**The MAGSORB Process for Bulk
Separation of Carbon Dioxide**

Final Report

**R.A. Knight
R.H. Carty
Institute of Gas Technology**

**R.G. Duthie
P.A. Pechtl
Bechtel Group, Inc.**

Work Performed Under Contract No.: DE-AC21-90MC26364

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880**

**By
Institute of Gas Technology
3424 S. State Street
Chicago, Illinois 60616**

April 1992

EXECUTIVE SUMMARY

The work performed during the reporting period from November 28, 1989 to February 28, 1992 on the research program, "The MAGSORB Process for Bulk Separation of Carbon Dioxide," is presented in this report. The research program, which was carried out by the Institute of Gas Technology (IGT), consists of the following eight tasks:

1. Test Plan Preparation
2. Facility Preparation and Equipment Modification
3. Preparation of Sorbent
4. Thermobalance Sorbent Tests
5. Cycle Tests of Sorbent in Packed-Bed Reactor
6. Analysis of Chemical and Physical Properties of Sorbent
7. Test Data Analysis and Interpretation
8. Systems Analysis and Technoeconomic Evaluation

The goal of this study was to investigate the removal of carbon dioxide from a synthesis gas which was produced by a coal gasifier. Potassium carbonate-modified magnesia (K_2CO_3 -modified MgO) was used in the process. The work consisted of measurements of capacity and rates of absorption as a function of temperature, pressure, and gaseous contaminants. In addition, the effects of repeated absorption and desorption cycling on the physical and chemical properties of the sorbent was studied.

Three techniques were used to prepare the MAGSORB pellets, as follows:

- Method 1. Basic magnesium carbonate (BMC) was slurried with KOH or K_2CO_3 , followed by extrusion into pellets, drying, and calcining at 900°F
- Method 2. BMC and KOH were slurried as in method 1, followed by regrinding, dry compressive pelletization, and calcination at 900°F
- Method 3. BMC and KOH were slurried as in method 1, followed by regrinding, blending with a pore structure control agent (ammonium bicarbonate), dry pelletization, and calcination.

Method 1 (which is described in the literature,^{1,2}) yielded MAGSORB pellets with the highest reactivity, but uneven distribution of potassium

resulted in Mg:K atomic ratios that varied widely among individual pellets. This introduced a large potential error into thermobalance test results.

Method 2 yielded denser MAGSORB pellets with acceptable Mg:K intradistribution, but sharply reduced reactivity. These pellets were approximately 2.4 times as dense as the Method 1 pellets, and had 73% lower pore volume.

Method 3 yielded pellets with good homogeneity and reactivity close to that of the Method 1 formulation. These pellets were 1.5 times as dense as Method 1 pellets and had 40% less total pore volume. MAGSORB pellets made by method 3 were used in most of the parametric thermobalance tests and all of the packed-bed cycle tests.

MAGSORB pellets were tested for reaction with CO_2 in a high-pressure, high-temperature thermobalance for temperature ranges from 650°F to 950°F and system pressures from atmospheric to 600 psig. Thermobalance and differential scanning calorimeter testing of Method 1 pellets showed that CO_2 absorption and desorption rates were negligible below a minimum temperature of about 750°F, but increased rapidly as temperature approached 800°F. Various temperature and pressure combinations for desorption of the CO_2 were studied. A sweep gas was required to enact complete desorption at 800°F and atmospheric pressure. It was found that desorption could occur without a sweep gas if reduction of CO_2 partial pressure was accompanied by a temperature increase. For example, CO_2 was desorbed by reducing CO_2 partial pressure from 139 to 46 psi while increasing temperature from 800° to 900°F.

A series of thermobalance tests was performed to show reproducibility in a standard gas mixture averaging 42 vol% CO_2 , 42 vol% He, and 16 vol% H_2O . These tests were conducted at 820° to 830°F and 300 psig system pressure, with a CO_2 partial pressure of 131 to 134 psi. These tests gave typical asymptotic weight gain curves with a mean CO_2 absorption of $70.1\% \pm 12.2\%$ of the stoichiometric limit after 30 minutes. The stoichiometric weight gain limit, based on the Mg, K, and CO_2 analyses of the MAGSORB, represented an absolute weight gain of 76.9%. The error limits given above are for 95% confidence.

Thermobalance tests under similar conditions as above, but containing syngas components (H_2 , CO, N_2), steam, H_2S , and NH_3 proved that these components did not react with the sorbent or reduce its reactivity. In fact,

the sorbent prepared by Method 3 showed higher CO₂ absorption rates and capacities in the presence of syngas, H₂S, or NH₃, with 30-minute weight gains ranging from 86.4% to 96.7% of the stoichiometric limit. Desorption was essentially complete in less than 12 minutes with standard gas with or without H₂S or NH₃, but took about 30 minutes in the syngas mixture.

A packed-bed reactor was constructed to conduct cycle testing of a selected MAGSORB formulation with a 50 vol% CO₂/He mixture. The conditions selected were 800°F and 300 psig for absorption, and 800°F and atmospheric pressure for desorption using pure N₂ as a sweep gas. The reactor consisted of a 6-inch-deep bed of sorbent inside a 1-inch-nominal 316SS tube, with external electric heating. The exit gas was continuously analyzed for CO₂ content. MAGSORB pellets that were made by Method 3 were tested for 3, 7, and 20 cycles of absorption and desorption. The reactor was pressurized from ambient pressure to 300 psig by reactant gas. A constant flow of reactant gas was maintained. Breakthrough was determined when the CO₂ concentration in the exit gas rose rapidly. Desorption was initiated at that point. Desorption was accomplished by reducing the pressure to atmospheric while flowing N₂ as a sweep gas until the CO₂ concentration dropped to less than 2.5%.

In the first cycle, the breakthrough time was approximately 25 minutes. Subsequent breakthrough times then decreased to 15-16 minutes, which included 13 minutes for repressurization. These results suggest some deactivation of the sorbent after one complete cycle, and are supported by physical test data showing decreases in porosity and surface area. During desorption, when the reactor temperature was increased from 750°-770°F to 800°-820°F, the exit gas CO₂ concentration dropped to zero, indicating that no further CO₂ desorption was occurring at those conditions, but subsequent breakthrough times still indicated deactivation. This deactivation does not appear to be the result of CO₂ retention. Pellet strength, measured by diametrical compression, declined by 9% after 3 cycles and by 38% after 7 cycles. No further strength decrease occurred after 20 cycles.

Bechtel National, Inc. completed a preliminary reactor design and technoeconomic analysis of the MAGSORB process for integration into a coal-to-methanol plant design. The gas conditioning system with MAGSORB was compared to a conventional system using Rectisol technology to remove CO₂ and H₂S from synthesis gas. Their initial findings indicated that the rate of the highly

exothermic CO₂ absorption by MgO may be heat-transfer limited, requiring design considerations to remove heat from the sorbent during the absorption cycle.

These findings were taken into account in designing a suitable MAGSORB reactor. In the process, fixed beds of the KOH-modified MgO/MgCO₃ sorbent are alternately cycled between absorption and desorption. During absorption, the MgO is exposed to the high-pressure CO₂-rich gas and must be cooled to remove the heat released during the production of the MgCO₃. During desorption, the saturated bed (MgCO₃) is reduced in pressure and heated to release the absorbed CO₂. The absorption/desorption beds are configured so that heat released during absorption is employed as heat input during regeneration. To transfer this heat, the beds are contained in thin parallel tubes arranged to facilitate heat transfer between absorbing and desorbing beds.

In the technoeconomic assessment, it was found that the use of the MAGSORB process for bulk separation of CO₂ offers three potential major advantages over conventional processes:

- A lower heat loss associated with gas cooling and reheating
- A conventional desulfurization process that is simplified and reduced in cost and energy consumption by prior CO₂ removal
- A potential for integration with advanced hot gas desulfurization

Two cases of coal-derived syngas desulfurization were compared. Each case was based on Texaco coal gasification at a scale equivalent to 11,000 bbl/day of methanol. Case 1 employed Rectisol low-temperature (refrigerated) methanol absorption/stripping for both CO₂ and H₂S removal. Case 2 used MAGSORB for CO₂ removal and Rectisol for removal of H₂S. In both cases, H₂S was removed in a concentrated stream for Claus plant sulfur production.

Case 1 was estimated to have a capital cost of \$156.2 million and an annual operating cost of \$17.2 million. Case 2 had an estimated capital cost of \$64.7 million and an annual operating cost of \$8.0 million, resulting in capital and operating cost savings, respectively, of \$91.5 million and \$9.1 million for Case 2 employing MAGSORB. These savings are calculated with a 20% additional cost allowance for MAGSORB because it is an unproven technology.

