Development of a Catalyst/Sorbent for Methane Reforming

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DOE Grant No. DE-FG26-2NT41549

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Research Objectives

Overall objective

Develop a combined catalyst and sorbent to promote and improve the efficiency of steam reforming which will improve the overall efficiency of producing hydrogen from coal.

Specific objectives

- Develop a combined catalyst/sorbent material
- Demonstrate the usefulness of the material for steam reforming
- Optimize the preparation conditions

Chemical Reactions for Producing H_2 from CH_4

Steam methane reforming (SMR) reaction:

$$CH_{4(g)} + H_2O_{(g)} \leftrightarrow 3H_{2(g)} + CO_{(g)}$$

$$K_{SMR} = \frac{\left(Y_{H_2}\right)^3 \left(Y_{CO}\right)}{\left(Y_{CH_4}\right)\left(Y_{H_2O}\right)} P^2$$

Water gas shift (WGS) reaction:

$$CO_{(g)} + H_2O_{(g)} \leftrightarrow H_{2(g)} + CO_{2(g)}$$

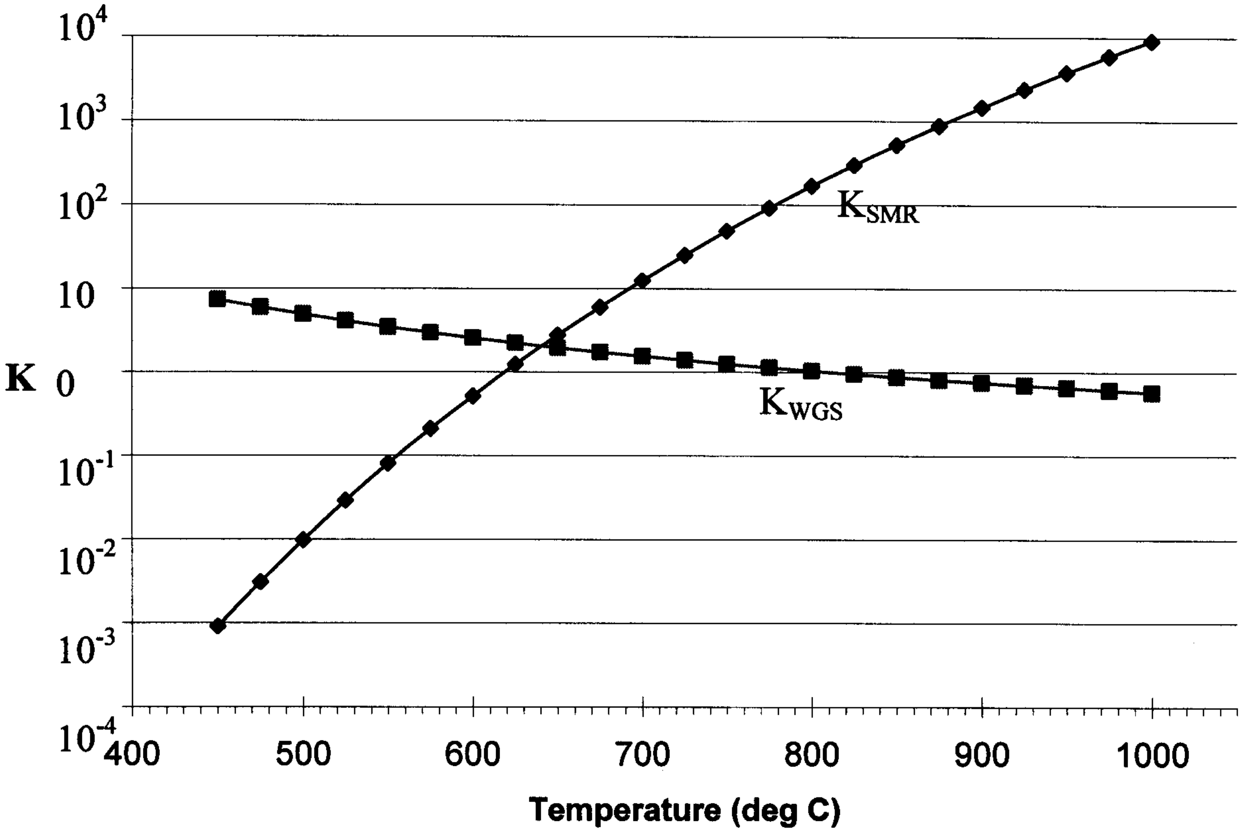
$$K_{WGS} = \frac{\left(Y_{H_2}\right)\left(Y_{CO_2}\right)}{\left(Y_{CO}\right)\left(Y_{H_2O}\right)}$$

Equilibrium modifying (EM) reaction:

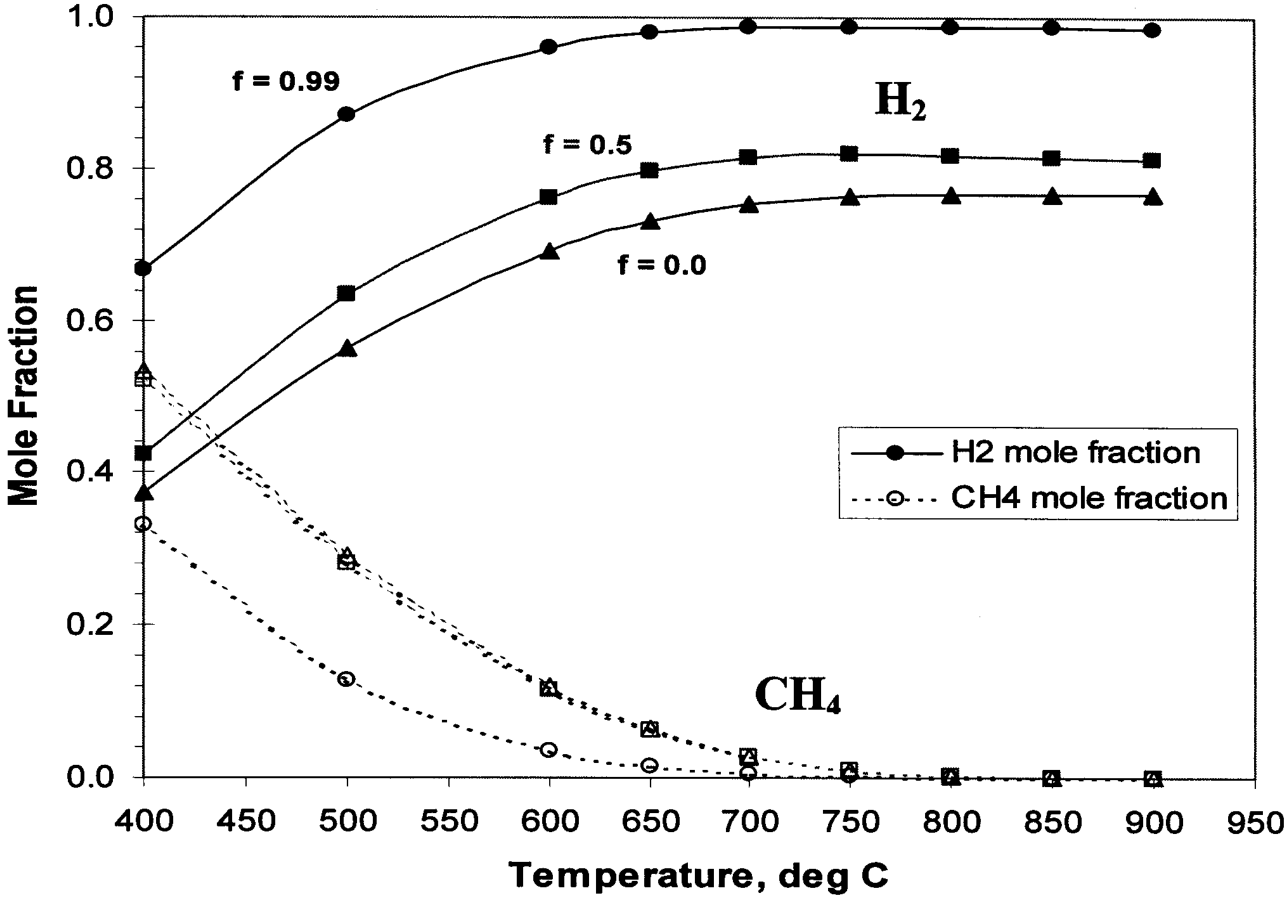
$$CaO_{(S)} + CO_{2(g)} \leftrightarrow CaCO_{3(S)}$$

