate salt dissolved in solution was mixed with the alumina using a mortar and pestle to produce a thick paste. After the paste had been mixed thoroughly and allowed to dry at room temperature, it was placed in a drying oven at 110°C for at least 5 hr. After drying, the resulting powder was reground if necessary and used to make tablets by first adding a 5 wt% lignin solution to produce a viscous, well mixed suspension that was then placed in a mold with a mold releasing agent. When calcium, lanthanum or zinc nitrate was mixed with alumina, tetrahydrofuran (THF) was used as the solvent. However, barium nitrate required using water as the solvent because of its low solubility in THF. This method also produced about 45 cast tablets.

All the samples were calcined at high temperature in an atmosphere of flowing air to increase the physical integrity of the tablets and pellets. Some samples were calcined at 900°C for 3 hr after being heated gradually from room temperature over a two-hour period. Other samples were calcined at 1100°C for 2 hr following a 3 hr heating ramp to 1100°C. All of the calcined materials were cooled using a 2 hr ramp back to room temperature.

Calcined tablets or pellets that subsequently were stored or exposed to air for some time before testing were recalcined to destroy any hydroxides or carbonates that could have formed on exposure to the atmosphere. The re-calcination was conducted at 750°C for 0.5 hr, and then the calcined materials were cooled immediately before conducting breaking force tests.

### **Shell Material Characterization**

The force required to break tablets or pellets was determined with an Accuforce EZ 250 instrument. A single pellet or tablet was placed between two flat plates, and the top plate was lowered at a rate of 10 mm/min. Cylindrical tablets were placed with their flat surfaces facing the plates. A small piece of cardboard was placed on either side of a tablet to distribute the force evenly over the sample; cardboard was not used in compressive force measurements of spherical core-in-shell pellets. The force that caused the pellet to break was taken to be the breaking force. In the case of a cylindrical tablet, the breaking force was divided by the flat surface area to provide the compressive strength that was recorded as the pressure required to break a sample in MPa. In the case of cylindrical tablets made with added limestone, the measurement was repeated with 40 different tablets to determine an average value and the 95% confidence limits. When a nitrate salt was substituted for the limestone, only 20 different tablets were broken.

The surface area of selected tablets was determined with a Micromeritics ASAP 2020 instrument that employed the BET method using nitrogen at -196°C. Five intact cast tablets which altogether weighed about 1.5 g were utilized for each test.

Powder X-ray diffraction (XRD) was used to determine reaction products formed when the tablets were calcined. A Siemens D-500 Diffractometer using Cu K $\alpha$  radiation with a graphite monochromator was used for this purpose. Samples, which had previously been used for measuring breaking force, were ground with an agate mortar and pestle and back-loaded into

a holder. A voltage of 50 kV and a current of 27 mA were employed. The divergence slits used were  $1.0^\circ$ , and the detector slit used was  $0.15^\circ$ . A counting time of 4 sec was engaged while rotating the sample at 54 rpm.

A semi-quantitative analysis of relevant crystalline phases was carried out on the results obtained by XRD measurements. The height of the most intense peak, or  $I_{100}$ , of the reported phase and the height of  $I_{100}$  of the  $\alpha\text{-Al}_2\text{O}_3$  phase were determined. The ratio of  $I_{100}$  (reported phase)/ $I_{100}(\alpha\text{-Al}_2\text{O}_3)$  is reported in order to relay the relative amount of the reported phase present. Powder diffraction files (PDF's) provided by The International Centre for Diffraction Data were consulted for the location of  $I_{100}$  in the measured diffractograms.

The pore sized distribution of selected tablets, which had been calcined, was determined by employing mercury intrusion porosimetry. The measurements were conducted with a Quantachrome PoreMaster mercury porosimeter. For each determination a sample consisting of three intact cylindrical cast tablets having a total mass of 0.9 g was used. The cumulative mercury intrusion curve was recorded, and the volume/pressure relationship was calculated using the Washburn equation. For this calculation a mercury contact angle of  $140^\circ$  and a surface tension of  $480 \text{ erg/cm}^2$  were used. The pore distribution was calculated as the derivative of the volume of the mercury intrusion curve with respect to the log of the pore diameter, or  $dV/d(\log d)$ .

### **Preparation of Core-in-shell Pellets for Testing**

Spherical core-in-shell pellets were prepared by first pelletizing powdered limestone in a rotating conical drum pelletizer that had a maximum diameter of 25 cm and was operated at 30 rpm. A small quantity of Microna 3 limestone powder was placed in the revolving drum, and it was sprayed with water intermittently so that it balled up into small pellets as the drum

revolved. Pellet cores were built up in this way until about 20 g of pellets ranging between 5 and 6 mesh, or between 3.96 mm and 3.35 mm in diameter, were produced. The cores were then hardened by operating the drum at the following speeds for the indicated times: 10 rpm for 10 min., 30 rpm for 20 min., 60 rpm for 30 min., and 90 rpm for 30 min.

The cores were subsequently coated with a shell formulation in powder form by using the revolving drum pelletizer. As the prepared cores rolled and tumbled in the pelletizer, the shell powder was added gradually while the pellets were sprayed intermittently either with deionized water or with a 5.0 wt% lignin in water solution. As the process continued, the coating of shell material increased in thickness until the pellets were between 4 and 5 mesh in size or between 4.76 and 3.96 mm in diameter. The core-in-shell pellets were subsequently hardened by using the same procedure described above for the cores.

Two types of shell formulations were employed for coating the pellet cores, although each type was composed largely of powdered alumina having the following composition: 30 wt% DD-290, 30 wt% T-64, and 40 wt% A-16SG. The first type also contained a small amount of Microna 3 limestone powder which was readily mixed with the alumina by using a small plastic drum that was alternately rolled and shaken. The second type contained a small quantity of lanthanum nitrate in addition to the alumina. It was prepared by dissolving lanthanum nitrate in tetrahydrofuran (THF), which was then mixed with the alumina powders by using a mortar. By controlling the quantity of solvent, a relatively thick paste was prepared which was partially dried at room temperature and then at 110°C for 4-5 hr. The dried material was ground subsequently with a mortar and pestle. Either of these shell formulations could be applied to the pellet cores as described above.

The core-in-shell pellets were calcined at high temperature to increase their physical integrity. Some samples were calcined at 900°C for 3 hr after being heated gradually from room temperature over a 2 hr period, whereas other samples were calcined at 1100°C for 2 hr.

Pellets that were subsequently impregnated with a Ni catalyst for reaction testing were calcined at 900°C followed by recarbonation which was conducted at 650°C in flowing CO<sub>2</sub>. The recarbonated pellets were put in a 50 ml round bottom flask which was then placed in a vacuum oven at 110°C for 3 hr. After this treatment, the flask was removed from the oven, capped, and allowed to cool for 5 min. Then without further cooling, 25 ml of 2 M Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in tetrahydrofuran (THF) was slowly added to the pellets. The pellets were allowed to soak for 1 hr in this solution whereupon the pellets were removed from the solution and allowed to dry under atmospheric conditions overnight. After drying, the pellets were placed in an oven at 1.0 atm and 110°C for 4 hr. The pellets were then heated in a tube oven as the temperature was ramped from room temperature to 500°C at 25°C/min in flowing air. Once 500°C was reached, the pellets remained in the oven for 2.0 hr to convert nickel nitrate into NiO. The impregnation process was then repeated so that the pellets were impregnated with nickel twice prior to testing in the fixed bed reactor. The gain in weight of the pellets resulting from impregnation corresponded to an added Ni content of 6 wt%. Prior to reaction testing of the core-in-shell pellets, the NiO was reduced in-situ by raising the catalyst bed temperature to 550°C and flowing H<sub>2</sub> at 1.3 mmol/min for 4 hr through the bed.

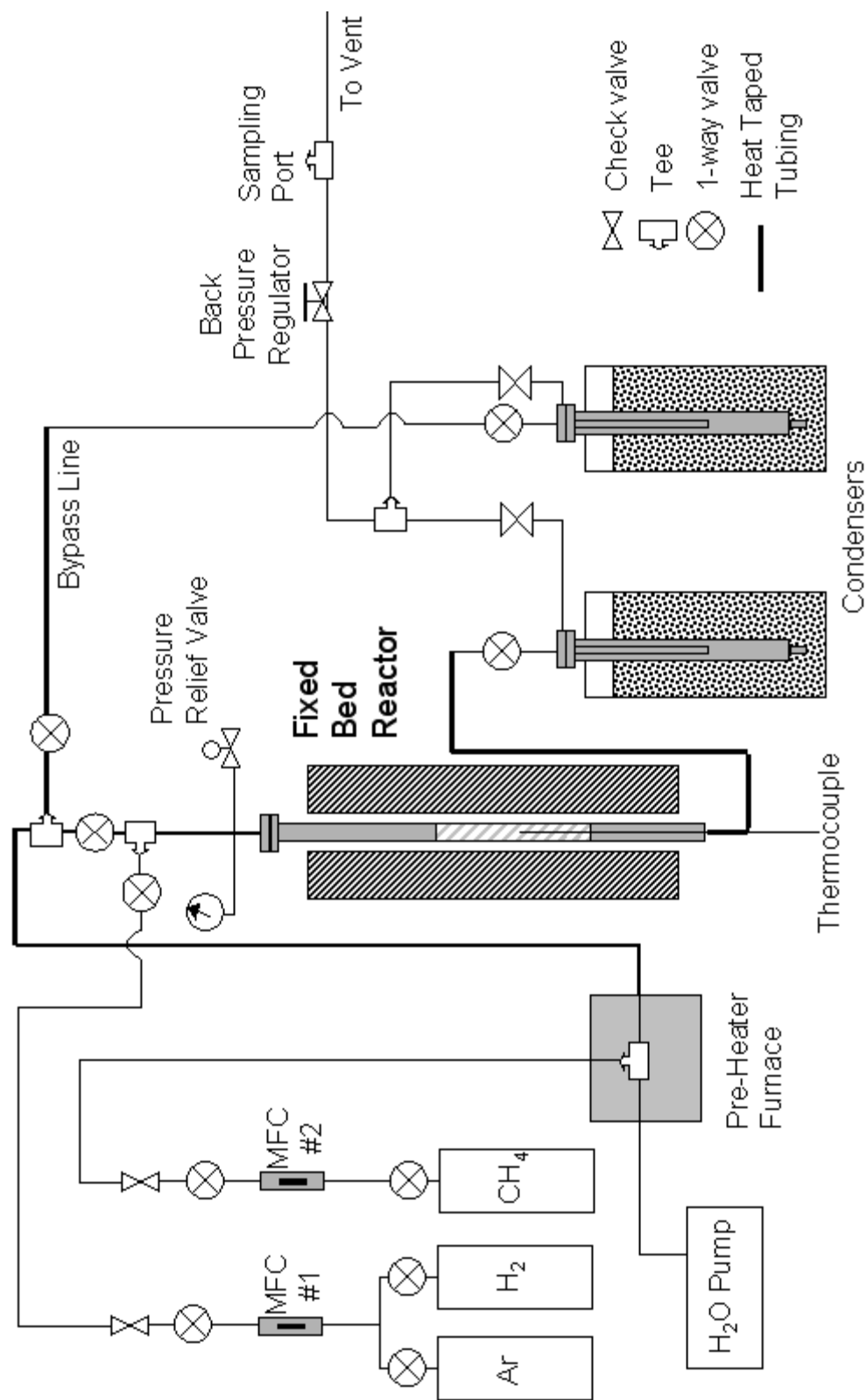
### **Performance Testing of Core-in-Shell Pellets**

The performance of the prepared core-in-shell pellets with a Ni catalyst was evaluated by conducting a number of test runs in which CH<sub>4</sub> was reformed with steam in the presence of the

combined catalyst and sorbent. These runs were conducted with a fixed bed reactor which had been packed with the prepared pellets (Figure 3). The body of the vertical tubular reactor consisted of a stainless steel tube having an inside diameter of 1.58 cm and overall length of 61 cm. The bottom of the reactor was fitted with a stainless steel plate having many small holes drilled in it. The plate supported the bed of pellets which consisted of several layers. For tests conducted at pressures between 1.0 and 5.0 atm, the bottom layer consisting of 0.63 cm diameter spherical pellets of SiC was 23 cm deep. On top of this layer was placed a 2.5 cm deep layer of extruded cylindrical pellets of SiC, each having a diameter of 0.32 cm. These layers of inert SiC supported the bed of core-in-shell pellets that was 10-11 cm deep and consisted of a mixture of core-in-shell pellets (13.7 g) interspersed with smaller SiC pellets (8.2 g). The core-in-shell pellets ranged from 3.6 to 4.4 mm in diameter while the spherical SiC pellets had a diameter of 1.3 mm. On top of the core-in-shell pellets was placed a 10 cm deep layer of the 0.32 cm diameter SiC extrudes. The layered arrangement insured that the bed of core-in-shell pellets was in the middle third of the region heated by the electric furnace which surrounded the reactor. A thermocouple was inserted through the bottom of the reactor to measure the temperature in the middle of the catalyst/sorbent bed.

For tests conducted at 10.0 atm it proved necessary to double the bed of catalyst/sorbent material. Therefore, 27.4 g of core-in-shell pellets were mixed with 16.4 g SiC pellets resulting in a bed depth of 21 cm. Consequently, the depth of the bottom layer of SiC pellets had to be reduced to 16.5 cm, while the other layers of SiC pellets remained the same.

The fixed bed reactor could be supplied with CH<sub>4</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O or argon individually or in appropriate mixtures. The H<sub>2</sub>O was always supplied as steam generated in a pre-heater where deionized water was vaporized. The flow of feed water was controlled by a Lab Alliance



**Figure 3.** Schematic diagram of the fixed bed reactor used for performance and lifecycle testing of the combined catalyst and sorbent, core-in-shell pellets.

Series I HPLC metering pump. Mass flow controllers made by Brooks Instruments were used to control the flow rate of  $\text{CH}_4$ , CO or other gases.

For tests of  $\text{CH}_4$  reforming,  $\text{CH}_4$  and steam were mixed in the preheater and then passed through heated stainless steel tubing to the heated fixed bed reactor. After passing through the reactor, the gas mixture was cooled to condense unreacted steam and then vented through a line with a back pressure regulator that maintained the required system pressure. A bypass line was provided around the reactor for use before starting a test run. Reactants could be fed through the bypass line at the appropriate flow rate and pressure for the particular conditions being tested, which insured that a well-mixed, steady flow of reactants could be introduced into the fixed bed reactor at the beginning of a performance test.

Before starting a test run, the bed of core-in-shell pellets was heated to  $850^\circ\text{C}$  to ensure that the sorbent was fully regenerated. This step was conducted by passing steam and  $\text{CH}_4$  in a 3:1 mole ratio at a flow rate of 2.41 mmol/min through the bed for 1.0 to 1.5 hr. After this step was completed, the flow of  $\text{CH}_4$  and steam was diverted around the reactor through the bypass while the reactor was cooled to the required temperature for the test run. During this cooling period, no gas was passed through the reactor when it was to be used for a test conducted at 1.0 atm. However, when it was to be used at higher pressures, argon at a rate of 3.08 mmol/min was supplied to the reactor to pressurize the system. The flow of argon was continued until other preparations had been completed. At this point an appropriate flow rate of  $\text{CH}_4$  and steam was established through the bypass line. At elevated pressures, the reactants were then passed through the bypass line for at least 15 min to ensure that a steady stream of reactants of the required composition would be supplied to the fixed bed reactor. For tests at elevated pressures, the argon flow was stopped just before introducing the reactant mixture into the fixed bed.

As the test run proceeded, samples of the reactor effluent were periodically drawn with Gastight syringes manufactured by the Hamilton Company. The effluent gas was analyzed with an SRI 8610C gas chromatograph (GC) equipped with a thermal conductivity detector and flame ionization detector. The samples were analyzed and the concentrations of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  were normalized to 100%. The gas concentrations reported are the average of several samples drawn during reaction testing at a given temperature and pressure.

For lifecycle testing of the core-in-shell pellets the reactor was loaded as described above. The pellets were reduced initially at  $550^\circ\text{C}$  and 1.0 atm by passing  $\text{H}_2$  through the reactor at a rate of 1.3 mmol/min for 4 hr. The bed temperature was then increased to  $650^\circ\text{C}$  for a series of lifecycle tests. One cycle consisted of passing a reactant stream through the bed of pellets at this temperature for 155 min to demonstrate  $\text{CH}_4$  reforming with  $\text{CO}_2$  absorption followed by sorbent regeneration at  $850^\circ\text{C}$ . The sorbent was considered regenerated when the  $\text{CO}_2$  concentration stabilized, which usually required 1.0-1.5 hr. Throughout the cycle  $\text{CH}_4$  and steam were supplied in a 1:3 mole ratio at a total flow rate of 2.41 mmol/min. Therefore, reducing conditions were maintained throughout the cycle so that the Ni catalyst remained reduced. Also throughout the cycle, samples of the reactor effluent were drawn at 10 min. intervals for analysis.

At the end of each cycle the reactant stream was diverted through the bypass line and around the reactor while it was cooled from  $850^\circ\text{C}$  to  $650^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ . Once the reactor temperature reached  $650^\circ\text{C}$ , the reactant stream was returned to the reactor and a new cycle began. Because of the time consuming nature of each cycle, lifecycle testing was limited to 10 cycles for each sample of pellets. However, the 10<sup>th</sup> cycle was interrupted before regenerating the sorbent so that it remained in the more stable  $\text{CaCO}_3$  form for further evaluation.

Also because of the time required to complete 10 cycles, it was not always possible to complete a 10 cycle test without interruption. Therefore, when a test had to be interrupted, it was stopped at the end of a  $\text{H}_2$  production period so that the pellet cores were left in the  $\text{CaCO}_3$  form. During such pauses, argon was passed through the reactor at 0.44 mmol/min. In addition, the temperature was left at 650°C to limit the amount of thermal stress experienced by the core-in-shell pellets.

### **Physical Characterization of Core-in-Shell Pellets**

Physical characterization of the core-in-shell pellets was also conducted before and after lifecycle testing. The BET surface area of the core-in-shell pellets was determined by using  $\text{N}_2$  adsorption measurements. A Micromeritics ASAP 2020 instrument was used for surface area determination. Approximately 1.0 g of core-in-shell pellets was analyzed. Pellets that were analyzed prior to lifecycle testing did not undergo a reduction treatment to convert NiO to metallic Ni.

Selective  $\text{H}_2$  chemisorption by the metallic Ni surface was used to determine the Ni surface area present in core-in-shell pellets.  $\text{H}_2$  chemisorption measurements were conducted with a Micromeritics ASAP 2020 instrument with the chemisorption attachment. Chemisorption measurements were conducted at 35°C. In order to reduce NiO to Ni prior to chemisorption measurements, each sample was reduced at 550°C for 4 hr in flowing  $\text{H}_2$  as part of the chemisorption program carried out by the ASAP 2020. Only the results of  $\text{H}_2$  chemisorption measurements of core-in-shell pellets that had not been subjected to lifecycle testing are reported. When  $\text{H}_2$  chemisorption measurements were carried out on core-in-shell pellets that had been subjected to lifecycle testing, the amount of  $\text{H}_2$  chemisorbed was very low, which was probably due to coking and the deposition of carbon on the Ni surface.

The size of Ni crystallites was determined through powder X-ray diffraction (XRD) measurements using a Siemens D-500 Diffractometer and Cu K $\alpha$  radiation with a graphite monochromator. A voltage of 50 kV and a current of 27 mA were employed. The divergence slits used were 1.0°, and the detector slit used was 0.15°. A counting time of 2 sec was used. The Scherrer equation was used to calculate the mean crystallite dimensions from the measured line breadth of the peaks. Since metallic Ni was required to measure the Ni crystallite size, samples that had been previously subjected to H<sub>2</sub> chemisorption measurements were used as the fresh core-in-shell samples. Core-in-shell pellets that had been subjected to lifecycle testing were also subjected to XRD measurements to determine the Ni crystallite size after being unloaded from the fixed bed reactor.

The effect of lifecycle testing on the physical integrity of core-in-shell pellets was also investigated. Core-in-shell pellets that were broken or otherwise found to contain visual shell cracks following lifecycle testing were considered “fractured.” The percentage of pellets fractured during lifecycle testing is reported.

The compressive force required to break the core-in-shell pellets was also determined. For this determination, the diameter of an individual pellet was measured with digital calipers, and then the compressive force required to break the pellet was measured with an Accuforce EZ 250 instrument. For this measurement the pellet was placed between two flat plates, and the top plate was lowered at a rate of 10 mm/min until the pellet broke. The force required to break the pellet was recorded. The crushing force divided by the pellet diameter is reported. Fifteen pellets were individually measured during this test and the average of the breaking force per unit of pellet diameter, or N/mm, was determined. This average is reported with 95% confidence intervals. Pellets that had not been reduced or subjected to lifecycle testing were used for

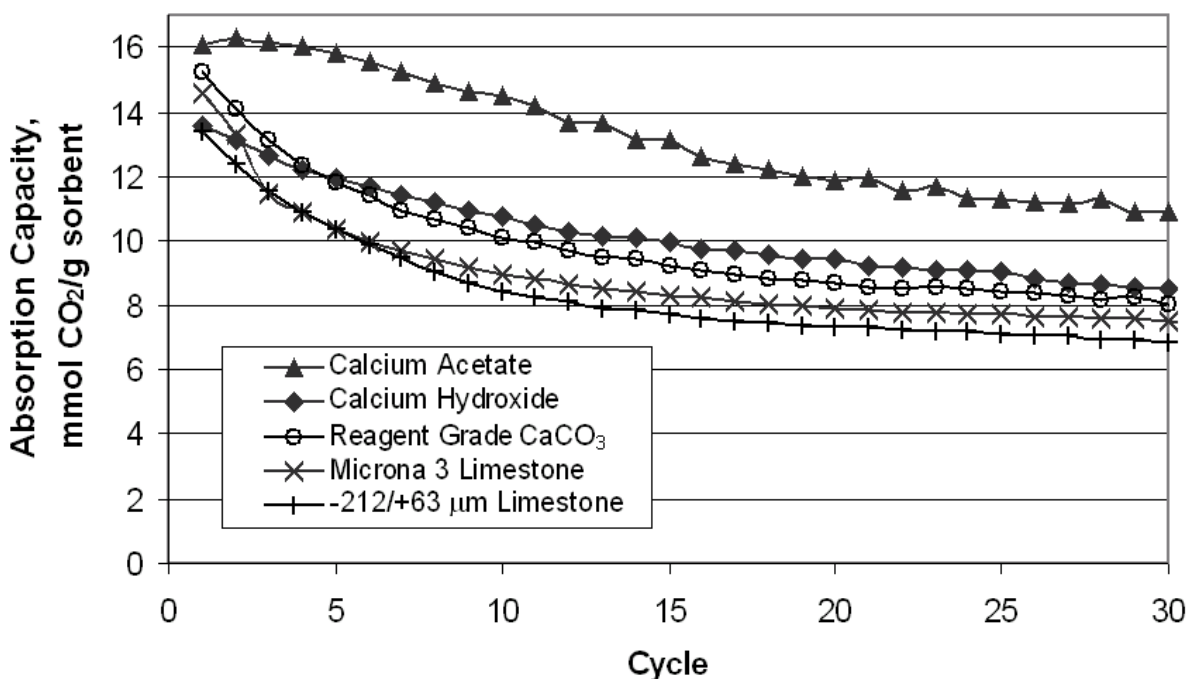
determining the average breaking force of fresh pellets. In the case of pellets subjected to lifecycle testing, only intact and fracture-free pellets were selected for the breaking force determination.

## RESULTS AND DISCUSSION

### Improvement of the Sorbent Core Material

The first major task of the present project was to improve the stability and lifecycle performance of the Ca-based sorbent by employing one or more of the following methods: (1) utilizing a more appropriate precursor, (2) adding an inert material such as MgO, or (3) controlling the initial sintering of the material. Although limestone and dolomite are the most obvious precursors for the preparation of CaO, an alternative precursor that has been shown to produce more stable CaO is calcium acetate.<sup>10</sup> These and several other precursors were utilized to prepare sorbents for evaluation in the present study. After each material had been calcined at 900°C for 3 hr, it was subjected to a multicycle test of CO<sub>2</sub> absorption and regeneration conducted at 750°C and 1.0 atm with the TGA system. The results of a preliminary series of tests are presented in Figure 4. In this and subsequent figures the CO<sub>2</sub> apparent absorption capacity of the calcined material is indicated. Figure 4 shows that the absorption capacity of each material decreased with usage. The theoretical maximum absorption capacity of the limestone with 97 wt% CaCO<sub>3</sub> and 3 wt% inert material is 16.9 mmol CO<sub>2</sub>/g calcined sorbent. Although CaO derived from calcium acetate displayed the highest absorption capacity, the material was not completely stable.

Because of their higher purity, reagent grade calcium hydroxide and calcium carbonate provided sorbents with a slightly greater absorption capacity than those provided by either

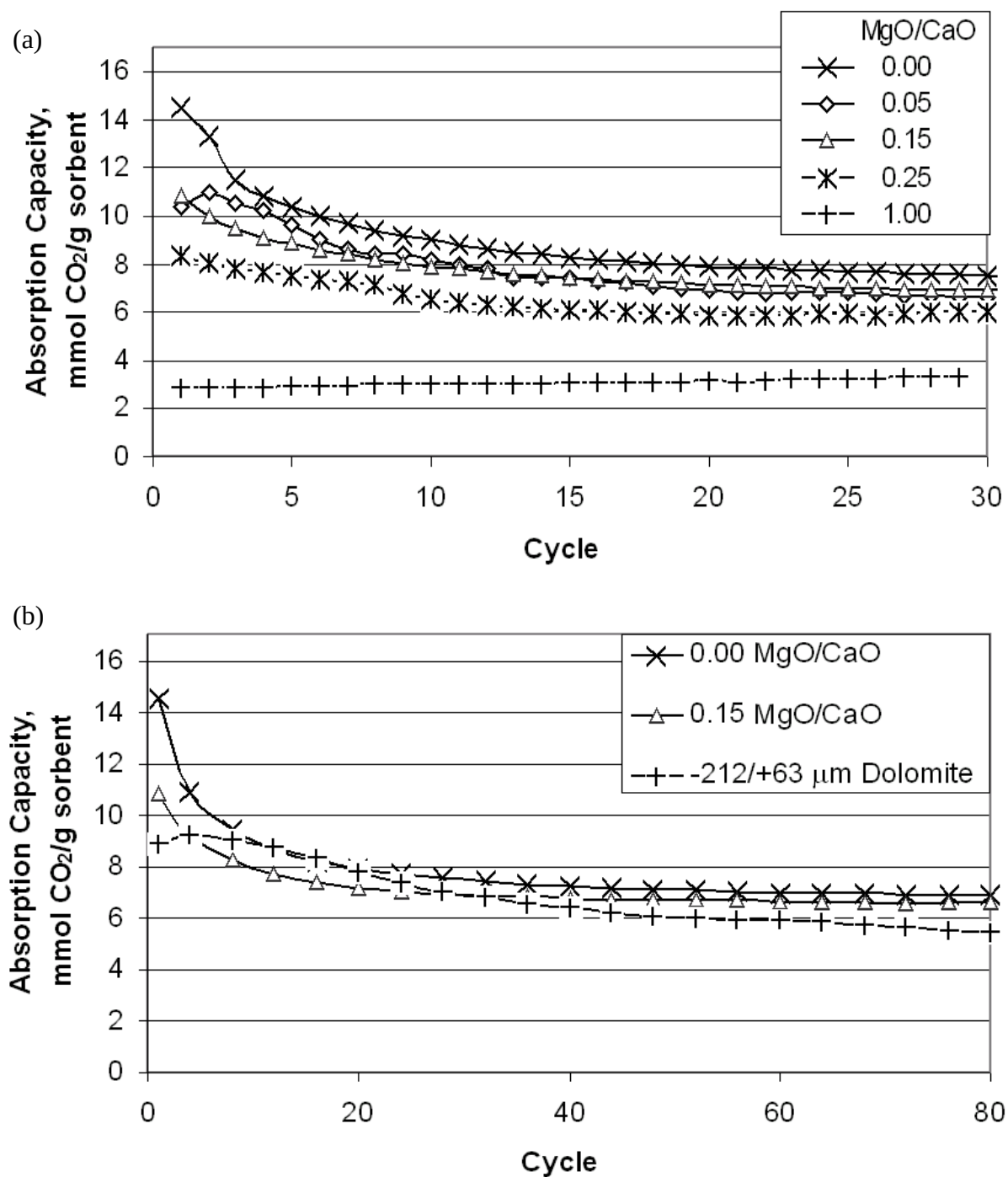


**Figure 4.** The apparent absorption capacity of CaO prepared by calcining various source materials at 900°C for 3 hr.

limestone. However, the reagent grade materials were not chosen for further investigation because of their higher cost.

Since Bandi et al.<sup>11</sup> had shown previously that the absorption capacity of CaO was more stable when derived from dolomite or huntite than from limestone, the possibility of stabilizing CaO with smaller concentrations of MgO was investigated by impregnating Microna 3 limestone with  $\text{Mg}(\text{NO}_3)_2$  followed by calcination at 900°C for 3 hr to decompose the nitrate. Sorbents with different levels of MgO were then subjected to 30-cycle tests of absorption and regeneration. The results presented in Figure 5a indicate the variation in absorption capacity of each material identified by the mass ratio of MgO to CaO.

The indicated values of the mass ratio of MgO to CaO encompass that of dolomitic lime (0.72 g MgO/g CaO). It is apparent that the initial absorption capacity decreased as the MgO



**Figure 5.** Effect of MgO expressed as g MgO/g CaO on the apparent absorption characteristics of CaO derived from Microna 3 limestone or dolomite. All samples were initially calcined at 900°C for 3 hr before testing. (a) Effect of different MgO loading levels; (b) Effect of extended lifecycle testing.

content increased, but at the same time the sorbent became more stable so that its capacity decreased less with usage. The decrease in absorption capacity was largely due to the decrease in CaO content of a given sample as the MgO content was increased. The absorption capacity may also have declined because MgO covered the CaO particles. Of special interest is the increase in absorption capacity with usage of the sorbent with 1.0 g MgO/g CaO. Such an increase is not well understood although it was likely due to rearrangement of the pore structure or crystal structure.

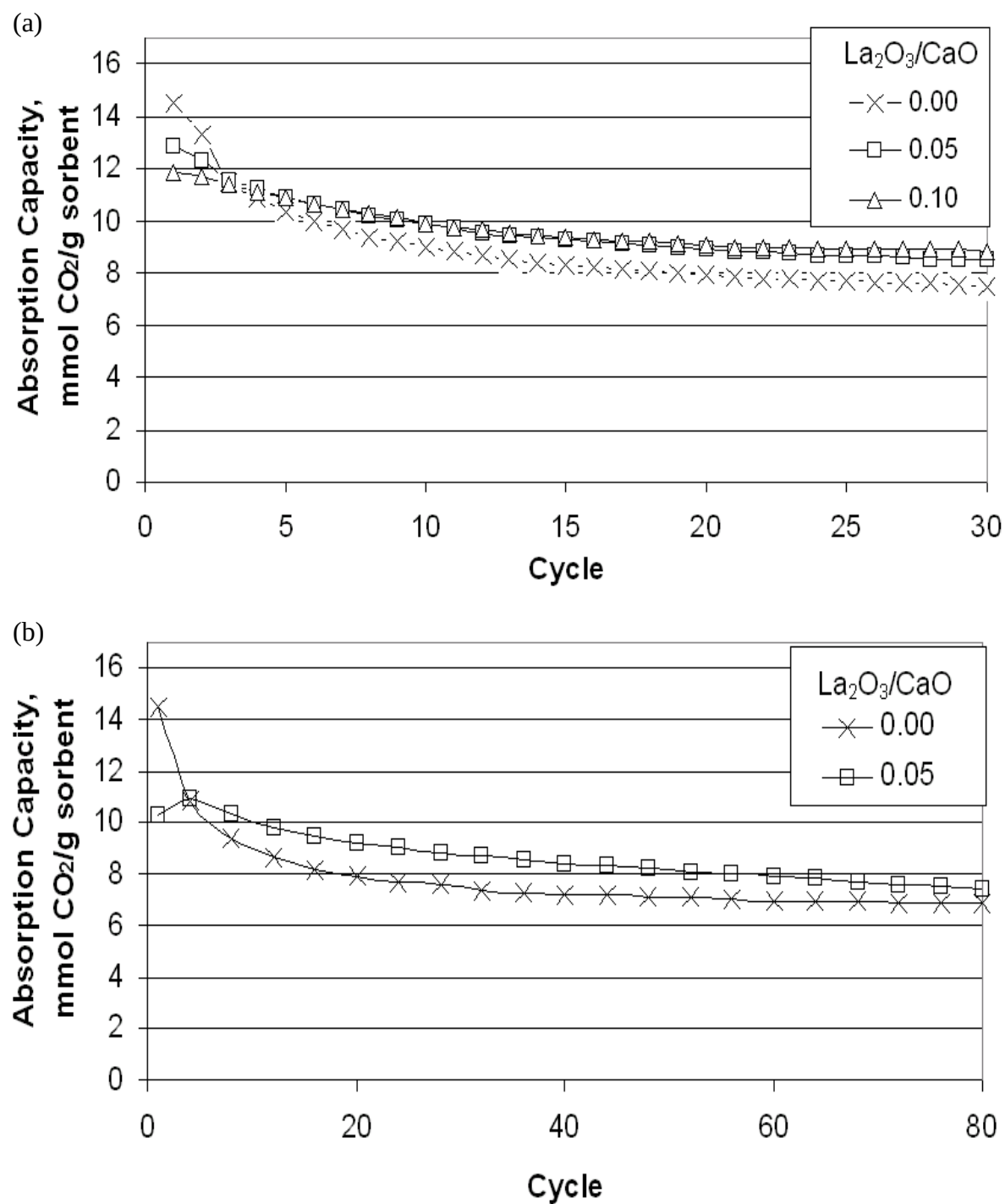
A longer lifecycle test was conducted with several samples, and the results are presented in Figure 5b. Although the initial absorption capacity of the sorbent without MgO present was greater than that of the sorbent with 0.15g MgO/g CaO, both materials absorbed about the same amount of CO<sub>2</sub> at the end of 80 cycles. This result indicates that more of the CaO in the sorbent containing MgO was available for absorption of CO<sub>2</sub>. The dolomitic lime absorbed the same amount of CO<sub>2</sub> as the Microna 3 lime between 10 and 20 cycles even though the dolomitic lime was equivalent to a sorbent with 0.72 g MgO/g CaO. Thus, more of the CaO in dolomitic lime was available for reaction. Others have attributed such behavior to the increased porosity of the dolomitic lime formed upon calcination.<sup>12</sup>

Another material considered as a potential stabilizing agent for the CaO sorbent was La<sub>2</sub>O<sub>3</sub>. This material had been shown previously to stabilize alumina when alumina had been used as a catalyst support.<sup>13, 14</sup> However, unlike MgO, La<sub>2</sub>O<sub>3</sub> cannot be considered completely inert for the conditions used in the present investigation. Shirsat et al.<sup>15</sup> reported that lanthanum dioxycarbonate, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, is a semi-stable intermediate in the decomposition of lanthanum carbonate, La(CO<sub>3</sub>)<sub>3</sub>. La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> decomposes above 720°C via the reaction:



However, the equilibrium partial pressure of  $\text{CO}_2$  for reaction 4 at  $750^\circ\text{C}$  is 0.06 atm. Therefore, the carbonation of  $\text{La}_2\text{O}_3$  appeared likely. To investigate this possibility, a sorbent derived from Microna 3 limestone was impregnated with lanthanum to provide a mixture with 0.10 g  $\text{La}_2\text{O}_3/\text{g}$   $\text{CaO}$ . After this material was subjected to a 30-cycle test of  $\text{CO}_2$  absorption and regeneration in the TGA, it was analyzed by x-ray diffraction and was found to contain a small amount of crystalline  $\text{La}_2\text{O}_2\text{CO}_3$ . In order to determine the amount of  $\text{CO}_2$  that could be absorbed by  $\text{La}_2\text{O}_3$ , a pure  $\text{La}_2\text{O}_3$  sample was prepared by calcining  $\text{La}(\text{NO}_3)_3$  at  $900^\circ\text{C}$  for 3 hr, and then it was subjected to a four-cycle absorption/regeneration test at  $750^\circ\text{C}$ . It was found that after four cycles less than 0.1 mmol  $\text{CO}_2/\text{g}$  sorbent was being absorbed. Therefore,  $\text{La}_2\text{O}_3$  was not absorbing a large amount of  $\text{CO}_2$ , but was also not completely inert.