In conclusion, this study has shown that MAGSORB can selectively and reversibly absorb CO₂ from a synthesis gas, and does not react appreciably with other syngas components. However, more work is needed to optimize reactivity and physical properties, and develop improved durability over repeated cycling. The use of this technology has the potential to significantly reduce costs of methanol synthesis from a CO₂-rich synthesis gas, such as that generated by coal gasification, which is available at a moderate temperature of 800°F and pressure of 300 psig. Suggested research includes investigation of alternate sorbent preparation methods, including coprecipitation of marginally soluble Mg and K species. A better technoeconomic analysis would require additional heat transfer and engineering data.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
TECHNICAL DISCUSSION	3
Task 1. Test Plan Preparation	3
Objective	3
Summary	3
Task 2. Facility Preparation and Equipment Modification	3
Objective	3
Summary	3
Task 3. Preparation of Sorbent Material	5
Objective	5
Summary	5
Task 4. Thermobalance Sorbent Tests	14
Objective	14
Summary	14
Task 5. Cycle Tests of Sorbent in Packed-Bed Reactors	30
Objective	30
Summary	32
Task 6. Analysis of Chemical and Physical Properties of Sorbent	35
Objective	35
Summary	35
Task 7. Test Data Analysis and Interpretation	42
Task 8. Systems Analysis and Technoeconomic Evaluation	42
Objective	42
Summary	43
Technical Discussion	45
MAGSORB Reactor Modeling	59
CONCLUSIONS AND RECOMMENDATIONS	69
REFERENCES CITED	73
APPENDIX. REACTOR SIMULATION MODEL	A-1

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1	Equilibrium Curve for CO ₂ Absorption/Desorption on MgO	2
2	Schematic Diagram of High-Temperature Thermobalance	4
3	Simplified Diagram of Thermobalance Internals	4
4	Schematic Diagram of Packed-Bed Reactor System	6
5	Thermobalance Curves for Batch 1 at 650° to 800°F and 300 to 850 psig System Pressure	17
6	Thermobalance Curves for Batches 1 and 2 at 800°F and 150 psi CO ₂ Partial Pressure	17
7	Absorption/Desorption Curve for Batch 1 at 800°F Without Nitrogen Purge	18
8	Absorption/Desorption Curves for Batches 1, 2, and 3 at 800°F and 150 psi CO ₂ Partial Pressure	19
9	Absorption/Desorption Curve for Batch 1: Absorption at 800°F, Desorption at 950°F/300 psig	20
10	Absorption/Desorption Curve for Batch 1: Absorption at 800°F/300 psig, Desorption at 925°F/200 psig	20
11	Absorption/Desorption Curve for Batch 1: Absorption at 800°F/300 psig, Desorption at 900°F/100 psig	21
12	Absorption Curve for Batch 18 at 800°F/300 psig	22
13	Absorption Curve for Batch 19 at 800°F/300 psig	23
14	Absorption Curve for Batch 20 at 800°F/300 psig	23
15	Absorption Curves for Batch 21 at 800°F/300 psig	25
16	Thermobalance Curves for Batch 23 Tests With Standard gas	26
17	Thermobalance Curves for Batch 23 Tests With Standard Gas Containing H ₂ S	27
18	Thermobalance Curves for Batch 23 Tests With Simulated Synthesis Gas	28
19	Thermobalance Curves for Batch 23 Tests With Standard Gas Containing NH ₃	29

LIST OF FIGURES, continued

<u>Figure No.</u>		<u>Page</u>
20	Thermobalance Curve for Batch 23 Test With Dry Standard Gas	30
21	Thermobalance Curves for Batch 25 (Lower Mg:K Ratio) Tests With Standard Gas	31
22	Thermobalance Curves for Batch 26 (Higher Mg:K Ratio) Tests With Standard Gas	31
23	CO ₂ Absorption Exotherm for Batch 1	39
24	CO ₂ Absorption Exotherm for Batch 2	40
25	CO ₂ Absorption Exotherm For Batch 3	40
26	Conventional and MAGSORB Sour Gas Removal Flow Diagrams	47
27	Block Flow Diagram for the Removal of CO ₂ and Sulfur by a Conventional Process	49
28	Block Flow Diagram for the Removal of CO ₂ and Sulfur by the MAGSORB Process	49
29	Coal-Gasification-Based Syngas Production Using a Conventional Low-Temperature Methanol (LTM) Process for Syngas Preparation	50
30	Coal-Gasification-Based Syngas Production Using the MAGSORB CO ₂ Removal and Modified LTM Process for Syngas Preparation	51
31	MAGSORB Reactor Configuration and Tubular Array	57
32	MAGSORB Reactor Fin Design	58
33	Absorbent Temperature Distribution in Tube Pair With Reaction Rate Limited by Heat Transfer	61
34	Absorbent Temperature Distribution in Tube Pair With Reaction Rates Based on Thermobalance Data	63
35	Simulation Breakthrough Lines for 6-Minute Cycle	66
36	Simulation Breakthrough Lines for 20-Minute Cycle	66
37	Schematic Diagram of MAGSORB Process Unit	67
38	Simulation of Thermally Coupled MAGSORB Absorption/Desorption Cycle	71

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
1	Summary of MAGSORB Batch Preparation and Analyses	7
2	Summary of Thermobalance Tests	16
3	Summary of Conditions in Packed-Bed Cycle Tests	33
4	Chemical Analyses of MAGSORB Batches	38
5	Detailed Analyses of Selected MAGSORB Batches	39
6	Results of Differential Scanning Calorimeter Analyses	39
7	Sorbent Capacity Comparison on Weight and Volumetric Basis -- Weight Gain for 30 Minutes Absorption	41
8	Physical Properties of Sorbents From Cycle Tests	42
9	CO ₂ Absorption Rate Basis for Reactor Design	46
10	Capital and Utility Cost Comparison of Conventional and Modified LTM Processes (\$ Basis: Oct 89)	55
11	Preliminary Reactor Design	64

INTRODUCTION

Gasification of coal for synthesis gas production yields a mixture of CO, CO₂, H₂, H₂O, H₂S, and NH₃. The composition of the resulting gas is adjusted as required for various uses by removing or enhancing the concentration of the various components. For example, the use of the gas for methanol synthesis requires the enhancement of the H₂ content with respect to CO, removal of the bulk of the CO₂ and H₂O, and complete removal of the H₂S. This program dealt with the bulk separation of carbon dioxide using the novel MAGSORB process.

In the MAGSORB process, the CO₂ is removed from the raw fuel gas using MgO/K₂CO₃ sorbent at 650° to 1000°F and 300 to 850 psig. These temperatures and pressures match with pressurized coal gasification and high-temperature water-gas shift operations. The CO₂ removal is conducted in a swing-bed absorption/desorption cycle in which MgO absorbs the CO₂ and the MgCO₃-containing spent sorbent is regenerated either by decreasing the pressure or by elevating the temperature to convert the MgCO₃ to MgO and CO₂. The equilibrium curve for the reaction is shown in Figure 1.

The MAGSORB process has the potential to significantly reduce the capital and operating costs for converting raw fuel gas to synthesis gas. Specific objectives of this study were:

- Preparation of a CO₂ sorbent material composed of MgO modified with K₂CO₃
- Investigation of the CO₂ absorption and desorption rates of the MgO/K₂CO₃ sorbent as a function of the system temperature and pressure
- Determination of the effects of H₂S and NH₃ on the absorption characteristics of the MgO/K₂CO₃ sorbent
- Testing of the change in absorption and desorption characteristics of the sorbent after 3, 7, and 20 absorption/desorption cycles
- Examination of the chemical and physical changes in the sorbent as a function of absorption/desorption cycles
- A technoeconomic analysis and comparison of conventional CO₂ separation to CO₂ separation using MAGSORB.

Figure 1. EQUILIBRIUM CURVE FOR THE REACTION $\text{MgO} + \text{CO}_2 \rightleftharpoons \text{MgCO}_3$

TECHNICAL DISCUSSION

Task 1. Test Plan Preparation

Objective

The objective of this task was to prepare a test plan including a baseline experimental program, including chemical and physical analyses, and data and systems analyses to be acquired in the project, and to define the schedule for performing these tasks.

Summary

The Test Plan for the project, which detailed the experiments to be conducted, their rationale, the analyses to be performed, and the handling of the experimental results, was completed and submitted for approval during the first quarter of the program. The implementation of the Test Plan was begun in January, 1990.

Task 2. Facility Preparation and Equipment Modification

Objective

The objective of this task was to modify existing equipment and to fabricate new apparatus to be used in the experimental work. In addition, this task also included the operational shakedown of the apparatus to ensure minimal downtime during the tests. This task included operational checks of the thermobalance that was to be used in Task 4 and construction of a laboratory packed-bed reactor for the cycle tests that were performed in Task 5.

Summary

The experimental testing was performed in both a high-temperature thermobalance and a packed-bed reactor system.