$$K_{EM} = \left(Y_{CO_2}\right)^{-1} P^{-1}$$

Reaction Equilibrium Constants for SMR & WGS



Effect of CO2 Removal on Product Composition (R=3.0)



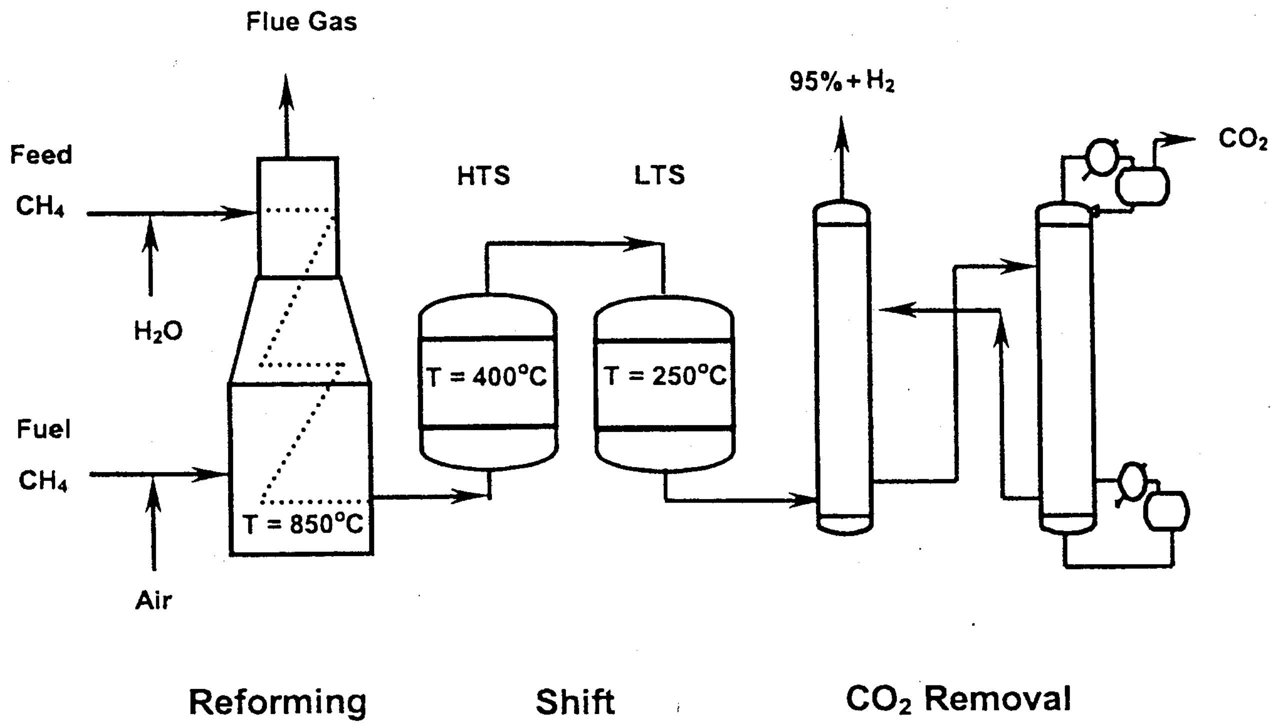


Fig. 9. Simplified flow diagram of the conventional steam methane reforming process.