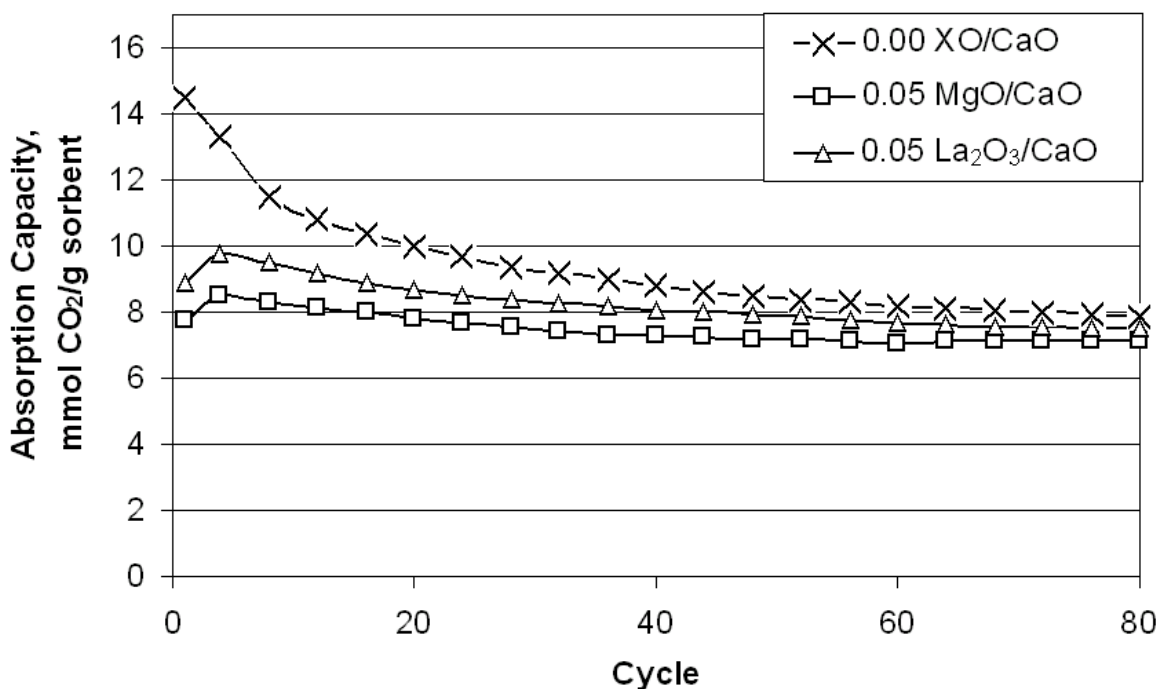
To see what effect  $\text{La}_2\text{O}_3$  would have on the stability of the sorbent, samples were prepared with different ratios of  $\text{La}_2\text{O}_3$  to  $\text{CaO}$ , based on Microna 3 limestone. After the samples had been calcined for 3 hr at  $900^\circ\text{C}$ , some were treated to 30 cycles of absorption and regeneration at  $750^\circ\text{C}$ . The results presented in Figure 6a show that the samples containing small amounts of  $\text{La}_2\text{O}_3$  had a higher absorption capacity through 30 cycles than the sample of untreated limestone. On the other hand, different levels of  $\text{La}_2\text{O}_3$  had little effect. Extending the sorbent performance to 80 cycles produced the results shown in Figure 6b. It can be seen that as the number of cycles was extended beyond 30, the absorption capacity advantage of the sorbent with  $\text{La}_2\text{O}_3$  gradually faded and almost disappeared entirely after 80 cycles. Consequently, this is an excellent example of the need for extended testing of  $\text{CaO}$  sorbents. While it could



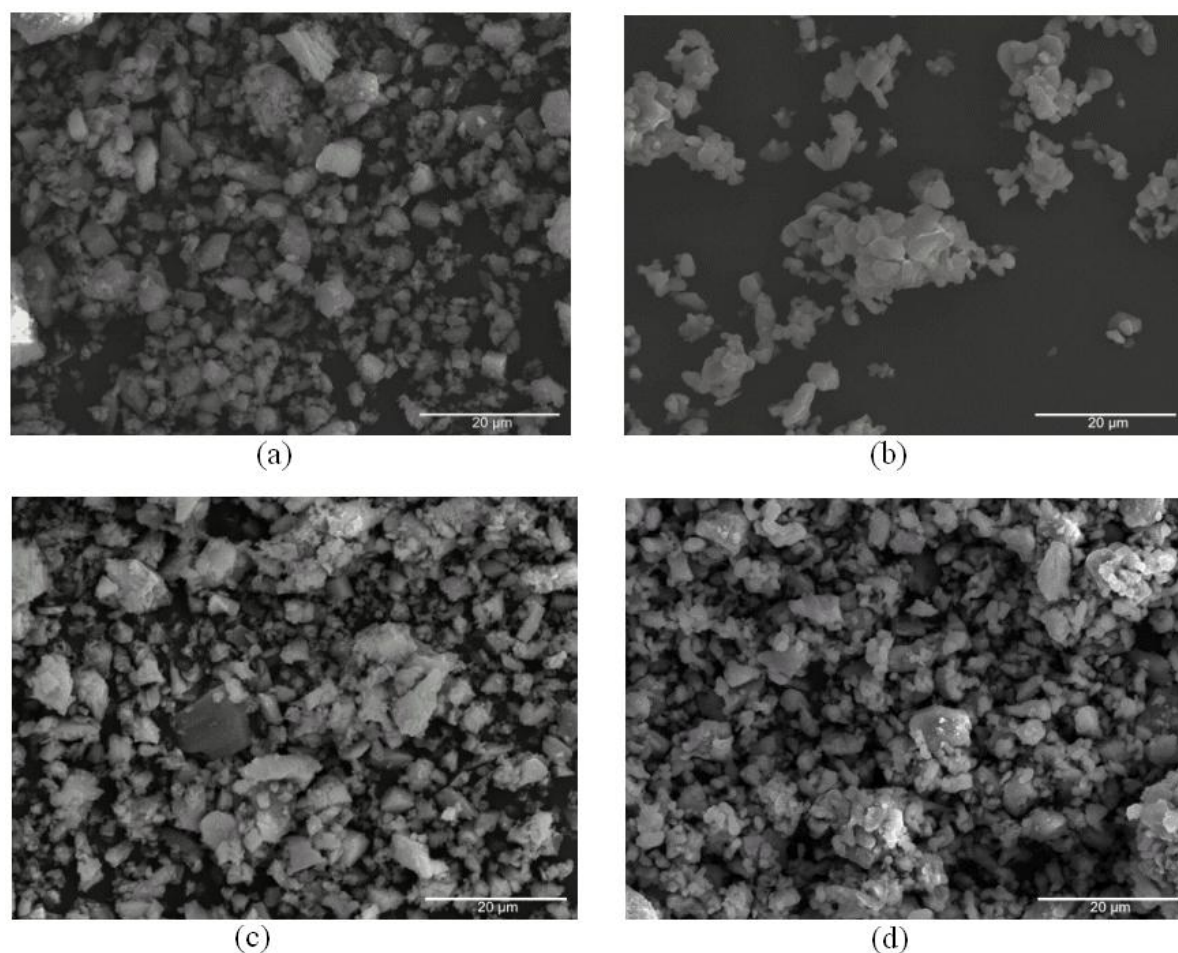
**Figure 6.** Effect of  $\text{La}_2\text{O}_3$  expressed as g  $\text{La}_2\text{O}_3/\text{g CaO}$  on the apparent absorption characteristics of  $\text{CaO}$  derived from Microna 3 limestone. The samples were initially calcined at  $900^\circ\text{C}$  for 3 hr before testing. (a) Effect of different  $\text{La}_2\text{O}_3$  loading levels; (b) Effect of extended lifecycle testing.

reasonably be assumed from Figure 6a that the addition of lanthanum is indeed beneficial, further testing showed that the benefit gradually disappeared after many more cycles.

An alternative method of preparing the sorbents with added MgO or  $\text{La}_2\text{O}_3$  was also investigated. Microna 3 limestone with little initial porosity was calcined at  $750^\circ\text{C}$  for 5 hr in air before adding the nitrates. This increased the porosity of the sorbent and presumably allowed more of the dissolved nitrates to penetrate the particles. The nitrate-impregnated samples were subsequently calcined at  $900^\circ\text{C}$  for 3 hr and then tested, which produced the results shown in Figure 7. A comparison of the results in Figure 7 with results presented in Figures 5 and 6 shows that the initial absorption capacity of the sorbents produced by the alternative method was less than that produced before. However, after 80 cycles the absorption capacities of the sorbents



**Figure 7.** A comparison of the effects of MgO and  $\text{La}_2\text{O}_3$  expressed as g XO/g CaO on the apparent absorption characteristics of CaO derived from Microna 3 limestone. The limestone was calcined at  $750^\circ\text{C}$  for 5 hr before adding  $\text{Mg}(\text{NO}_3)_2$  or  $\text{La}(\text{NO}_3)_3$ . The mixture was then calcined at  $900^\circ\text{C}$  for 3 hr.



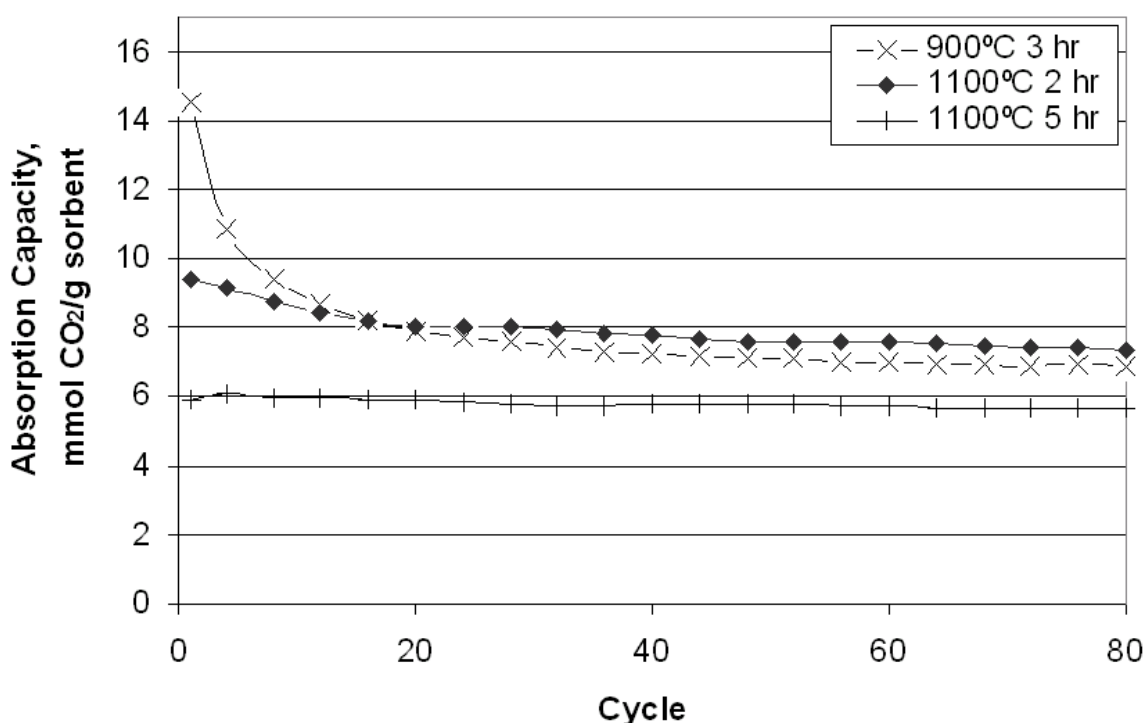
**Figure 8.** SEM micrographs of Microna 3 limestone samples after initial calcination at 900°C for 3 hr and after 30 cycles of CO<sub>2</sub> absorption and desorption at 750°C. (a) After initial calcination without MgO; (b) After 30 cycles without MgO; (c) After initial calcination with 0.05 g MgO/g CaO; (d) After 30 cycles with 0.05 g MgO/g CaO.

prepared by the alternative method were not significantly different from those prepared by the first method. On the other hand, the sorbents prepared by the alternative method were more stable, at least for 30 cycles.

The purpose of adding MgO to the Microna 3 limestone was to improve the stability of the sorbent by inhibiting sintering. SEM images were obtained of Mg-free samples and of samples with a 0.05 g MgO/g CaO both before and after being subjected to a 30-cycle test. The samples were calcined initially at 900°C for 3 hr. Figure 8a is an image of the calcined

limestone before testing, while Figure 8b is an image after testing. Although Figure 8a shows that the pure limestone experienced some sintering during initial calcination, it experienced more severe sintering during the 30 cycle test (Figure 5b). By comparison, the samples with MgO may have undergone slightly more sintering during initial calcination (Figure 5c) but much less sintering during the 30-cycle test (Figure 5d). Overall, it appeared that a small amount of MgO was beneficial.

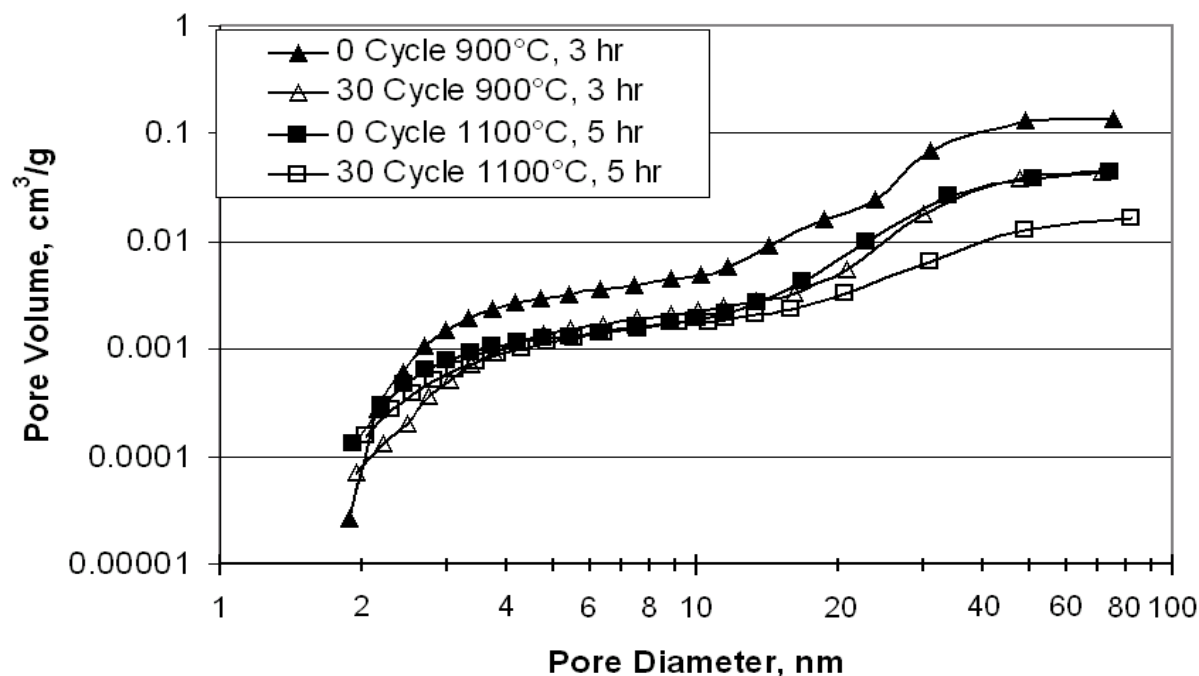
The effects of initial calcination conditions on Microna 3 limestone prior to cyclic testing were also studied, and the results are shown in Figure 9. It was hypothesized that increasing the severity of the initial calcination conditions would produce larger pores in the mesoporous region, which would then allow  $\text{CO}_2$  to penetrate deeper into a CaO particle because of reduced mass transfer limitations. However, this could also reduce the surface area available for sorption



**Figure 9.** Effect of initial calcination conditions on the apparent absorption capacity of CaO derived from Microna 3 limestone.

and reduce the absorption capacity. On the other hand, it could also result in a more stable material. Figure 9 shows that calcining the Microna 3 limestone at 1100°C for 2 hr produced a somewhat more stable sorbent than that produced by calcining the material at 900°C for 3 hr. Increasing the calcination time to 5 hr while maintaining the 1100°C temperature produced an even more stable sorbent but with less capacity. Also, the sample that was calcined at 1100°C for 5 hr may have become slightly more active between the first and second cycles. This increase in activity may have been due to the development of new pores and cracks during the initial cycle of carbonation and regeneration of the CaO.

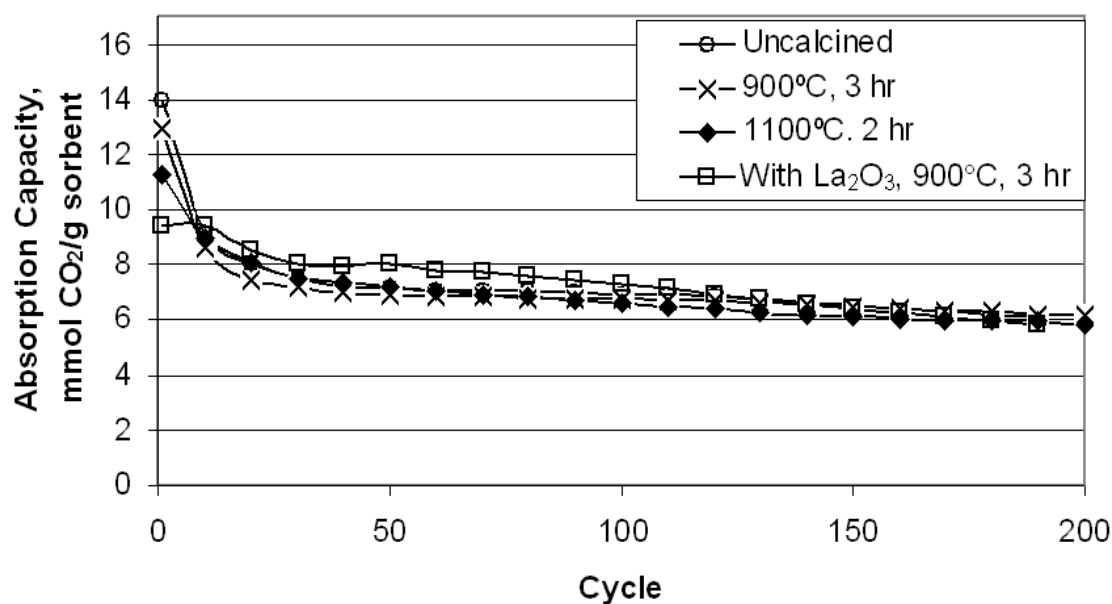
To provide greater insight into the effects of initial calcination conditions and repeated absorption and regeneration on the physical properties of the sorbent, samples of Microna 3 limestone were calcined initially either at 900°C for 3 hr or 1100°C for 5 hr and then subjected to a 30-cycle test of absorption and regeneration at 750°C. The pore volume distribution of the samples was then determined after the initial calcination and after the 30-cycle test. Figure 10 shows on a logarithmic scale the cumulative pore volume of the samples that had received the different treatments. The sample calcined initially at 900°C for 3 hr had the largest cumulative pore volume whereas the sample that had been calcined initially at 1100°C for 5 hr had a lower cumulative pore volume. Therefore, the more severe calcination conditions reduced both the pore volume and absorption capacity of the material, which was not desirable. However, these conditions did produce a more stable material. This increase in stability was not only reflected by absorption capacity in Figure 9 but also by the porosity results which are reported in Figure 10. The results of this test showed that after 30 absorption cycles the cumulative pore volume of the pores smaller than 10 nm was reduced only 6% for the sorbent calcined at 1100°C for 5 hr compared to a reduction of 54% for the sorbent calcined at 900°C for 3 hr.



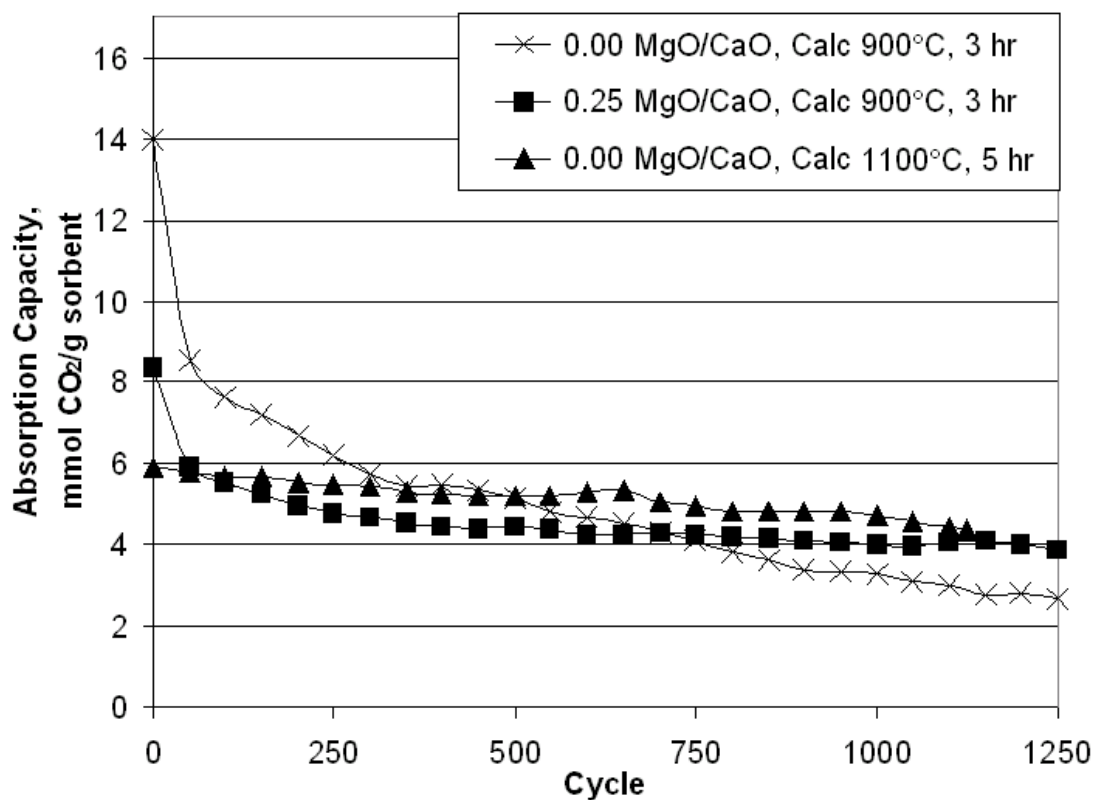
**Figure 10.** Cumulative pore volume distribution of Microna 3 limestone after it had been subjected to various initial calcination conditions.

Since it appeared that the lifecycle performance of a sorbent could be better determined by extended testing, several sorbent samples were subjected to a 200 cycle test and three samples were even subjected to a test of 1100 cycles or more. The results are presented in Figures 11 and 12, respectively. In Figure 11, it can be seen that pre-calcining the sorbent had some effect initially, as did the calcination temperature. However, after 50-60 cycles there was little difference in the absorption capacity. It is also apparent that while a small amount of  $\text{La}_2\text{O}_3$  was beneficial initially, any benefit disappeared after 120-130 cycles. These results again emphasize the importance of extended lifecycle testing of any proposed sorbent.

Further confirmation of this observation is provided by the results of the more prolonged testing presented in Figure 12. The first and third set of results were obtained with unmodified Microna 3, whereas the second set of results was achieved with Microna 3 which had been impregnated with  $\text{Mg}(\text{NO}_3)_2$  to provide a material with 0.25 g  $\text{MgO/g}$   $\text{CaO}$  after calcining at



**Figure 11.** Various sorbents derived from Microna 3 limestone were tested after being initially calcined at the indicated conditions. One sorbent contained 0.05 g La<sub>2</sub>O<sub>3</sub>/g CaO.



**Figure 12.** Absorption capacity of CaO derived from Microna 3 limestone. One sorbent contained 0.25 g MgO/g CaO. The sorbents had been initially calcined at either 900°C for 3 hr or 1100°C for 5 hr.

900°C for 3 hr. The first two sets of results encompassed the full 1250 cycles, while the third set ended with 1124 cycles. By the completion of 1124 cycles, the absorption capacity of the sorbent stabilized with MgO and calcined at 900°C for 3 hr was equal to that of the unmodified Microna 3 which had been calcined at 1100°C for 5 hr. In addition, the absorption capacity of either sorbent was decidedly greater than that of the unmodified Microna 3 which had been calcined at 900°C for 3 hr. Furthermore, the absorption capacity of this material was still trending downward after 1250 cycles whereas that of the sorbent with MgO seemed to have reached a relatively stable value. However, the stability of this material could only have been verified by extending the test even further.

Another interesting result displayed by Figure 12 was the difference in absorption capacity of the CaO by the end of the test. At the end of the 1250 cycle test, the Microna 3 sample initially calcined at 900°C for 3 hr absorbed 2.68 mmol CO<sub>2</sub>/g sorbent, which corresponded to a 15.8% conversion of CaO. However, the sorbent with 0.25 g MgO/g CaO absorbed 3.85 mmol CO<sub>2</sub>/g sorbent, which corresponded to a 28.1% conversion of CaO. Thus, the presence of the inert MgO increased the absorption capacity of the CaO portion.

The results in Figure 12 are important because they show that the lifecycle performance of the sorbent was improved significantly either by the addition of MgO or by the use of a higher initial calcination temperature.

### **Improvement of the Catalytic Shell Material**

The goal of the second major task was to improve the physical strength, catalytic activity and lifecycle performance of the shell material and supported Ni catalyst. The goal was achieved by investigating the effects of shell composition and preparation conditions on the compressive strength and surface area of the shell material and on the activity of the Ni catalyst. Surface area

was important because it had been found previously that the quantity of Ni deposited within the shell, and hence its activity, was proportional to the surface area.<sup>4</sup> Of course, the final test of catalytic activity was to see how well the catalyst performed while reforming CH<sub>4</sub> with steam.

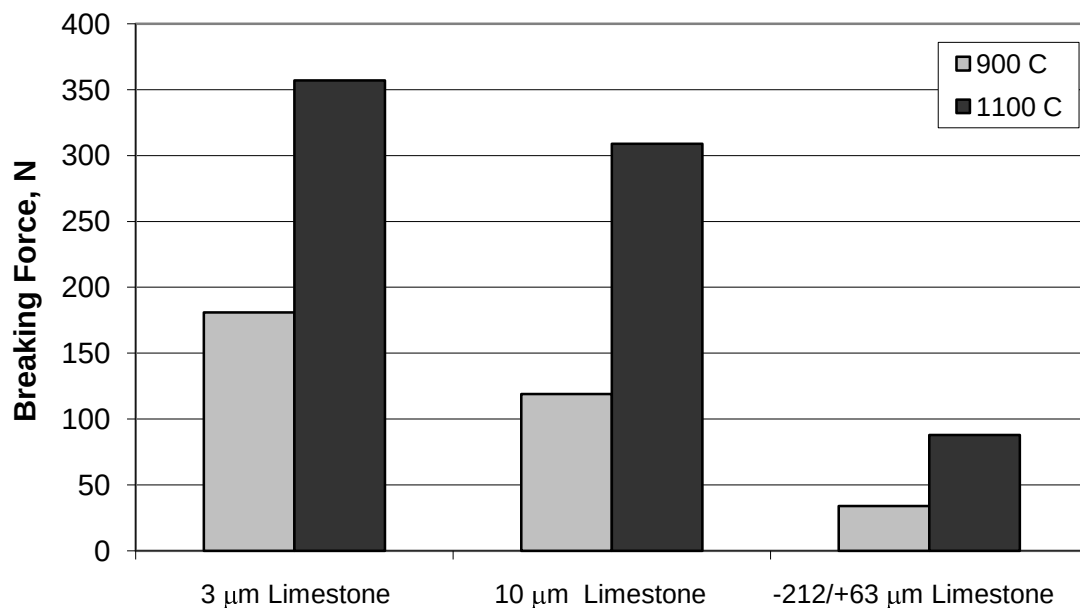
The composition of the shell material had evolved through several previous studies. Initially it had been shown that a strong porous shell material could be made by combining T-64  $\alpha$ -alumina (48 wt%), A-16SG  $\alpha$ -alumina (32 wt%), and limestone (-297/+44  $\mu$ m, 20 wt%) and then calcining the material at 1100°C for 2 hr.<sup>6-8</sup> A subsequent study showed that core-in-shell pellets prepared with a similar material and impregnated with a Ni catalyst were capable of steam reforming propane but not methane which requires a more active catalyst. To increase the catalytic activity of the catalyst, the surface area of the alumina support was greatly increased by replacing half of the T-64  $\alpha$ -alumina with CP-7 amorphous alumina.<sup>4, 5</sup> As a result of this change, the activity of the catalyst made with the revised shell material was increased sufficiently to provide for methane reforming, but the compressive strength of the shell material decreased too much for the intended application. During the course of the present investigation it was discovered that the compressive strength of the shell material could be restored substantially by using much smaller limestone particles in lower concentrations than had been tested previously. Therefore, limestone particles as small as 3  $\mu$ m and in concentrations as low as 3 wt% were selected for testing. The limestone was combined with a mixture of alumina having the following composition which had also evolved from the previous studies: 30 wt% CP-7, 30 wt% T-64, and 40 wt% A-16SG.

For physical testing, the alumina mixture and limestone were combined, mixed with water, and cast into cylindrical tablets having a diameter of 6 mm and thickness of 6 mm. The tablets were formulated either with 5 wt% or 10 wt% limestone, the balance being alumina.

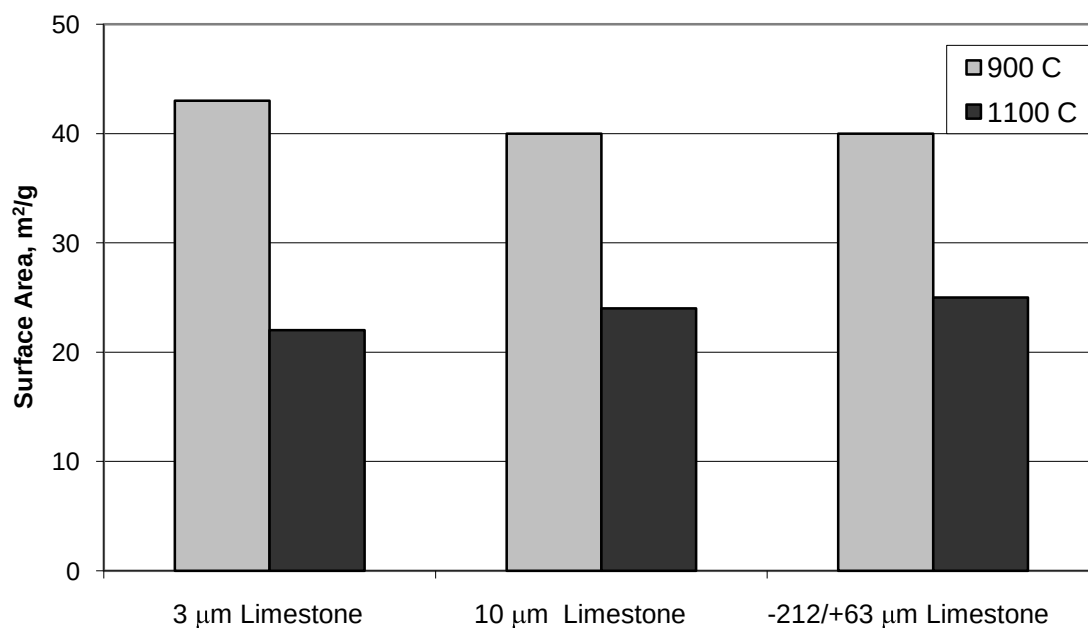
After air drying, the tablets were calcined either at 900°C for 3 hr or at 1100°C for 2 hr. The calcined tablets were subsequently tested to measure their compressive strength and surface area.

**Preliminary tests with ultrafine size limestone.** Tablets prepared with only 5% limestone were used to show the effect of limestone particle size. The results are given in Figures 13 and 14 where it can be seen that the strongest tablets were made with the 3  $\mu\text{m}$  limestone and the weakest with -212/+63  $\mu\text{m}$  limestone. However, the tablets made with 10  $\mu\text{m}$  limestone were nearly as strong as those made with 3  $\mu\text{m}$  limestone. It is also apparent that the particles calcined at 1100°C were much stronger than those calcined at 900°C (Figure 13). On the other hand, Figure 14 shows that tablets calcined at 1100°C had a much smaller surface area than those calcined at 900°C. The surface area of the pellets was only slightly affected by limestone particle size which is not surprising since most of the surface area was generated by the presence of the CP-7 alumina. As expected, the results demonstrate that the CP-7 is unstable at 1100°C.