The thermobalance was calibrated by measuring the weight loss versus time for a known decomposition of MgCO_3 . The system operated satisfactorily with the recorded weight loss indicated by the calibrated transducer output agreeing with that determined by sample weights within $\pm 2\%$. A schematic diagram of the thermobalance apparatus is shown in Figure 2. A simplified diagram of the reactor internals is shown in Figure 3. The thermobalance is

Figure 2. SCHEMATIC DIAGRAM OF HIGH-TEMPERATURE THERMOBALANCE

Figure 3. SIMPLIFIED DIAGRAM OF THERMOBALANCE INTERNALS

designed to operate at temperatures up to 1800°F. The operating pressure limits are 1000 psig at ambient pressure, 500 psig at 1700°F, and 200 psig at 1800°F. A detailed description of the operating procedure is provided with the discussion in Task 4.

The packed-bed reactor system was constructed in December 1991, shaken down in January 1992, and operated in February 1992. A schematic diagram of the packed-bed reactor as operated is shown in Figure 4. The reactor is fabricated from 1.00-inch-OD x 0.834-inch-ID seamless 316SS tubing. The sample is captured between glass wool plugs in the center of the heated zone, and the reactor volumes upstream and downstream of the sorbent bed are filled with non-reacting Kimax beads. An Optical Filter Corporation Model 702D infrared CO₂ analyzer is used to continuously monitor and record the CO₂ concentration in the treated gas stream. A detailed discussion of the operating procedure is in Task 5.

Task 3. Preparation of Sorbent Material

Objective

The purpose of this task was to prepare the primary reference sorbent to be tested. Compositional variants of this sorbent and a standard sorbent material consisting of unmodified MgO pellets were also prepared for comparisons. The sorbents that were used in the experimental tests included the following:

- A MgO standard
- A K₂CO₃-modified MgO reference sorbent with an approximate Mg:K molar ratio of 7:1
- A K₂CO₃-modified MgO sorbent with an approximate Mg:K molar ratio of 6:1
- A K₂CO₃-modified MgO sorbent with an approximate Mg:K molar ratio of 8:1

Summary

This task was pursued throughout the first eight quarters of the program. Table 1 summarizes the various preparation methods and Mg:K analyses for the 26 sorbent batches prepared during the program.

Figure 4. SCHEMATIC DIAGRAM OF PACKED-BED REACTOR SYSTEM

The original preparation procedure, based on previous IGT work, was as follows:

1. Basic magnesium carbonate (BMC), $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, was blended by hand with 50% aqueous KOH solution in relative quantities to yield an Mg:K atomic ratio of 7:1 (BMC is essentially insoluble)
2. Additional distilled water was added to obtain a smooth grout-like consistency
3. The slurry was extruded in 0.125-inch diameter strings and divided into cylindrical pellets of 0.125 inch length
4. The pellets were air-dried overnight and calcined at 500°C for 30 minutes to convert MgCO_3 to MgO

The first MAGSORB batch (Batch 1) was analyzed by x-ray diffraction and found to be composed of $\text{K}_2\text{CO}_3 \cdot 1/2\text{H}_2\text{O}$ and MgO . Elemental analysis of Batch 1 showed an Mg:K atomic ratio of 7.0, acceptably close to the calculated value based on weights of starting materials. Two more batches were then prepared

Table 1, part 1. SUMMARY OF MAGSORB BATCH PREPARATION AND ANALYSES

Batch	Comments	Mg/K Ratio			
		Calc	Meas	Meas/ Calc	% Rel Std Dev ^a
1	BMC mixed with conc KOH sol'n, hand-mixed, extruded, dried, calcined in air	7.0	7.0 ^b (8.4) ^c	1.0 ^b (1.2) ^c	NA ^b (17.5) ^c
2	Same as Batch 1	6.0	6.8	1.1	NA
3	Same as Batch 1	8.0	8.4	1.1	NA
4	Same as Batch 1	7.0	NA	NA	NA
5	Blank, same procedure as Batch 1, but no KOH	--	--	--	--
6	Same as Batch 1, but possible contamination	6.0	NA	NA	NA
7	KOH sol'n diluted with water prior to BMC addition	6.0	8.1	1.4	21.9
8	Same as Batch 7	7.0	8.8	1.3	21.8
9	Same as Batch 7	8.0	10.3	1.3	25.3
10	Used K ₂ CO ₃ instead of KOH, calcined in CO ₂ ; pellets were soft	6.0	8.5	1.4	18.9
10	Same batch calcined in air; pellets were firm	6.0	8.3	1.4	19.8
11	Used KOH, analyzed before calcining	6.0	7.3	1.2	36.4
11	Same batch calcined in CO ₂ ; pellets were soft	6.0	7.2	1.2	31.5
12	BMC ball-milled with K ₂ CO ₃ sol'n, analyzed before calcining	6.0	8.2	1.4	27.5
	Same batch after calcining	6.0	9.6	1.3	24.5

^a Based on analysis of 10 pellets or representative sub-samples

Table 1, part 2. SUMMARY OF MAGSORB BATCH PREPARATION AND ANALYSES

Batch	Comments	Mg/K Ratio			
		Calc	Meas	Meas/ Calc	% Rel Std Dev ^a
13	Added powder to KOH solution in homogenizer; before calcining	6.0	6.6	1.1	9.7
13	After calcining in air	6.0	9.5	1.6	27.7
14	Same mixing method as batch 13, but used more water in KOH solution for thinner slurry; before calcining	7.0	7.4	1.1	36.0
14	After calcining in tube furnace in 75% H ₂ /25% CO ₂	7.0	9.3	1.3	21.0
14	After calcining in air	7.0	9.7	1.4	27.0
15	Same mixing method as batches 13 and 14, after thickening paste in vacuum oven at 104°F	6.0	6.8	1.1	NA
15	Extruded paste	6.0	8.9	1.5	21.7
15	Pellets air-dried overnight; not calcined	6.0	5.7	0.95	27.9
16	Revised mixing order: slurried 4MgCO ₃ ·Mg(OH) ₂ ·5H ₂ O in water, then added KOH solution; unthickened paste	6.0	6.2	1.03	1.9
16	After thickening and extrusion	6.0	7.1	1.2	7.7
16	After overnight air-drying of pellets	6.0	7.8	1.3	32.6
16	After calcining in air	6.0	7.2	1.2	27.8
17	Same mixing method as batch 16, but used rapid drying of paste; uncalcined	6.0	7.9	1.3	17.8
17	After calcining in air	6.0	14.5	2.4	80.5

^a Based on analysis of 10 pellets or representative sub-samples

Table 1, part 3. SUMMARY OF MAGSORB BATCH PREPARATION AND ANALYSES

Batch	Comments	Mg/K Ratio			
		Calc	Meas	Meas/ Calc	% Rel Std Dev ^a
18	Batch 16D calcined pellets crushed, re-blended, and pelletized by compression	6.0	6.7	1.1	3.7
19	Batch 11A (uncalcined) pellets crushed, re-blended, and pelletized by compression, then calcined in air	6.0	6.6	1.1	5.7
20	Paste made from Batch 14-15 method, slurry air-dried, ground to powder, and mixed; powder rewetted with water and paste extruded into pellets	6.0	9.1	1.5	24.7
21	Batch 1 pellets crushed, NH_4HCO_3 added (50 wt%), pelletized, cured at 60°C, calcined in air	6.0	8.0	1.3	1.1
22	Blank (no K) made with 50 wt% NH_4HCO_3	NA	NA	NA	NA
23	Batches 10-12 crushed, NH_4HCO_3 added (50 wt%), processed as Batch 21	6.0	6.8	1.1	2.7
24	Batches 10-12 crushed, NH_4HCO_3 added (45 wt%), processed as Batch 21; used for packed-bed tests	6.0	7.3	1.2	NA
25	Lower Mg:K ratio made from BMC and KOH, dried, crushed, repelletized with 45% NH_4HCO_3 added	5.3	5.7	1.1	NA
26	Lower Mg:K ratio made from BMC and KOH, dried, crushed, repelletized with 45% NH_4HCO_3 added	7.1	7.5	1.1	NA

^a Based on analysis of 10 pellets or representative sub-samples

with lower and higher K content. With Batches 2 and 3, however, the analyzed Mg:K ratios were higher than expected based on calculations. The measured Mg:K ratio in Batch 2 was 6.8, versus a calculated value of 6.0, and the measured Mg:K ratio in Batch 3 was 8.38, versus a calculated value of 8.0. X-ray diffraction, density, and porosity measurements were also made on Batches 1, 2, and 3. Details are provided under Subtask 6.

Upon observation of the discrepancies between calculated and measured Mg:K ratios, steps were taken to improve mixing of components. The water required to achieve an extrudable slurry consistency was added to the KOH solution prior to blending with the BMC powder. This was done to ensure a uniform distribution of potassium throughout the slurry, which was then allowed to equilibrate for one hour before extrusion. Batch 4 was prepared with this method.

An MgO standard without potassium (Batch 5) was also prepared at this time to serve as a control.