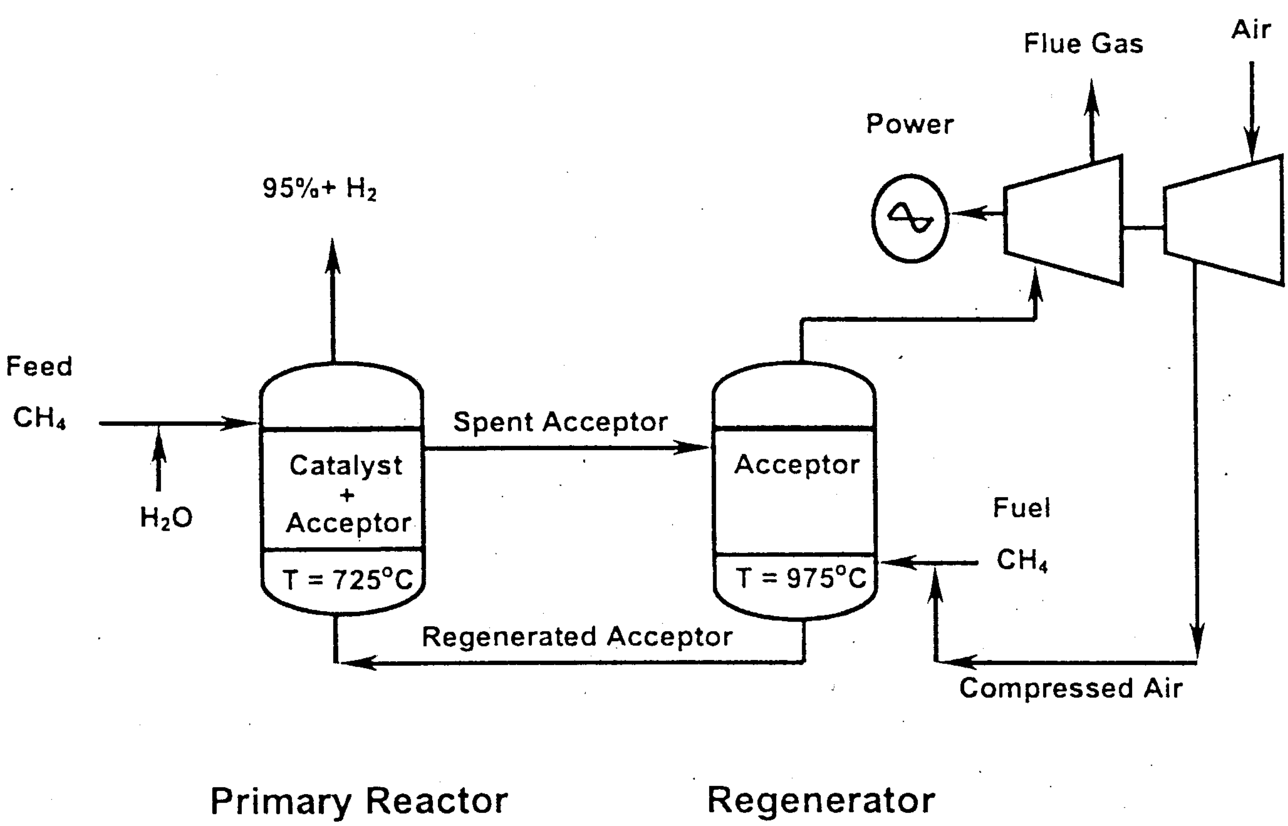


Fig. 10. Simplified flow diagram of the single-step steam methane reforming process.

Relevant Technical Literature

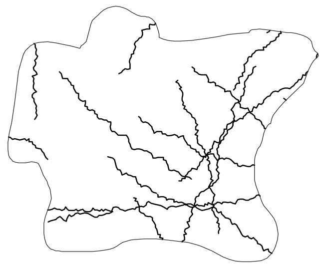
B. Balasubramanian et al., "Hydrogen from methane in a single-step process," *Chem. Eng. Sci.*, 54, 3543-3552 (1999).

Y. Ding and E. Alpay, "Adsorption-enhanced steam-methane reforming," *Chem. Eng. Sci.*, 55, 3929-3940 (2000).

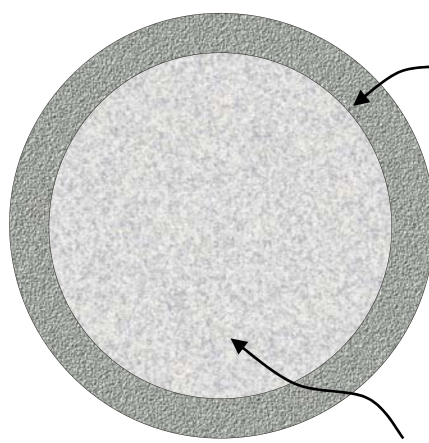
J. R. Hufton et al., "Sorption-Enhanced Reaction Process for Hydrogen Production," *AIChE Jour.*, 45, 248-256 (1999).

W. E. Waldron et al., "Production of Hydrogen by Cyclic Sorption Enhanced Reaction Process," *AIChE Jour.*, 47, 1477-1479 (2001).

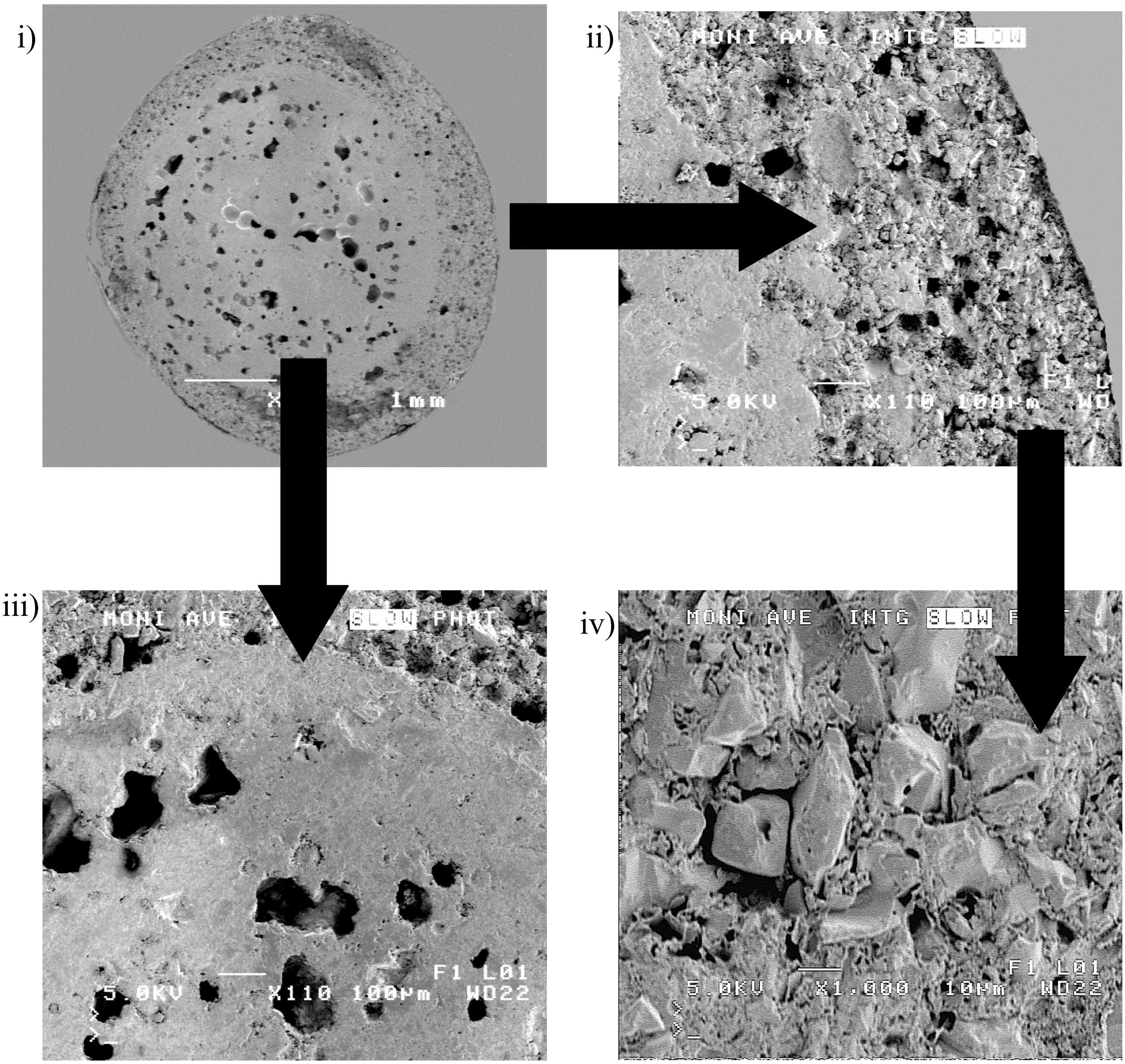
Limestone Particle



Core-in-Shell Pellet



The core-in-shell structure overcomes the inherent weakness of lime particles.