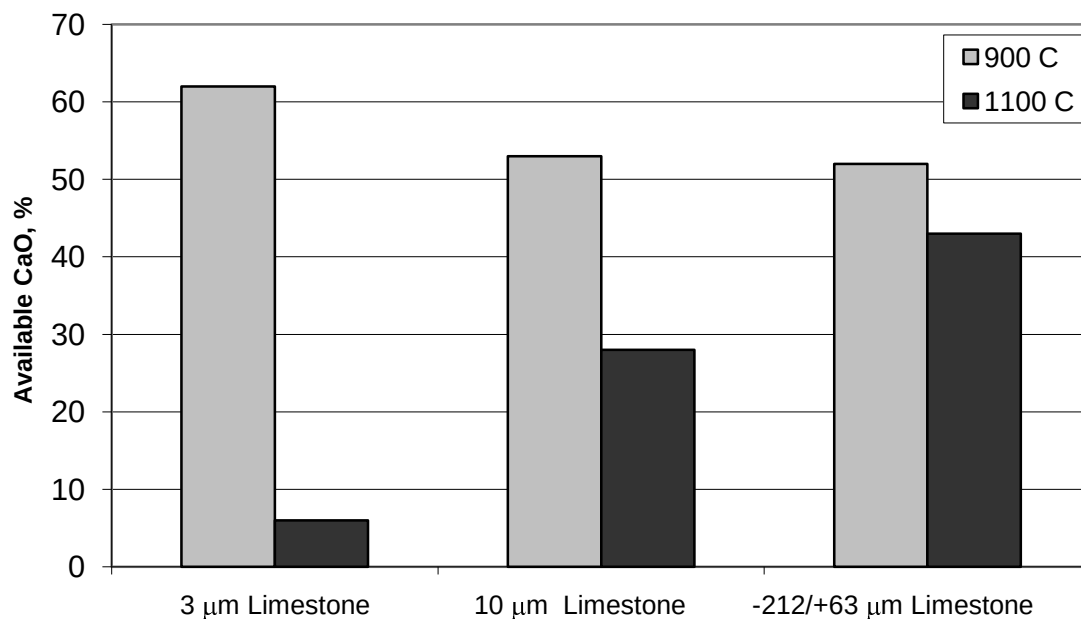
Since not all of the CaO present in the tablets was likely to react with the  $\text{Al}_2\text{O}_3$  during calcination, the apparent fraction of unreacted CaO in the calcined tablets was determined by thermogravimetric analysis which in effect measured the quantity of  $\text{CO}_2$  absorbed at 650°C by the tablets after calcination at a given temperature. The results, which are presented in Figure 15, indicate that for tablets calcined at 900°C, from 52 to 62% of the CaO seemed to be unreacted and, therefore, capable of absorbing  $\text{CO}_2$ . While the tablet material made with 3  $\mu\text{m}$  limestone had the highest apparent concentration of unreacted CaO when calcined at 900°C, it had the lowest concentration when calcined at 1100°C. The low concentration of unreacted CaO correlated with high strength of the tablets as shown in Figure 13. The relatively large



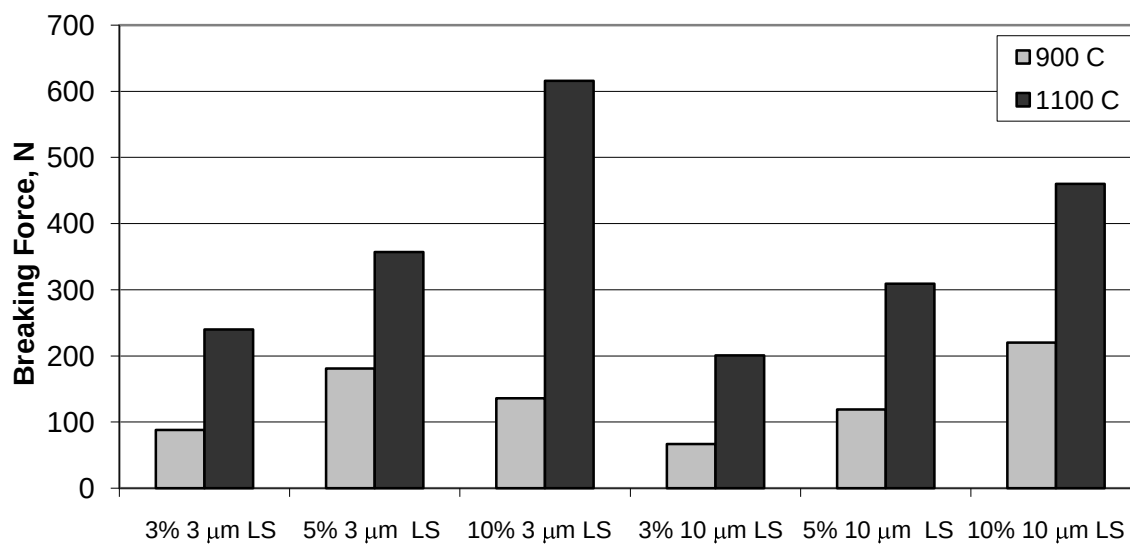
**Figure 13.** Force required to break cast tablets formulated with 5 wt.% limestone particles of various sizes and calcined at different temperatures.



**Figure 14.** Surface area of cast tablets formulated with 5 wt.% limestone particles of various sizes and calcined at different temperatures.



**Figure 15.** Apparent fraction of the CaO supplied that was still available for absorbing CO<sub>2</sub>.



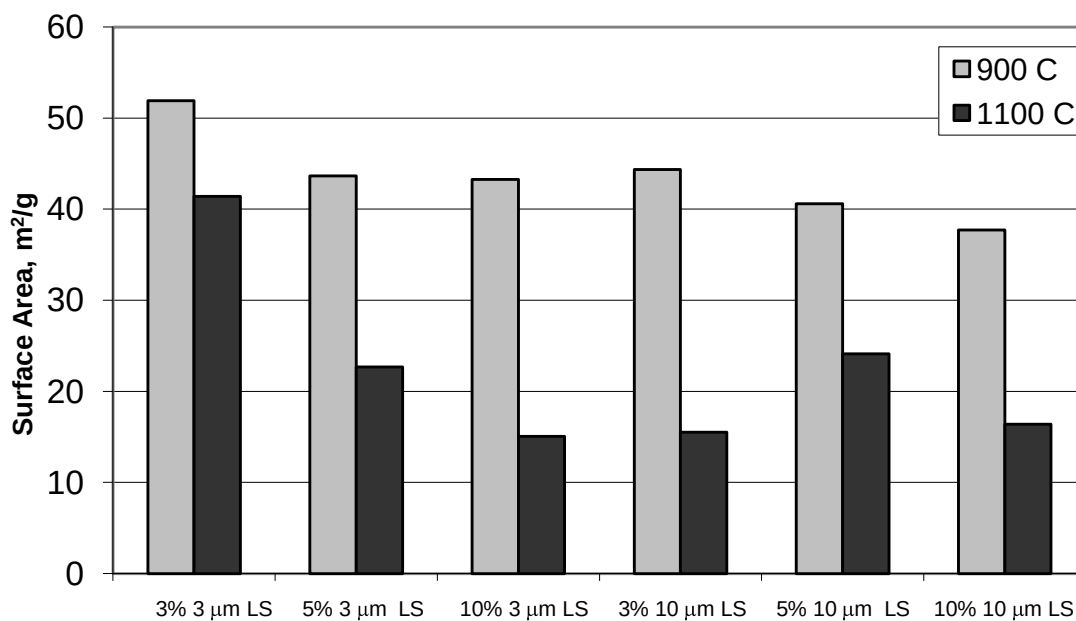
**Figure 16.** Force required to break cast tablets formulated with limestone particles of different sizes and supplied in different concentrations.

concentration of unreacted CaO (43%) in the tablets made with -212/+63  $\mu\text{m}$  limestone and calcined at 1100°C probably accounted for the low strength of these tablets.

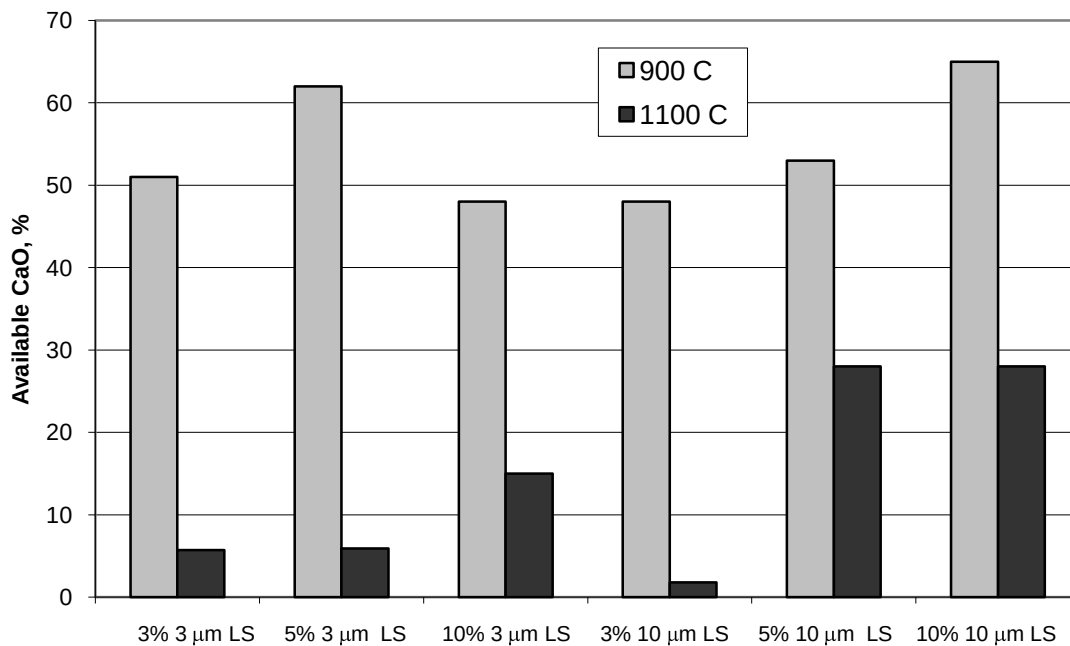
Further tests were conducted to explore the effect of limestone particle concentration over a range of 3 to 10% in the preparation mixture made with either 3  $\mu\text{m}$  or 10  $\mu\text{m}$  limestone while again employing CP-7 as the third component of the alumina mixture. The results of these tests presented in Figure 16 show that the force required to break the tablets increased with increasing limestone concentration for both limestone particle sizes. Furthermore, the force required to break the tablets was generally greater for the tablets made with the 3  $\mu\text{m}$  limestone than for those made with the 10  $\mu\text{m}$  material. In addition, the tablets calcined at 1100°C were always much stronger than those calcined at 900°C.

Figure 17 shows that limestone concentration did not have a large effect on the surface area of tablets calcined at 900°C. The effect of limestone concentration was more apparent with tablets calcined at 1100°C, particularly with tablets made with 3  $\mu\text{m}$  limestone. In this case, the surface area trended sharply downwards as the limestone concentration increased.

Tablets made with different limestone concentrations were also tested after calcination to determine the apparent fraction of unreacted CaO in the calcined tablets. The results presented in Figure 18 indicate that 48 to 65% of the CaO remained unreacted for tablets calcined at 900°C regardless of limestone particle size. For tablets calcined at 1100°C the unreacted CaO decreased to 15% or less in the majority of cases, the exceptions being observed with 10  $\mu\text{m}$  limestone in either 5 or 10% concentration. A comparison of the results in Figures 16 and 18 reveals some correlation between the breaking force and unreacted CaO.



**Figure 17.** Surface area of cast tablets formulated with limestone particles of different sizes and supplied in different concentrations.

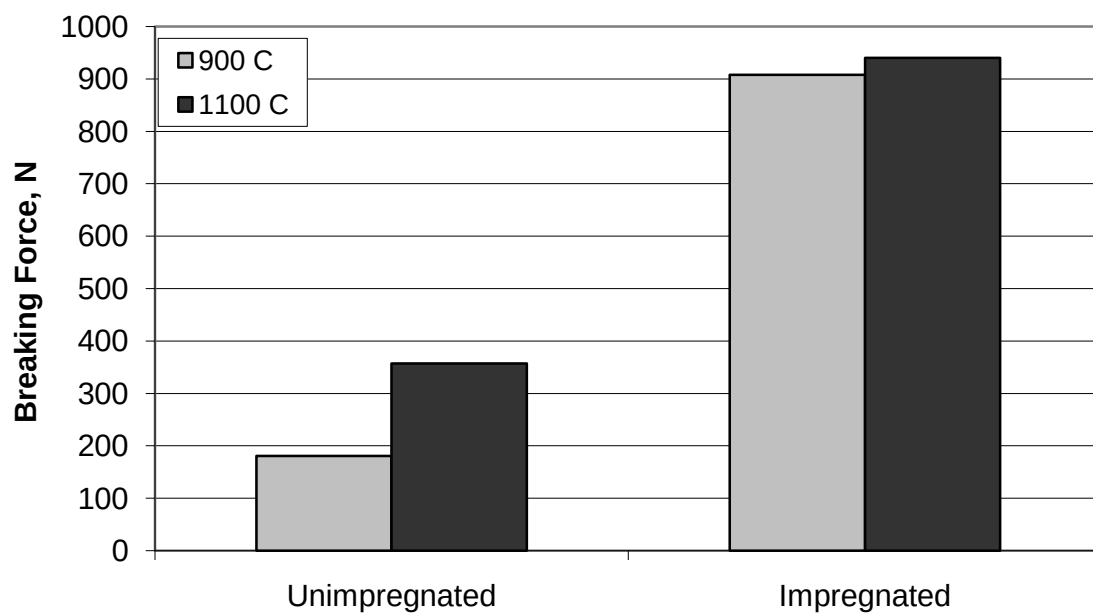


**Figure 18.** Apparent fraction of the CaO supplied which was still available for absorbing CO<sub>2</sub>.

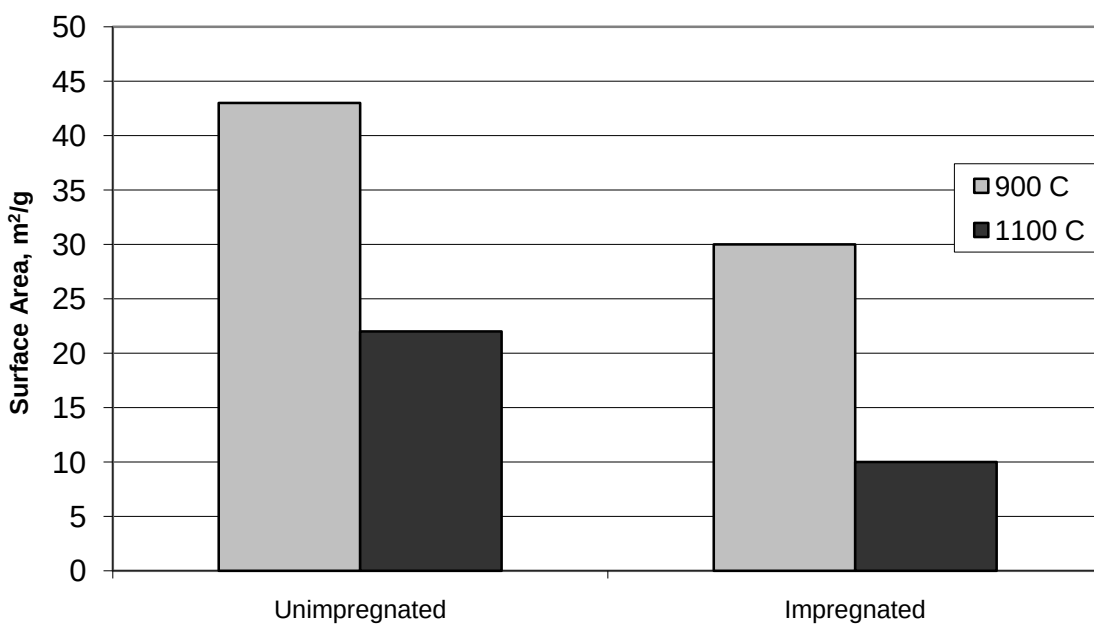
Samples of tablets made with different limestone particle sizes and concentrations and then calcined at either 900 or 1100°C were also subjected to X-ray diffraction (XRD) analysis to determine the presence of new crystalline phases. The analysis revealed the presence of calcium monoaluminate ( $\text{CaAl}_2\text{O}_4$ ) in samples calcined at 1100°C but not in samples calcined at 900°C. It appeared that this new crystalline phase was the principal reaction product formed as  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  reacted, and it could have accounted for the greater strength of the materials calcined at 1100°C.

Some of the cast tablets, which had been prepared with 5 wt.% limestone (3  $\mu\text{m}$ ) and 95 wt.% alumina containing 30 wt.% CP-7, were also impregnated with a 2 M solution of  $\text{La}(\text{NO}_3)_3$  in tetrahydrofuran and tested. The results are compared with similar tablets which had not been impregnated in Figures 19 and 20. It is apparent that the impregnated tablets were much stronger than those which had not been impregnated, but they also suffered a loss of surface area. Interestingly, the impregnated tablets calcined at 900°C seemed as strong as those calcined at 1100°C, while the surface area for the two cases was quite different. It was hypothesized that during calcination the  $\text{La}(\text{NO}_3)_3$  would be converted to  $\text{La}_2\text{O}_3$  which could react with  $\text{Al}_2\text{O}_3$  to form  $\text{LaAlO}_3$ . This material could serve as a particle binder and thereby strengthen the tablets. This hypothesis was partially confirmed by XRD analysis of the calcined tablets which showed  $\text{LaAlO}_3$  to be present in tablets calcined at 1100°C, but not in tablets calcined at 900°C. Therefore, it fails to explain why the tablets calcined at 900°C were as strong as those calcined at 1100°C.

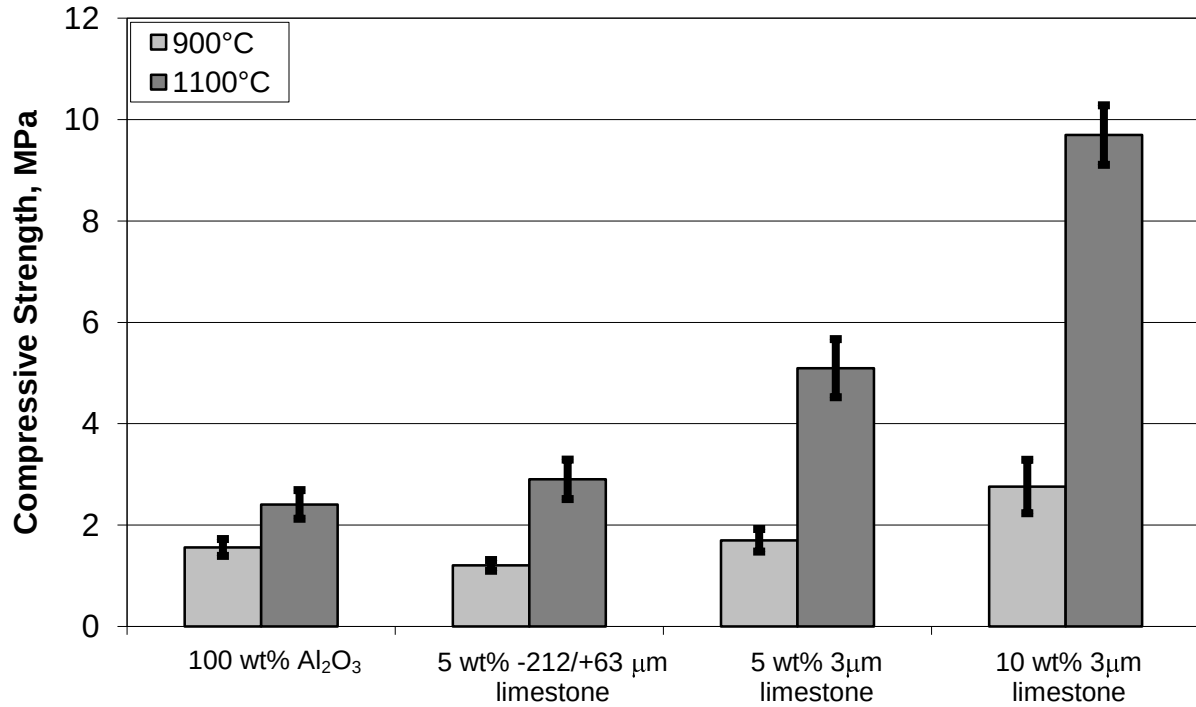
**Further tests with ultrafine size limestone.** While the preceding results provided a preliminary indication of the effects of limestone particle size and concentration on the physical



**Figure 19.** Effect of  $\text{La}(\text{NO}_3)_3$  impregnation on the force required to break the cast tablets.



**Figure 20.** Effect of  $\text{La}(\text{NO}_3)_3$  impregnation on the surface area of cast tablets.



**Figure 21.** Compressive strength of cast alumina tablets made with limestone in various concentrations and particle sizes and calcined at either 900°C for 3 hr or 1100°C for 2 hr.

properties of cast tablets composed largely of alumina oxide, further experimental work was conducted to improve the accuracy of the results. By repeating certain critical tests and measurements several times, it became possible to calculate the 95% confidence limits that are shown in Figure 21 and others that follow.

Figure 21 shows that a 5 wt% concentration of 3 μm limestone had little effect on the compressive strength of tablets calcined at 900°C for 3 hr. However, a 10 wt% concentration did increase the compressive strength of tablets calcined at this temperature compared to that of pure alumina tablets. Also it can be seen that the compressive strength of tablets calcined at 1100°C for 2 hr increased in direct proportion to the concentration of Microna 3 limestone.

**Table 3.** The ratio of the height of the most intense peak ( $I_{100}$ ) of the reported phase to the  $I_{100}$   $\alpha$ - $\text{Al}_2\text{O}_3$  peak obtained from XRD measurements of cast tablets made of  $\text{Al}_2\text{O}_3$  and Microna 3 limestone after calcination at different temperatures.

| Additive Material        | Temperature, °C | $I_{100}$ (Reported Phase)/ $I_{100}(\alpha\text{-Al}_2\text{O}_3)$ |                           |                           |
|--------------------------|-----------------|---------------------------------------------------------------------|---------------------------|---------------------------|
|                          |                 | CaO                                                                 | $\text{CaAl}_2\text{O}_4$ | $\text{CaAl}_4\text{O}_7$ |
| 2.7 wt% CaO <sup>a</sup> | 900             | 0.17                                                                | 0.00                      | 0.00                      |
|                          | 1100            | 0.07                                                                | 0.05                      | Observed <sup>c</sup>     |
| 5.7 wt% CaO <sup>b</sup> | 900             | 0.27                                                                | 0.00                      | 0.00                      |
|                          | 1100            | 0.05                                                                | 0.18                      | 0.56                      |

<sup>a</sup>Corresponds to 5 wt.% limestone.

<sup>b</sup>Corresponds to 10 wt.% limestone.

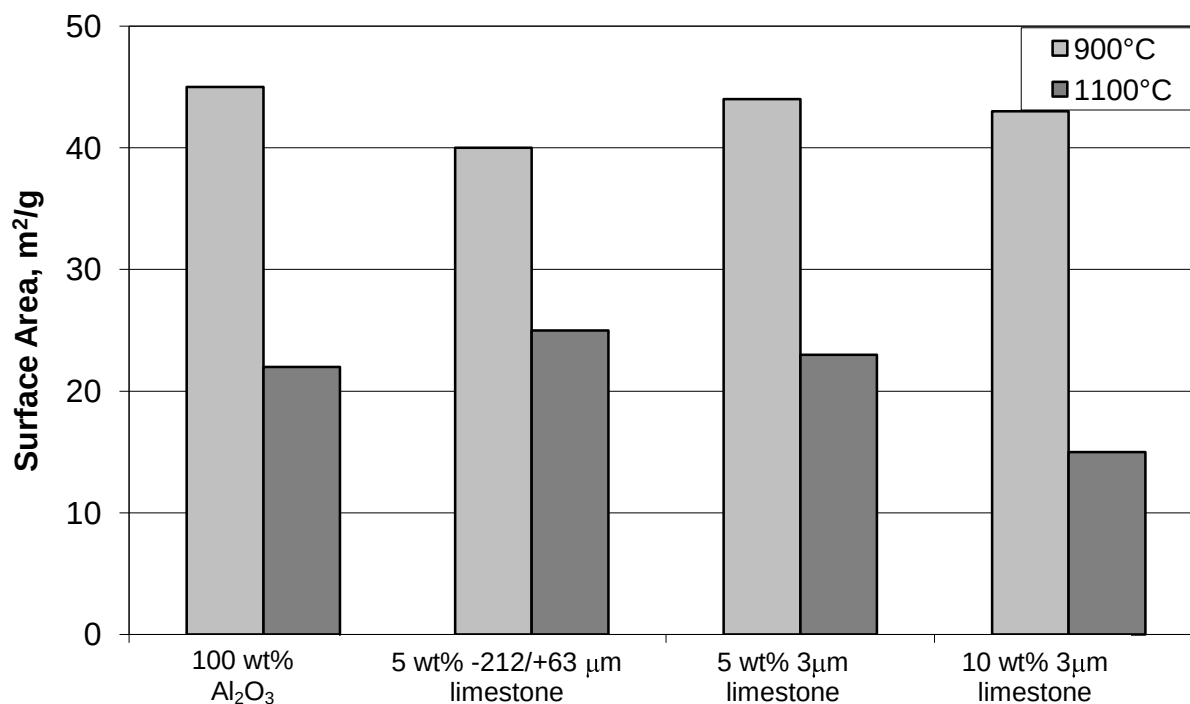
<sup>c</sup> $\text{CaAl}_4\text{O}_7$  was observed but the major peak was obscured under a minor  $\alpha$ - $\text{Al}_2\text{O}_3$  peak.

Furthermore, it is apparent that 5 wt% concentration of Microna 3 limestone was much more effective than a similar concentration of  $-212/+63\ \mu\text{m}$  limestone, especially at the higher calcination temperature. Selected samples of tablets that gave the results displayed in Figure 21 were analyzed by X-ray diffraction and the results are shown in Table 3. In all samples with limestone present and calcined at 900°C for 3 hr, no calcium aluminate phases were detected. However, in the samples calcined at 1100°C for 2 hr, the first expected calcium aluminate phase,  $\text{CaAl}_2\text{O}_4$  was detected. The second calcium aluminate phase,  $\text{CaAl}_4\text{O}_7$ , formed by the reaction of  $\text{CaAl}_2\text{O}_4$  with  $\text{Al}_2\text{O}_3$ , was also detected. The phase  $\text{CaAl}_4\text{O}_7$  was weakly observed in the 2.7 wt% CaO sample calcined at 1100°C for 2 hr even though a minor  $\alpha$ - $\text{Al}_2\text{O}_3$  peak obscured the strongest XRD peak. The trend in the appearance of the calcium aluminate phases appeared to correlate with the increase in the compressive strength of the tablets demonstrated in Figure 21. Also of interest is the decrease in the amount of crystalline CaO present in the XRD results in samples calcined at 1100°C.

The appearance of the calcium aluminate phases could account for the increase in compressive strength of tablets with Microna 3 limestone that were calcined at 1100°C. The melting points of  $\text{CaAl}_2\text{O}_4$  and  $\text{CaAl}_4\text{O}_7$  are 1602°C and 1762°C, respectively,<sup>16</sup> whereas melting points of  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  are 2054°C and 2613°C, respectively.<sup>17</sup> Thus, at 1100°C the sintering of the calcium aluminate phases is more likely to take place than the sintering of either  $\text{CaO}$  or  $\text{Al}_2\text{O}_3$ . The formation of calcium aluminate in the  $\text{CaO-Al}_2\text{O}_3$  system occurs by ionic  $\text{Ca}^{2+}$  diffusion into  $\text{Al}_2\text{O}_3$ ,<sup>18</sup> which would account for the decrease in the quantity of the crystalline  $\text{CaO}$  phase present. Since the Tamman temperature for  $\text{CaO}$  is about 1000-1250°C,<sup>19</sup> calcination at 1100°C would facilitate sintering of  $\text{CaO}$ , which presumably would enhance the diffusion of  $\text{Ca}^{2+}$  ions to form calcium aluminate.

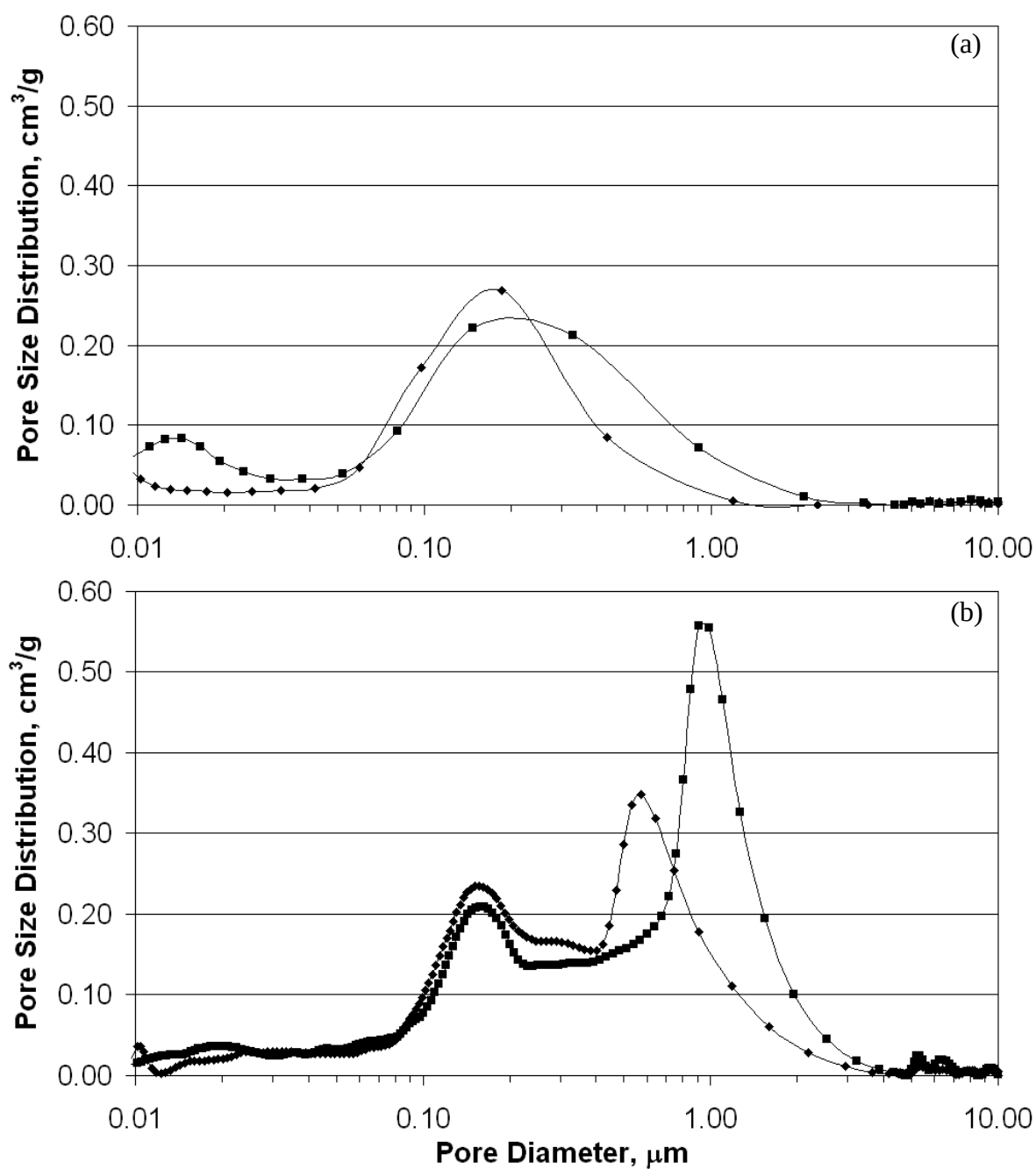
Surface area measurements of the tablets made with limestone are presented in Figure 22. As expected, the surface area decreased in samples calcined at 1100°C for 2 hr when compared with similar samples calcined at 900°C for 3 hr. This was most likely due to sintering of small pores in the high surface area DD-290 alumina. Samples calcined at 900°C appeared to yield a surface area of 40 m<sup>2</sup>/g or more, whereas most samples calcined at 1100°C for 2 hr yielded a surface area of only 22-25 m<sup>2</sup>/g. In addition, the sample with 10 wt% Microna 3 limestone calcined at 1100°C resulted in a surface area of only 15 m<sup>2</sup>/g.

In order to obtain further insight into the nature of the interaction between particles during sintering, intact cast tablets were subjected to mercury intrusion porosimetry. This technique provides the means for determining the pore size distribution between particles. The intact calcined tablets were subjected to the mercury intrusion technique, and the results are shown in Figure 23 parts (a) and (b).



**Figure 22.** BET surface area of cast alumina tablets made with various limestone concentrations and particle sizes and calcined at either 900°C for 3 hr or 1100°C for 2 hr.

Figure 23 (a) illustrates the pore size distribution curves for pure alumina cast tablets, which appear as a broad distribution that reaches a maximum at a pore diameter of 0.15 μm for tablets calcined at 900°C for 3 hr and at a pore diameter of 0.20 μm for tablets calcined at 1100°C for 2 hr. The small peak in the pore size distribution curve centered around a pore diameter of 0.015 μm in the sample calcined at 1100°C for 2 hr is believed to represent an increase in the size of pores within particles of amorphous DD-290 alumina as smaller pores within particles coalesce into larger pores. The shift in the distribution curves above a pore diameter of 0.06 μm was probably due to particle sintering as the temperature was increased, resulting in a wider interstitial pore size distribution with a larger mean pore diameter. As smaller particles fused together through sintering, the smaller spaces between particles would be closed, changing the pore size distribution observed in Figure 23 (a). Figure 23 (b) shows the



**Figure 23.** Pore size distributions obtained by mercury intrusion porosimetry of (a) 100% Al<sub>2</sub>O<sub>3</sub> tablets and (b) tablets with 10 wt.% Microna 3. Samples were calcined at 900°C for 3 hr (◆) or 1100 °C for 2 hr (■).

pore size distribution curves obtained by testing cast tablets with 10 wt% Microna 3 limestone in the alumina mixture. Above a pore diameter of 0.10  $\mu\text{m}$  there was a shift from a unimodal distribution to a bimodal distribution with addition of the Microna 3 limestone. Instead of a single broad peak, two sharper peaks appeared in each curve. Both curves displayed a smaller peak centered on a pore diameter of 0.15  $\mu\text{m}$  and a larger peak centered around a pore diameter of 0.57  $\mu\text{m}$  in one case (900°C) and 0.9  $\mu\text{m}$  in a second case (1100°C). Interestingly, the smaller peak in each curve appeared to be largely independent of the calcination temperature, which suggests that it was due to the change in the particle size distribution of the physical mixture. In direct contrast, the larger peak in each curve was highly temperature dependent so that an increase in calcination temperature produced a taller peak. The limestone particles, which became CaO particles upon calcination, could have reacted with alumina particles directly adjacent to them at high temperature resulting in the formation of calcium aluminate with a lower melting point than either  $\text{Al}_2\text{O}_3$  or CaO. Thus, enhanced sintering could have taken place at the interface between CaO and  $\text{Al}_2\text{O}_3$  particles due to the formation of calcium aluminate.