Batch 6 was made by the same method as Batch 4, but was not tested because of possible contamination. Sorbent batches 7, 8, and 9 with intended Mg:K atomic ratios of 6:1, 7:1, and 8:1, respectively, were prepared using the revised preparation method, but with the appropriate changes in relative amounts of BMC and KOH. Ten pellets of each of these sorbents were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPAES) to determine variations in the Mg:K ratio. These analyses showed Mg:K ratios of 8.1, 8.8, and 10.3, which were 26% to 35% higher than expected. In addition, the relative standard deviation of M:/K ratio for 10 pellets in each batch were quite large, ranging from 22% to 25%.

One explanation for these variations was the possibility of volatilization of K species during pellet calcination. Data from fuel cell studies have shown that volatile K species were formed in the presence of water vapor at elevated temperatures, possibly according the reactions:

To reduce these side reactions, sorbent Batch 10 was formulated using aqueous K_2CO_3 instead of KOH as a potassium source. The solution was made

with CO₂-saturated water and calcined under CO₂ atmosphere to favor the stable K₂CO₃ form during drying and calcination. A portion of the batch 10 pellets were also calcined in the previous manner, in a muffle furnace under air. The results of analyses of both of these batches showed no improvement in the variability of the Mg:K ratio among pellets. It was also noted that the pellets calcined under CO₂ were quite soft compared to pellets calcined in air.

Batch 11 was prepared using KOH solution and calcining under a CO₂ atmosphere. The pellets were analyzed before and after calcining. Both analyses still showed a large standard deviation in the Mg:K ratio. These results indicated that the principal cause for the nonhomogeneity must have been in the method for dispersing BMC in the KOH solution, not in the conversion of K to volatile forms during calcining.

At that point, efforts were concentrated on mixing techniques. Batch 12 was prepared by mixing KOH solution and BMC, then ball milling the mixture to ensure crushing of agglomerates and distribute the solid evenly. Again, there was no improvement in pellet-to-pellet homogeneity before or after calcining. Batch 13 was prepared using a laboratory homogenizer for high-shear mixing while slowly adding the BMC to the KOH solution. The dried pellets displayed a standard deviation of 9.7% in Mg:K ratio, which is within the experimental error limits of the analytical procedure, indicating that this method resulted in a sorbent slurry with more uniformly dispersed potassium. However, when the pellets were calcined, analysis of 10 pellets gave an average Mg:K atomic ratio of 9.5 with a relative standard deviation of 27.7%, again calling into question the role of potassium loss during calcination. Batch 14 was also made with the homogenizer, but more water was used in mixing. Half of the pellets were calcined under an atmosphere of 75% H₂/25% CO₂ to minimize potassium volatilization reactions, and the remainder were calcined in air. Again, the calcined sorbent appeared to show reduced potassium levels, but the variability among pellets was too great to support any firm conclusion of the role of calcination in effecting possible potassium loss. For Batch 15, variations in homogenizer operation were tested, and the sorbent was analyzed for Mg:K ratio at each step in the process. The uncertainty in true Mg:K ratio was again very large. For batch 16, the mixing procedure was altered, with BMC first slurried in water followed by the addition of concentrated KOH

solution. This was done to avoid possible uneven absorption of KOH by the dry powder before attaining adequate dispersion in the liquid phase. Analyses at each process step showed that both the increase in Mg:K atomic ratio and the increase in pellet-to-pellet homogeneity began in the paste vacuum-drying step and accelerated through the air-drying and calcination steps. This suggested that maldistribution of potassium in the solid could be occurring from uneven localized crystallization of KOH from solution during the drying phase. The next variation in preparation procedure was an attempt to inhibit high-KOH-concentration crystal growth domains by rapid drying of the paste. Batch 17 was therefore prepared in a similar manner as Batch 16, except that the initial slurry was dried to an extrudable paste rapidly, in air at 212°F, instead of slowly in a vacuum oven at 140°F. Analyses of uncalcined and calcined material showed no improvement in homogeneity, in fact showing an even larger inconsistency among pellets in the calcined material (relative standard deviation = 80.5%).

At that point, a determination was made to abandon attempts to make the sorbent directly from slurry extrusion, but rather to prepare pellets by crushing, remixing, and repelletizing previously calcined batches, in order to ensure a uniform MAGSORB material to continue thermobalance testing. A mechanical pelletizing device was used to reconstitute calcined material from batch 16, which had an average Mg/K ratio of 7.2. Approximately 25 g of reconstituted material was made in this way, and designated batch 18. A 10-pellet sample of Batch 18 was found to be acceptably uniform. The Mg:K atomic ratio was 6.68, and the relative standard deviation was 3.7%. This degree of variation is well within the error limits of the analytical technique. The CO₂ content of the batch was 11.1%, which, after accounting for K₂CO₃, indicated that about 8% of the magnesium was present as MgCO₃. Thermobalance tests, however, indicated lower reactivity than previous batches made by slurry extrusion. These results are discussed in more detail under Task 4.

To prepare Batch 19, uncalcined pellets from Batch 11 were crushed, homogenized, and pelletized in the pellet press. These pellets were then calcined in an oven at 900°F. It was felt that this procedure would result in a more open pore structure than the technique used for batch 18, in which pellets were made from previously calcined material. Batch 19 analyses showed

an average Mg:K atomic ratio of 6.64 with a relative standard deviation of 5.7%. This confirmed acceptable uniformity of composition for the batch. When thermobalance tests again showed low reactivity toward CO₂, Batch 20 was prepared from reagents by the original slurring technique, and the paste was air-dried. The dry cake was then ground, and the fine powder mixed to increase uniformity. However, instead of pelletizing the dried powder in a pellet press, the fine powder was rewetted and the paste extruded into pellets similar to the technique used for the original pellets. This method of preparation did not increase the reactivity, and the composition of the 10-pellet sample showed an average Mg:K ratio of 9.1 with a relative standard deviation of 24.7%, again confirming that the nonhomogeneity resulted from slurring the sorbent.

To restore reactivity without sacrificing homogeneity, a modified procedure was used to make pellets with increased pore surface area. Batch 21 was prepared using the following procedure:

- Pellets from Batch 1 were crushed by hand to -100 mesh
- The batch 1 powder was blended with 50 wt% of -100-mesh ammonium bicarbonate (NH₄HCO₃) in a glove box under nitrogen (to prevent absorption of atmospheric moisture); NH₄HCO₃ is a pore structure control agent
- The MAGSORB-ammonium bicarbonate mixture was re-pelletized using a pellet press
- The pellets were heated slowly under partial vacuum at 140°F to decompose NH₄HCO₃, increasing the void volume of the pellets
- The pellets were calcined at 900°F for 30 minutes to convert MgCO₃ to MgO.

Analyses of Batch 21 showed that the pellets were acceptably uniform, with an average Mg:K ratio of 8.0 and a relative standard deviation of 1.1%. Because the Mg:K ratio was so high, pellets from Batch 1 were reanalyzed prior to testing both Batch 21 and Batch 1 in the thermobalance. The measured Mg:K ratio of Batch 1 was found to be 8.4, with a relative standard deviation of 17.5%. Also, it was found that the measured CO₂ content of Batch 1 in the latest analysis was 39.4%, compared to 8.9% CO₂ in a March 1990 analysis, indicating significant pickup of atmospheric carbon dioxide during storage.

The significance of these observations are discussed in conjunction with thermobalance tests in Task 4.

Based on the results of analyses and thermobalance tests, it was decided to use the Batch 21 preparation procedure to prepare sorbent pellets for the remainder of the thermobalance and packed-bed tests. Batch 22 was an MgO blank that included the use of NH_4HCO_3 in the pellet preparation. This batch was prepared to determine whether NH_4HCO_3 alone could increase the CO_2 chemisorption rate in the absence of the potassium additive. Batch 23 was a large batch of NH_4HCO_3 -modified MAGSORB pellets made from ground and repelletized material from combined batches 10, 11 and 12.

Detailed analyses of Batch 23 and other selected MAGSORB batches are also given later in the discussion of Task 6, Analysis of Chemical and Physical Properties of Sorbent.

Task 4. Thermobalance Sorbent Tests

Objective

The objectives of this task were to determine the practicable ranges of operating temperature and pressure for absorption and desorption of CO_2 by MAGSORB sorbent, to investigate the effects of various syngas components on sorbent performance, and to investigate the effects of variation in K_2CO_3 content of the sorbent. All of the tests in this task were conducted in a high-pressure thermobalance containing the sorbent in a fixed bed exposed to excess flowing gas.