Micrographs of a freshly made limestone-based pellet; i) section of an entire pellet at 17X, ii) the shell at 110X, iii) the core at 110X, and iv) the shell at 1000X.

Desired Characteristics of Core-in-Shell Catalyst/Sorbent

Shell:

- Physically strong and abrasion resistant
- Adequate surface area for supporting Ni catalyst
- Sufficiently porous to allow CO_2 to diffuse readily into and out of the core

Core:

- Large CO_2 absorption capacity
- Easily regenerated
- Highly stable to prevent loss in reactivity as it is repeatedly loaded and regenerated

CaO Based Sorbent

Advantages:

- Excellent absorption capacity at high temperature
- Raw materials (i.e., limestone or dolomite) are plentiful and inexpensive
- Easily regenerated by heating or depressurizing

Problems:

- Chemically reactive CaO is a weak, friable material
- At high temperature CaO becomes less reactive due to sintering

Scope of Work

Material preparation and development

- Prepare pellets with CaO cores and Al_2O_3 shells
- Impregnate shells with Ni
- Vary pellet composition and preparation conditions

Material characterization

- Measure BET surface area and pore volume
- Estimate and/or measure Ni content
- Measure compressive strength of pellets
- Measure abrasion resistance of pellets

Performance testing

- Conduct steam reforming tests on a bench-scale
- Use results to improve pellet formulation

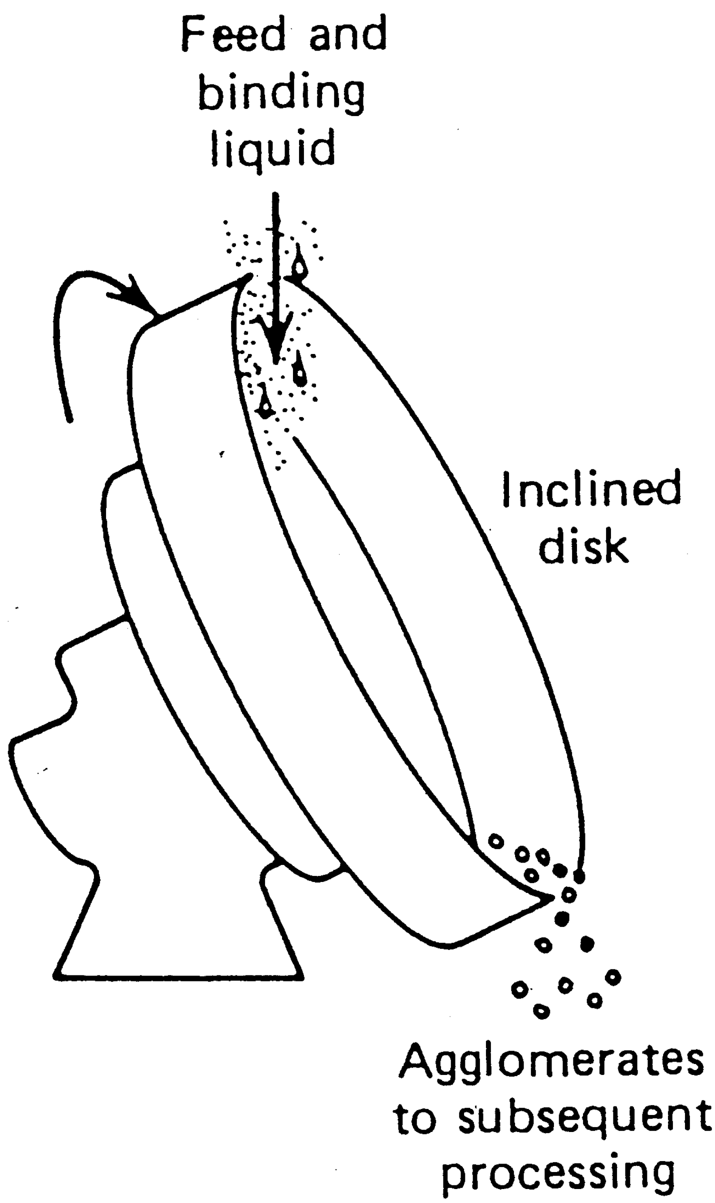
Materials Used for Preparing Pellets

Core Materials:

• Iowa Limestone:	98% $CaCO_3$	
	-325 mesh	
• Dolime:	$Ca(OH)_2 \cdot Mg(OH)_2$	Fresh
	$CaCO_3 \cdot Mg(OH)_2$	As used

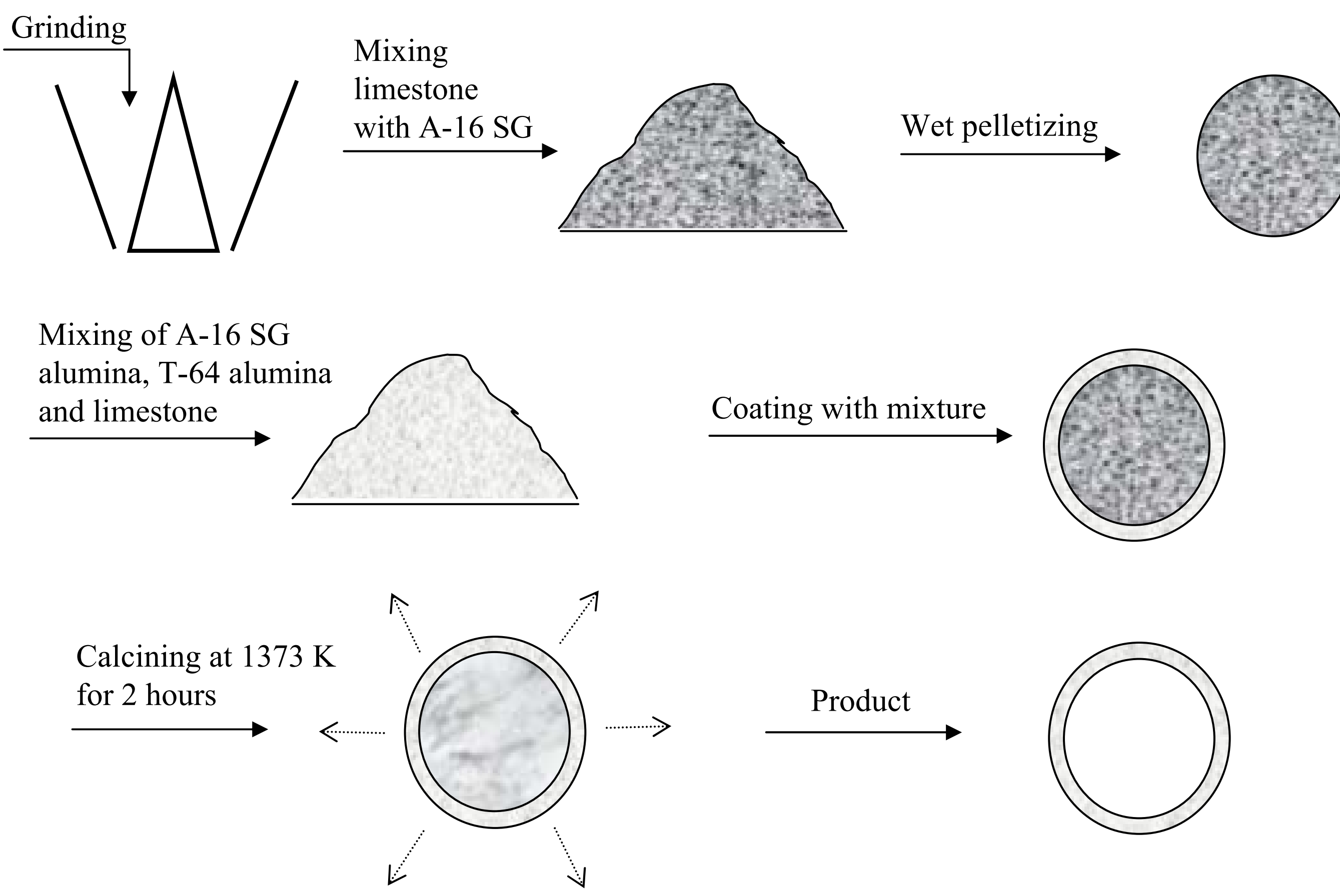
Shell materials:

• α-alumina (T-64 from Alcoa)	8 μm (average)
• α-alumina (A-16SG from Alcoa)	1 μm (average)
• γ-alumina (CP-7) from Alcoa)	8 μm (average
	280 m^2/g

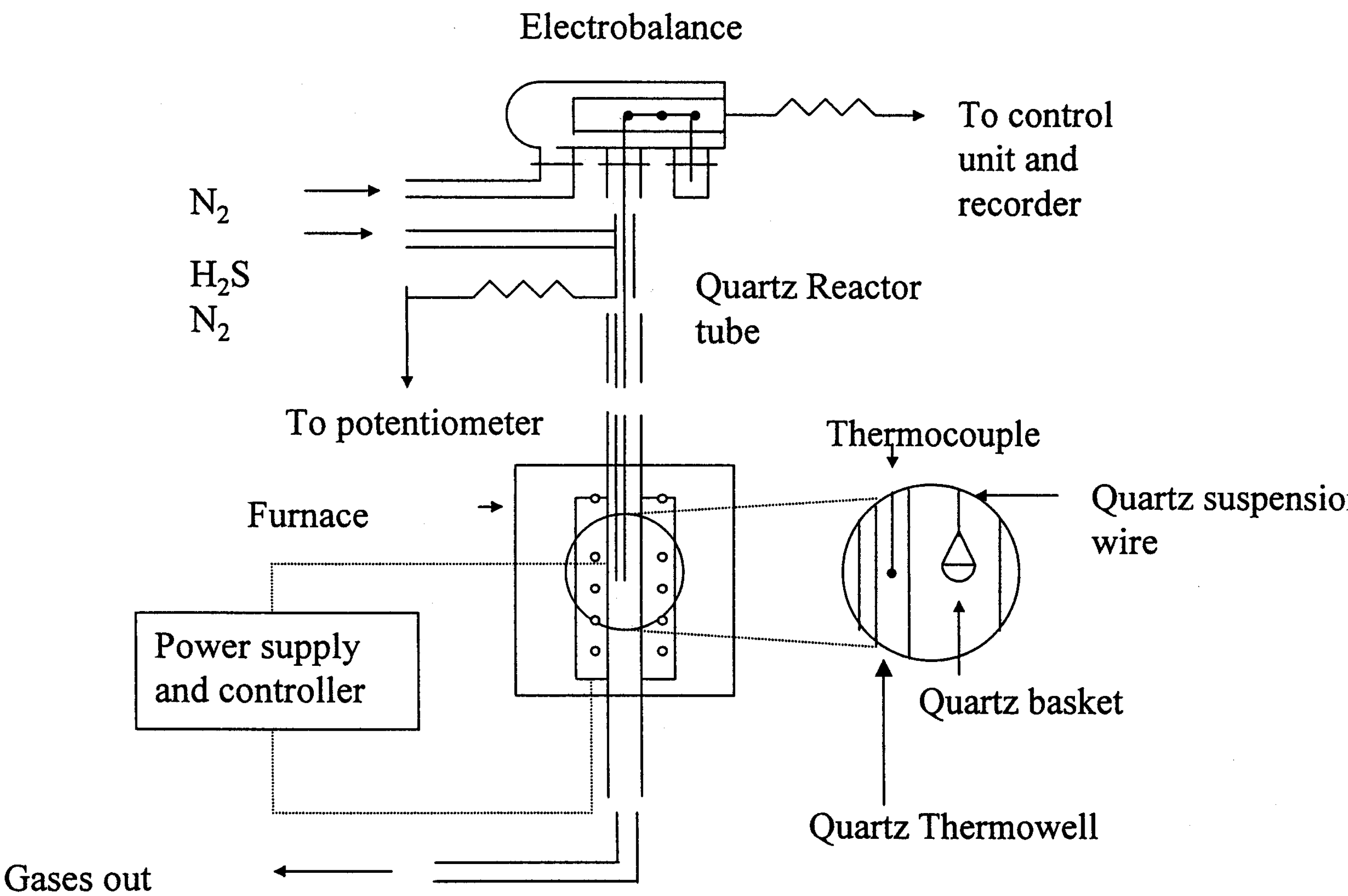


Schematic of an inclined-disk agglomerator.