Table 4, which shows selected physical properties of the compounds CaO,  $\text{Al}_2\text{O}_3$ , and  $\text{CaAl}_2\text{O}_4$  among others, indicates that  $\text{CaAl}_2\text{O}_4$  with a Tamman temperature of 801°C would be more likely to sinter at the calcination temperatures employed than would  $\alpha\text{-Al}_2\text{O}_3$  or CaO with their higher Tamman temperatures.

Although crystalline calcium aluminate was not observed with XRD in samples calcined at 900°C for 3 hr (Table 3), amorphous calcium aluminate could still have been present. Thus, the pore size distributions with maxima located at pore sizes of 0.57  $\mu\text{m}$  and 0.90  $\mu\text{m}$  for samples calcined at 900°C for 3 hr or 1100°C for 2 hr, respectively, could have been due to neck growth and grain coarsening of the particles as the particles fused together by the formation of

**Table 4.** Selected properties of various phases present during the preparation and testing of cast tablets and core-in-shell pellets.

| Phase                                    | Density,<br>g/cm <sup>3</sup> | Melting Point,<br>°C    | Tamman Temperature,<br>°C <sup>a</sup> |
|------------------------------------------|-------------------------------|-------------------------|----------------------------------------|
| $\alpha$ -Al <sub>2</sub> O <sub>3</sub> | 3.99 <sup>17</sup>            | 2054 <sup>17</sup>      | 1027                                   |
| CaO                                      | 3.34 <sup>17</sup>            | 2613 <sup>17</sup>      | 1000-1250 <sup>19</sup>                |
| CaAl <sub>2</sub> O <sub>4</sub>         | 2.51 <sup>20</sup>            | 1602 <sup>16</sup>      | 801                                    |
| La <sub>2</sub> O <sub>3</sub>           |                               | 2304 <sup>17</sup>      | 1152                                   |
| LaAlO <sub>3</sub>                       | 4.89 <sup>21</sup>            | 2031-2049 <sup>22</sup> | 1015-1024                              |
| ZnAl <sub>2</sub> O <sub>4</sub>         | 4.68 <sup>23</sup>            | 1950 <sup>24</sup>      | 975                                    |
| BaAl <sub>2</sub> O <sub>4</sub>         | 4.04 <sup>25</sup>            | 1829 <sup>26</sup>      | 915                                    |

<sup>a</sup>Taken as half the melting point unless otherwise noted

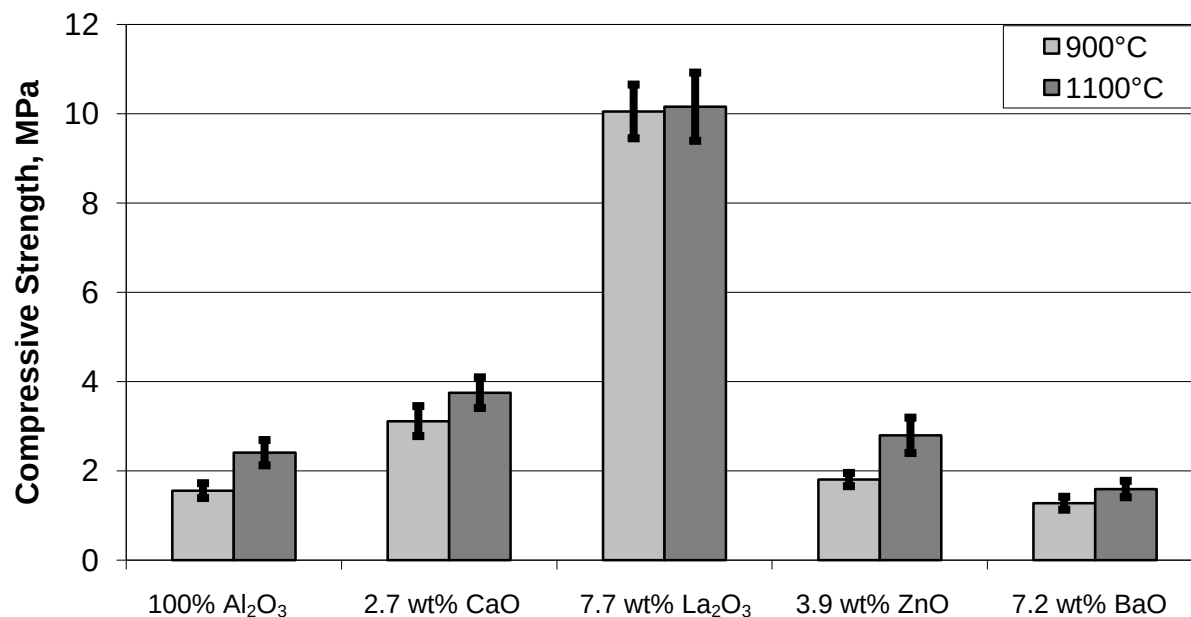
calcium aluminate. Some alumina particles may not have had limestone particles adjacent to them, causing sintering that also may have led to the smaller peak in each distribution curve centered around a pore diameter of 0.15  $\mu$ m.

The sintering mechanism that appeared to take place during calcination with the addition of Microna 3 limestone was probably a non-densifying mechanism produced by surface diffusion or lattice diffusion from the surface that formed necks.<sup>27</sup> The cumulative pore volume between particles was measured in the pore range from 0.05  $\mu$ m to 10.0  $\mu$ m for all samples. The cumulative pore volume for the pure alumina tablets calcined at 900°C for 3 hr was 0.20 cm<sup>3</sup>/g and for tablets calcined at 1100°C for 2 hr was 0.23 cm<sup>3</sup>/g. When Microna 3 limestone was present in 10 wt% concentration in the cast tablets, the pore volume for samples calcined at 900°C for 3 hr was 0.26 cm<sup>3</sup>/g and for samples calcined at 1100°C for 2 hr was 0.32 cm<sup>3</sup>/g. Thus, the interstitial pore volume increased with the addition of Microna 3 limestone. Therefore,

the increase in compressive strength of the material was most likely due to the formation of a binding calcium aluminate phase that resulted in neck growth between CaO and Al<sub>2</sub>O<sub>3</sub> particles, but did not result in densifying of the particle mixture. The lack of densification is a beneficial result since decreased pore volume could impede the diffusion of CO<sub>2</sub> to the core of a core-in-shell pellet.

**Impregnation of shell material with metal nitrates.** An alternative method for introducing various metal oxides into the alumina particle mixture was also investigated. This method involved doping the alumina with a solution of the nitrate salt of the metal that upon calcination was converted to the oxide. The metal oxides were chosen to provide a range of optical basicity which is a numerical expression of the average electron donor power of an oxide, and thus it provides a measure of the acid-base properties of an oxide. The basic oxides tested in order of increasing basicity were CaO, La<sub>2</sub>O<sub>3</sub>, ZnO, and BaO with optical basicities of 1.00, 1.07, 1.08, and 1.21, respectively. Alumina is classified as an acidic oxide.<sup>28</sup> It was hypothesized that the difference between the optical acidity of the alumina and optical basicity of the additive would act as a driving force to produce an aluminate phase. The aluminate phase produced during sintering would ideally act as a binder for the material, thus increasing the compressive strength of the tablets.

In order to produce results comparable to tablets made with added limestone, tablets with other oxides were made for testing with the same atomic ratio of each metallic element to that of aluminum as the atomic ratio of Ca:Al indicated in Table 2. The tablets were prepared by first mixing the alumina powders with a solution of the metal nitrate, which was then dried. The dried mixture was then mixed with a 5 wt.% lignin solution and cast. After drying at room temperature, the tablets were calcined at 900°C for 3 hr or at 1100°C for 2 hr.



**Figure 24.** Compressive strength of cast tablets made with equivalent concentrations of basic oxides derived from nitrate salts and calcined at 900°C for 3 hr or 1100°C for 2 hr. All of the samples with basic oxides had an atomic ratio X/Al of 0.026 where X was Ca, La, Zn, or Ba.

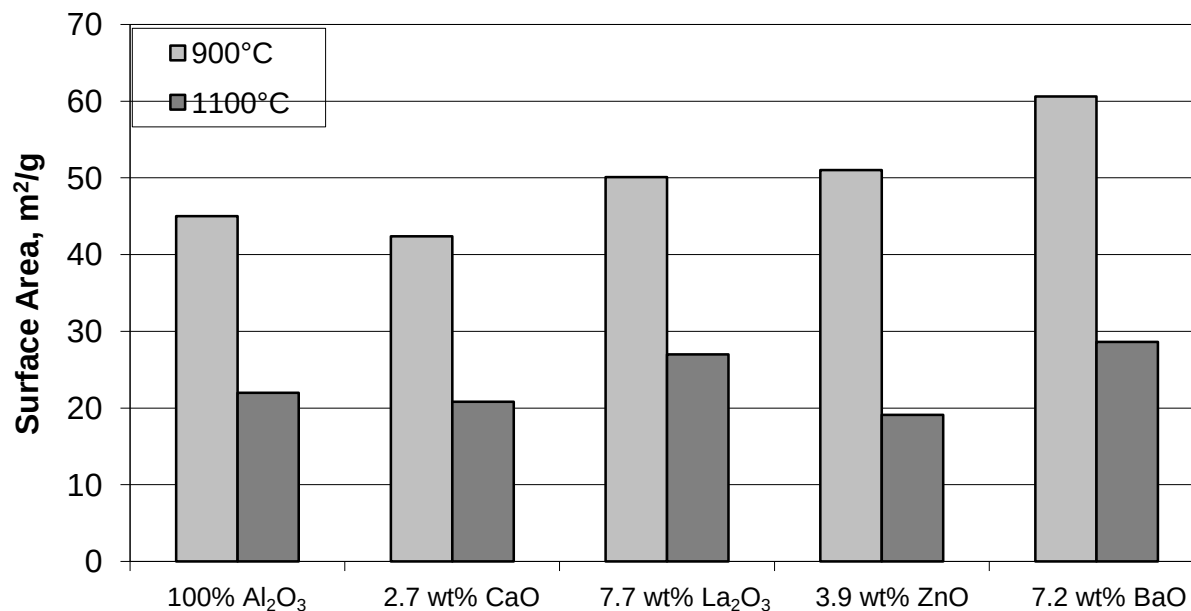
The compressive strength of tablets made with equivalent concentrations of different metal oxides and subsequently calcined at either 900°C for 3 hr or 1100°C for 2 hr is indicated in Figure 24. All of the results in Figure 24 that were obtained with added basic oxides that employed the same atomic ratio of 0.026 mol X/mol Al, where X is the basic oxide atom. While results are presented in order of increasing basicity, the compressive strength does not increase in a similar manner. However, the incorporation of lanthanum oxide in the material greatly increased the compressive strength of the samples, and the increase in compressive strength was the same for both calcination temperatures. The fact that a large compressive strength could be achieved at the lower calcination temperature is highly fortuitous since it would permit calcining core-in-shell pellets at a temperature where less of the high surface area alumina would be degraded.

**Table 5.** The ratio of the height of the most intense peak ( $I_{100}$ ) of the reported phase to the  $I_{100}$   $\alpha$ - $\text{Al}_2\text{O}_3$  peak obtained from XRD measurements of cast tablets made of  $\text{Al}_2\text{O}_3$  and added metal nitrates after calcination at different temperatures.

| Additive Material               | Temperature, °C | $I_{100}$ (Reported Phase)/ $I_{100}$ ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) |                  |                           |                           |
|---------------------------------|-----------------|------------------------------------------------------------------------------|------------------|---------------------------|---------------------------|
|                                 |                 | $\text{CaAl}_2\text{O}_4$                                                    | $\text{LaAlO}_3$ | $\text{ZnAl}_2\text{O}_4$ | $\text{BaAl}_2\text{O}_4$ |
| 2.7 wt% CaO                     | 900             | 0.00                                                                         |                  |                           |                           |
|                                 | 1100            | 0.00                                                                         |                  |                           |                           |
| 7.7 wt% $\text{La}_2\text{O}_3$ | 900             |                                                                              | 0.02             |                           |                           |
|                                 | 1100            |                                                                              | 0.17             |                           |                           |
| 3.9 wt% ZnO                     | 900             |                                                                              |                  | 0.07                      |                           |
|                                 | 1100            |                                                                              |                  | 0.10                      |                           |
| 7.2 wt% BaO                     | 900             |                                                                              |                  |                           | 0.08                      |
|                                 | 1100            |                                                                              |                  |                           | 0.28                      |

X-ray diffraction (XRD) measurements were also performed on tablets containing metal oxides derived from the corresponding nitrates. The XRD results are presented in Table 5.

While increasing the basicity of the metal oxide incorporated in the tablets did not produce an increase in the compressive strength of cast tablets, it can be seen from Table 5 that in general an increase in basicity of the metal oxide did increase the amount of the crystalline aluminate phase formed. The addition of CaO derived from heat treating cast tablets with calcium nitrate present did not produce an observable calcium aluminate phase, which contrasted sharply with the results achieved by incorporating limestone in the tablets (see Table 3). However, lanthanum, zinc and barium oxides all produced crystalline aluminate phases in tablets calcined at 900°C for 3 hr or 1100°C for 2 hr. Thus, the large increase in compressive strength achieved by adding  $\text{La}_2\text{O}_3$  could not be explained by the presence or the amount of the crystalline aluminate phases observed.



**Figure 25.** BET surface areas of cast tablets made with equivalent concentrations of basic oxides derived from nitrate salts and calcined at 900°C for 3 hr or 1100°C for 2 hr. All of the samples with basic oxides had an atomic ratio X/Al of 0.026 where X was Ca, La, Zn, or Ba.

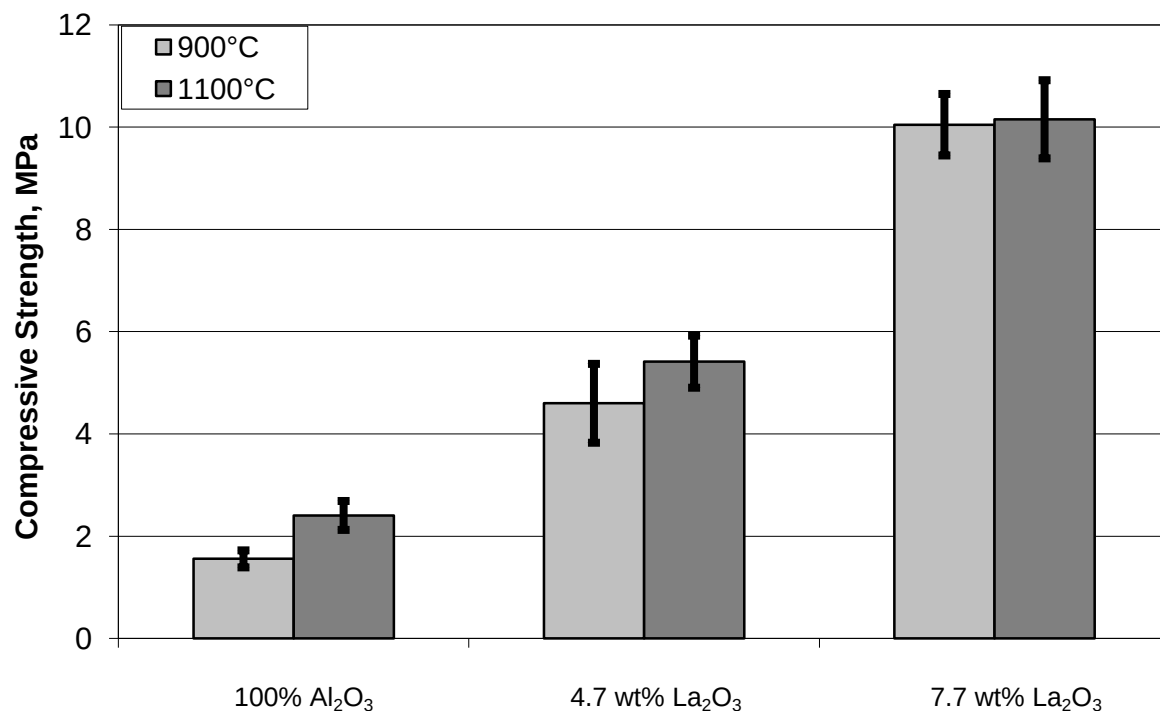
The addition of lanthanum nitrate to the alumina mixture prior to casting and calcination resulted in an increase in compressive strength that was statistically similar for tablets calcined either at 900°C for 3 hr or at 1100°C for 2 hr. Thus, the strength of the samples could be increased sufficiently by the addition of lanthanum nitrate even at the lower calcination temperature. The advantage of using the lower calcination temperature is that it had less effect on the BET surface area of the shell material as indicated by Figure 25. This surface area was determined by nitrogen adsorption measurements carried out on alumina tablets made by the same procedure as that employed to make the tablets used for measuring the breaking force. These measurements showed that the samples calcined at 900°C for 3 hr did retain a higher surface area compared to similar samples calcined at 1100°C for 2 hr. More than likely, the

large loss in surface area experienced by the tablets calcined at 1100°C was due to sintering of the amorphous DD-290 alumina, which had a large surface area initially.

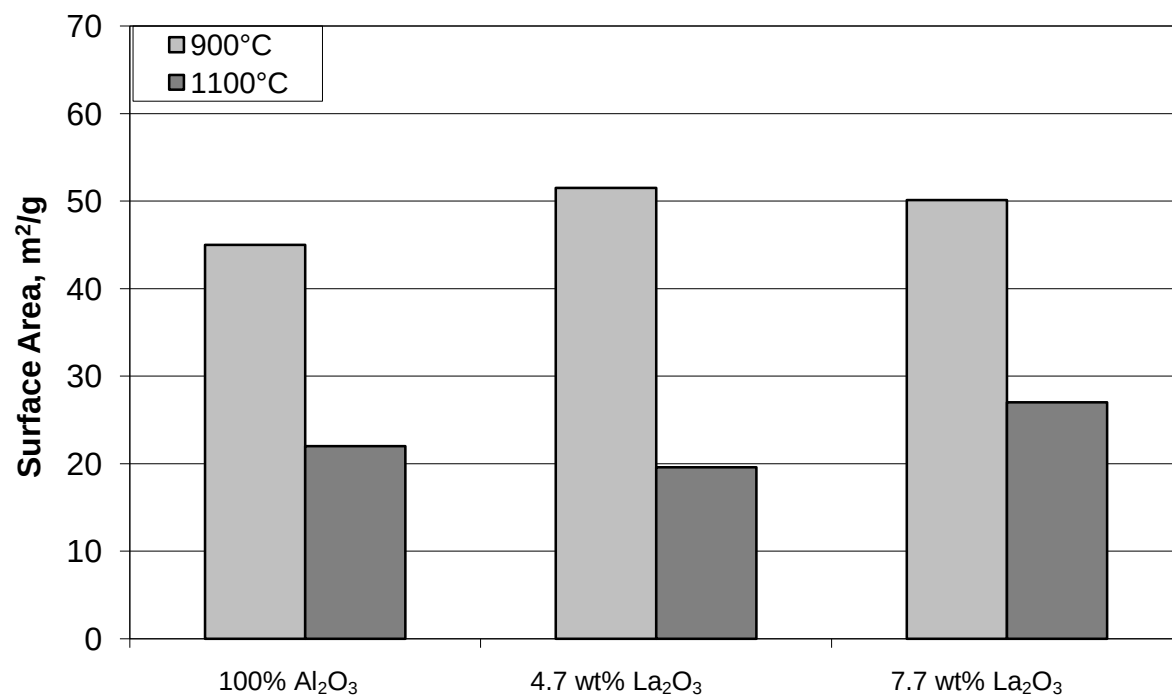
**Further tests with lanthanum oxide.** Since the incorporation of  $\text{La}_2\text{O}_3$  in the shell material produced a dramatic increase in the compressive strength of the cast tablets, further consideration was given to the effect of  $\text{La}_2\text{O}_3$  concentration in the tablets. When a lower concentration corresponding to an atomic ratio of 0.15 La:Ca or a mass concentration of 4.7 wt%  $\text{La}_2\text{O}_3$  was used, the results presented in Figures 26 and 27 were achieved. Figure 26 shows that the increase in compressive strength of the tablets due to the addition of  $\text{La}_2\text{O}_3$  is directly proportional to its concentration. Furthermore, the results show that at either  $\text{La}_2\text{O}_3$  concentration, the effect of calcination temperature on the compression strength was not statistically significant.

As shown in Figure 27, the BET surface area of the tablets calcined at 900°C was slightly greater for tablets with  $\text{La}_2\text{O}_3$  than for pure  $\text{Al}_2\text{O}_3$  tablets, but the surface area was not affected by the concentration of  $\text{La}_2\text{O}_3$ . The apparently greater surface area of tablets with lanthanum compared to pure alumina tablets agrees with earlier results that showed that lanthanum oxide has a stabilizing effect on the surface area of alumina at high temperatures.<sup>29</sup> This effect may also have accounted for the slightly greater surface area of tablets calcined at 1100°C that contained 7.7 wt%  $\text{La}_2\text{O}_3$ .

To determine the effects of  $\text{La}_2\text{O}_3$  on the porosity of intact cast tablets, mercury intrusion porosimetry was applied to selected samples that contained 7.7 wt%  $\text{La}_2\text{O}_3$  and had been calcined at either 900°C or 1100°C (Figure 28). For ease of comparison the porosity of pure  $\text{Al}_2\text{O}_3$  tablets presented in Figure 23 (a) are reproduced in Figure 28 (a). Figure 28 (b) shows the pore size distribution within tablets containing 7.7 wt%  $\text{La}_2\text{O}_3$  and calcined at 900°C for 3 hr or



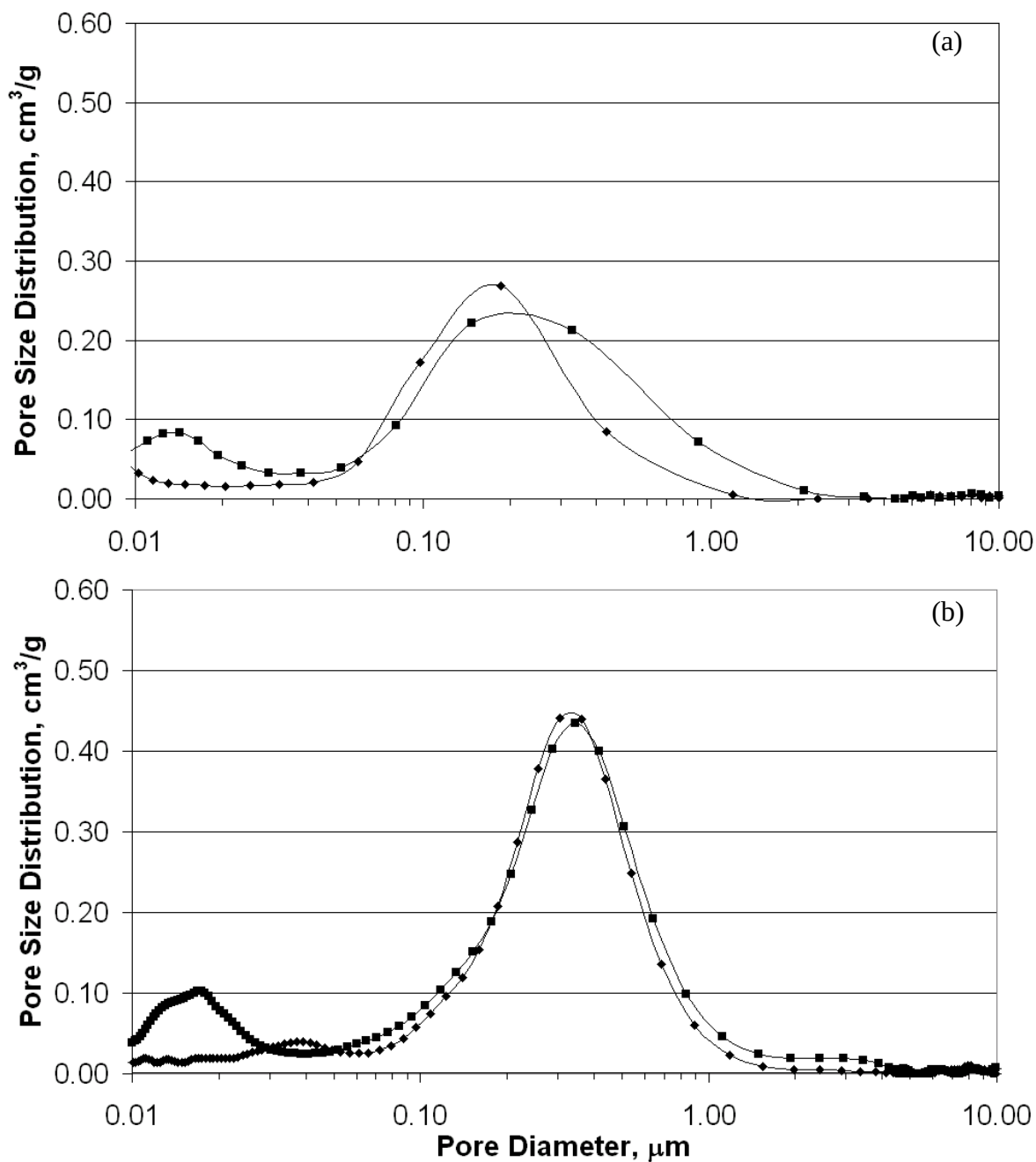
**Figure 26.** Compressive strength of cast tablets made with various concentrations of  $\text{La}_2\text{O}_3$  derived from the nitrate salt and calcined at 900°C for 3 hr or 1100°C for 2 hr.



**Figure 27.** BET surface area measurements of cast tablets made with various concentrations of  $\text{La}_2\text{O}_3$  derived from the nitrate salt and calcined at 900°C for 3 hr or 1100°C for 2 hr.

1100°C for 2 hr. The two large peaks centered around a pore diameter of 0.35  $\mu\text{m}$  are most likely due to the pore space between particles or interparticle porosity while the smaller peak centered around a pore diameter of 0.015  $\mu\text{m}$  probably is due to the pore space within particles of amorphous DD-290 alumina. Figure 28 indicates that the addition of  $\text{La}_2\text{O}_3$  shifts the pore size distribution so that the interparticle porosity is more narrowly focused about a larger mean size. It also indicates that the pore size distribution in Figure 28 (b) is essentially independent of the calcination temperature between 900°C and 1100°C, which correlates with the effect of calcination temperature over this range on the compressive strength.

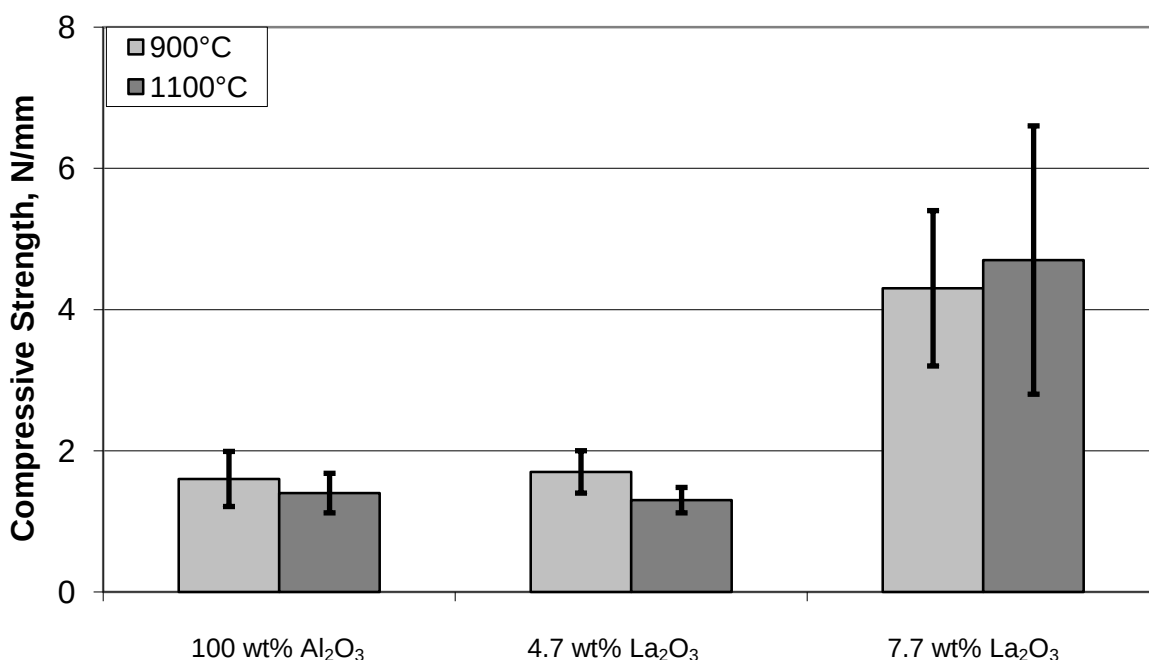
The dramatic increase in compressive force required to break the cast tablets made with lanthanum nitrate appeared to be due to local bonding and not due to densification of the cast tablets while being calcined. The lack of densification was attributed to the interstitial pore volume between particles in the cast tablets as determined by mercury porosimetry. The cumulative pore volume of the cast tablets was determined over a range of pore diameters from 0.05  $\mu\text{m}$  to 10.0  $\mu\text{m}$ . Over this range the pore volume should have been largely due to the interstitial space between particles. For pure alumina cast tablets calcined at 900°C for 3 hr, the measured pore volume was 0.20  $\text{cm}^3/\text{g}$ , while for similar tablets calcined 1100°C for 2 hr the measured pore volume of 0.23  $\text{cm}^3/\text{g}$ . In contrast, cast tablets made with added lanthanum and calcined under similar conditions had measured pore volumes of 0.27  $\text{cm}^3/\text{g}$  and 0.28  $\text{cm}^3/\text{g}$ , respectively. Thus, local binding of the alumina particles and not an overall densification of the cast tablets seemed to take place. The same trend was observed when Microna 3 limestone was introduced to strengthen the tablets. The lack of densification is beneficial because it permits gas to diffuse through the material when it is used as a shell around a core of sorbent material.



**Figure 28.** Pore size distribution obtained by mercury intrusion porosimetry of (a) 100%  $\text{Al}_2\text{O}_3$  tablets and (b) tablets with 7.7 wt%  $\text{La}_2\text{O}_3$ . Samples were calcined at 900°C for 3 hr (◆) or at 1100 °C for 2 hr (■).

Since  $\text{LaAlO}_3$  was observed by XRD analysis of the calcined tablets, it is quite likely that this material served as a binding agent for the  $\text{Al}_2\text{O}_3$  particles. While  $\text{LaAlO}_3$  may have been produced by the solid state reaction between  $\text{La}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , since the estimated Tamman temperature of  $\text{La}_2\text{O}_3$  is  $1152^\circ\text{C}$  (see Table 4), a more likely possibility is that  $\text{Al}_2\text{O}_3$  reacted with one of the decomposition products of lanthanum nitrate as the shell material was being calcined. A likely decomposition product is  $\text{LaO}(\text{NO}_3)$  which can form at  $440^\circ\text{C}$  and is known to be unstable and reactive.<sup>30</sup>

**Core-in-shell pellets.** Since the addition of lanthanum had greatly increased the compressive strength of cast alumina tablets, further tests were conducted to see if lanthanum addition would have a similar effect on the compressive strength of core-in-shell pellets when it was added to the shell material. The breaking force of spherical core-in-shell pellets and cylindrical tablets would likely have different modes of fracture and the compressive strengths are not directly comparable. Therefore, spherical core-in-shell pellets with and without lanthanum were produced in order to compare compressive strength testing results. To control the amount of  $\text{La}_2\text{O}_3$  present in the alumina shell, lanthanum was added to the shell mixture prior to pelletization. Measured quantities of the specific alumina mixture used previously and a lanthanum nitrate solution were mixed and then allowed to dry. The resulting material was reground and applied as a shell material to spherical pellets made of Microna 3 limestone. As in the preparation of the cast alumina tablets, a 5% lignin solution was employed for applying the shell material to the pellet cores. The core-in-shell pellets were subsequently calcined at either  $900^\circ\text{C}$  for 3 hr or  $1100^\circ\text{C}$  for 2 hr. A compressive strength test of the calcined pellets produced the results presented in Figure 29. Since the spherical pellets did not have a flat surface over which a force could be applied, the results are presented in terms of the breaking force in



**Figure 29.** Compressive strength of core-in-shell spherical pellets with lanthanum nitrate added to the Al<sub>2</sub>O<sub>3</sub> shell mixture prior to pelletization. The cores were made of Microna 3 limestone. The samples were calcined at 900°C for 3 hr or 1100°C for 2 hr.

Newtons divided by the pellet diameter in millimeters. The pellets that were produced with only alumina present in the shell composition were weak, which was expected. Surprisingly, the addition of 4.7 wt% La<sub>2</sub>O<sub>3</sub> to the shell material seemed to have no effect on the compressive strength, whereas the addition of 7.7 wt% La<sub>2</sub>O<sub>3</sub> improved the compressive strength significantly. However the improvement in compressive strength was not as large as that observed with the cast tablets. On the other hand, as with the cast tablets, the calcination temperature over the 900°C to 1100°C range did not have a significant effect on the compressive strength.

**Catalyst development.** The catalytic material development work during the first phase emphasized developing a nickel catalyst that would give a high methane conversion while steam reforming at a temperature of 600°C. In a commercial process, methane steam reforming is

typically conducted at higher temperature and pressure (800-900°C, 100 bars). However, for the utilization of a combined catalyst and sorbent, the optimal operating temperature for the combined methane reaction and CO<sub>2</sub> absorption reaction by CaO is 600°C or lower when at atmospheric pressure. Thus it is important for the nickel catalyst to have high activity at this temperature. In the future, it would be desirable for the catalyst formulation to also be resistant to coke deposition and sulfur.

The first phase of this investigation showed that while a shell material composed entirely of  $\alpha$ -alumina and limestone was very strong, its surface area available for supporting a catalyst was limited. Therefore, when the material was impregnated with a nickel catalyst, the resulting activity of the catalyst was limited. However, when part of the  $\alpha$ -alumina was replaced with CP-7 alumina so that it constituted approximately 30% of the alumina mixture, the surface area of the catalyst support increased greatly as did the activity of the nickel catalyst but the physical strength declined.