Summary

In a thermobalance test, the sample pellets were contained in a stainless-steel wire mesh basket suspended in the upper portion of the reactor which is purged and cooled by a downflow of inert gas as shown in Figure 3. The desired temperature and pressure conditions were established in the lower, heated portion of the reactor in the presence of flowing reactant gases. The test was initiated by lowering the basket into the heated reaction zone. This procedure took 5 to 6 seconds. The sample was kept in the heated portion of the reactor for a predetermined time while its weight was continuously monitored and recorded by means of a load transducer from which the sample was

suspended. Mass calibrations were made at regular intervals to verify the validity of mass change measurements. The test was terminated either by raising the basket back to the upper, cooled portion of the reactor, or, in the case of absorption/desorption experiments, by changing the operating conditions.

During the course of the program, a total of 52 thermobalance experiments were performed, 10 of which were essentially shakedown experiments and 39 of which are considered successful data-producing experiments. Absorption cycles took at least 32 minutes, with longer cycles being used for samples of low reactivity. Desorption cycles were run until the weight loss appeared to be complete. Table 2 lists conditions used in the 39 successful experiments that were performed, and the experiments are discussed individually or in groups below.

Absorption Screening Tests: Thermobalance tests were first conducted on MAGSORB Batch 1 to determine the conditions required for absorption of the CO_2 . Figure 5 shows the results of Tests 01-11 through 01-17B, which were conducted at various temperatures and pressures. The plots show the weight gain with time, where weight is given as percent of the stoichiometric maximum calculated from the sorbent composition. It is apparent that the reaction rate increases dramatically between 650° and 750°F, regardless of the CO_2 partial pressure. Also, it is interesting to note that the rate decreases slightly as system pressure is increased from 600 to 850 psig, which may indicate diffusional effects on mass transfer.

The CO_2 absorption of Batch 2 was tested in thermobalance test 01-18 at 800°F and 300 psig. Figure 6 compares the weight-vs-time plots for Batches 1 and 2 at these conditions in Tests 01-12 and 01-18. The results of these tests indicate that absorption rates were similar. At that time, the interparticle Mg:K distribution problem had not yet been detected.

Desorption Screening Tests: The next series of tests was made to determine conditions required for CO_2 desorption. In the first attempt at a desorption without inert gas sweep (Test 01-23A), which is shown in Figure 7, the total system pressure was lowered in stages to reduce the CO_2 partial pressure below the equilibrium value. There was no desorption of CO_2 even at

Table 2. SUMMARY OF THERMOBALANCE TESTS

Test	Sorbent Batch	Temp, °F	Pres, psig	Gas Comp ^a	Mode
01-11	1	650	300	Std	Abs
01-12	1	800	300	Std	Abs
01-13	1	650	600	Std	Abs
01-14	1	800	600	Std	Abs
01-16A	1	800	850	Std	Abs
01-17B	1	750	300	Std	Abs
01-18B	2	800	300	Std	Abs
01-21	2	800, 800	300, 0	Std, N ₂	Abs/Des
01-22	3	800, 800	300, 0	Std, N ₂	Abs/Des
01-23A	1	800, 800	300, step ^b	Std, Std	Abs/Des
01-23B	1	800, 800	300, 0	Std, Std	Abs/Des
01-24	1	800, 950	300, 300	Std, Std	Abs/Des
01-25	1	800, 925	300, 200	Std, Std	Abs/Des
01-26	1	800, 900	300, 100	Std, Std	Abs/Des
02-14	18	800	300	Std	Abs
02-15	18	800	300	Std	Abs
02-17	18	800	300	Std	Abs
02-18	19	800	300	Std	Abs
02-19	20	800	300	Std	Abs
02-20	1	800	300	Std	Abs
02-21	21	800	300	Std	Abs
02-22	21	800	300	Std	Abs
02-23	21	800	300	Std	Abs
02-24	22	830	300	Std	Abs
02-25	23	830	300	Std	Abs
02-26	23	830	300	Std	Abs
02-27	23	830, 830	300, 0	Std, N ₂	Abs/Des
02-28	23	830, 830	300, 0	Std+H ₂ S, N ₂	Abs/Des
02-29	23	830	300	Std+H ₂ S	Abs
02-30	23	820	300	Syngas	Abs
02-31	23	820, 820	300, 0	Syngas, N ₂	Abs/Des
02-32	23	830	300	Dry std	Abs
02-34	23	820	300	Std+NH ₃	Abs
02-35	23	820, 820	300, 0	Std+NH ₃ , N ₂	Abs/Des
02-36	23	830, 830	300, 0	Std+NH ₃ , N ₂	Abs/Des
03-02	26	820	300	Std	Abs
03-04	26	820	300	Std	Abs/Des
03-05	25	820	300	Std	Abs
03-06	25	820	300	Std	Abs/Des

Notes:

^a "Std" = standard gas: 41.5% CO₂, 41.5% He, 17% H₂O; "Syngas" = 11.03% H₂, 25.8% CO, 42.4% CO₂, 4.0% N₂, 17% H₂O; "Dry std" = 50% CO₂, 50% He.

^b Stepwise system pressure decrease: 200 psig, 100 psig, 50 psig, 0 psig

Figure 5. THERMOBALANCE CURVES FOR BATCH 1 AT 650° TO 800°F AND 300 TO 850 PSIG SYSTEM PRESSURE

Figure 6. THERMOBALANCE CURVES FOR BATCHES 1 AND 2 AT 800°F AND 150 PSI CO₂ PRESSURE

Figure 7. ABSORPTION/DESORPTION CURVE FOR BATCH 1 AT 800°F
WITHOUT NITROGEN PURGE

ambient system pressure, which gave a CO₂ partial pressure of approximately 7.5 psi.

The desorption procedure was then changed to introduce a purge gas. In tests 01-21, 01-22, and 01-23B, complete absorption/desorption cycles were performed by depressurizing to atmospheric pressure and switching from CO₂/He/steam to N₂. The thermobalance curves for these tests with batches 1, 2, and 3 are shown in Figure 8. All of the absorptions in the tests were conducted at a total system pressure of 300 psig and a temperature of 800°F, and desorption was virtually complete in every test. The absorption rates indicated by the initial slopes of the absorption curves, varied significantly between the three samples, but the later discovery of pellet-to-pellet variations in Mg:K ratio suggested that no firm conclusions could be drawn regarding these differences, since the chemical compositions of the actual pellets used in the tests may not have been representative of each batch as a whole.

Figure 8. ABSORPTION/DESORPTION CURVES FOR BATCHES 1, 2, AND 3
AT 800°F AND 150 PSI CO₂ PRESSURE

Temperature Swing Tests: The next series of tests was conducted to investigate combined pressure and temperature swing for desorption. In Test 01-24, shown in Figure 9, the system pressure was maintained at 300 psig, resulting in a CO₂ partial pressure of approximately 151 psi for both the absorption and desorption. At the end of the absorption period, the temperature was raised until weight loss began, at approximately 950°F, and desorption was carried to completion at that temperature. In Test 01-25, shown in Figure 10, the system pressure for the desorption was lowered to 200 psig resulting in a CO₂ partial pressure of approximately 105 psi. The temperature was then raised until desorption of CO₂ began at approximately 925°F. In Test 01-26, shown in Figure 11, the system pressure for the desorption was lowered to 100 psig resulting in a CO₂ partial pressure of approximately 46 psia. At that pressure, desorption of the CO₂ began at a temperature of approximately 900°F.

At the time these test data were first analyzed, the discovery of Mg:K atomic ratio variation among pellets was discovered, and further thermobalance testing was halted until a satisfactory sorbent formulation procedure could be developed. When Batch 18 was prepared and found to be acceptably uniform,

**Figure 9. ABSORPTION/DESORPTION CURVE FOR BATCH 1:
ABSORPTION AT 800°F, DESORPTION AT 950°F**

**Figure 10. ABSORPTION/DESORPTION CURVE FOR BATCH 1:
ABSORPTION AT 800°F/300 PSIG, DESORPTION AT 925°F/200 PSIG**

Figure 11. ABSORPTION/DESORPTION CURVE FOR BATCH 1:
ABSORPTION AT 800°F/300 PSIG, DESORPTION AT 900°F/100 PSIG

thermobalance testing was resumed.

Screening Tests with Reformulated Sorbents: Tests 02-14, 02-15, and 02-17 were conducted with Batch 18 at 800°F and 300 psig in the standard gas mixture (41.5% CO₂/41.5% He/17% steam). The resulting weight gain-vs-time plots are shown in Figure 12. Test 02-14 resulted in a 42% weight gain over 32.3 minutes, representing 58% of the limiting stoichiometric weight gain. Test 02-15 was similar to Test 02-14, but was extended to 60 minutes, and showed a weight gain of 48% absolute, or 66% of the theoretical limit. The rate of weight gain in both of these tests was low compared with previous tests using MAGSORB prepared from extruded slurry batches. In order to determine whether this may have been due to decreased surface porosity caused by compressive pelletization, Test 02-17 was made with batch 18 pellets broken into pieces approximately the size of earlier pellets to increase surface area and expose fresh surface. However, the results of Test 02-17 actually showed further decreased reactivity, with a weight gain of only about 24% in 30 minutes. It was later concluded that exposure to atmospheric moisture and/or CO₂ was probably responsible for this deterioration of reactivity with time. This phenomenon is discussed later in the report.