Preparation procedure for a core-in-shell sorbent



Adsorption testing



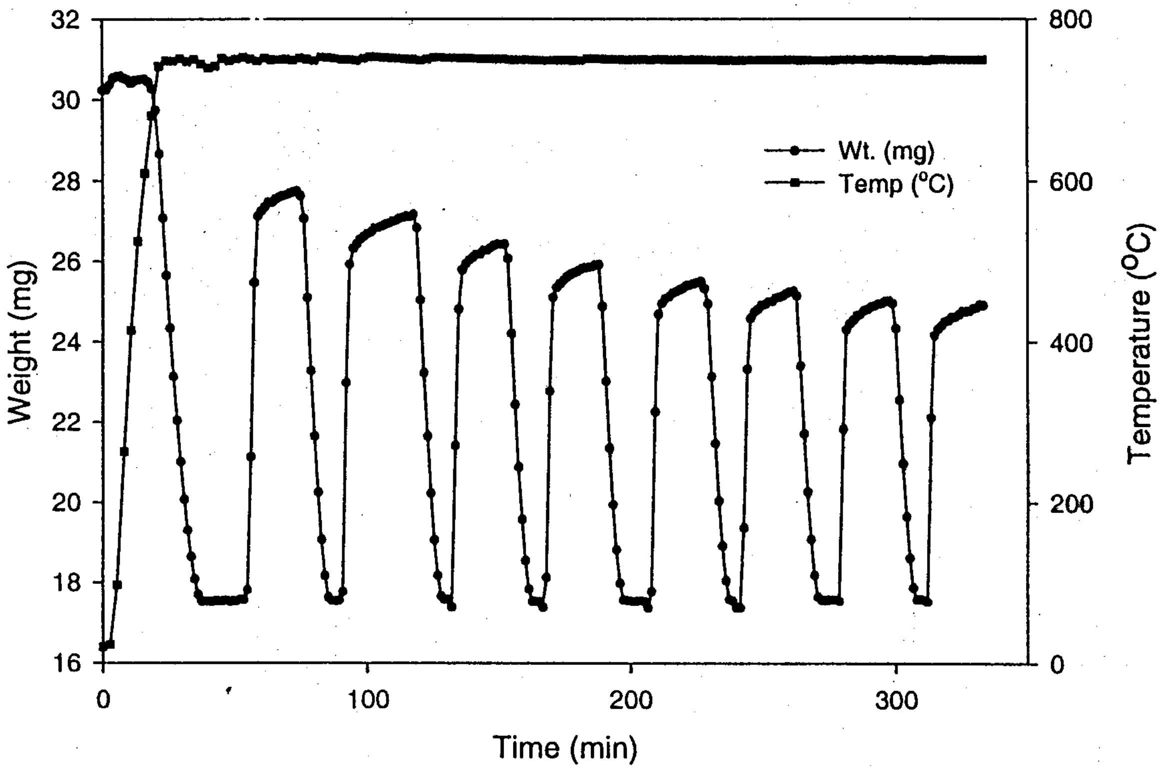


Figure 1. Results of a multicycle CO_2 absorption test with a limestone pellet.

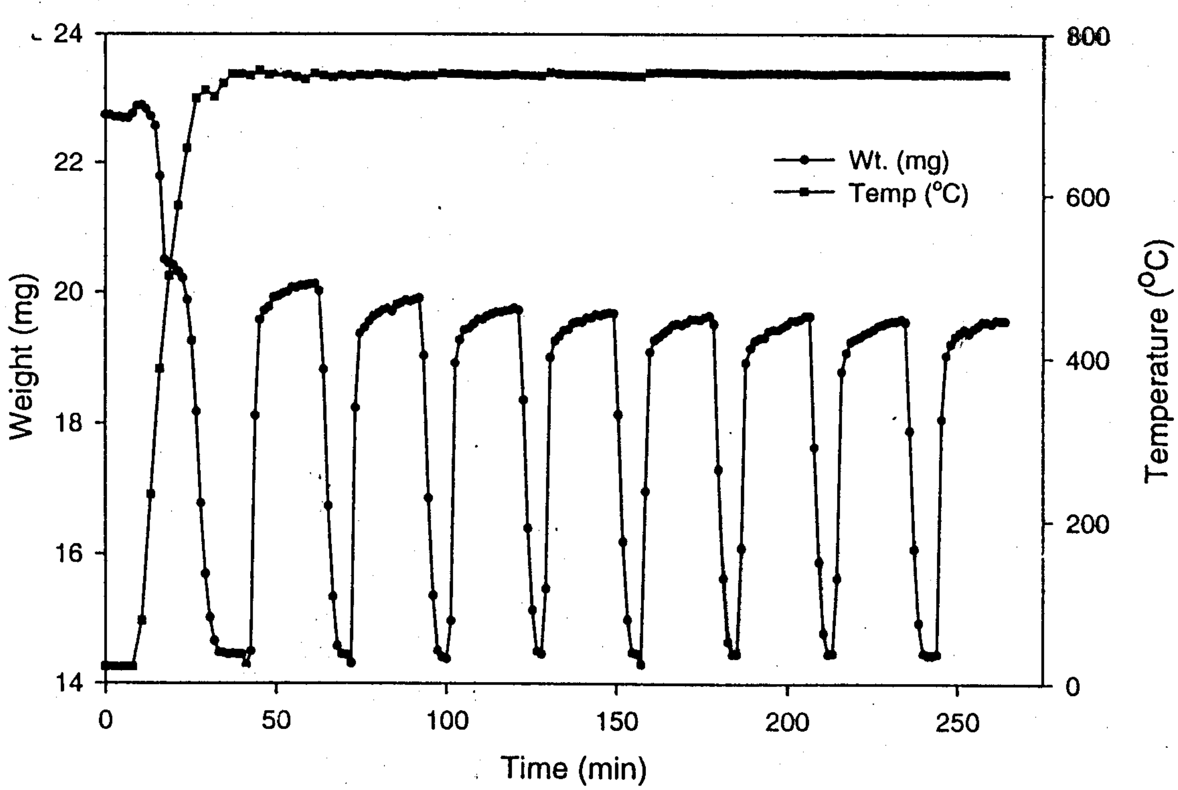
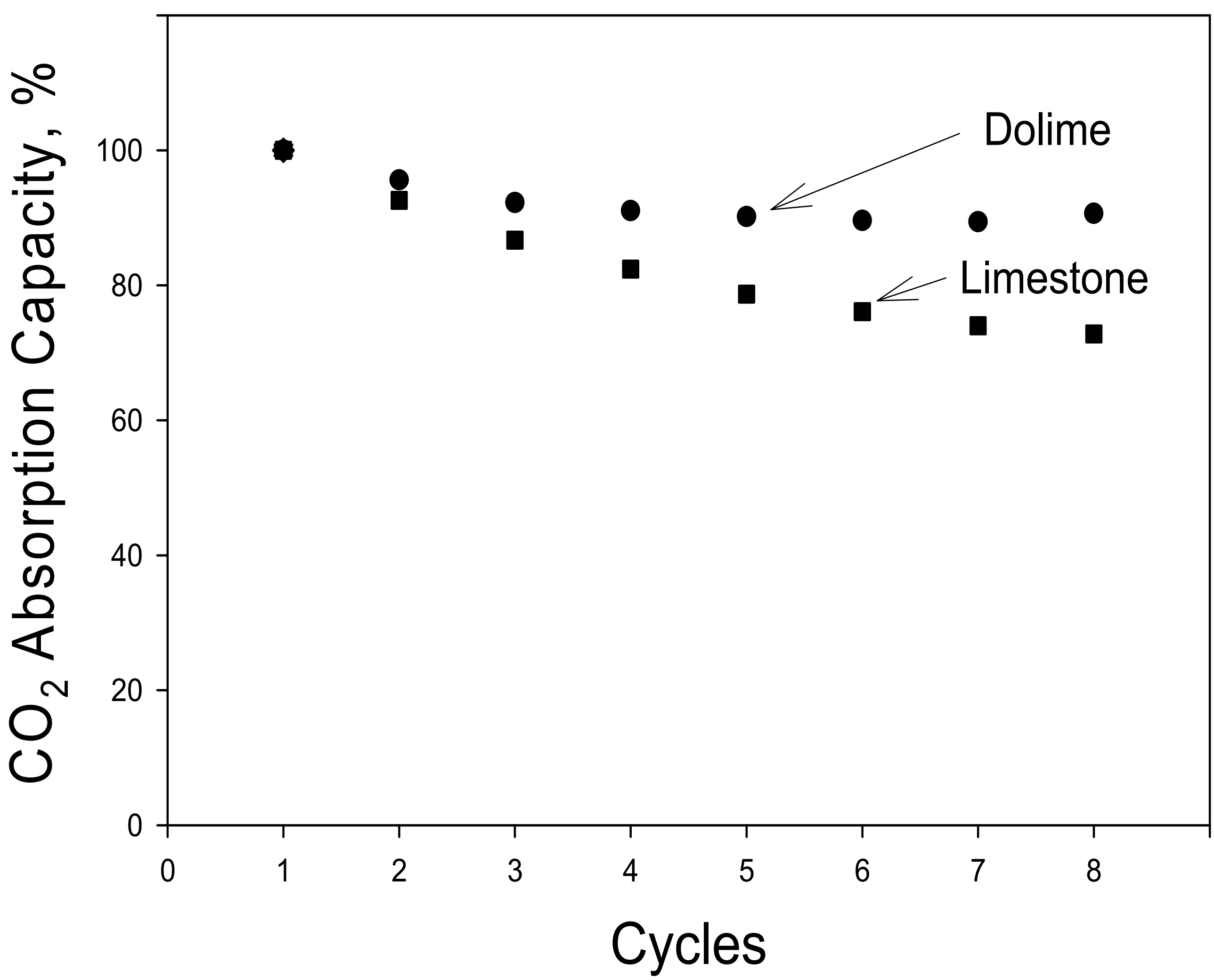