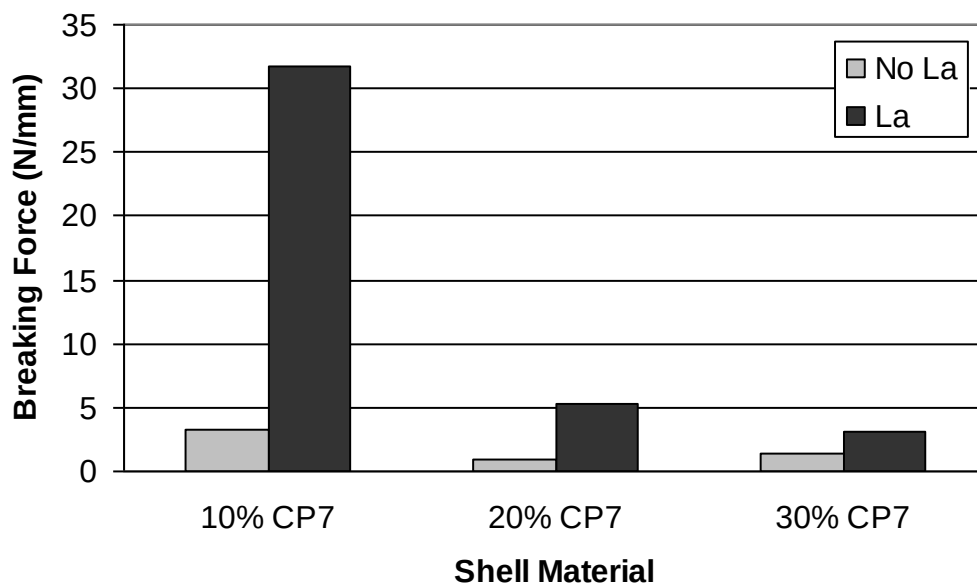
The dilemma posed by the trade-off between catalytic activity and physical strength of the material was addressed in the present, second phase of the investigation. Since it had been shown that the addition of lanthanum to the shell material had the opposite effect as the introduction of CP-7, it seemed likely that a balance of the two materials could solve the dilemma, i.e., produce a material which had both the necessary surface area and strength. To explore this possibility, a series of spherical pellets was prepared of only shell material but with different concentrations of CP-7, and while some of the pellets were impregnated with lanthanum, others were not. The composition of the different batches of pellets before lanthanum impregnation and calcination is shown in Table 6. After the preparation had been

**Table 6.** Composition of the shell and catalyst support material before lanthanum impregnation and calcination.

| Level |         | Composition (wt%)          |                                       |                                         |                        |
|-------|---------|----------------------------|---------------------------------------|-----------------------------------------|------------------------|
|       |         | CP-7, 8 $\mu$ m<br>alumina | T-64, 8 $\mu$ m,<br>$\alpha$ -alumina | A-16SG, 1 $\mu$ m,<br>$\alpha$ -alumina | 3 $\mu$ m<br>limestone |
| 1     | 10% CP7 | 9.5                        | 47.5                                  | 38                                      | 5                      |
| 2     | 20% CP7 | 19                         | 38                                    | 38                                      | 5                      |
| 3     | 30% CP7 | 28.5                       | 28.5                                  | 38                                      | 5                      |

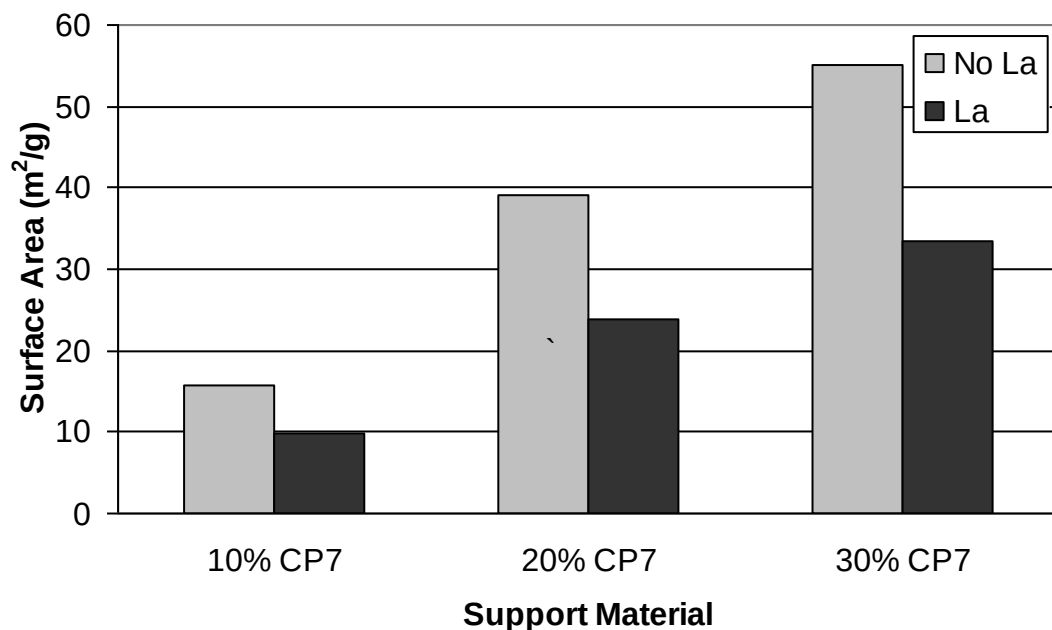
completed, including calcination at 900°C for 2 hr, the pellets were tested and the results are presented in Figures 30 and 31. As seen in Figure 30 the breaking force of the shell material decreased as more CP-7 alumina was incorporated in the mixture. For the catalyst pellets to be practical for commercial use, the desired breaking force is at least 9 N/mm pellet diameter. None of the pellets that were calcined at 900°C without pre-treatment with lanthanum nitrate satisfied this strength requirement. Pretreatment with lanthanum nitrate prior to calcination significantly increased the breaking force of the pellets. The strength improvement was most dramatic with the 10% CP-7 material formulation, which showed approximately an eight fold strength improvement. Even with the lanthanum pretreatment, the 10% CP-7 support material formulation was the only one that satisfied the minimum 9 N/mm breaking force requirement.

Figures 31 (a) and (b) show the effects of CP-7 concentration and lanthanum nitrate pretreatment on the surface area and microporosity of the calcined pellets. Pretreatment of the support materials with lanthanum nitrate resulted in decreased surface area by approximately 30% for all of the pellets. The porosity also decreased, although the extent of reduction seemed

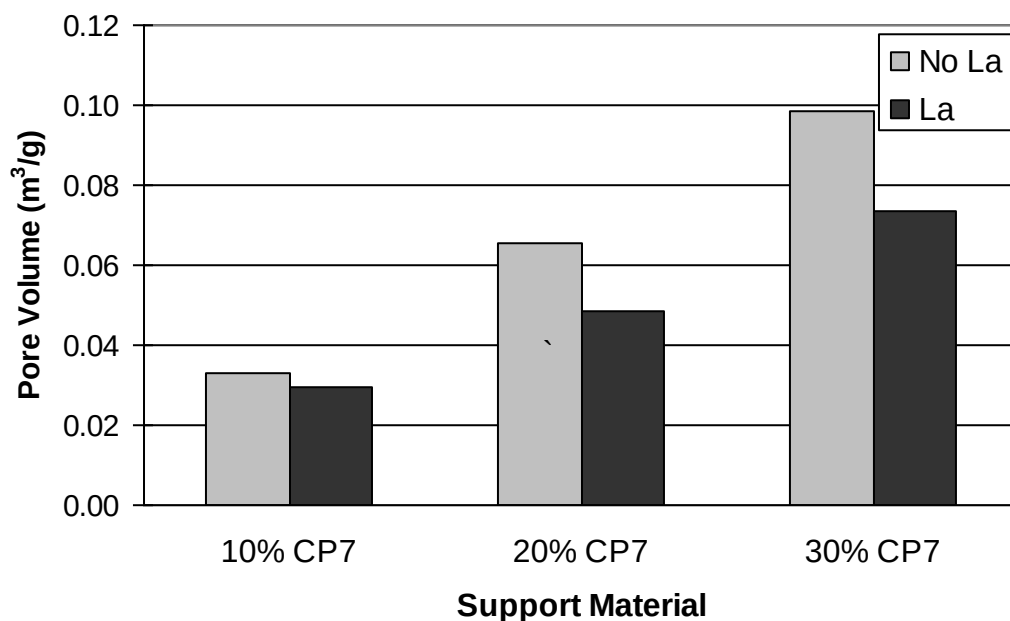


**Figure 30.** Breaking force of spherical pellets with different compositions (10%, 20%, 30% CP-7), with and without lanthanum nitrate pretreatment (La = lanthanum added, No La = no lanthanum added) and with no nickel. Pellets were calcined at 900°C.

to be more pronounced for support materials with higher surface area and porosity. The microporosity reduction might have been caused by blockage of the pores by lanthanum oxide, which possibly also caused the increase in the strength of the materials. The 10% CP-7 pellets, which showed a dramatic breaking force improvement when pretreated with lanthanum nitrate, showed only a small reduction in microporosity. This suggests that the effect of lanthanum oxide addition in increasing the material strength was not only due to the reduction of porosity, but also possibly due to partial sintering of lanthanum oxide upon calcination. However, since the melting point of lanthanum oxide is 2304°C, it would be unlikely to sinter when calcined at 900°C. Therefore, as suggested above a more likely possibility was the interaction of alumina with one of the decomposition products of lanthanum nitrate to form lanthanum aluminate with an increase in the strength of the material.



(a)



(b)

**Figure 31.** Nitrogen absorption results for support material formulation (10%, 20%, 30% CP-7) and pellet pretreatment (No La = no lanthanum added, La= lanthanum added). (a) surface area, (b) pore volume. The pellets had been calcined at 900°C for 2 hr.

The nickel content of the Ni impregnated shell material seemed likely to depend on several parameters which included the (1) shell material formulation, (2) lanthanum pre-treatment, (3) method of Ni impregnation, and (4) number of Ni impregnations. To explore this dependency in greater detail and with some consideration of the possible interactions between parameters, an organized study of the parameters was conducted. The parameter levels which were selected are indicated in Table 7. Three levels of CP-7 were included in the shell material formulation which resulted in the corresponding shell compositions listed in Table 6. Some of the pellets were impregnated with lanthanum before calcination at 900°C for 2 hr, whereas other pellets were only calcined. Two nickel impregnation methods were applied to the calcined pellets. In the first method, the pellets were soaked in an aqueous solution having a 2 M concentration of  $\text{Ni}(\text{NO}_3)_2$  and an 8 M concentration of urea, whereas in the second method the pellets were soaked in a THF solution with a 2 M concentration of  $\text{Ni}(\text{NO}_3)_2$ . Finally, some pellets were impregnated with Ni only once while other pellets were impregnated twice. In all,

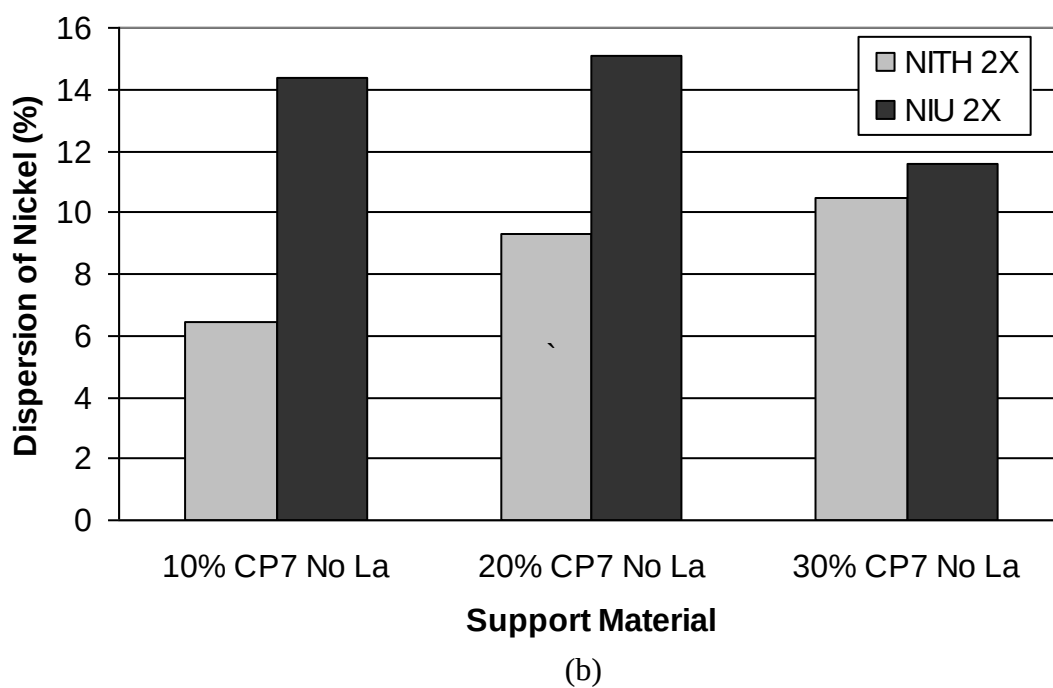
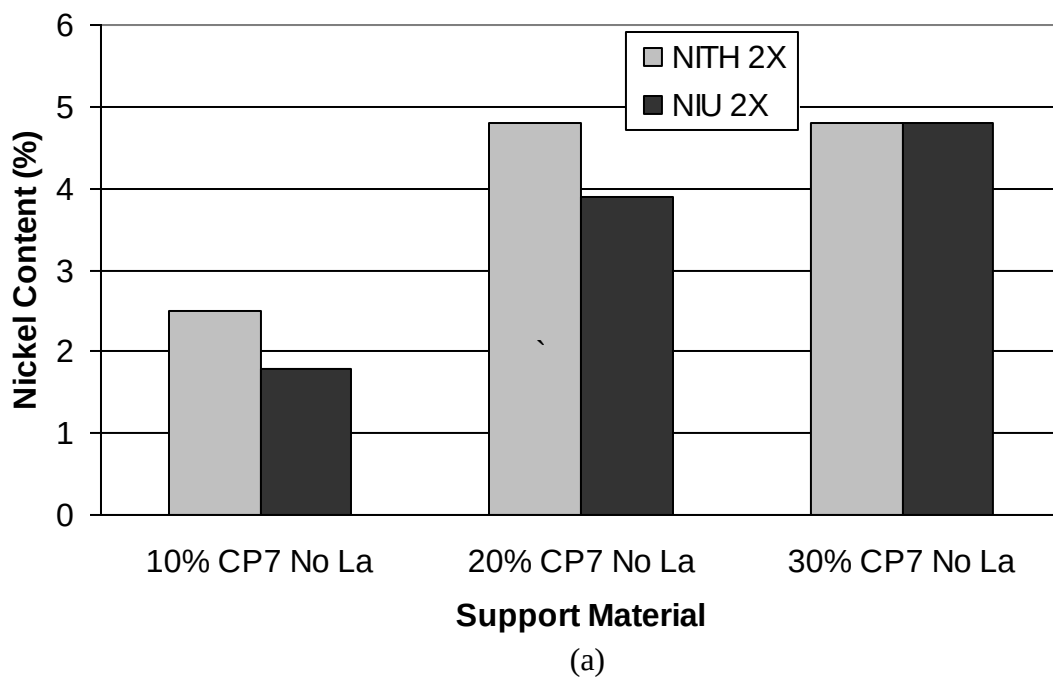
**Table 7.** Parameters known to affect the Ni loading of the catalyst support.

| Parameter                     | Parameter level |                                                                   |
|-------------------------------|-----------------|-------------------------------------------------------------------|
|                               | No.             | Description                                                       |
| I. Shell material formulation | 1               | 10% CP7                                                           |
|                               | 2               | 20% CP7                                                           |
|                               | 3               | 30% CP7                                                           |
| II. Pellet pretreatment       | 1               | Calcined at 900°C                                                 |
|                               | 2               | La treated + Calc. at 900°C                                       |
| III. Ni impregnation method   | 1               | NIU [ $\text{Ni}(\text{NO}_3)_2$ in urea + $\text{H}_2\text{O}$ ] |
|                               | 2               | NITH [ $\text{Ni}(\text{NO}_3)_2$ in THF]                         |
| IV. No. of Ni impregnations   | 1               | One impregnation                                                  |
|                               | 2               | Two impregnations                                                 |

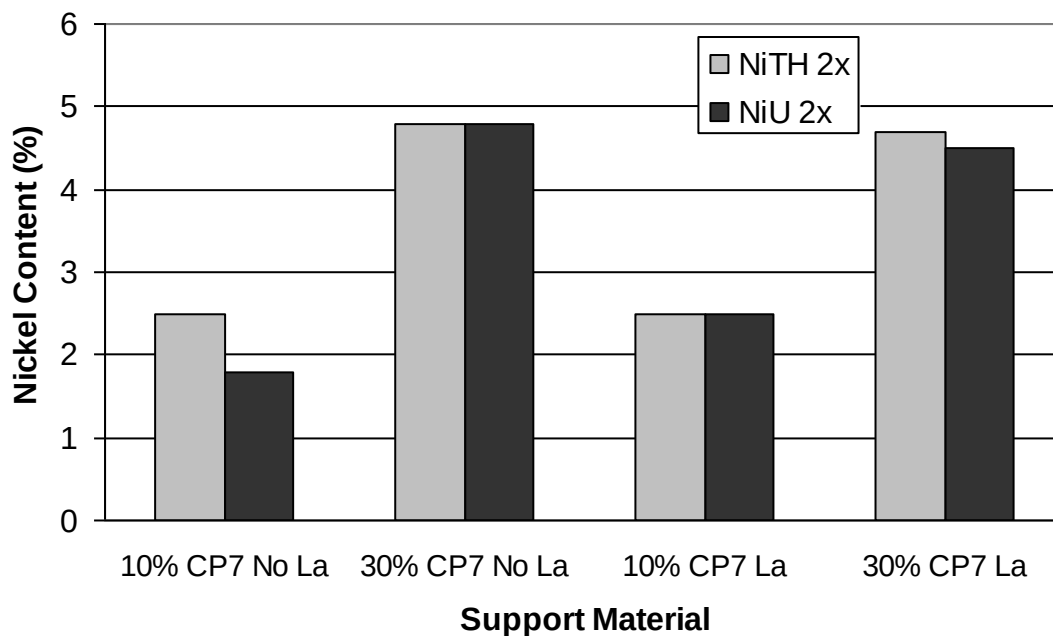
**Table 8.** Batches of Ni-impregnated material and their nickel content.

| No.    | CP-7<br>wt.% | La<br>Present | Ni impreg.<br>Method | Ni Content, wt.% |            |
|--------|--------------|---------------|----------------------|------------------|------------|
|        |              |               |                      | 1X impreg.       | 2X impreg. |
| 1, 2   | 10           | No            | NIU                  | 0.96             | 1.79       |
| 3, 4   | 10           | No            | NITH                 | 1.39             | 2.53       |
| 5, 6   | 10           | Yes           | NIU                  | 1.47             | 2.54       |
| 7, 8   | 10           | Yes           | NITH                 | 1.36             | 2.50       |
| 9, 10  | 20           | No            | NIU                  | 1.77             | 3.91       |
| 11, 12 | 20           | No            | NITH                 | 2.41             | 4.87       |
| 13, 14 | 20           | Yes           | NIU                  | 2.42             | 4.10       |
| 15, 16 | 20           | Yes           | NITH                 | 2.47             | 4.50       |
| 17, 18 | 30           | No            | NIU                  | 2.00             | 4.77       |
| 19, 20 | 30           | No            | NITH                 | 2.35             | 4.77       |
| 21, 22 | 30           | Yes           | NIU                  | 2.38             | 4.52       |
| 23, 24 | 30           | Yes           | NITH                 | 2.55             | 4.74       |

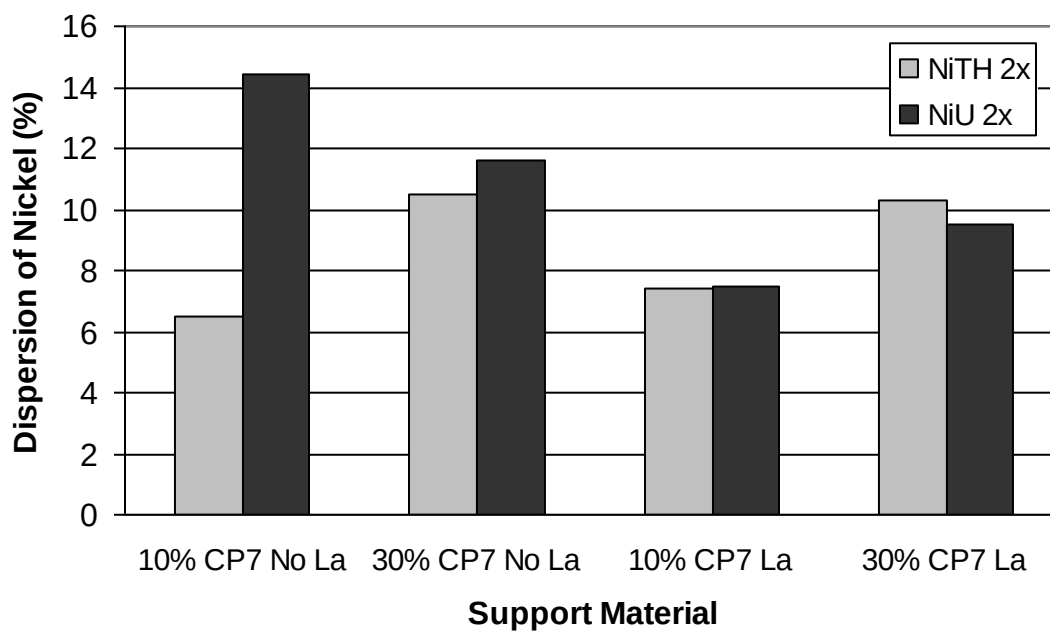
24 batches of the Ni-impregnated material were prepared. The nickel content of these batches is listed in Table 8 and also indicated in Figures 32-34. These figures also show the nickel dispersion. As seen in Figure 32 (a) the Ni content increased with increasing concentration of CP-7 alumina in the support material. The Ni nitrate solution choice had a small effect on the Ni content and a much larger effect on the Ni dispersion (Figure 32b), particularly at lower CP-7 concentrations. This result confirms the benefit of using a urea/water impregnation solution to increase Ni dispersion. Similar trends were observed whether lanthanum was incorporated or not (see Figures 33 (a) and (b)). However, the lanthanum pretreatment appeared to eliminate the positive effect of urea/water in increasing the Ni dispersion. Figures 34 (a) and (b) show that



**Figure 32.** Effect of CP-7 content in the support and Ni impregnation methods (NITH = Ni nitrate/THF, NIU = Ni nitrate/urea in water) on Ni loading and dispersion. (a) Ni content, (b) Ni dispersion.

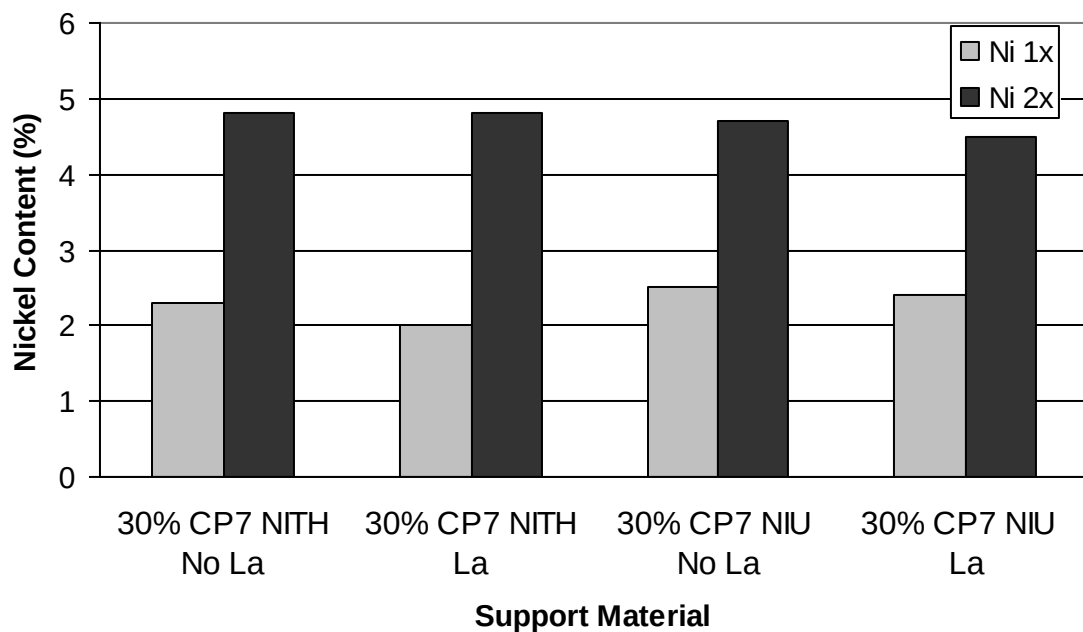


(a)

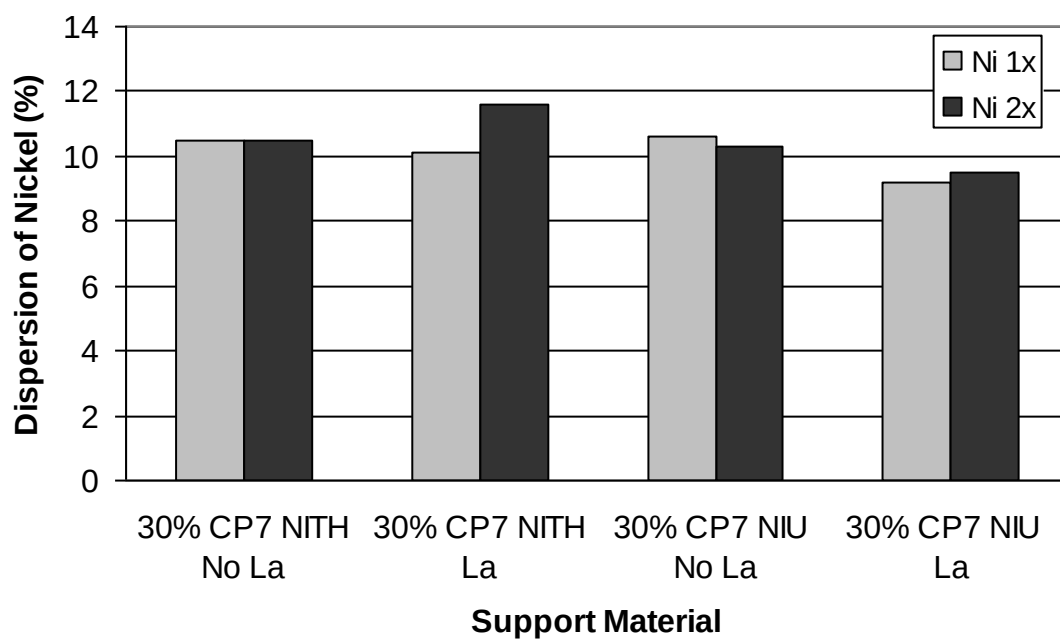


(b)

**Figure 33.** Effect of lanthanum incorporation and nickel loading method (NITH = Ni nitrate/THF, NIU = Ni nitrate/urea in water) on Ni loading and dispersion. (a) Ni content, (b) Ni dispersion.

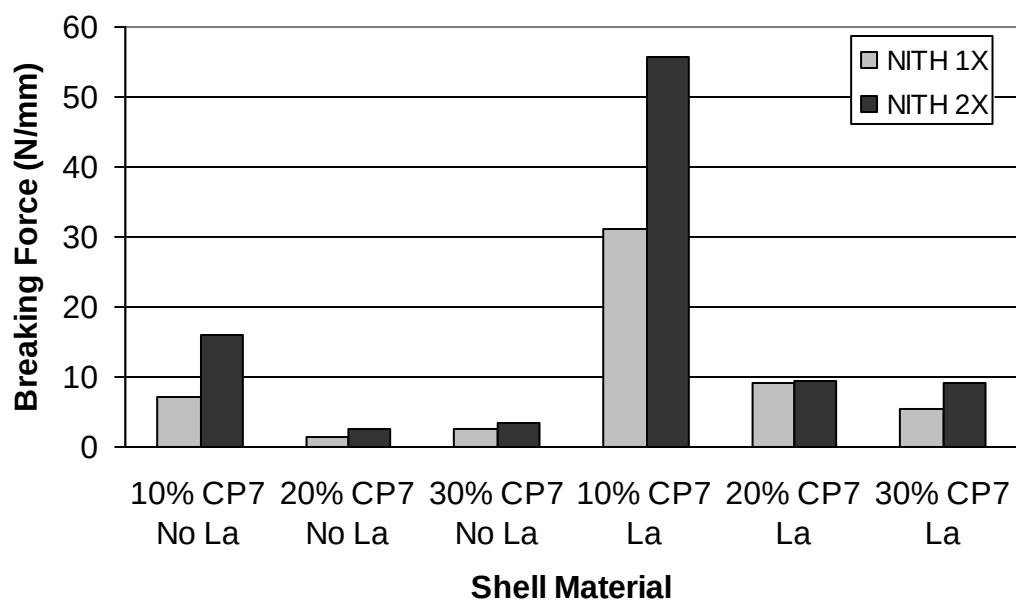


(a)

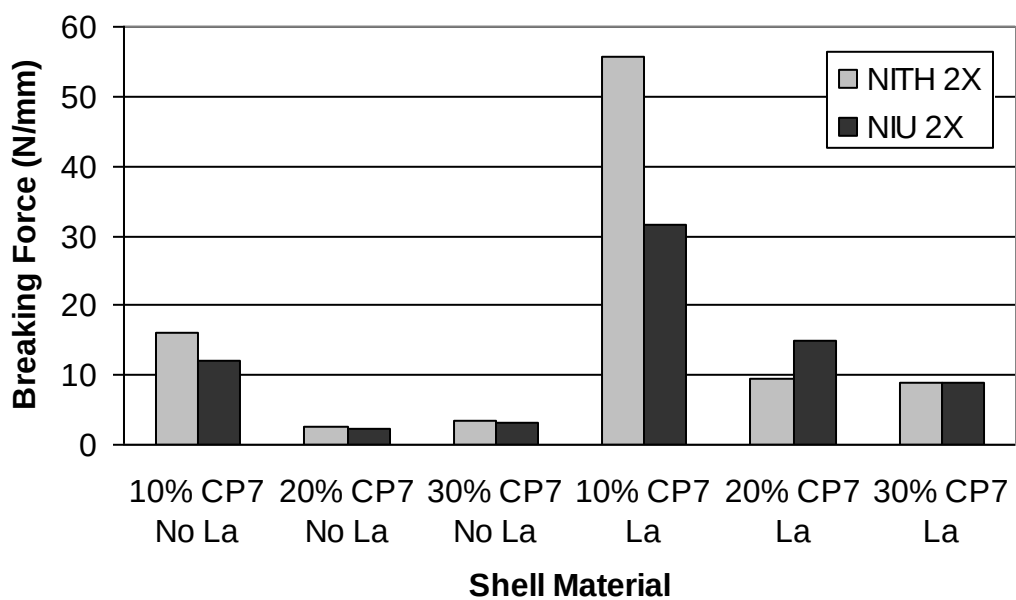


(b)

**Figure 34.** Effect of number of Ni impregnations on Ni loading and dispersion (1x or 2x impregnations). (a) Ni content, (b) Ni dispersion.



(a)



(b)

**Figure 35.** Breaking force of spherical pellets with different compositions, with and without lanthanum nitrate pretreatment, and with different Ni impregnation solutions.  
 (a) Effect of number of impregnations, (b) Effect of Ni nitrate impregnation solution.

**Table 9.** Effect of a single Ni impregnation by the NITH method on pellet breaking force.

| Level | CP-7<br>Conc., % | Breaking Force (N/mm) |         |            |         |
|-------|------------------|-----------------------|---------|------------|---------|
|       |                  | No La Present         |         | La present |         |
|       |                  | w/o Ni                | with Ni | w/o Ni     | with Ni |
| 1     | 10               | 3.3                   | 7.0     | 31.7       | 31.1    |
| 2     | 20               | 0.9                   | 1.4     | 5.2        | 9.1     |
| 3     | 30               | 1.3                   | 2.5     | 3.1        | 5.4     |

repeating the impregnation of Ni a second time increased the nickel content by almost 100%.

The metal dispersion did not appear to be affected by multiple impregnation cycles.

Figure 35(a) shows the breaking force of the calcined pellets with or without La and either with one or two Ni impregnations. This figure shows that a second Ni impregnation only affected the breaking force at the lowest CP-7 concentration where it had a beneficial effect.

Figure 35(b) indicates that the NITH solution had a beneficial effect on the breaking force at the lowest CP-7 concentration whereas the nature of the Ni solution had little effect at higher CP-7 concentrations.

The effect of Ni impregnation by the NITH method on the pellet breaking force can be seen in Table 9 where a comparison is made of results produced with pellets which had not been impregnated and those produced after a single impregnation by the NITH method. It can be seen that in all cases except one, the breaking force was considerably greater for the Ni-impregnated pellets regardless of whether lanthanum was present or not. Of course, the breaking force for the lanthanum treated pellets was always greater than for the untreated pellets.

### **Preparation and Testing of Core-in-Shell Pellets with a Ni Catalyst**

The purpose of the third major task was to prepare and test core-in-shell pellets made with the improved core and shell materials and impregnated with a Ni catalyst. The product was

subjected to a thorough performance evaluation by reforming methane with steam at different temperatures and pressures. The evaluation also included limited lifecycle tests of the most promising catalyst/sorbent materials. These tests showed to what extent the process performance and physical properties of the materials changed with use.

Two of the most promising shell formulations were utilized in preparing the core-in-shell pellets. One formulation consisted of 90 wt%  $\text{Al}_2\text{O}_3$  and 10 wt% Microna 3 limestone having a mean particle size of 3.2  $\mu\text{m}$ . Another formulation consisted of  $\text{Al}_2\text{O}_3$  and lanthanum nitrate prepared by mixing the  $\text{Al}_2\text{O}_3$  with a solution of the lanthanum salt in tetrahydrofuran (THF) followed by drying and then regrinding the resulting powder. When this mixture was applied to the pellet cores, and the resulting core-in-shell pellets were calcined, the  $\text{La}(\text{NO}_3)_3$  was converted to  $\text{La}_2\text{O}_3$ , so the resulting shell formulation was equivalent to one composed of 92.3 wt%  $\text{Al}_2\text{O}_3$  and 7.7 wt%  $\text{La}_2\text{O}_3$ . In either shell formulation the alumina fraction was composed of 30 wt% DD-290, 30 wt% T-64, and 40 wt% A16-SG.