Figure 12. ABSORPTION CURVE FOR BATCH 18 AT 800°F/300 PSIG

One thermobalance adsorption test (Test 02-18) was conducted with Batch 19, which resulted in the weight gain-vs-time curve shown in Figure 13 at test conditions of 800°F and 300 psig. The results indicate that the low reactivity which was previously observed for Batch 18 is also characteristic of Batch 19. It appears that the crushing and re-pelletizing method, while preserving the uniform composition of the pellets, reduces the reactivity of the MAGSORB on a weight basis. The compression of the material may be collapsing the pore structure and inhibiting the access of reactants to the inside of the pellet.

Another thermobalance test (Test 02-19) was conducted with Batch 20, which had been prepared by paste formation, drying, crushing, rewetting with water, and extrusion. As shown in Figure 14, the results indicate a reactivity similar to that previously observed for Batch 18, higher than that of Batch 19 but lower than that of early batches made with the original slurry extrusion technique.

Because of what appeared at the time to be poor reproducibility between replicate tests made with the same batch, a series of operational tests were performed on the thermobalance. The results of these tests indicated

Figure 13. ABSORPTION CURVE FOR BATCH 19 AT 800°F/300 PSIG

Figure 14. ABSORPTION CURVE FOR BATCH 20 AT 800°F/300 PSIG

satisfactory operation of the thermobalance. Test 02-20 was conducted to further confirm correct operation of the equipment. In Test 02-20, a previous MAGSORB batch (batch 1) which had shown high reactivity for CO₂ absorption in earlier tests was reanalyzed and retested in the thermobalance. Test 02-20 was conducted with standard gas at 800°F and 300 psig. The results were similar to those observed in an earlier test with Batch 1 (Test 01-20). The absorption rates were comparable, and the maximum absorption was also similar, with 75% of stoichiometric CO₂ absorption in the recent test, compared with 81% in the earlier test. As noted earlier, the Batch 1 pellets appear to have absorbed a substantial amount of atmospheric CO₂ during storage, but their reactivity was not affected.

By this time, the sorbent preparation technique using the pore structure control agent NH₄HCO₃ had been devised, and Batch 21 was prepared by that method. Three thermobalance tests (Test 02-21, 02-22, and 02-23) were performed to assess reactivity of Batch 21 at 800°F and 300 psig with 50 vol% CO₂. The results are shown in Figure 15, which plots the results of Tests 02-21, 02-22, and 02-23 along with previous tests using dry pelletization only (Test 02-17, batch 18) and using the slurry extrusion technique (Test 02-20, batch 1). The relative standard deviations in Mg/K ratio for ten-pellet samples are also given, showing clearly that the dry pelletization technique gives much more homogeneous material than the extruded slurry, while the addition of the pore structure control agent, NH₄HCO₃, increases reactivity significantly compared to dry pelletization alone. However, declining reactivity was observed with each consecutive test with Batch 21, as shown by the comparison of Tests 02-21, 02-22, and 02-23. A chemical analysis of the sorbent from Test 02-23 after CO₂ absorption showed a CO₂ content of 31.9 wt%, which was almost identical with the thermobalance data which showed a weight gain corresponding to 31.5 wt% CO₂.

These results suggested that some sort of aging effect was taking place, and precautions were taken to isolate sorbent samples in a desiccator under vacuum to eliminate absorption of atmospheric moisture and CO₂.

Following preparation of batches 22 and 23, 12 thermobalance tests were conducted. One test was performed with the Batch 22 MgO blank and 11 tests with Batch 23. Each absorption cycle was run for 32 minutes, and desorption cycles were run until the weight loss appeared to be complete. Absorption

Figure 15. ABSORPTION CURVES FOR BATCH 21 AT 800°F/300 PSIG

cycles were performed at 820° to 830°F and 300 psig total system pressure, and desorption was conducted by switching to 100% N₂ at atmospheric pressure. The descriptions of the test results with each gas mixture are discussed individually below.

Performance Tests -- Standard Gas: The standard gas mixture used in thermobalance tests is provided by a 1:1 mol ratio mixture of CO₂ and He, with steam added to approximate the steam content of a typical coal gasifier. The resulting test gas has the following composition: 41.5% CO₂, 41.5% He, 17% H₂O. At 300 psig test pressure, the CO₂ partial pressure is 131 psi.

One test (02-24) was performed with the standard gas mixture and Batch 22, an MgO blank prepared with NH₄HCO₃. No detectable weight gain was recorded after 32 minutes at 800°F and 300 psig. This verifies the importance of the potassium additive in promoting CO₂ absorption.

Three tests (02-25, 02-26, and 02-27) were conducted with the standard gas mixture and Batch 23 sorbent, resulting in the weight gain/loss curves displayed in Figure 16. Two of the tests were absorption only, and one was absorption/desorption. The CO₂ absorption at 30 minutes residence time,

Figure 16. THERMOBALANCE CURVES FOR BATCH 23 TESTS WITH STANDARD GAS

expressed as percent of stoichiometric, ranged from 61.5% to 76.1%, with a mean of 70.1% and a standard deviation of 6.2%. In the desorption cycle of Test 02-27, the sorbent desorbed very rapidly. Because of an electrical problem with the chart recorder, the initial desorption signal was interrupted, so a portion of the desorption curve in Figure 16 is interpolated. However, the remaining data show that desorption was essentially complete in 10 minutes or less. The indicated weight loss curve excursion below baseline may be attributed to CO_2 and H_2O desorption beyond the content of the original sample, but is also within the precision limits of the instrumentation.

Performance Tests -- Standard Gas with H_2S : Two tests (02-28, 02-29) were conducted with the standard gas containing 0.9 vol% H_2S , to determine if any reaction takes place between MAGSORB and H_2S or whether H_2S has any effect on the CO_2 absorption/desorption rates. One of the two tests also included the desorption cycle. Figure 17 shows the thermobalance curves for these tests. The mean CO_2 absorption at 30 minutes was 86.4%, with a standard deviation of 1.1%. These data indicated that H_2S did not inhibit the

Figure 17. THERMOBALANCE CURVES FOR BATCH 23 TESTS WITH STANDARD GAS CONTAINING H_2S

CO_2 absorption rates at these conditions, but in fact appeared to significantly enhance it. Analyses of the sorbents recovered from the tests showed no detectable sulfur, confirming the absence of a chemical reaction between H_2S and MAGSORB. Analyses also showed Mg:K ratios of 6.47 for Test 02-28 sorbent and 6.55 for Test 02-29 sorbent, indicating no significant changes in these ratios. The CO_2 content of the recovered sorbent from Test 02-29 was 40.4 wt%, corresponding to 87.3% of the stoichiometric limiting weight gain and adequately confirming the thermobalance data.

In the desorption cycle of Test 02-28, desorption was complete in about 10 minutes. As observed with the standard gas, the desorption weight loss curve falls slightly below baseline, but the discrepancy is within the precision limits of the instrumentation.

Performance Tests -- Synthesis Gas: Two tests, one absorption (02-30) and one absorption/desorption (02-31), were conducted with a simulated syngas mixture based on a Texaco coal gasifier. The syngas composition was 11.0% H_2 , 25.8% CO , 42.4% CO_2 , 4.0% N_2 , and 17% H_2O . Figure 18 shows the

Figure 18. THERMOBALANCE CURVES FOR BATCH 23 TESTS WITH SIMULATED SYNTHESIS GAS

results of these thermobalance tests, giving an average CO_2 absorption of 96.7% of stoichiometric limit at 30 minutes, with a standard deviation of 5.0%. As with the standard gas plus H_2S , there was a significant increase in the CO_2 absorption rate from the syngas compared to the standard gas. These results were confirmed by analyzing the reacted sorbent from Test 02-30, which indicated a CO_2 content of 45.3 wt%, corresponding to a weight gain of 95.5% of the stoichiometric limit. The desorption data show that the desorption rate is slowed somewhat in synthesis gas compared to the standard gas, taking about 30 minutes for essentially complete CO_2 desorption (within 5% of baseline).

Performance Tests -- Standard Gas With NH_3 : Three tests (02-34, 02-35, and 02-36) were performed with the standard gas plus 0.2 vol% NH_3 added by including ammonia in the water which is used to produce the steam. Figure 19 shows the thermobalance curves for these tests, indicating a mean 30-minute weight gain of 92.1% of stoichiometric, with a standard deviation of 3.6%. This mean absorption rate is significantly higher than the absorption rate with standard gas. Analysis of the recovered sorbent from Test 02-34

Figure 19. THERMOBALANCE CURVES FOR BATCH 23 TESTS WITH STANDARD GAS CONTAINING NH_3

showed no detectable N in the solid, and, based on analyzed CO_2 content, confirmed the absorption recorded on the thermobalance at 96.6% of the stoichiometric limit.