Figure 2. Results of a multicycle CO_2 absorption test with a dolime pellet.



The CO_2 absorption capacity of pellets prepared from different materials.

Cast Pellets Used for Studying Shell Material

Preparation Method

- Mix alumina and limestone powders with a dilute lignin solution to prepare a flowable slurry
- Fill cavities in a plastic mold with the slurry
  - Cavities are 6 mm in diameter and 6 mm deep
  - Mold rests on a plaster base to aid dewatering
- Allow to dry for 24 hr or more
- Remove pellets from mold and store or
- Calcine and impregnate with nickel

Characterization Methods

- Measure crushing strength
- Measure BET surface area
- Determine the specific volume of micropores

Procedure for Loading Nickel on Shell Material

1. Calcine pellets at 1100^oC for 2 hr to partially sinter shell material
2. Treat core-in-shell pellets with CO_2 at 700^oC to convert CaO back to $CaCO_3$
3. Soak pellets in $Ni(NO_3)_2$/THF solution
4. Dry pellets in open air to vaporize THF
5. Calcine pellets at 600^oC to convert $Ni(NO_3)_2$ to NiO
6. Reduce pellets with H_2 at 600^oC to convert NiO to Ni

Note: If pellets are stored following step 2, they will need to be dried in a vacuum oven before proceeding with step 3.

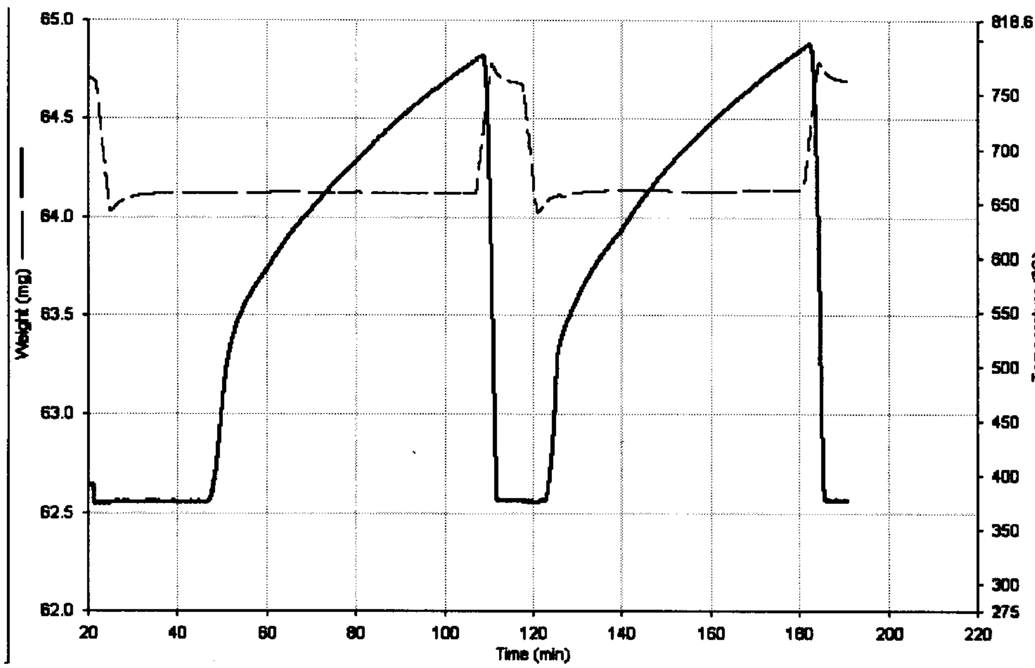
Properties of cast tablets of shell material

(Tablets also contained 32% A-16SG alumina and 20% limestone)