The spherical core-in-shell pellets were prepared by first pelletizing the cores made entirely of Microna 3 limestone and then coating the cores with either the mixture of  $\text{Al}_2\text{O}_3$  and Micron 3 limestone or the mixture of  $\text{Al}_2\text{O}_3$  and lanthanum nitrate. After calcining the pellets at 900°C for 3 hr, the pellets were recarbonated and then impregnated twice with nickel nitrate in THF. After each impregnation, the pellets were heated to 500°C to convert the nickel nitrate into NO. The gain in weight of the pellets corresponded to an added Ni content of 6 wt%. Prior to reaction testing, the NiO was reduced in-situ by raising the catalyst bed temperature to 550°C and passing  $\text{H}_2$  through the bed. The catalyst prepared by this procedure was highly active and could be used directly for reforming methane.

During the first phase of this project a different procedure had been employed for preparing the Ni catalyst, and the catalyst proved to be much less active.<sup>4</sup> Although the fresh catalyst was capable of steam reforming propane or toluene, it required an extended period of activation by reforming propane at 750-770°C for several hours before it was capable of catalyzing the reaction of CH<sub>4</sub> and steam. To determine why such a long activation period was required, the present phase of the project focused initially on changes in the composition of the core-in-shell pellets that had taken place during preparation. Pellets prepared by the method employed during the first phase were examined by X-ray fluorescence (XRF) before and after catalyst activation. This examination revealed the presence of sulfate in the freshly prepared pellets. After the Ni catalyst had been activated by reforming propane for several hours, the concentration of sulfur compounds was reduced significantly. The source of the sulfur was traced to the lignin solution that had been used as a binder while the shell material was being applied to the pellet cores. It was found subsequently that only water was required as a binder for the shell material, and the problem was solved. Consequently, the core-in-shell pellets used in the present phase of the project were made without lignin and no period of activation was required.

Core-in-shell pellets with the different shell formulations and loaded with the Ni catalyst were tested in the fixed bed reactor by conducting a series of runs in which methane was reformed with steam at different temperatures, pressures, and feed rates. The reactor with an inside diameter of 1.58 was packed with core-in-shell pellets that had an outside shell diameter between 3.96 and 4.76 mm and a sorbent core diameter between 3.35 and 3.96 mm. These pellets were interspersed with smaller SiC pellets to reduce channeling and to improve heat transfer. A catalyst bed depth of 10.5 cm was employed for runs made at lower pressures (1 to

5 atm), while a bed depth of 21 cm was used for runs made at 10 atm. A 10 cm deep layer of extruded SiC pellets was placed above the catalyst bed to mix and preheat the reactants. A quantity of SiC pellets was also placed below the catalyst pellets. A thermocouple was placed in the middle of the catalyst bed to record the temperature.

The experimental conditions employed for the series of test runs are indicated in Table 10. For the runs conducted at pressures between 1 and 5 atm, a constant mass of pellets was used, whereas for runs conducted at 10 atm, the mass was doubled so that an adequate amount of sorbent was present. Also for the runs conducted between 1 and 5 atm the feed rate was increased as the pressure rose to keep the apparent reactor space time,  $\theta_F$ , nearly constant. The apparent space time was taken to be the ratio of the empty reactor volume occupied by the catalyst bed to the volumetric feed rate based on reactor inlet conditions. However, for the runs conducted at 10 atm it became necessary to double the space time as well as the volume of the catalyst bed to ensure sufficient sorbent capacity.

**Table 10.** Summary of experimental conditions employed for testing core-in-shell pellets by reforming  $\text{CH}_4$  with a 3:1 mole ratio of steam to  $\text{CH}_4$  in the fixed bed reactor.

| Bed Mass,<br>g | Bed Vol.,<br>$\text{cm}^3$ | Temp.,<br>$^\circ\text{C}$ | Press.,<br>atm. | Feed Rate,<br>$\text{mmol/min}$ | $\theta_F$ ,<br>sec. |
|----------------|----------------------------|----------------------------|-----------------|---------------------------------|----------------------|
| 13.7           | 13.3                       | 550                        | 1               | 2.41                            | 4.90                 |
| 13.7           | 13.3                       | 600                        | 1               | 2.41                            | 4.62                 |
| 13.7           | 13.3                       | 600                        | 3               | 7.23                            | 4.62                 |
| 13.7           | 13.3                       | 600                        | 5               | 12.05                           | 4.60                 |
| 27.4           | 26.6                       | 600                        | 10              | 24.10                           | 9.25                 |
| 13.7           | 13.3                       | 650                        | 1               | 2.41                            | 4.37                 |
| 13.7           | 13.3                       | 650                        | 3               | 7.23                            | 4.37                 |
| 13.7           | 13.3                       | 650                        | 5               | 12.05                           | 4.36                 |
| 27.4           | 26.6                       | 650                        | 10              | 24.10                           | 8.75                 |

For the experimental conditions listed in Table 10 it proved instructive to calculate the equilibrium conversion that could be achieved by steam reforming methane for the conditions given in this table. Two cases were considered. The first case assumed that the  $\text{CO}_2$  generated by the reactions of steam and  $\text{CH}_4$  and steam and  $\text{CO}$  would be absorbed by the reaction of  $\text{CO}_2$  and  $\text{CaO}$  under equilibrium conditions. The second case assumed no  $\text{CO}_2$  would be absorbed because the sorbent was fully loaded. Based on these equilibrium conversions, the corresponding gas compositions were calculated and the results are given in Table 11. These results show that with an active  $\text{CaO}$  sorbent present the equilibrium concentration of hydrogen would range from 93.6 mol% to 97.9 mol% for the listed conditions. Without the  $\text{CaO}$  sorbent, the maximum hydrogen concentration attainable would be considerably smaller. Furthermore, without the sorbent the concentration of hydrogen would decrease rapidly with increasing system pressure. Consequently for systems operating at higher pressures, the role played by the sorbent became even more important.

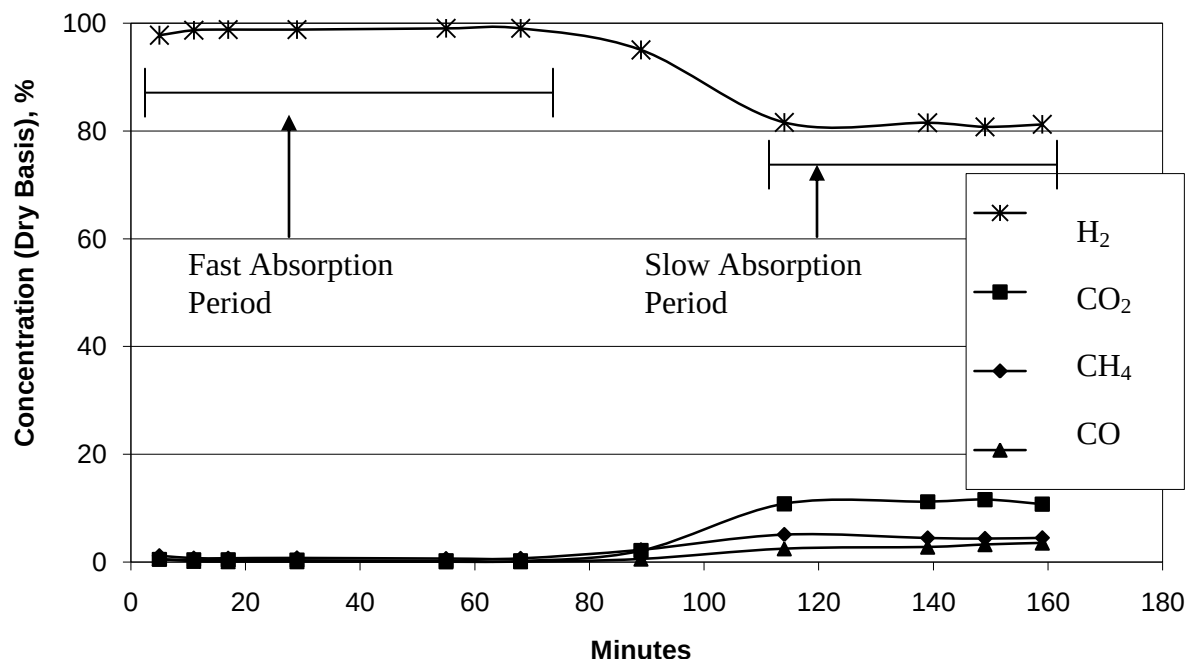
**Performance tests at atmospheric pressure.** The performance evaluation of core-in-shell pellets with the improved shell compositions and impregnated with a Ni catalyst was initiated by first conducting a series of runs at atmospheric pressure. These runs were conducted using the fixed bed reactor and experimental procedure described under Experimental Methods.

The results of a typical steam-methane reforming test with fresh core-in-shell pellets conducted with a 3:1 mole ratio of  $\text{H}_2\text{O}:\text{CH}_4$  at  $600^\circ\text{C}$  and 1.0 atm are presented in Figure 36. During the initial 70 min of the test, most of the  $\text{CH}_4$  was converted and virtually all of the  $\text{CO}_2$  was absorbed, resulting in a high  $\text{H}_2$  product concentration. This period will be referred to as the Fast Absorption period. As time progressed, the  $\text{CaO}$  sorbent was gradually converted to  $\text{CaCO}_3$ ,

**Table 11.** Calculated equilibrium gas concentrations for the test conditions listed in Table 10 including a 3:1 mole ratio of steam to CH<sub>4</sub>.

| Temperature,<br>°C | Pressure,<br>atm | CO <sub>2</sub> Absorption | Concentration (Dry Basis), % |      |                 |                |
|--------------------|------------------|----------------------------|------------------------------|------|-----------------|----------------|
|                    |                  |                            | CH <sub>4</sub>              | CO   | CO <sub>2</sub> | H <sub>2</sub> |
| 550                | 1                | With                       | 1.9                          | 0.1  | 0.1             | 97.9           |
|                    |                  | Without                    | 12.4                         | 4.6  | 13.8            | 69.2           |
| 600                | 1                | With                       | 1.6                          | 0.5  | 0.4             | 97.5           |
|                    |                  | Without                    | 6.0                          | 7.8  | 12.5            | 73.6           |
| 600                | 3                | With                       | 3.4                          | 0.1  | 0.1             | 96.3           |
|                    |                  | Without                    | 14.5                         | 5.1  | 13.0            | 67.4           |
| 600                | 5                | With                       | 4.5                          | 0.1  | 0.1             | 95.4           |
|                    |                  | Without                    | 19.5                         | 4.0  | 12.9            | 63.6           |
| 600                | 10               | With                       | 6.3                          | 0.0  | 0.0             | 93.6           |
|                    |                  | Without                    | 26.97                        | 2.82 | 12.35           | 57.86          |
| 650                | 1                | With                       | 1.3                          | 2.0  | 1.3             | 95.4           |
|                    |                  | Without                    | 2.3                          | 10.8 | 10.9            | 76.0           |
| 650                | 3                | With                       | 3.0                          | 0.7  | 0.4             | 95.9           |
|                    |                  | Without                    | 8.1                          | 8.2  | 11.8            | 71.9           |
| 650                | 5                | With                       | 4.1                          | 0.3  | 0.3             | 95.3           |
|                    |                  | Without                    | 12.2                         | 6.8  | 12.1            | 68.9           |
| 650                | 10               | With                       | 5.8                          | 0.1  | 0.1             | 93.9           |
|                    |                  | Without                    | 18.83                        | 5.05 | 12.19           | 63.92          |

and the rate of CO<sub>2</sub> absorption slowed significantly. However, an analysis performed on the gas concentrations observed during the Slow Absorption period revealed that the steam-methane reforming and water-gas shift reactions could not solely account for the observed reactor effluent concentrations. On the other hand, when CO<sub>2</sub> absorption was taken into account, the conversions obtained were consistent. Thus, slow absorption of CO<sub>2</sub> by the CaO sorbent



**Figure 36.** Gas concentrations observed in the reactor effluent during fixed bed reactor testing of a fresh batch of core-in-shell pellets with limestone added to the shell formulation and impregnated with Ni. Testing was conducted at 600°C and 1.0 atm.

appeared to be taking place even after an extended time. Hence, this phase of reaction testing will be referred to as the Slow Absorption period.

During the Slow Absorption period, the H<sub>2</sub> concentration was significantly lower than during the Fast Absorption period, whereas the CO, CO<sub>2</sub> and CH<sub>4</sub> concentrations were higher. The Slow Absorption period was characterized by a partially loaded CaO sorbent that continued to absorb CO<sub>2</sub> through a diffusion-limited reaction. The phenomenon of CaO slowly absorbing CO<sub>2</sub> after an initial rapid, kinetically controlled period is a well known property of CaO-based sorbents.<sup>31, 32</sup> A comparison of the gas concentrations observed during the Slow Absorption period with those recorded in Table 11 for the same temperature and pressure also indicated that the system had not yet reached an equilibrium state. For example, the observed H<sub>2</sub> concentration of over 80 mole % was significantly greater than the equilibrium value of 73.6 mole % reported in Table 11.

**Table 12.** The average product gas concentrations observed during the three periods of operation. Run conditions: 3:1 mole ratio  $\text{CH}_4\text{:H}_2\text{O}$ ; 2.41 mmole/min; 650°C, 1.0 atm.

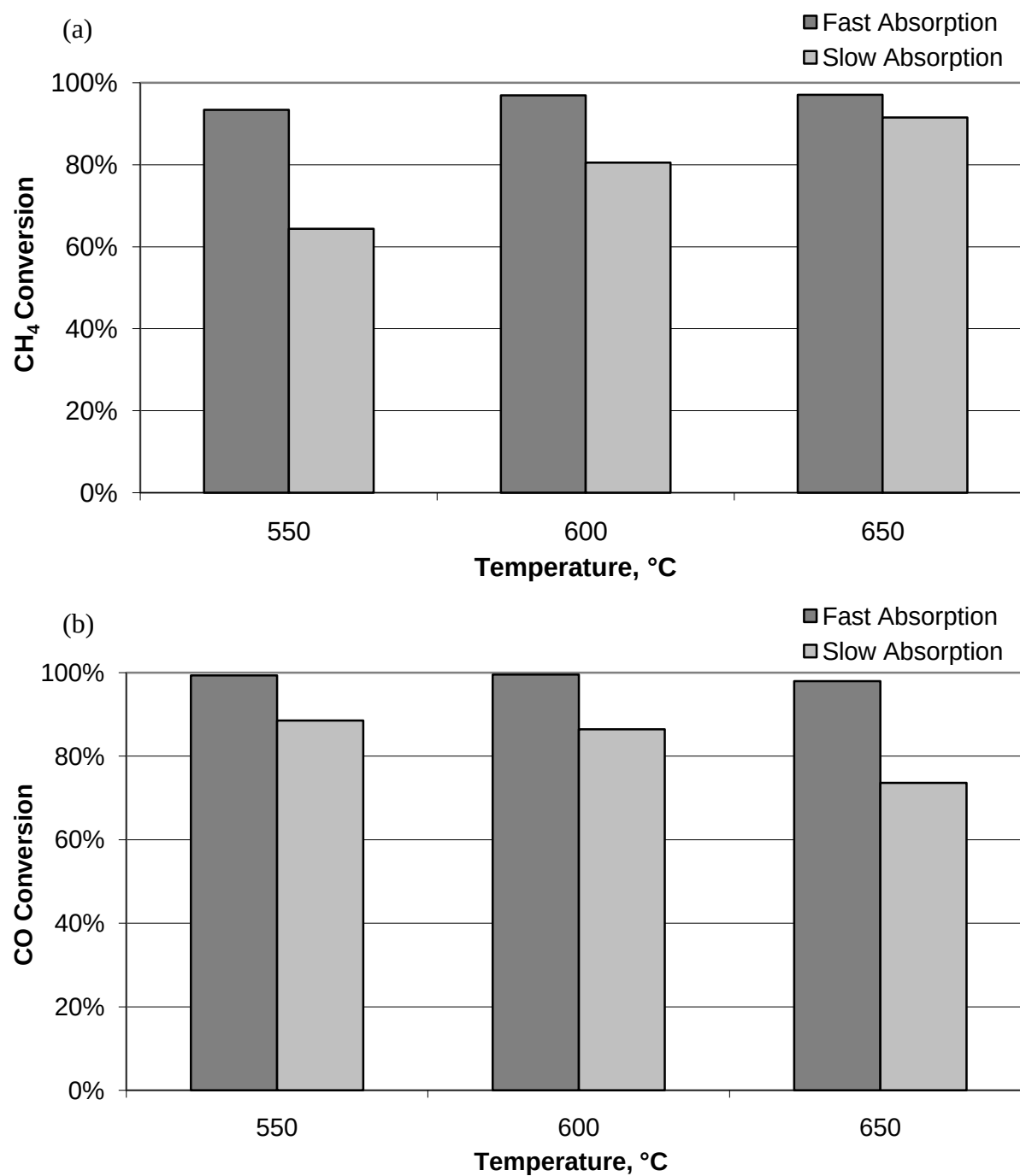
| Operating Period | Gas concentrations (dry basis), mole % |     |               |              |
|------------------|----------------------------------------|-----|---------------|--------------|
|                  | $\text{CH}_4$                          | CO  | $\text{CO}_2$ | $\text{H}_2$ |
| Fast Absorption  | 0.9                                    | 0.9 | 0.7           | 97.4         |
| Slow Absorption  | 2.3                                    | 4.7 | 12.1          | 80.9         |
| Steady-state     | 3.0                                    | 5.6 | 14.4          | 77.0         |

To gain some appreciation of how much more  $\text{CO}_2$  would have been absorbed if the test had been extended for a very long time, another run was conducted using similar conditions except that the temperature was increased to 650°C and the run was continued for 875 min. The results were generally similar to those shown in Figure 36. The Fast Absorption period lasted for approximately 100 min., and the Slow Absorption Period for another 100-150 min. After that the concentration of  $\text{CO}_2$  increased very gradually for another 300-400 min. before reaching an apparent steady state. The average product gas concentrations during these three periods of operation are shown in Table 12. The gas composition shown for the Steady State Absorption period is an average of the values recorded over the final 260 min. of the run. The steady state composition represents the gas concentrations that would have been obtained without a sorbent present. A comparison of this composition with that recorded during the Slow Absorption period shows that the differences are relatively small. Also a comparison of the results in Table 12 with the equilibrium composition listed in Table 11 indicates relatively good agreement between the gas composition noted during the Fast Absorption period and the equilibrium composition with  $\text{CO}_2$  absorption. In addition, the  $\text{H}_2$  concentration of 77 mole % and  $\text{CH}_4$  concentration of 3.0 mole % observed during the Steady-state period agree well with

the corresponding equilibrium values of 76 mole %  $\text{H}_2$  and 2.3 mole %  $\text{CH}_4$  in Table 11. On the other hand, this agreement did not extend to the CO and  $\text{CO}_2$  components of the gas mixture.

Additional runs were conducted at 1.0 atm with core-in-shell pellets to gain a better understanding of the effects of temperature. For the runs containing limestone in the shell formulation, the reactor effluent composition is presented in Table 13 and the conversions of  $\text{CH}_4$  and CO are presented in Figures 37 (a) and (b), respectively. A comparison of these conversions with the equilibrium conversions shown in Figure 2 indicates that the rates of the steam-methane reforming reaction, water-gas shift reaction and reaction of CaO and  $\text{CO}_2$  were rapid enough to produce conversions limited by equilibrium during the Fast Absorption period. A product stream with 98 mol%  $\text{H}_2$  was produced between 550 and 650°C. The level of  $\text{CH}_4$  conversion during the Fast Absorption period increased slightly as the temperature increased, which was expected due to the endothermic nature of the steam-methane reforming reaction. Additionally, conversions observed during the Fast Absorption period were greater than the conversions during the Slow Absorption period. The greatest enhancement in  $\text{CH}_4$  conversion due to rapid  $\text{CO}_2$  absorption was experienced at 550°C, which allowed for the endothermic steam-methane reforming reaction to be enhanced. The greatest enhancement in CO conversion due to rapid  $\text{CO}_2$  absorption was observed at 650°C, which allowed for the exothermic water-gas shift reaction to be enhanced. Thus, rapid  $\text{CO}_2$  absorption resulted in  $\text{CH}_4$  and CO conversions at levels greater than those possible without a sorbent.

The gas compositions shown for the Slow Absorption period can best be explained by the slow absorption of  $\text{CO}_2$  during this period. Furthermore, the absorption of some  $\text{CO}_2$  during this period could explain why the CO conversions recorded in Figure 37 (b) are higher than the equilibrium CO conversions indicated in Figure 2 (b) for 1.0 atm and no  $\text{CO}_2$  absorption. A



**Figure 37.** The observed  $\text{CH}_4$  (a) and  $\text{CO}$  (b) conversions recorded during fixed bed reactor testing of core-in-shell pellets with a Ni catalyst and with limestone in the shell formulation. Testing was conducted at 1.0 atm.

**Table 13.** Reactor effluent concentrations observed while reaction testing core-in-shell pellets with a Ni catalyst and with limestone in the shell formulation. Testing was conducted at 1.0 atm.

| Temperature,<br>°C | Absorption<br>Period | Concentration (dry basis), mol% |     |                 |                |
|--------------------|----------------------|---------------------------------|-----|-----------------|----------------|
|                    |                      | CH <sub>4</sub>                 | CO  | CO <sub>2</sub> | H <sub>2</sub> |
| 550                | Fast                 | 1.7                             | 0.2 | 0.2             | 97.9           |
|                    | Slow                 | 10.4                            | 2.2 | 14.3            | 73.1           |
| 600                | Fast                 | 0.8                             | 0.1 | 0.4             | 98.7           |
|                    | Slow                 | 5.0                             | 2.8 | 12.8            | 79.4           |
| 650                | Fast                 | 0.8                             | 0.5 | 0.8             | 98.0           |
|                    | Slow                 | 2.0                             | 5.7 | 12.3            | 80.1           |

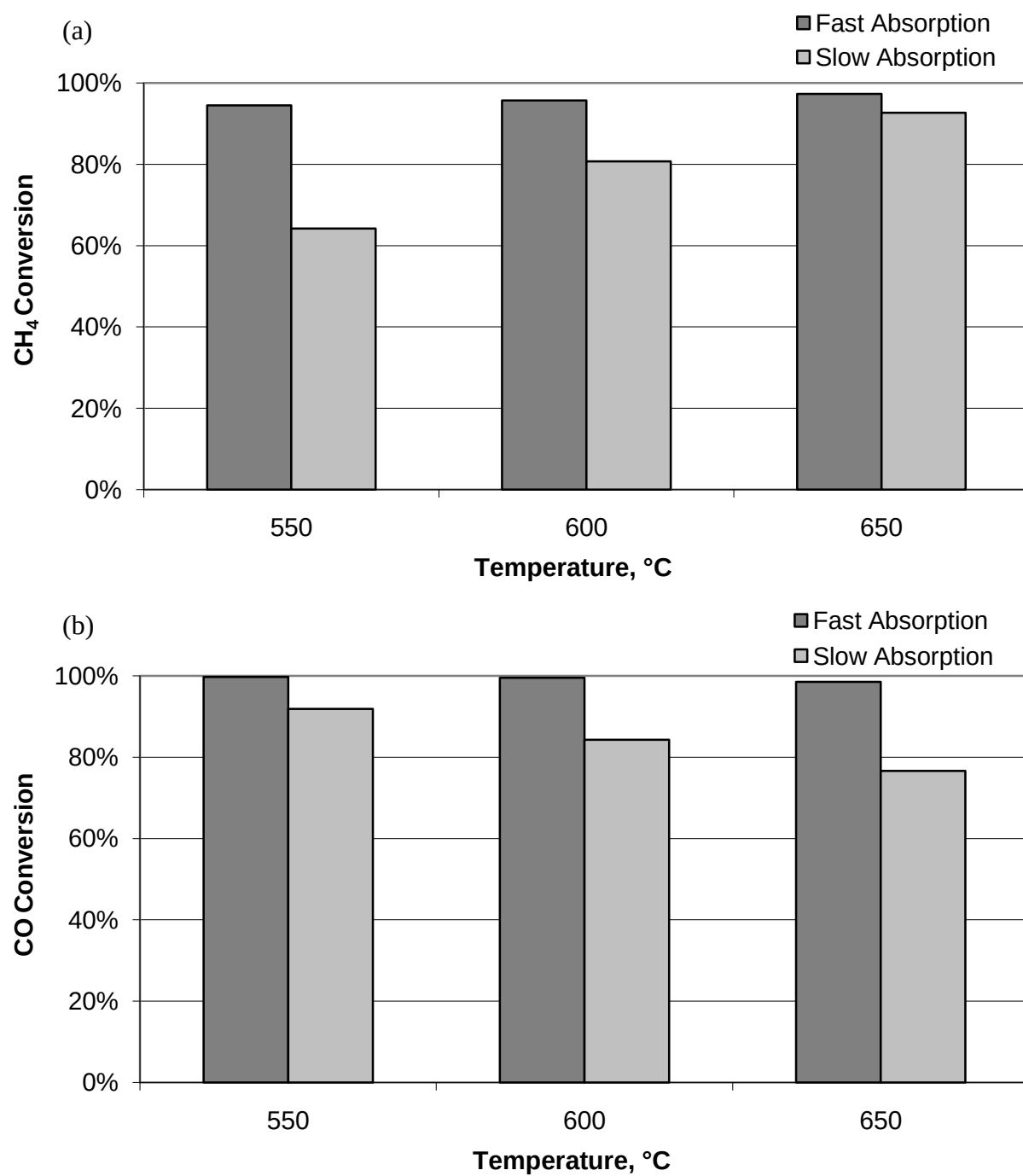
possible alternative explanation is that a temperature gradient across the fixed bed could have been present due to the large endothermicity of the steam-methane reforming reaction. Since the bed temperature was measured at the center of the bed, the bed exit temperature could have been cooler, which would have resulted in a higher than expected CO conversion due to the exothermic nature of the water-gas shift reaction. Overall, the CO conversion decreased with increasing temperature, which was probably due to the exothermic nature of the water-gas shift reaction.

For the next group of runs, core-in-shell pellets with lanthanum added to the alumina shell formulation were prepared and then tested in the fixed bed reactor using the same conditions as before. In the previous major section of this report it was shown that the addition of lanthanum nitrate to the alumina shell formulation produced a stronger shell material upon calcination. Therefore, lanthanum was added to the shell formulation and reaction testing was conducted to determine any effects that the addition of lanthanum might have on the production of H<sub>2</sub>.

**Table 14.** Reactor effluent concentrations observed while reaction testing core-in-shell pellets with a Ni catalyst and with lanthanum in the shell formulation. Testing was conducted at 1.0 atm.

| Temperature,<br>°C | Absorption<br>Period | Concentration (dry basis), mol% |     |                 |                |
|--------------------|----------------------|---------------------------------|-----|-----------------|----------------|
|                    |                      | CH <sub>4</sub>                 | CO  | CO <sub>2</sub> | H <sub>2</sub> |
| 550                | Fast                 | 1.4                             | 0.1 | 0.4             | 98.1           |
|                    | Slow                 | 10.7                            | 1.6 | 12.3            | 75.4           |
| 600                | Fast                 | 1.1                             | 0.1 | 0.6             | 98.1           |
|                    | Slow                 | 4.9                             | 3.2 | 12.8            | 79.1           |
| 650                | Fast                 | 0.7                             | 0.4 | 0.5             | 98.5           |
|                    | Slow                 | 1.7                             | 5.0 | 12.3            | 81.0           |

The product gas composition observed during testing of the pellets with the lanthanum shell formulation is presented in Table 14. The gas concentrations in Table 14 were used to determine the CH<sub>4</sub> and CO conversions reported in Figure 38 (a) and (b), respectively. The results obtained with the lanthanum shell formulation were very similar to the results obtained with the limestone shell formulation. The CH<sub>4</sub> and CO conversions observed during the Fast Absorption period of reaction testing were near calculated equilibrium levels (Figure 2). The absorption of CO<sub>2</sub> by CaO, which took place rapidly during the Fast Absorption period, resulted in the production of a product stream with over 98 mol% H<sub>2</sub> on a dry basis between 550 and 650°C. Additionally, CH<sub>4</sub> and CO conversions were enhanced by the rapid absorption of CO<sub>2</sub>, which allowed for greater conversions than would have otherwise been possible without the sorbent. Again, during the Slow Absorption period the product gas composition could best be explained by allowing for some absorption of CO<sub>2</sub>. Overall, the addition of lanthanum to the shell formulation did not hinder the ability of the pellets to produce H<sub>2</sub> in high concentrations.



**Figure 38.** The observed  $\text{CH}_4$  (a) and  $\text{CO}$  (b) conversions recorded during fixed bed reactor testing at 1.0 atm of core-in-shell pellets with lanthanum and a Ni catalyst added to the shell formulation.

Furthermore, the results obtained with the different pellet formulations were consistent and reproducible.

**Performance testing at elevated pressures.** The performance of core-in-shell pellets was also evaluated at absolute pressures of 3.0, 5.0 and 10.0 atm and at temperatures of 600°C and 650°C. Core-in-shell pellets with limestone or with lanthanum added to the shell formulation were tested separately. A steam to methane feed ratio of 3:1 was employed throughout the series of tests while the total molar flow rate of feed was increased in proportion to the pressure. Thus, the space time of the reactants passing through the bed remained the same at 1.0, 3.0 and 5.0 atm. At 10.0 atm, the increased flow rate necessitated doubling the mass of core-in-shell pellets so that adequate sorbent was present for the Fast Absorption period. Doubling the mass of pellets also doubled the length of the catalyst bed, effectively doubling the space time of the gas passing through the bed.

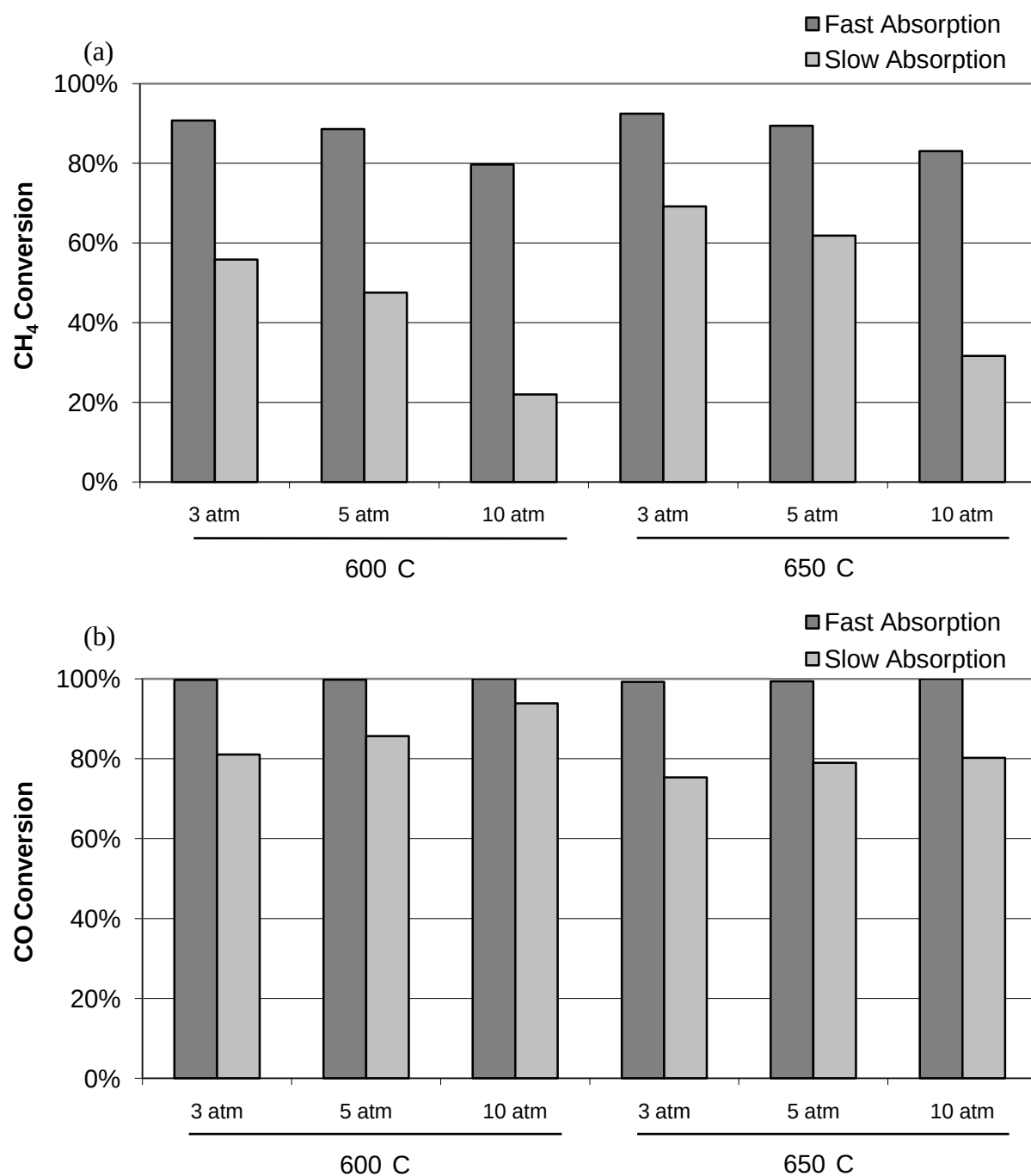
The product gas concentrations observed while operating the reactor filled with pellets having the limestone shell formulation are shown in Table 15 for the runs made at higher pressures. The CH<sub>4</sub> and CO conversions based on the gas concentrations presented in Table 15 are illustrated in Figure 39 (a) and (b). The CH<sub>4</sub> conversions for the Fast Absorption period are approximately equal to the thermodynamic equilibrium levels shown in Figure 2. Additionally for tests conducted at 3 and 5 atm, the observed concentrations in Table 15 are comparable to the calculated equilibrium concentrations in Table 11. In both Figures 2 and 39 (a) it can be seen that for a given pressure, CH<sub>4</sub> conversion does not have a strong dependence on temperature during the Fast Absorption period. This result is probably due to the balance between the endothermic and exothermic heats of reaction for the three reactions involved.