The desorption curves for Tests 02-35 and 02-36 flatten out after about 12 minutes, but remain well above baseline, which seems to indicate about 12% residual weight. However, these data are inconsistent with the actual measured weights of the samples recovered from the thermobalance, which showed 1% and 6% residual weight, respectively, for Tests 02-35 and 02-36. No explanation was found for this observation.

Performance Tests -- Dry Standard Gas: In Test 02-32, which was intended to be a test with standard gas + NH_3 , a pump malfunction prevented the entry of NH_3 -spiked water into the system. The decision was made to continue the test, resulting in a gas atmosphere of 50% CO_2 /50% He. The data, shown in Figure 20, indicate 73.5% of limiting CO_2 absorption at 30 minutes. Because the CO_2 partial pressure was 157 psi, compared to 131 psi in the standard gas tests with steam, the data is not directly comparable. However,

Figure 20. THERMOBALANCE CURVE FOR BATCH 23 TEST WITH DRY STANDARD GAS

if first-order kinetics are assumed for the chemisorption, the absorption rate for this gas mixture would fall within the 95% confidence limits observed for the standard gas. This indicates that there is no significant difference in CO_2 absorption rate with or without steam.

Performance Tests -- Variations in Sorbent Mg:K Atomic Ratio: In Tests 03-02 and 03-04, Batch 26 with an Mg:K atomic ratio of 7.5:1 was tested at 800°F and 300 psig in the standard gas. In Tests 03-05 and 03-06, Batch 25 with an Mg:K ratio of 5.7:1 was tested under similar conditions. The results of these tests are shown graphically in Figures 21 and 22. These results do not differ significantly from those obtained with Batch 23 (Mg:K ratio of 6.8:1).

Task 5. Cycle Tests of Sorbent in Packed-Bed Reactors

Objective

The objective of this task was to perform absorption/desorption cycle tests in a laboratory packed-bed reactor to determine the effects of cycling

Figure 21. THERMOBALANCE CURVES FOR BATCH 25 (LOWER Mg:K RATIO) TESTS WITH STANDARD GAS

Figure 22. THERMOBALANCE CURVES FOR BATCH 26 (HIGHER Mg:K RATIO) TESTS WITH STANDARD GAS

on the reactivity and physical integrity of the sorbent. Tests of 3, 7, and 20 cycles were performed in duplicate using a simulated syngas atmosphere.

Summary

A description of the packed-bed reactor system was given in the Task 2 discussion, and a schematic diagram of the equipment was shown in Figure 4. Five shakedown tests were performed using MAGSORB Batch 6 to test various combinations of gas flow rate, CO₂ concentration, and testing procedures. The selected test procedure consists of the following steps:

- The 6-inch-deep MAGSORB bed is captured between plugs of glass wool in reactor; swept volumes above and below the bed are filled with Kimax beads
- The reactor is heated to 800°F under N₂ at 300 psig for leak-testing
- The reactor is depressurized to atmospheric pressure and isolated (bypass mode)
- The CO₂-containing reactant gas is flowed, bypassing the reactor, until the CO₂ concentration indicated on the infrared monitor is steady.
- The gas flow is diverted to the reactor at atmospheric pressure; MAGSORB absorbs CO₂ while pressure rises to 300 psig; upon attaining 300 psig, the exit gas is continuously analyzed for CO₂ content
- The gas flow is maintained at constant input rate until CO₂ output concentration increases rapidly, indicating breakthrough (approximately 25 minutes)
- Nitrogen is introduced while pressure is reduced to atmospheric; depressurization takes four minutes
- Desorption is continued at atmospheric pressure until entire cycle time reaches 60 minutes, at which time the CO₂ concentration is less than 5% of the inlet gas CO₂ concentration

The upper and lower bed temperatures and the outlet gas CO₂ concentration were continuously recorded.

Because thermobalance test 02-32 indicated that the sorbent reactivity was essentially the same with and without steam in the reactant gas, it was decided to run the packed bed with a dry gas consisting of 50 vol% CO₂ in helium. This simplified operation and data analysis.

Six packed-bed absorption/desorption cycle tests were conducted, three with three absorption/desorption cycles, two with seven cycles, and one with

20 cycles. The conditions and operating results of the tests are given in Table 3. All of the tests used Batch 24 pellets, and were operated at 300 psig system pressure, which corresponded to a CO₂ partial pressure of 155 psi. The results of chemical analyses and physical testing of the sorbent before and after cycling are discussed in detail under Task 6.

Table 3. SUMMARY OF CONDITIONS IN PACKED-BED CYCLE TESTS

Test No.	Cycle No.	Min/max temperature, °F ^a		Breakthrough CO ₂ conc, vol%	Breakthrough time, min ^b
		Absorption	Desorption		
C3-1	1	850	765	40.5	24.0
	2	850	765	41.5	15.5
	3	850	765	43.5	15.5
C3-2	1	830	750	35.8	27.5
	2	830	750	41.0	15.0
	3	835	750	42.5	15.5
C3-3	1	850	760	40.0	28.0
	2	840	765	40.8	15.0
	3	840	770	43.0	15.0
C7-4	1	830	750	35.8	27.5
	2	830	750	41.0	15.5
	3	835	750	42.5	15.5
	4	855	805	40.0	16.5
	5	825	800	40.7	15.0
	6	820	780	42.5	15.0
	7	820	770	43.2	15.0
C7-5	1	850	760	40.0	28.0
	2	840	765	40.8	15.0
	3	840	770	43.0	15.0
	4	830	780	38.7	15.5
	5	825	780	38.7	15.5
	6	820	770	39.8	15.5
	7	815	760	41.0	15.5
C20-6	8	820	775	39.5	15.0
9 - 20		810 - 820	750 - 770	42.0 - 43.0	15.0 - 18.0

Notes:

- ^a Maximum temperature at beginning of absorption cycle, minimum temperature at beginning of desorption cycle (see text)
- ^b Includes 13-14 minutes required to pressurize reactor to 300 psig, during which no measurement of CO₂ concentration was made

In test C3-1, the first of the three-cycle tests, the absorption and desorption cycles were each run for 30 minutes, and the reactor furnace temperature was held constant at 820°-850°F. The initial reactor temperature was about 820°F, but quickly rose to 850°F from the exothermic absorption reaction when CO₂ gas was introduced. The inlet gas flow rate was maintained at a rate whereby the reactor took 13 to 14 minutes to reach 300 psig. It was calculated that the amount of CO₂ absorbed during pressurization would be less than 10% of the expected sorbent capacity based on thermobalance data. Upon desorption, the bed temperatures dropped rapidly from the endothermic desorption reaction. The upper portion of the bed cooled first to 765°F, but quickly reheated, while the lower bed began to cool. With 30 minutes of desorption, the outlet CO₂ composition dropped to about 3.5 vol%. Because breakthrough occurred after a total CO₂ input time of 22 minutes in the first cycle and only 15 minutes in later cycles, the absorption/desorption time split was changed to 25/35 minutes for subsequent tests. Two obvious points were noted:

- The outlet CO₂ concentration under dynamic equilibrium conditions prior to breakthrough was quite high -- 40.5 vol% compared to 49 vol% CO₂ in the inlet gas
- The time to reach breakthrough decreased dramatically on the second and third cycles, indicating either incomplete desorption or deactivation of the sorbent.

In Test C3-2, the furnace temperature was reduced to about 820°F to reduce the bed temperature upon absorption and reduce the steady-state CO₂ outlet concentration. The breakthrough concentration was reduced slightly to about 36 vol% and the time to breakthrough increased to 14 minutes. However, the second and third cycles again showed drastically reduced breakthrough times and increased breakthrough concentrations. Outlet CO₂ concentrations after 33 minutes of desorption dropped to about 2.5 vol%. The product sorbent from Test C3-2 was analyzed for CO₂ content, and the analysis showed a residual weight gain of 14.6%, corresponding to 19% of the maximum theoretical weight gain based on analysis of the unreacted sorbent.

Test C3-3 was run under similar conditions as Test C3-2, and the results, as shown in Table 3, were quite similar.

For the 7-cycle tests, recovered sorbent from the 3-cycle tests was used and exposed to four additional cycles. A decision was made to include a

temperature swing component in the desorption, attempting to desorb more of the CO₂ from the sorbent and possibly improve the absorption performance in subsequent cycles. In Test C7-4, the reactor furnace temperature was set at 800°F for absorption, increased to 900°F at the beginning of desorption, and reduced to 800°F five minutes before the beginning of the desorption cycle. In the desorption cycle, the bed temperature rose rapidly after the initial cooling, gradually reaching 900°F at the top of the bed, but not exceeding 800°F at the lower part of the bed. Using this procedure, the outlet CO₂ concentration dropped essentially to zero after about 30 minutes of desorption at the higher temperature. However, as Table 3 shows, the deeper desorption did not significantly affect the breakthrough concentration or breakthrough times in subsequent absorption cycles.