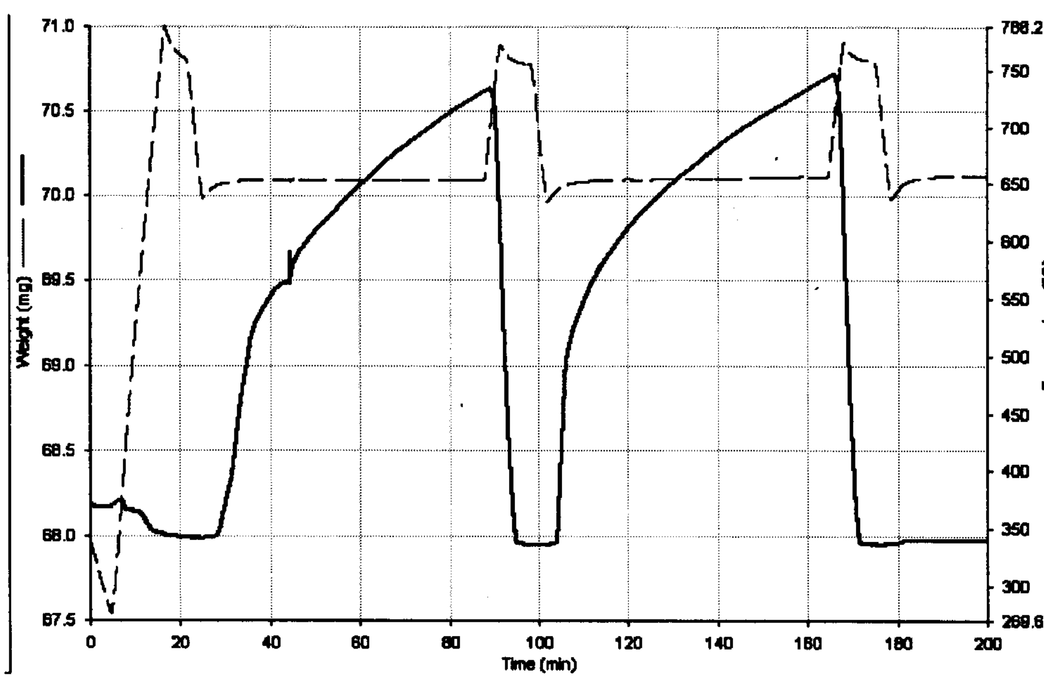
Shell Material	γ-Al_2O_3 CP-7, %	α-Al_2O_3 T-64, %	NiO %	Surf. Area, m^2/g	Pore Vol., cm^3/g	Strength, N
Standard	0	48	0	1.0	0.0018	409
(1) Ni impreg.			5.4	2.1	0.0065	
(2) Ni impreg.			11.4	2.3	0.0089	
CP-7 Mix #1	48	0	0	36.2	0.093	48
(1) Ni impreg.			7.8	13.0	0.048	
(2) Ni impreg.			14.0	12.4	0.039	
CP-7 Mix #2	24	24	0	5.3	0.015	98
(1) Ni impreg.			6.9	6.9	0.022	
(2) Ni impreg			12.0	7.8	0.027	
CP-7 Mix #3	36	12	0	23.9	0.067	32
(1) Ni impreg.			10.3	24.7	0.052	
(2) Ni impreg.			17.6			
CP-7 Mix #4	30	18	0	15.1		43
(1) Ni impreg.			7.5			
(2) Ni impreg.			13.2			
CP-7 Mix #5	18	30	0	7.4		95
(1) Ni impreg.			7.3			
(2) Ni impreg.			11.1			

Absorption of 5% CO_2 at 650°C by Core-in-Shell Pellets

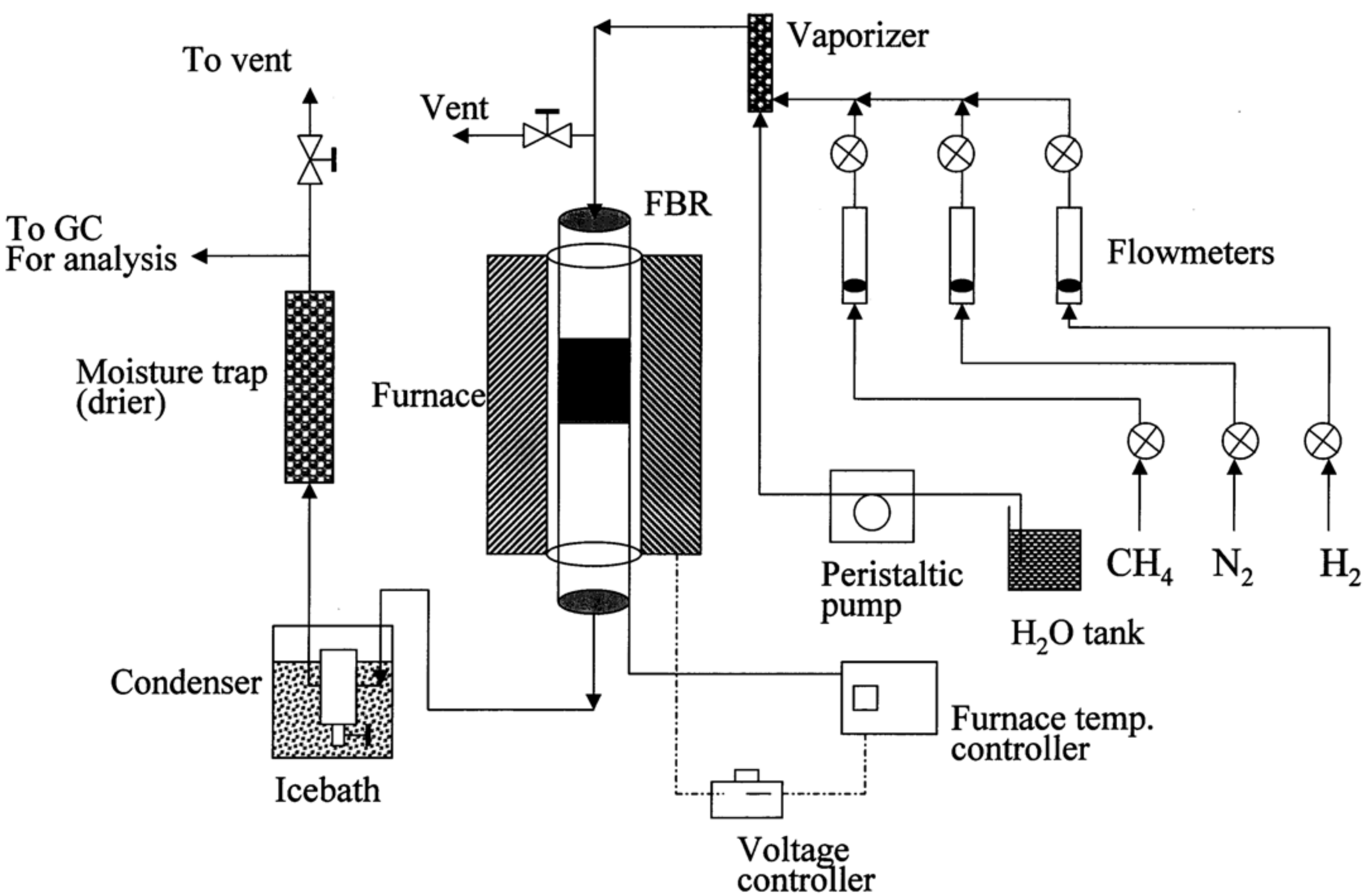
a). Core-in-Shell Pellet without Ni



b) Core-in-Shell Pellet Impregnated with Ni (4% NiO)



Fixed Bed Reactor System



Accomplishments

1. Determined the effects of temperature, $H_2O:CH_4$ ratio, and degree of CO_2 removal on the equilibrium conversion and product composition

2. Compared the relative stability of sorbents derived from limestone and dolime

3. Determined the effects of replacing α-alumina with γ-alumina in the shell material

4. Demonstrated an appropriate method for nickel impregnation

5. Showed that significant amounts of Ni can be supported by the shell material

6. Showed that the presence of Ni in the shell does not interfere with CO_2 absorption by the core.

Future Work

1. Complete assembling a fixed bed reactor for testing the combined catalyst/sorbent under appropriate reaction conditions

2. Conduct a series of performance tests with the fixed bed reactor to evaluate the combined catalyst/sorbent

3. Further characterize the catalyst/sorbent material by SEM, XRD, and AAS

4. Utilize the results to improve the material