**Table 15.** Reactor effluent concentrations observed while reaction testing core-in-shell pellets with a Ni catalyst and with limestone in the shell formulation. Testing was conducted at higher pressures.

| Temperature,<br>°C | Pressure,<br>atm | Absorption<br>Period | Concentration (dry basis), mol% |                  |                 |                |
|--------------------|------------------|----------------------|---------------------------------|------------------|-----------------|----------------|
|                    |                  |                      | CH <sub>4</sub>                 | CO               | CO <sub>2</sub> | H <sub>2</sub> |
| 600                | 3                | Fast                 | 2.5                             | 0.1              | 0.3             | 97.2           |
|                    |                  | Slow                 | 14.5                            | 3.5              | 12.2            | 69.9           |
|                    | 5                | Fast                 | 3.1                             | 0.1              | 0.2             | 96.6           |
|                    |                  | Slow                 | 19.0                            | 2.5              | 12.3            | 66.3           |
|                    | 10               | Fast                 | 6.0                             | 0.0 <sup>a</sup> | <0.1            | 93.8           |
|                    |                  | Slow                 | 41.8                            | 0.7              | 9.2             | 48.2           |
| 650                | 3                | Fast                 | 2.0                             | 0.2              | 0.2             | 97.6           |
|                    |                  | Slow                 | 8.9                             | 4.9              | 11.7            | 74.5           |
|                    | 5                | Fast                 | 2.9                             | 0.1              | 0.6             | 96.4           |
|                    |                  | Slow                 | 11.7                            | 4.0              | 12.3            | 72.0           |
|                    | 10               | Fast                 | 4.8                             | 0.0 <sup>a</sup> | <0.1            | 95.1           |
|                    |                  | Slow                 | 31.0                            | 2.8              | 11.1            | 55.0           |

<sup>a</sup>Below detection limits

It can also be seen in Figure 39 (a) that an increase in pressure reduced the CH<sub>4</sub> conversion, which was expected based on the change in the number of moles of gas as all three reactions take place during the Fast Absorption period. Table 15 shows that during the Fast Absorption period H<sub>2</sub> in high concentrations was produced at all pressures and temperatures investigated. Also, unreacted CH<sub>4</sub> was the principle impurity while CO and CO<sub>2</sub> were present in very low concentrations. At 10.0 atm, the concentration of CO<sub>2</sub> was less than 0.1 mol%, and the concentration of CO was below the detection limits of the GC. Thus increasing the system pressure during the Fast Absorption period diminished CH<sub>4</sub> conversion and increased CO conversion, resulting in lower concentrations of H<sub>2</sub>, CO and CO<sub>2</sub>. A comparison of the actual



**Figure 39.** The observed  $\text{CH}_4$  (a) and  $\text{CO}$  (b) conversions recorded during fixed bed reactor testing of core-in-shell pellets with a Ni catalyst and with limestone in the shell formulation. Testing conducted at elevated pressures.

CH<sub>4</sub> conversions for the Slow Absorption period in Figure 39 with the equilibrium values appearing in Figure 2 shows good agreement except for the values at 10.0 atm where the actual CH<sub>4</sub> conversions were considerably lower than the equilibrium values. The diminished CH<sub>4</sub> conversion during the Slow Absorption period at 10.0 atm was most likely due to heat transfer limitations that diminished the conversion of CH<sub>4</sub> relative to equilibrium levels because of the strongly endothermic steam-methane reforming reaction. Of greater interest were the effects of temperature and pressure on the CO conversion during the Slow Absorption period where at any specific temperature and pressure the actual CO conversion was always greater than the equilibrium conversion that did not account for CO<sub>2</sub> absorption. Therefore, these results further indicate that CO<sub>2</sub> was being absorbed during the Slow Absorption period.

Core-in-shell pellets with lanthanum added to the shell formulation were also tested at pressures of 3.0, 5.0 and 10.0 atm and at both 600 and 650°C. The effluent gas concentrations observed during these tests are presented in Table 16, and the calculated CH<sub>4</sub> and CO conversions based on these concentrations are presented in Figure 40.

The results with pellets having lanthanum in the shell formulation were very similar to the results obtained with pellets having limestone in the shell formulation. The gas compositions in Table 16 for the lanthanum shell formulation were very similar to those in Table 15 for the limestone shell formulation. Furthermore, the CH<sub>4</sub> and CO conversions indicated by Figure 40 for the lanthanum formulation were very similar to those shown in Figure 39 for the limestone formulation.

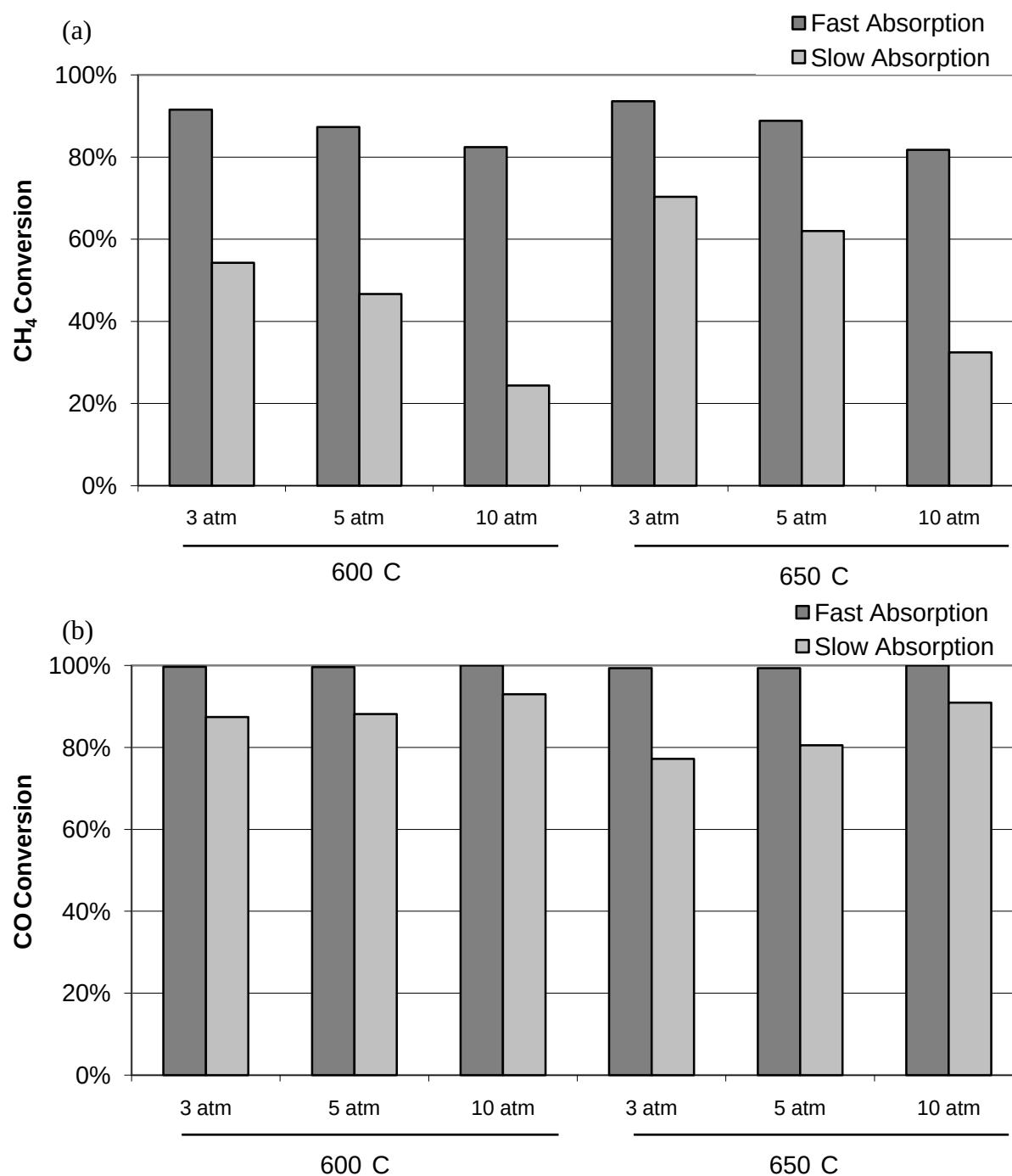
**Lifecycle testing of core-in-shell pellets with a Ni catalyst.** Limited lifecycle testing of the core-in-shell pellets was conducted to evaluate the performance of the pellets as they were subjected to 10 cycles of H<sub>2</sub> production and subsequent sorbent regeneration. Selected physical

**Table 16.** Reactor effluent concentrations observed while reaction testing core-in-shell pellets with a Ni catalyst and with lanthanum in the shell formulation.

| Temperature,<br>°C | Pressure,<br>atm | Absorption<br>Period | Concentration (dry basis), mol% |                  |                 |                |
|--------------------|------------------|----------------------|---------------------------------|------------------|-----------------|----------------|
|                    |                  |                      | CH <sub>4</sub>                 | CO               | CO <sub>2</sub> | H <sub>2</sub> |
| 600                | 3                | Fast                 | 2.2                             | 0.1              | 0.2             | 97.5           |
|                    |                  | Slow                 | 15.3                            | 2.3              | 11.9            | 70.5           |
|                    | 5                | Fast                 | 3.5                             | 0.1              | 0.2             | 96.2           |
|                    |                  | Slow                 | 19.7                            | 2.0              | 11.6            | 66.7           |
|                    | 10               | Fast                 | 5.1                             | 0.0 <sup>a</sup> | <0.1            | 94.9           |
|                    |                  | Slow                 | 39.9                            | 0.9              | 8.6             | 50.6           |
| 650                | 3                | Fast                 | 1.7                             | 0.2              | 0.8             | 97.4           |
|                    |                  | Slow                 | 8.4                             | 4.5              | 11.9            | 75.2           |
|                    | 5                | Fast                 | 3.0                             | 0.2              | 0.6             | 96.2           |
|                    |                  | Slow                 | 11.7                            | 3.7              | 12.0            | 72.6           |
|                    | 10               | Fast                 | 5.3                             | 0.0 <sup>a</sup> | <0.1            | 94.7           |
|                    |                  | Slow                 | 30.5                            | 1.3              | 11.0            | 57.2           |

<sup>a</sup>Below detection limits

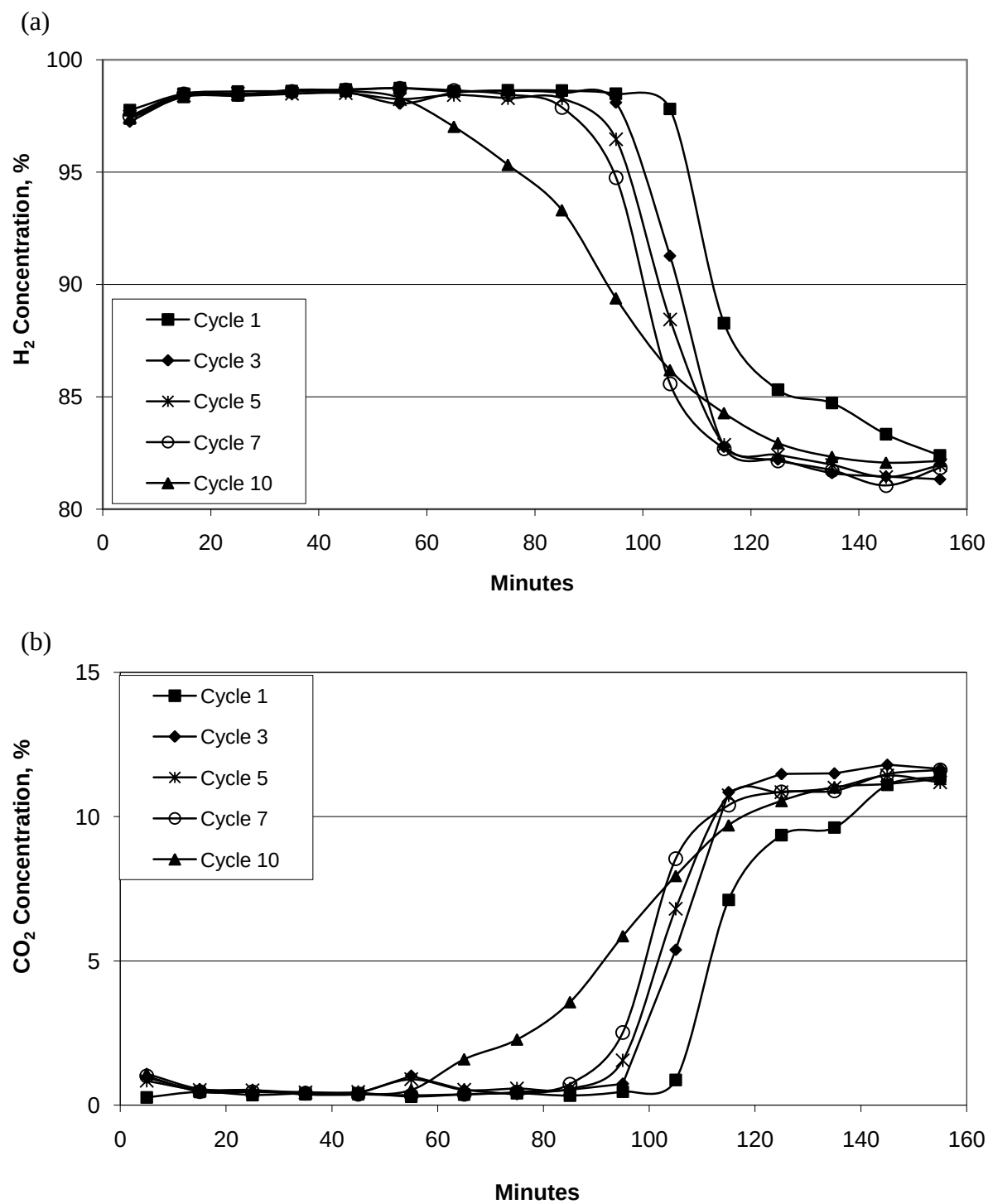
properties of the pellets were also measured before and after lifecycle testing. Core-in-shell pellets with either the limestone shell formulation or the lanthanum shell formulation were prepared for fixed bed reactor testing. A fresh batch of 13.7 g of core-in-shell pellets was loaded into the fixed bed reactor for each test. After an initial reduction of the NiO catalyst to Ni by flowing H<sub>2</sub> at 550°C, the pellets were ready for the first cycle. The reactor temperature was increased to 650°C, and steam and CH<sub>4</sub> in a 3:1 mole ratio were fed to the reactor at a rate of 2.41 mmol/min. During this time, a sample of the reactor effluent was drawn every 10 min for analysis in order to record the reactor response curve. After 155 min, the reactor temperature was raised from 650°C to 850°C at a rate of 10°C/min while continuing the flow of reactants to regenerate the CaO sorbent. When the CO<sub>2</sub> concentration in the reactor effluent reached a



**Figure 40.** The observed CH<sub>4</sub> (a) and CO (b) conversions recorded during fixed bed reactor testing of core-in-shell pellets with a Ni catalyst and with lanthanum in the shell formulation. Testing conducted at higher pressures.

constant level at 850°C, the sorbent was considered regenerated. During regeneration the flow of reactants was continued to ensure that the Ni catalyst remained reduced. Regeneration took 1.0 to 1.5 hr at 850°C. The period of reaction testing for 155 min at 650°C followed by the regeneration step at 850°C constituted a complete cycle. Each pellet formulation was subjected to 10 cycles. However, the sorbent was not regenerated after the 10th reaction stage at 650°C so that it was left in the more stable  $\text{CaCO}_3$  form for further evaluation.

Core-in-shell pellets with limestone added to the shell formulation were tested first. As each test cycle proceeded, the concentrations of  $\text{H}_2$  and  $\text{CO}_2$  in the reactor effluent were recorded during the  $\text{CH}_4$  reforming phase [see Figure 41 (a) and (b), respectively]. At the beginning of each cycle and for an extended period,  $\text{CO}_2$  was rapidly absorbed so the concentration of  $\text{CO}_2$  was only 0.8 mol% in the reactor effluent. During this period, the rates of the steam-methane reforming reaction, water-gas shift reaction and reaction between  $\text{CaO}$  and  $\text{CO}_2$  were sufficiently rapid to produce  $\text{H}_2$  in 98 mol% concentration. Eventually as time progressed, the rate of  $\text{CO}_2$  absorption by  $\text{CaO}$  slowed so its concentration rose to about 12 mol% while the  $\text{H}_2$  concentration fell to 81-82 mol%. As the number of cycles increased, the time that  $\text{H}_2$  was produced in 98 mol% concentration also decreased from 95-100 min for the first cycle to 50 min for the last cycle. Also, Figure 41 (b) indicates that as the number of cycles increased the period during which  $\text{CO}_2$  was rapidly absorbed decreased from 100 min for the first cycle to 50 min for the last cycle. Thus the amount of  $\text{CO}_2$  that was absorbed rapidly diminished as the sorbent absorption capacity decreased. While the length of time that  $\text{CO}_2$  was rapidly absorbed decreased as the number of cycles increased,  $\text{H}_2$  in high concentration was produced during a portion of each cycle. Thus, more mature samples of combined catalyst and sorbent were still capable of producing  $\text{H}_2$  in

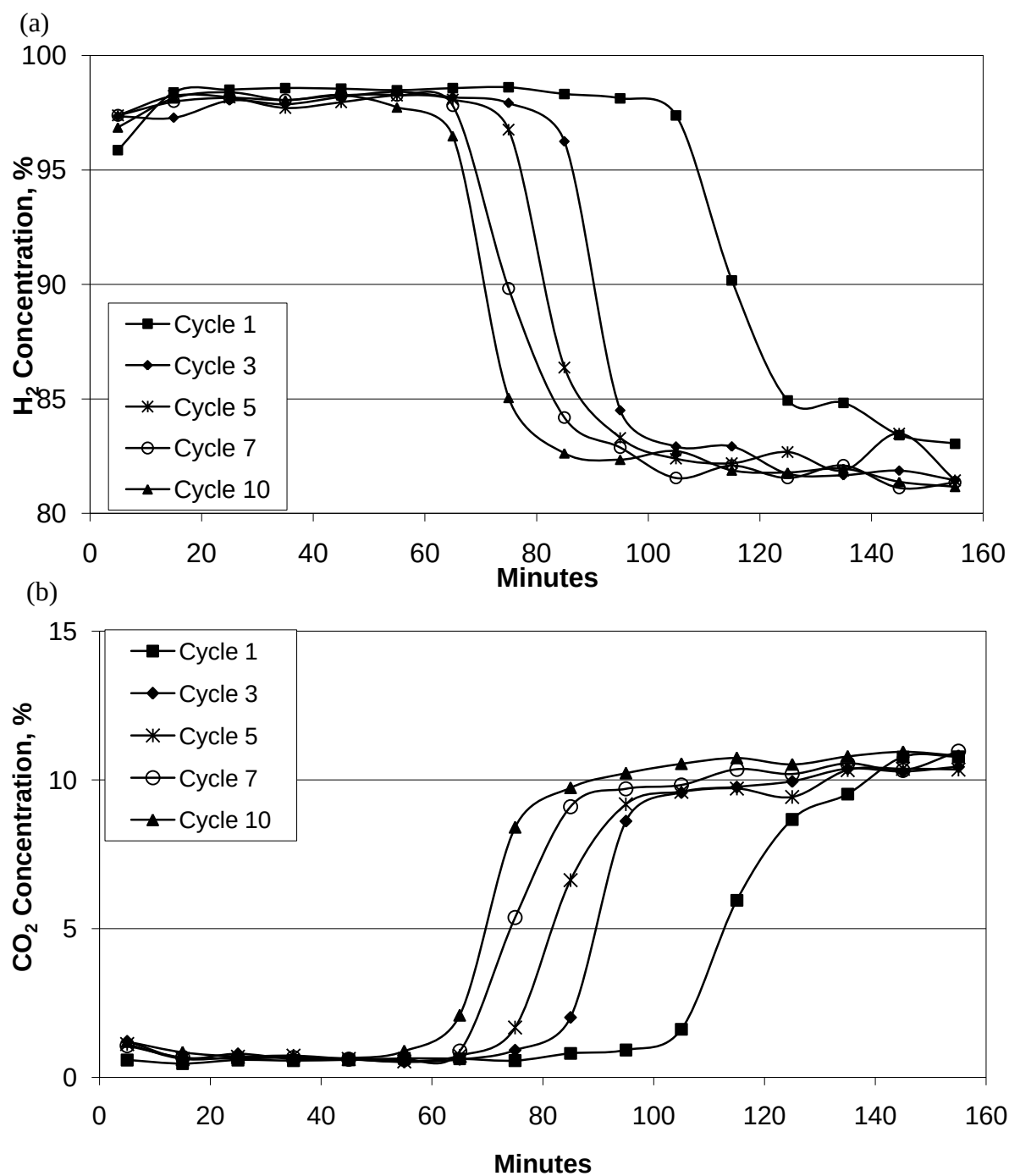


**Figure 41.** The concentration of (a)  $H_2$  and (b)  $CO_2$  in the reactor effluent during lifecycle testing of core-in-shell pellets with the limestone shell formulation. Tests were conducted at 1.0 atm and 650°C during the  $CH_4$  reforming phase shown here.

high concentration, but the length of time the high concentration of  $\text{H}_2$  was produced decreased with each cycle.

For the first seven cycles the transition time between the rapid and slow  $\text{CO}_2$  absorption periods was relatively short. However, the transition time between the 7<sup>th</sup> and 10<sup>th</sup> cycles was longer, which could have been due to changes either in the core material or shell material. As the number of cycles increased, the CaO cores may have become denser due to expansion and contraction associated with the change in molar volume as the sorbent was transformed between CaO and  $\text{CaCO}_3$ . Also, since the melting point of  $\text{CaCO}_3$  is  $1330^\circ\text{C}$ ,<sup>17</sup> it would have a Tamman temperature of  $665^\circ\text{C}$ . Therefore, enhanced sintering of the core could have taken place at  $650^\circ\text{C}$  when the core was in the form of  $\text{CaCO}_3$ , or before the core was completely regenerated at  $850^\circ\text{C}$ . Densification and sintering of the core would tend to reduce the rate of diffusion of  $\text{CO}_2$  into the core and thereby reduce its overall rate of absorption.

The performance of core-in-shell pellets with lanthanum added to the shell formulation was also investigated over 10 cycles of reaction and sorbent regeneration. Figure 42 shows the concentrations of  $\text{H}_2$  and  $\text{CO}_2$  observed during lifecycle testing of the pellets. While the results were generally similar to those observed with the previous pellets, there were some important differences that seemed due to the difference in shell formulations. In both cases,  $\text{H}_2$  in 98 mol% concentration was produced during the initial rapid  $\text{CO}_2$  absorption period followed by the production of  $\text{H}_2$  in 82 mol% concentration during the slow  $\text{CO}_2$  absorption period. However, after the first cycle, the concentration profiles differed appreciably between shell formulations for the transition from one  $\text{CO}_2$  absorption period to the next. Furthermore, this difference appeared to increase as the number of cycles increased. The results suggest that the two



**Figure 42.** The concentration of  $H_2$  (a) and  $CO_2$  (b) in the reactor effluent during lifecycle reaction testing of core-in-shell pellets with the lanthanum shell formulation. Tests were conducted at 1.0 atm and 650°C during the  $CH_4$  reforming phase shown here.

**Table 17.** Physical properties of core-in-shell pellets with limestone or lanthanum added to the shell formulation before and after lifecycle testing in the fixed bed reactor.

|                                                 | Limestone Shell Formulation |                         | Lanthanum Shell Formulation |                         |
|-------------------------------------------------|-----------------------------|-------------------------|-----------------------------|-------------------------|
|                                                 | Before Lifecycle Testing    | After Lifecycle Testing | Before Lifecycle Testing    | After Lifecycle Testing |
| BET Surface Area, m <sup>2</sup> /g             | 8                           | 5                       | 8                           | 6                       |
| Ni Crystallite Size, nm <sup>a</sup>            | 12                          | 54                      | 8                           | 39                      |
| Ni Surface Area, m <sup>2</sup> /g <sup>b</sup> | 3.1                         | --                      | 3.3                         | --                      |
| Ni Dispersion, %                                |                             |                         |                             |                         |
| By XRD                                          | 8                           | 2                       | 12                          | 3                       |
| By H <sub>2</sub> Chemisorption                 | 7                           | --                      | 9                           | --                      |
| Fractured Pellets, %                            | --                          | 18                      | --                          | 26                      |
| Compressive Strength, N/mm                      | 4.9 ± 1.0                   | 9.0 ± 2.2               | 5.5 ± 1.0                   | 12.6 ± 2.3              |

<sup>a</sup>Measured with X-ray diffraction (XRD)<sup>b</sup>Measured with H<sub>2</sub> chemisorption

materials will need to be tested over many more cycles before a definite conclusion can be reached about their relative performance.

To determine the effect that lifecycle testing had on the physical properties of the core-in-shell pellets, various methods were used to characterize the pellets before and after testing, and the results are presented in Table 17. The BET method was used to determine the surface area of the pellets by measuring the quantity of N<sub>2</sub> absorbed at 77 K. This method showed that the initial surface area was 8 m<sup>2</sup>/g for pellets with either shell formulation and that after lifecycle testing, the surface area decreased to 5 m<sup>2</sup>/g for the limestone formulation and 6 m<sup>2</sup>/g for the lanthanum formulation. The loss of surface area was most likely due to sintering of the

amorphous DD-290 alumina in the shell formulation. The slightly higher surface area observed in the lanthanum shell formulation after testing could have been due to the stabilizing effect of lanthanum on alumina at high temperatures.<sup>29</sup> However further testing would be required to verify that the observed difference in surface area was indeed statistically significant.

The effect of lifecycle testing on the size of the Ni crystallites present in the core-in-shell pellets was determined by X-ray diffraction measurements (XRD). The mean Ni crystallite size was determined with the Sherrer equation using the measured line breadth of the Ni crystallite peak. Since metallic Ni was required for these measurements, pellets that had been subjected to H<sub>2</sub> chemisorption measurements but not lifecycle testing were used for the “fresh” pellet XRD measurements. Such measurements were also conducted on core-in-shell pellets that had been subjected to lifecycle testing in the fixed bed reactor. The results of these measurements are presented in Table 17, and they indicate that sintering of the Ni crystallites occurred in both the limestone and lanthanum shell formulations. Consequently, the size of the Ni crystallites in the limestone shell formulation grew from 12 nm to 54 nm as a result of lifecycle testing. Also, the size of the Ni crystallites in the lanthanum formulation grew from 8 nm to 39 nm. By comparison, Ortiz and Harrison<sup>2</sup> reported that the size of Ni crystallites in an industrial reforming catalyst grew from 19.8 nm to 32.2 nm as a result of being subjected to 15 cycles of H<sub>2</sub> production and sorbent regeneration. While sintering of the Ni catalyst did occur during the present testing of the core-in-shell pellets, the catalytic activity of both pellet formulations was sufficient to reform CH<sub>4</sub> to nearly equilibrium levels during each lifecycle test.

The surface area of the Ni catalyst was measured by selective H<sub>2</sub> chemisorption on the catalyst present in core-in-shell pellets. Only the results of selective H<sub>2</sub> chemisorption on fresh core-in-shell pellets are reported in Table 6 because very little H<sub>2</sub> was chemisorbed on pellets

that had been subjected to lifecycle testing, which may have been due to carbon deposition on the Ni surface from coking. The Ni surface area of fresh pellets was found to be 3.1 m<sup>2</sup>/g and 3.3 m<sup>2</sup>/g for the limestone and lanthanum shell formulations, respectively. By comparison, the Ni surface area of Süd Chemie Reformax 330 LDP, an industrial reforming catalyst, was 3.5 m<sup>2</sup>/g of sample. Thus, the Ni surface area of the fresh core-in-shell pellets was similar to that of an industrial reforming catalyst.

The dispersion of the Ni catalyst was also evaluated. The dispersion is the fraction of metallic Ni atoms in a crystallite that are exposed on the surface and, thus, assumed to be catalytically active. The dispersion of Ni was determined by two different methods. In the first method, XRD was used to determine the dispersion of Ni atoms based on the size of the Ni crystallites. If spherical crystals are assumed, the dispersion of Ni and crystallite size are related by the equation:

$$D(\%) = \frac{C}{d} \quad (5)$$

where  $D$  is the dispersion,  $d$  is the crystallite diameter in nm obtained from XRD measurements, and  $C$  is a constant specific for the metal that incorporates several physical properties of the metal catalyst.<sup>33</sup>  $C$  is equal to 97 for Ni. The dispersion of Ni atoms based on the size of Ni crystallites determined by XRD measurements is shown in Table 17. Due to sintering of the Ni crystallites, the dispersion of Ni atoms decreased from 8% to 2% as a result of lifecycle testing of the core-in-shell pellets with limestone added to the shell formulation. Likewise, sintering of the Ni crystallites in the pellets with lanthanum added in the shell reduced the dispersion of Ni from 12% to 3% as a result of lifecycle testing.

In the second method, H<sub>2</sub> chemisorption is used as a basis for determining the dispersion of Ni by relating the amount of H<sub>2</sub> adsorbed to the total concentration of Ni present. This

method showed that the dispersion of Ni was 7% and 9% in fresh pellets containing limestone and lanthanum, respectively, in the shell formulations. As noted above, pellets subjected to lifecycle testing did not adsorb significant amounts of  $H_2$  and, therefore, could not be used for application of the second method. However, the Ni dispersion determined by the two methods was in good general agreement for fresh, untested core-in-shell pellets.

The effect of lifecycle testing on the physical integrity of the core-in-shell pellets was also evaluated. During lifecycle testing, it was observed that some core-in-shell pellets were fractured, which could have been due to thermal stress as the pellets were heated and cooled, or to expansion and contraction of the cores as  $CO_2$  was absorbed and desorbed or to mechanical stress as the pellets were loaded and unloaded. The percentage of fractured pellets resulting from lifecycle testing is listed in Table 17, where it can be seen that a higher percentage of pellets with lanthanum were fractured than with limestone. This result could have been due to the formation of different aluminate phases. When limestone was added to the formulation,  $CaO$  would have been formed, which could have reacted with  $Al_2O_3$  to form  $CaAl_2O_4$ . On the other hand, the addition of  $La(NO_3)_3$  could have resulted in the formation of  $LaAlO_3$ . Since the thermal expansion coefficients of the alumina phases are  $7.1 \text{ ppm}/^\circ\text{C}^{34}$  and  $9.8 \text{ ppm}/^\circ\text{C}^{35}$  for  $CaAl_2O_4$  and  $LaAlO_3$ , respectively, the larger coefficient of thermal expansion of  $LaAlO_3$  may have produced more thermal stress during lifecycle testing, resulting in more fracturing of the core-in-shell pellets. However, further testing is needed to justify this supposition.

Finally, the compressive force required to break the core-in-shell pellets before and after lifecycle testing was determined since this is an important physical property of pellets that will be subjected to mechanical stresses in various practical applications. For this determination, 15 unreduced, core-in-shell pellets were taken from each batch used to load the fixed bed reactor for

lifecycle testing. The core-in-shell pellets were subjected individually to a compression test after the diameter of the pellet had been measured. The results are reported in terms of the force required to break a pellet divided by its diameter. An average of 15 measurements and the corresponding 95% confidence limits are reported for each batch in Table 17. Likewise, 15 intact core-in-shell pellets from each batch that had completed lifecycle testing were also subjected to the breaking force test.

The addition of 7.7 wt.%  $\text{La}_2\text{O}_3$  in the alumina shell formulation was previously shown to enhance the strength of the core-in-shell pellets compared to pellets with only alumina in the shell formulation (see Figure 29). However, in the present study, the compressive strength of fresh, unreduced core-in-shell pellets was almost the same for pellets made with either lanthanum or limestone added to the shell formulation. The difference was not statistically significant. But the present study also included the Ni catalyst in the shell whereas the previous study of the compressive strength did not. Overall, the recorded compressive strength of the fresh core-in-shell pellets reported in Table 17 is similar to the 4.3 N/mm indicated in Figure 29 for core-in-shell pellets calcined at 900°C but without the Ni catalyst.

Table 17 also includes the measured compressive strength of core-in-shell pellets that had been subjected to lifecycle testing. Average values are reported with 95% confidence intervals. Interestingly, the compressive strength of the tested pellets was approximately twice that of the fresh pellets. Further examination of the core-in-shell pellets revealed that the increase in compressive strength may not have been due entirely to strengthening of the shell material but also to densification of the core material. As the CaO core absorbed  $\text{CO}_2$  and was subsequently regenerated, it appeared to become more compact and denser. The shell of pellets that had been subjected to lifecycle testing could be separated from the core which remained intact and seemed

much stronger. Thus, the increase in compressive strength of the pellets subjected to lifecycle testing could have been due to densification of the core as well as further sintering of the shell.

### **Application for the Water Gas Shift Reaction**

The purpose of the fourth major task was to determine the applicability of the core-in-shell pellets for converting CO into H<sub>2</sub> by means of the water gas shift reaction shown below:



This reaction is likely to become more widely used for the production of H<sub>2</sub> from synthesis gas (CO + H<sub>2</sub>) produced by gasifying coal or biomass.

The results presented in the preceding section of this report indicate that the core-in-shell pellets with a Ni catalyst are not only capable of catalyzing the CH<sub>4</sub> reforming reaction, but that they are also capable of catalyzing the water gas shift reaction. Otherwise the concentration of CO would increase as CH<sub>4</sub> is reformed by the reaction:



Instead the concentration of CO was always low whenever CH<sub>4</sub> was reformed in this investigation.

On the other hand, the Ni catalyst may not have been required because Han and Harrison<sup>36</sup> had shown that the water gas shift reaction can be catalyzed by several other materials including CaO and Al<sub>2</sub>O<sub>3</sub>, which were also present in the core-in-shell pellets. Therefore, the CaO and Al<sub>2</sub>O<sub>3</sub> may also have contributed to the overall catalytic activity of the pellets.

The experimental work described below was undertaken to see whether the Ni catalyst is actually required when the core-in-shell pellets are used for conducting the water gas shift reaction. In addition, since iron oxide has been shown to catalyze the water gas shift reaction, some consideration was also given to the use of an iron oxide catalyst in place of the Ni catalyst.

**Table 18.** Core-in-shell pellet formulations tested for the water-gas shift reaction.

| Sample I.D.                                  | Limestone Core         | Shell Formulation, wt% |      |        |                 | Calcination Conditions |
|----------------------------------------------|------------------------|------------------------|------|--------|-----------------|------------------------|
|                                              |                        | A16-SG                 | T-64 | DD-290 | Limestone       |                        |
| F( $\text{Al}_2\text{O}_3$ )                 | Microna 3              | 36                     | 27   | 27     | 10 <sup>c</sup> | 900°C, 3 hr            |
| F( $\text{Fe}_2\text{O}_3$ ) <sup>a</sup>    | Microna 3              | 32.4                   | 24.3 | 24.3   | 9 <sup>c</sup>  | 900°C, 3 hr            |
| F( $\text{Ni-Al}_2\text{O}_3$ ) <sup>b</sup> | -212/+63 $\mu\text{m}$ | 38                     | 28.5 | 28.5   | 5 <sup>d</sup>  | 800°C, 2 hr            |

<sup>a</sup>10 wt%  $\text{Fe}_2\text{O}_3$  was also added

<sup>b</sup>6.1 wt% Ni after being impregnated with  $\text{Ni}(\text{NO}_3)_2$

<sup>c</sup>Microna 3 limestone

<sup>d</sup>-212/+63  $\mu\text{m}$  limestone

To see whether a Ni catalyst was required or could be replaced, three different catalyst formulations were prepared and tested. These formulations were used for making the pellet shells, while the pellet cores were made of limestone. The composition of the three different core-in-shell formulations is indicated in Table 18.

The first formulation, denoted as F( $\text{Al}_2\text{O}_3$ ), had only limestone and alumina present in the shell before calcination. Microna 3 limestone was added to the shell formulation to enhance the physical strength of the shell material upon calcination at 900°C for 3 hr. This 3.2  $\mu\text{m}$  size material proved to be more effective than the -210/+44  $\mu\text{m}$  material used previously for strengthening the shell material.<sup>4, 5</sup> In addition, Microna 3 limestone was utilized as the CaO precursor for the cores of the core-in-shell pellets.

The second formulation, designated F( $\text{Fe}_2\text{O}_3$ ), was generally similar to the first except for the addition of  $\text{Fe}_2\text{O}_3$  to the shell material. The overall composition of the shell material included 10 wt%  $\text{Fe}_2\text{O}_3$  in addition to the four component concentrations listed. The inclusion of  $\text{Fe}_2\text{O}_3$  was designed to approximate a widely used high temperature shift (HTS) catalyst.

Industrial HTS catalysts are made with approximately 90 wt%  $\text{Fe}_2\text{O}_3$  and 10 wt%  $\text{Cr}_2\text{O}_3$ .<sup>37</sup> The active phase in HTS catalysts is  $\text{Fe}_3\text{O}_4$ , which forms upon reduction of  $\text{Fe}_2\text{O}_3$ . The  $\text{Cr}_2\text{O}_3$  acts as a refractory to stabilize the  $\text{Fe}_3\text{O}_4$  crystallites. For industrial applications, HTS catalysts undergo a controlled reduction procedure to ensure that  $\text{Fe}_3\text{O}_4$  is produced as the major phase. In this investigation, no initial reduction of iron oxide was performed. Microna 3 limestone was again utilized as the CaO precursor for the cores of the core-in-shell pellets.

The third shell formulation, denoted as F(Ni- $\text{Al}_2\text{O}_3$ ), was similar to one of the shell formulations used by Satrio et al.<sup>5</sup> for steam-methane reforming. In order to activate the Ni catalyst, methane and propane were reformed at 850°C for several hours after the Ni had been reduced with  $\text{H}_2$  at 550°C for 4 hr. A prolonged period of activation was required because the work was done before it was discovered that lignin-free water should be used for pelletizing the core and shell materials.

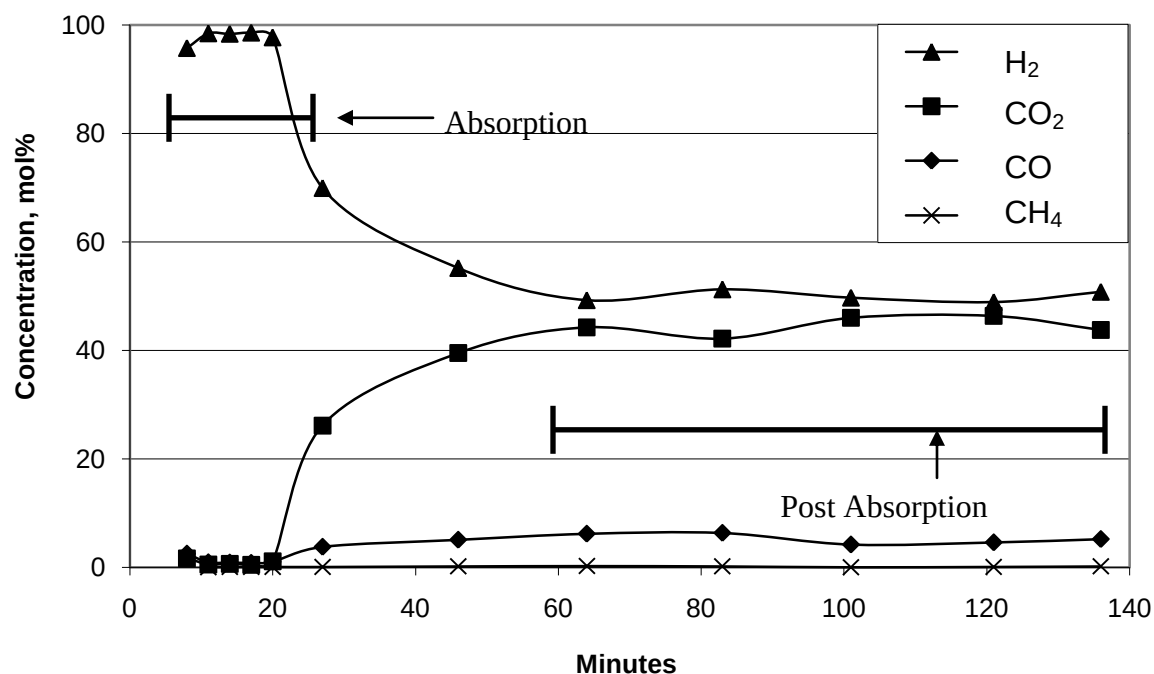
The core-in-shell pellets were prepared as described previously, and pellets with the third shell formulation were impregnated with a Ni catalyst as described before. The performance of the pellets was evaluated using the fixed bed reactor system shown in Figure 3. The reactor was packed with several layers of SiC pellets and core-in-shell pellets as described for conducting the  $\text{CH}_4$  reforming tests.

For testing a core-in-shell pellet formulation, the fixed bed reactor was supplied with a mixture of steam and carbon monoxide in a 3:1 mole ratio while also employing a total gas flow rate of 3.6 mmol/min. Steam was generated by pumping de-ionized water at a controlled flow rate into a preheater furnace where it was mixed with CO, which was metered by a Brooks mass flow controller. The mixture of steam and CO was conducted through heat-taped, stainless steel tubing to the reactor inlet.

Before undertaking a new test cycle of the core-in-shell pellets, the pellets were regenerated to desorb any  $\text{CO}_2$  absorbed during a previous cycle. The  $\text{F}(\text{Al}_2\text{O}_3)$  formulation was regenerated by increasing the bed temperature to  $775^\circ\text{C}$  with argon flowing through the bed at a rate of  $1.8\text{ mmol/min}$ . Under these conditions, desorption was slow and a long time was required for the reactor effluent to be devoid of  $\text{CO}_2$ . Therefore, a different procedure was employed for regenerating the sorbent in the case of other shell formulations. For these formulations, a  $\text{CO}$  and steam mixture flowing at  $3.6\text{ mmol/min}$  was used as the sweep gas while the bed temperature was raised to  $850^\circ\text{C}$ . Under these conditions, desorption of  $\text{CO}_2$  was considered complete when the  $\text{CO}_2$  concentration in the reactor effluent remained constant. Sorbent regeneration at  $850^\circ\text{C}$  typically took about  $1.0\text{--}1.5\text{ hr}$ . In addition, the use of  $\text{CO}$  and steam as the sweep gas ensured that the  $\text{Ni}$  catalyst remained reduced during sorbent regeneration of the  $\text{F}(\text{Ni-Al}_2\text{O}_3)$  sample.

After regenerating the sorbent, the reactor temperature was reduced to a temperature more appropriate for the water-gas shift reaction. While the reactor was being cooled, argon was passed through the bed at a rate of  $1.8\text{ mmol/min}$  in the case of the  $\text{F}(\text{Al}_2\text{O}_3)$  shell formulation. For the other shell formulations, no gas was passed through the bed during cooling. When the desired reaction temperature was achieved, the reactants were introduced in a  $1:3$  mole ratio of  $\text{CO}:\text{H}_2\text{O}$  while employing a total flow rate of  $3.6\text{ mmol/min}$ . Samples of the reactor effluent were periodically drawn with Gastight syringes supplied by the Hamilton Co. These samples were analyzed with an SRI 8610C gas chromatograph (GC) equipped with both a thermal conductivity detector and flame ionization detector to determine the concentrations of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$ , which were then normalized to  $100\%$ .

The performance of the different core-in-shell pellet formulations listed in Table 18 was evaluated by conducting the water-gas shift reaction in the fixed bed reactor starting with a freshly regenerated sample and continuing a run until the sorbent was saturated and CO<sub>2</sub> absorption effectively ceased. The results of such a run are presented in Figure 43. For this run the reactor was charged with the F(Ni-Al<sub>2</sub>O<sub>3</sub>) pellet formulation, and it was operated at 600°C. During the “Absorption” period, most of the CO<sub>2</sub> was absorbed and a high concentration of H<sub>2</sub> was produced. Later, as the sorbent became saturated, the concentration of H<sub>2</sub> fell to a level of approximately 50 mol% and the concentration of CO<sub>2</sub> reached a level of 43-47 mol%. This period where the sorbent had become saturated and CO<sub>2</sub> absorption had effectively ceased is identified as the “Post Absorption” period. Figure 43 illustrates a run with a F(Ni-Al<sub>2</sub>O<sub>3</sub>) sample that had undergone several absorption and regeneration cycles, which shortened the length of the Absorption period compared to that of a fresh sample.



**Figure 43.** Composition of the reactor effluent during testing of the F(Ni-Al<sub>2</sub>O<sub>3</sub>) formulation at 600°C. The composition is on an H<sub>2</sub>-free basis.

The Post Absorption phase should produce the gas concentrations that would result if no sorbent was present in the reactor. Interestingly, every test run observed in this investigation resulted in a  $\text{H}_2$  concentration slightly higher than the  $\text{CO}_2$  concentration during the Post Absorption period. This is interesting because  $\text{H}_2$  and  $\text{CO}_2$  should be present in equimolar quantities when only the water-gas shift reaction takes place. A check of the GC did not reveal an error in calibration that would account for the disparity. A possible explanation for the disparity is that  $\text{CO}_2$  continued to be slowly absorbed well into the so-called Post Absorption period. When  $\text{CaO}$  produced from limestone undergoes recarbonation after calcination, the  $\text{CaO}$  goes through a period of rapid, kinetically controlled reaction with  $\text{CO}_2$ , followed by the buildup of a carbonate layer. When the thickness of the carbonate layer becomes significant, the rate of absorption of  $\text{CO}_2$  becomes controlled by diffusion through the carbonate layer.<sup>31</sup> This slow, diffusion-controlled period of  $\text{CO}_2$  absorption can last for an extended period of time. Thus, it is likely that  $\text{CaO}$  continued to slowly absorb  $\text{CO}_2$  even during the Post Absorption period.

Each of the core-in-shell pellet formulations was subjected to a series of tests of the water-gas shift reaction conducted at four different temperatures. All of these tests were conducted at 1.0 atm and while feeding  $\text{CO}$  and steam in a 1:3 mole ratio. For these reactions conditions, the corresponding equilibrium gas composition is shown in Table 19. Of course, this composition represents that which would have been achieved had the tests proceeded to equilibrium.

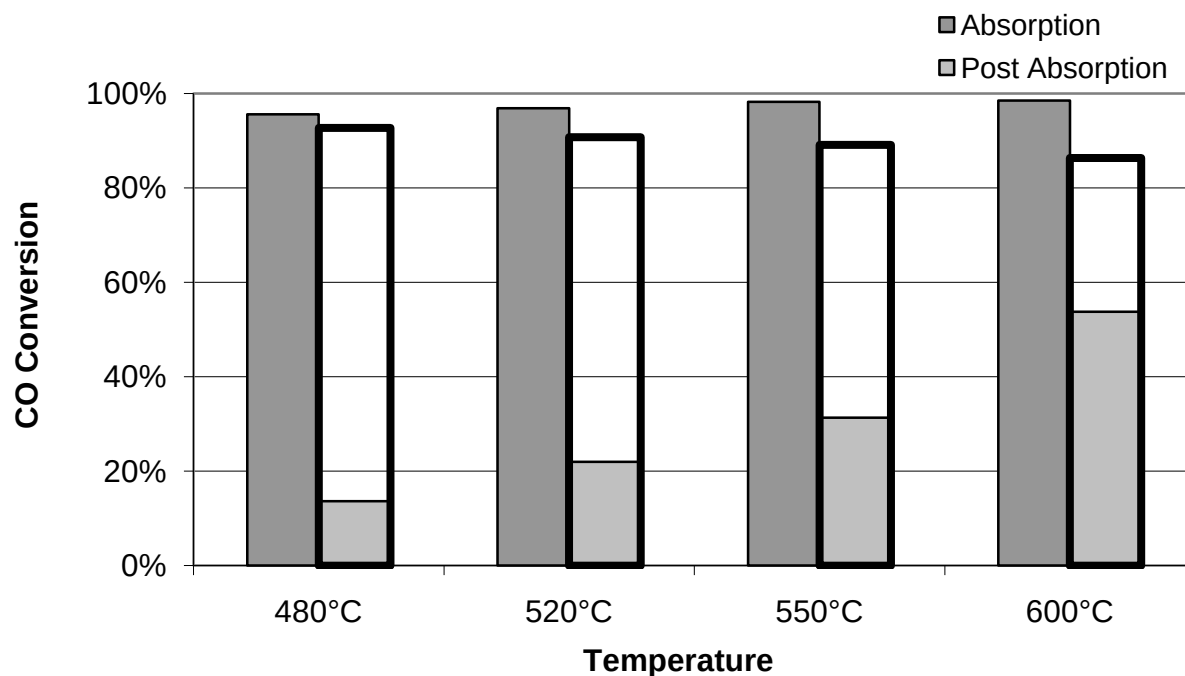
The actual results of the first series of tests conducted with the  $\text{F}(\text{Al}_2\text{O}_3)$  formulation are presented in Table 20. The gas concentrations in this table can be compared with the thermodynamic equilibrium gas concentrations in Table 19. The gas concentrations recorded in this table were used to calculate the  $\text{CO}$  conversions for both the Absorption and Post Absorption

**Table 19.** Calculated thermodynamic equilibrium gas concentrations based on a feed of 1 mol CO and 3 mol H<sub>2</sub>O and a reaction pressure of 1.0 atm.

| Temperature,<br>°C | CO <sub>2</sub> Absorption | Concentration (dry basis), mol% |                 |                |
|--------------------|----------------------------|---------------------------------|-----------------|----------------|
|                    |                            | CO                              | CO <sub>2</sub> | H <sub>2</sub> |
| 480                | With                       | 0.00                            | 0.00            | 100.00         |
|                    | Without                    | 3.79                            | 48.11           | 48.11          |
| 520                | With                       | 0.00                            | 0.10            | 99.90          |
|                    | Without                    | 4.88                            | 47.56           | 47.56          |
| 550                | With                       | 0.00                            | 0.20            | 99.80          |
|                    | Without                    | 5.76                            | 47.12           | 47.12          |
| 600                | With                       | 0.20                            | 0.79            | 99.01          |
|                    | Without                    | 7.35                            | 46.32           | 46.32          |

**Table 20.** Gas concentrations observed exiting the fixed-bed reactor during water-gas shift testing of the F(Al<sub>2</sub>O<sub>3</sub>) shell formulation.

| Temperature,<br>°C | Period of<br>Operation | Concentration (dry basis), mol% |      |                 |                |
|--------------------|------------------------|---------------------------------|------|-----------------|----------------|
|                    |                        | CH <sub>4</sub>                 | CO   | CO <sub>2</sub> | H <sub>2</sub> |
| 480                | Absorption             | 0.0                             | 4.4  | 0.1             | 95.4           |
|                    | Post Absorption        | 0.0                             | 76.0 | 8.5             | 15.5           |
| 520                | Absorption             | 0.0                             | 3.1  | 0.6             | 96.1           |
|                    | Post Absorption        | 0.0                             | 63.9 | 15.6            | 20.5           |
| 550                | Absorption             | 0.0                             | 1.8  | 0.6             | 97.6           |
|                    | Post Absorption        | 0.0                             | 52.3 | 20.5            | 27.2           |
| 600                | Absorption             | 0.0                             | 1.5  | 0.9             | 97.6           |
|                    | Post Absorption        | 0.0                             | 30.1 | 30.6            | 39.3           |



**Figure 44.** CO conversion observed during water-gas shift testing of the  $F(\text{Al}_2\text{O}_3)$  core-in-shell pellet formulation. The heavy lines outlining the shaded areas represent the calculated equilibrium conversion. The shaded areas represent actual conversion observed in all cases.

periods of operation, which are presented in Figure 44. The black bars outlining the Post Absorption period indicate the calculated equilibrium CO conversion for the water-gas shift reaction based on equilibrium data found in the *Catalyst Handbook*.<sup>37</sup> The equilibrium data for the reaction of  $\text{CaO}$  and  $\text{CO}_2$  present during the Absorption period was obtained from *Metallurgical Thermochemistry*.<sup>38</sup> For the Absorption period of operation, the calculated equilibrium conversion of CO was essentially 100% over the 480-600°C temperature range. Hence, black bars outlining the equilibrium conversion for the Absorption period are not shown in order to refrain from obscuring the experimental conversion.

A comparison of the results in Table 20 with those in Table 19, indicates that during the  $\text{CO}_2$  Absorption Period of testing, the actual product gas composition was approaching the equilibrium gas composition, especially at the higher temperatures. This result is also reflected

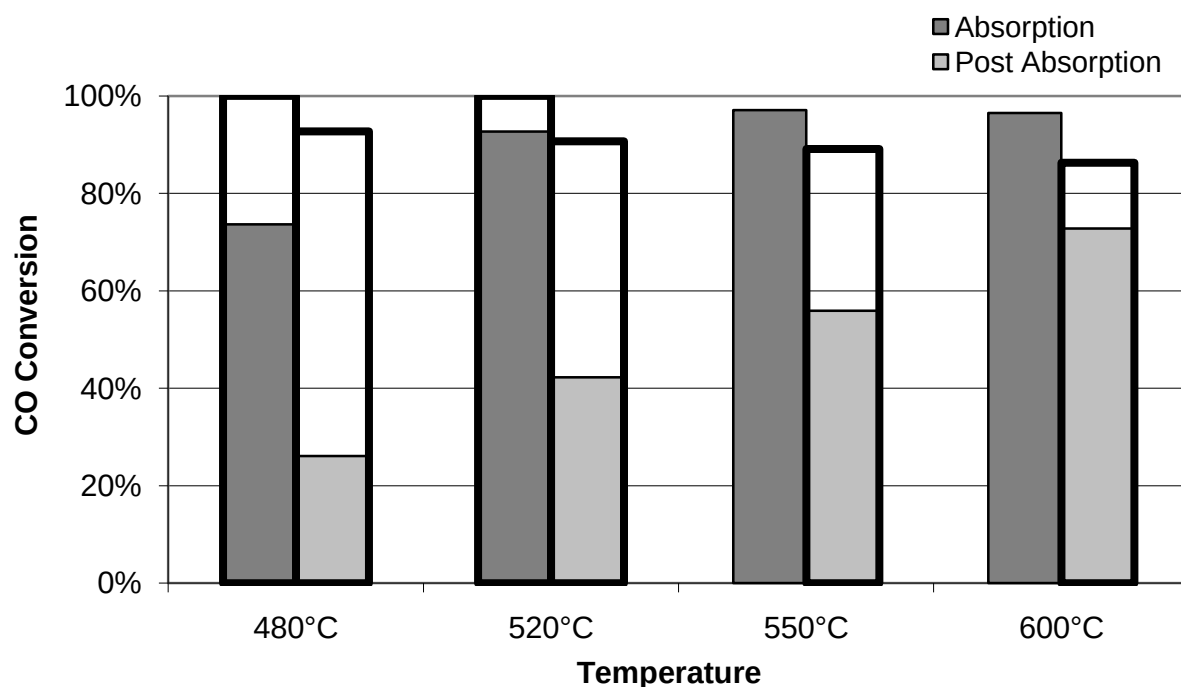
by the CO conversion which increased with temperature and approached 100% at the higher temperatures. However, during the Post CO<sub>2</sub> Absorption Period the observed gas composition and the CO conversion based on this composition differed greatly from the corresponding values based on thermodynamic equilibrium. Since the actual CO concentration was much greater and the corresponding product concentrations were much lower than the equilibrium values, the actual results appeared to have been limited by reaction kinetics. In other words, the results indicate that the catalytic activity of the F(Al<sub>2</sub>O<sub>3</sub>) formulation was not sufficient to achieve equilibrium CO conversion levels during the Post Absorption period.

During the Absorption period, the system appeared to approach equilibrium but was still slightly limited by either the rate of diffusion of CO<sub>2</sub> through the shell to the CaO core or the rate of reaction between CaO and CO<sub>2</sub>. The limitation is indicated by the gradual increase in CO conversion with increasing temperature, which is opposite to the decrease in CO conversion expected in an exothermic system limited by thermodynamic equilibrium (see Figure 2b). However, a comparison of actual CO conversion levels during the Absorption period with calculated equilibrium limited CO conversions for the Post Absorption period in Figure 44 indicates that the equilibrium limitation of the water-gas shift reaction was largely overcome by the absorption of CO<sub>2</sub>. In other words, since the CO conversion during the Absorption period as indicated by Figure 44 was higher than the equilibrium conversion indicated for the Post Absorption period, the absorption of CO<sub>2</sub> made it possible to overcome the thermodynamic equilibrium limitation of the water-gas shift reaction. The maximum benefit was observed at 600°C where a CO conversion of 98.5% was achieved when CO<sub>2</sub> was being absorbed compared to a calculated equilibrium conversion of 86.3% without CO<sub>2</sub> absorption.

**Table 21.** Gas concentrations observed exiting the fixed-bed reactor during water-gas shift testing of the  $F(Fe_2O_3)$  shell formulation.

| Temperature,<br>°C | Period of<br>Operation | Concentration (dry basis), mol% |      |                 |                |
|--------------------|------------------------|---------------------------------|------|-----------------|----------------|
|                    |                        | CH <sub>4</sub>                 | CO   | CO <sub>2</sub> | H <sub>2</sub> |
| 480                | Absorption             | 0.0                             | 26.1 | 1.2             | 72.8           |
|                    | Post Absorption        | 0.0                             | 58.6 | 15.8            | 25.6           |
| 520                | Absorption             | 0.0                             | 7.2  | 0.7             | 92.1           |
|                    | Post Absorption        | 0.0                             | 40.6 | 26.3            | 33.0           |
| 550                | Absorption             | 0.0                             | 2.9  | 0.7             | 96.5           |
|                    | Post Absorption        | 0.0                             | 28.3 | 31.1            | 40.6           |
| 600                | Absorption             | 0.0                             | 3.4  | 1.2             | 95.4           |
|                    | Post Absorption        | 0.0                             | 15.8 | 38.2            | 46.0           |

The second series of tests of the water-gas shift reaction was conducted with the  $F(Fe_2O_3)$  formulation of the core-in-shell pellets. The results of this series are reported in Table 21 and Figure 45. Gas concentrations that were observed in the reactor effluent during this series are shown in Table 21 and the CO conversions based on these concentrations are shown in Figure 45. The gas concentrations in this table can be compared with calculated thermodynamic equilibrium gas concentrations in Table 19. As before, the black borders above the unshaded areas correspond to calculated thermodynamic equilibrium values, whereas the shaded areas correspond to the actual conversion achieved. Of special interest was the higher conversion achieved with the  $F(Fe_2O_3)$  formulation compared to that achieved with the  $F(Al_2O_3)$  formulation at each temperature during the Post Absorption period. These results clearly indicate that the  $F(Fe_2O_3)$  formulation had a higher catalytic activity for the water-gas shift reaction than the  $F(Al_2O_3)$  formulation for this reaction when CO<sub>2</sub> was present because it was not being absorbed.



**Figure 45.** CO conversion observed during water-gas shift testing of the  $F(Fe_2O_3)$  formulation. The heavy lines outlining the shaded areas represent the calculated equilibrium conversion. The shaded areas represent actual conversions in all cases.

During the  $CO_2$  Absorption period when essentially no  $CO_2$  was present, the CO conversion achieved with the  $F(Al_2O_3)$  formulation was always greater than that obtained with the  $F(Fe_2O_3)$  formulation. Furthermore, a comparison of the results in Table 21 with those in Table 20 showed that the  $H_2$  concentration produced at each temperature was lower for the second formulation than for the first during the  $CO_2$  Absorption period. These results suggest that the kinetics of the water gas shift reaction are affected adversely by the presence of  $CO_2$ , with the effect being greater when the reaction is catalyzed by  $Al_2O_3$  than when it is catalyzed by  $Fe_2O_3$ . The effect could be due to the chemisorption of  $CO_2$  interfering with the chemisorption of CO. The difference in the performance of the two catalysts could also be due to a difference in absorptivity of the materials or to the addition of ultra-fine sized  $Fe_2O_3$  to the second formulation. This would have reduced the porosity of the shell and increased its

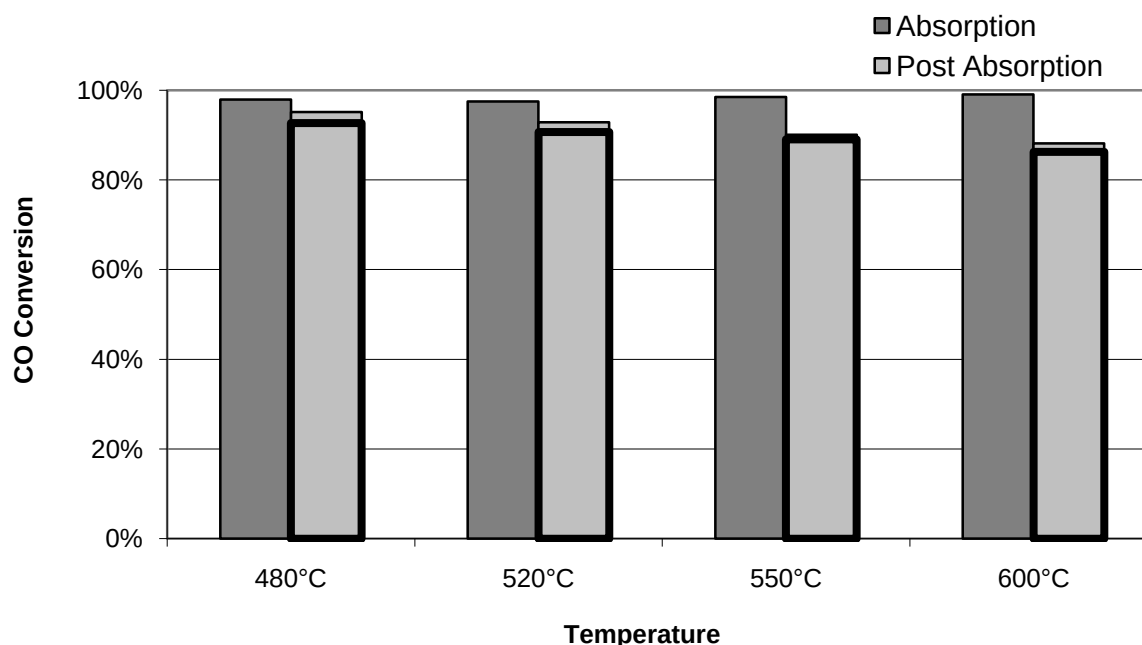
**Table 22.** Gas concentrations observed exiting the fixed-bed reactor during water-gas shift testing of the F(Ni-Al<sub>2</sub>O<sub>3</sub>) shell formulation.

| Temperature,<br>°C | Period of<br>Operation | Concentration (dry basis), mol% |     |                 |                |
|--------------------|------------------------|---------------------------------|-----|-----------------|----------------|
|                    |                        | CH <sub>4</sub>                 | CO  | CO <sub>2</sub> | H <sub>2</sub> |
| 480                | Absorption             | 0.6                             | 2.1 | 0.7             | 96.6           |
|                    | Post Absorption        | 0.6                             | 2.5 | 46.0            | 50.9           |
| 520                | Absorption             | 0.3                             | 2.3 | 1.1             | 96.3           |
|                    | Post Absorption        | 0.3                             | 3.7 | 47.8            | 48.2           |
| 550                | Absorption             | 0.3                             | 1.5 | 0.8             | 97.4           |
|                    | Post Absorption        | 0.3                             | 5.2 | 43.9            | 50.6           |
| 600                | Absorption             | 0.1                             | 0.9 | 0.7             | 98.2           |
|                    | Post Absorption        | 0.2                             | 6.3 | 43.2            | 50.2           |

resistance to diffusion of CO<sub>2</sub>. Consequently, the CO<sub>2</sub> produced by the water-gas shift reaction was not absorbed as rapidly. However, as the temperature was raised, the rate of CO<sub>2</sub> diffusion could have increased so that at the higher temperatures, this rate was virtually non-limiting. At both 550°C and 600°C, the CO conversion achieved with F(Fe<sub>2</sub>O<sub>3</sub>) was only slightly lower than that obtained with F(Al<sub>2</sub>O<sub>3</sub>) during the Absorption period.

The third series of tests was conducted with the F(Ni-Al<sub>2</sub>O<sub>3</sub>) formulation similar to the one used by Satrio et al.<sup>5</sup> for steam-methane reforming. It differed slightly from the Ni-containing formulation described in the preceding section of this report for reforming methane.

The results of applying the F(Ni-Al<sub>2</sub>O<sub>3</sub>) formulation to the water-gas shift reaction at different temperatures are presented in Table 22 and Figure 46. As before, the observed gas concentrations in Table 22 can be compared with calculated thermodynamic equilibrium gas concentrations in Table 19. These results indicate that for every temperature and during both the Absorption and Post Absorption periods the CO conversion was very large and similar in



**Figure 46.** CO conversion observed during water-gas shift testing of the F(Ni-Al<sub>2</sub>O<sub>3</sub>) formulation. The heavy lines outlining the shaded areas represent the calculated equilibrium conversion. The shaded areas represent actual conversions in all cases.

magnitude to that predicted by thermodynamic equilibrium provided the formation of CH<sub>4</sub> was neglected. Since the concentration of CH<sub>4</sub> in the product was only 0.1 to 0.6 mol%, it probably did not have a major effect on the outcome. In contrast to results obtained with the previous shell formulations, the CO conversion achieved with the F(Ni-Al<sub>2</sub>O<sub>3</sub>) formulation during the Post Absorption period was within 3% of the calculated equilibrium conversion for each temperature. Also, the conversion during the Post Absorption period declined as the temperature increased, which corresponded with the effect of temperature on the equilibrium conversion.

Although the performance of the F(Ni-Al<sub>2</sub>O<sub>3</sub>) formulation was clearly superior to that of the other formulations during the Post Absorption period, it was not significantly better than the performance of the F(Al<sub>2</sub>O<sub>3</sub>) formulation during the CO<sub>2</sub> Absorption period. Furthermore, the

F(Al<sub>2</sub>O<sub>3</sub>) did not appear to catalyze the reverse CH<sub>4</sub> reforming reaction shown below, since CH<sub>4</sub> was not observed in the reaction products when CO and steam were reacted.



On the other hand, the F(Ni-Al<sub>2</sub>O<sub>3</sub>) did appear to catalyze this reaction since CH<sub>4</sub> was found in the reaction products listed in Table 22. Also reaction 6 indicates that the use of a Ni catalyst for the water gas shift reaction at higher pressures could produce CH<sub>4</sub> in troublesome concentrations. Therefore, considering this disadvantage of a Ni catalyst together with the higher cost of Ni, its greater susceptibility to poisoning by sulfur, and its lower resistance to oxidation, it is apparent that the Fe(Al<sub>2</sub>O<sub>3</sub>) formulation would be the better choice for core-in-shell pellets used for the water gas shift reaction.

## CONCLUSIONS

The overall objective of this innovative research project was largely achieved. This objective was to develop a combined catalyst and sorbent material that will promote the reaction of CH<sub>4</sub> and/or CO with steam while simultaneously separating the reaction products, H<sub>2</sub> and CO<sub>2</sub>. The material combines a catalyst for both the methane reforming and water gas shift reactions with a sorbent for CO<sub>2</sub>, the principal byproduct of these reactions. It was shown that a practical and serviceable material can be prepared in the form of spherical pellets consisting of a core of powdered limestone encased in a shell composed largely of alumina. The shell is strengthened by calcining the pellets at 900 to 1100°C, and a catalyst is added by impregnating the material with Ni.

Although initial research showed that the absorption capacity of CaO derived from limestone decreases at a relatively rapid rate when it is used in a cyclic process involving CO<sub>2</sub> absorption and regeneration, it was shown that the rate of decrease is greatly reduced by

incorporating MgO in the material at a level of 0.25 g MgO/g CaO. Alternatively, the rate of decrease can be reduced by first calcining the material at 1100°C for an extended time (e.g., 5 hr). Both methods proved equally effective in a 1200 cycle test of the sorbent.

Initial research also showed that while strong shell material can be made by calcining a mixture of different sizes of  $\alpha$ - alumina particles, the resulting surface area of the calcined product is too limited for supporting an active Ni catalyst. This deficiency was corrected by replacing approximately 30% of the  $\alpha$ -alumina with a noncrystalline form of alumina having a large surface area, but this reduced the compressive strength of the shell material. This problem was largely overcome by incorporating either sufficient 3  $\mu\text{m}$  size limestone to provide 5.7 wt% CaO in the calcined shell material or sufficient lanthanum nitrate to provide 7.7 wt%  $\text{La}_2\text{O}_3$ .

Performance tests of core-in-shell pellets prepared with the improved shell materials and impregnated with a Ni catalyst produced excellent results over a range of temperatures (550 to 650°C) and pressure (1 to 10 atm). During each cycle while  $\text{CO}_2$  was being largely absorbed, the conversions of  $\text{CH}_4$  and CO approached thermodynamic equilibrium levels. In limited lifecycle tests of these pellets, the activity of the Ni catalyst remained high throughout the tests, whereas the absorption capacity of the sorbent appeared to decrease from cycle to cycle. For these lifecycle tests  $\text{CH}_4$  reforming was conducted at 650°C while sorbent regeneration was conducted at 850°C.

Additional performance tests showed that the core-in-shell pellets can also be used advantageously for conducting the water gas shift reaction to produce  $\text{H}_2$  by reacting steam and CO. Although the best results were achieved by using pellets impregnated with a Ni catalyst, results that were nearly as good were achieved with similar pellets which did not contain the Ni catalyst as long as  $\text{CO}_2$  was largely absorbed. This result indicates that alumina may be as useful

as Ni for catalyzing the water gas shift reaction besides being more stable, less costly and not as easily poisoned.

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