Test C7-5 was operated in a manner identical to Test C7-4, and the results were similar.

For Test C20-6, pellets from Test C7-4 were exposed to an additional 13 cycles, resulting in a total of 20 cycles. The data in Table 3 show the results from the first cycle of the test (eighth cycle for the sorbent) and a range of data points from the subsequent cycles, which were virtually identical in every respect.

The pellets from all of the tests were tested for crush strength and examined visually. The results of these investigations are discussed below under Task 6.

Task 6. Analysis of Chemical and Physical Properties of Sorbent

Objective

The objective of this task is to analyze relevant chemical and physical properties of the sorbents used in thermobalance and packed-bed tests.

Summary

The analyses and physical properties of the sorbents have been discussed briefly under Subtasks 3, 4, and 5 in conjunction with discussions of experimental results in those subtasks. More detailed discussions of sorbent properties are given in this section.

Each sorbent batch was analyzed for Mg and K content by inductively coupled plasma atomic emission spectroscopy (ICPAES). In most cases, 10 randomly selected pellets were analyzed to assess the homogeneity of the batch. The CO₂ content of sorbent batches was determined by the standard ASTM method D1756. Pore volume, pore diameter distribution, and particle density were all determined by analysis in a Micromeritics Model 9310 mercury porosimeter. BET surface area was determined in a Micromeritics Model 2100D N₂ porosimeter. Crystalline phases were determined by qualitative x-ray diffraction. The heat of CO₂ absorption was determined in a Differential Scanning Calorimeter (DSC).

The chemical analyses of the MAGSORB batches are shown in Table 4. Where multiple samples were analyzed, the mean values are shown. Mg:K atomic ratios have already been given in Table 1. These data were used primarily to calculate the stoichiometric CO₂ absorption limits for samples tested in the thermobalance. It was assumed that 100% of the potassium was in the form of K₂CO₃, and that residual CO₂ was tied up as MgCO₃. Batch 22 was a control batch with no added K, so the Mg and K analyses were not performed. It is of interest to note the results of two separate analyses of Batch 1 performed immediately after the batch was prepared and then after storage for 15 months in a closed bottle. The sample picked up a considerable amount of CO₂, increasing from 8.89 wt% to 39.84 wt% CO₂. This is more than could be accounted for by the CO₂ contained in the air trapped inside the storage bottle. It was assumed that air infiltration by diffusion and possible leakage through the cap seal must have allowed a gradual resupply of CO₂. In any case, these analyses point out the reactivity of this sorbent toward atmospheric CO₂, even at ambient conditions, over an extended time period.

Table 5 shows supplemental analyses of selected batches, including XRD, porosity, density, and surface area. The XRD data, where available, indicate that only MgO, K₂CO₃, and K₂CO₃·½H₂O were detectable in the unreacted solids. Density and pore volume measurements are based on Hg porosimeter analyses. The true density, which should be close to the density of a 4:1 by weight mixture of crystalline MgO and K₂CO₃ (≈3.3 g/cm³), varied over a relatively small range from 2.2 to 2.8 g/cm³. The particle density, however, which includes pores, varied over a wider range of 0.36 to 0.95 g/cm³.

Batches 1, 2, and 3, made by the original slurry extrusion method gave slightly lower particle densities (0.36 to 0.43 g/cm³) than Batches 23 and 24 made from regrinding and pelletizing with NH₄HCO₃ (0.58 to 0.60 g/cm³). Batch 19, which was made from regrinding and pelletization without NH₄HCO₃, gave a much higher pellet density of 0.95 g/cm³. These trends also occur for pore volume, which was lowest for the dense Batch 19 pellets, much higher for the Batch 23 and 24 pellets, and slightly higher for the slurry-extrusion pellets, which gave the highest initial reaction rates in thermobalance tests. It is worth noting that the density and porosity measurements on Batch 22, the control batch made without added potassium, are similar to those of the highly reactive Batch 1-3 pellets, which proves that available surface is not sufficient to promote reactivity with CO₂.

Surface area values were obtained from BET (N₂) analyses, but these analyses were not available for Batches 19, 22, and 23. The values obtained for slurry-extrusion Batches 1 through 3, however, show a surface area (44.8 m²/g average value) 2.2 times higher than that of Batch 24 (20.7 m²/g), made by the dry pelletization method with NH₄HCO₃.

The DSC was used to determine the exothermic heat release from the reaction, MgO + CO₂ = MgCO₃, for Batches 1, 2, and 3. A summary of the results of the DSC is given in Table 6 and the exotherms as a function of temperature for the three sorbents are given in Figures 23 through 25. These tests were conducted in pure CO₂ at 300 psig. The areas under the exotherms were measured by weighing and were used to calculate the heat of reaction using the exotherm for the melting of zinc powder as a standard. In calculating the heats of reaction, it was assumed that the sorbent had absorbed the stoichiometric amount of CO₂. The values in Table 6 should be compared with the heat of reaction for the formation of MgCO₃ from CO₂ and MgO, which is 23.41 kcal/gmol.

Table 4. CHEMICAL ANALYSES OF MAGSORB BATCHES

Batch	Wt% Mg ^a	W% K ^a	Wt% CO ₂	Stoichiometric CO ₂ absorption, wt%
1	41.1 ^b 31.0 ^c	9.47 ^b 6.01 ^c	8.89 ^b 39.84 ^c	70.8 ^b 19.7
2	40.9	9.67	9.64	69.8
3	44.1	8.46	7.87	76.7
7	44.4	9.07	NA	NA
8	44.2	8.29	NA	NA
9	45.4	7.47	NA	NA
10	45.0	8.76	NA	NA
11	44.7	10.9	NA	NA
12	45.0	7.84	NA	NA
13	46.5	8.45	9.58	79.3
14a	44.9	8.03	11.32	74.5
14b	46.8	8.50	8.62	80.9
16	43.6	10.6	NA	NA
17	46.8	7.97	NA	NA
18	43.6	10.5	11.1	73.7
19	42.8	10.38	11.1	72.2
20	46.3	8.60	11.1	77.5
21	45.4	9.17	8.45	78.8
23	40.2	9.51	10.0	77.3
24	44.5	9.80	9.20	76.9
25	43.0	12.1	9.81	74.8
26	42.6	9.12	11.1	71.2

Notes:

- ^a Entries in *italics* indicate an average value based on analyses of 10 pellets
- ^b Original analysis when batch was prepared
- ^c Later analysis made when batch was retested; CO₂ content increased during storage

Table 5. DETAILED ANALYSES OF SELECTED MAGSORB BATCHES

Batch	XRD		Mercury Porosimeter				N ₂ Porosimeter
	Major	Minor	Particle density, g/cm ³	True density, g/cm ³	Pore volume, cm ³ /g	Mean pore diameter, μ m	Surface area, m ² /g
1	MgO	K ₂ CO ₃	0.411	2.83	2.08	0.122	45.7
2	MgO	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O	0.429	2.67	1.96	0.097	40.1
3	MgO	K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O	0.360	2.85	2.43	0.137	48.5
19	--	--	0.952	2.22	0.60	0.092	--
22	--	--	0.410	2.23	1.99	0.087	--
23	--	--	0.598	2.62	1.29	0.230	--
24	MgO	K ₂ CO ₃ , K ₂ CO ₃ · $\frac{1}{2}$ H ₂ O	0.584	2.64	1.33	0.154	20.7

Table 6. RESULTS OF DIFFERENTIAL SCANNING CALORIMETER ANALYSES

Batch	Initiation of CO ₂ Absorption, °F	CO ₂ Absorption Peak, °F	Completion of CO ₂ Absorption, °F	Initiation of CO ₂ Desorption, °F	Heat of Reaction, kcal/gmol
1	729	793	932	1096	23.6
2	707	779	887	1089	21.0
3	725	788	887	1096	18.7

Figure 23. CO₂ ABSORPTION EXOTHERM FOR BATCH 1

Figure 24. CO₂ ABSORPTION EXOTHERM FOR BATCH 2

Figure 25. CO₂ ABSORPTION EXOTHERM FOR BATCH 3

One aspect of the physical property data specifically impacts the volumetric reactivity and/or CO₂ capacity of the sorbent. As indicated by thermobalance data, the reactivity of reground/repelletized MAGSORB modified with NH₄HCO₃ (Batches 23-24) is much higher on a weight basis than that of the unmodified sorbent (Batches 18-20). However, as Table 7 below shows, this advantage is smaller when the reactivity is calculated on a volumetric basis. The table data is based on thermobalance tests at 800°F/300 psig with standard gas, and shows the weight of CO₂ absorbed per unit weight or unit volume of unreacted sorbent. In a commercial installation, this may be important with regard to reactor size, which has a substantial impact on capital cost. The denser Batch 19 pellets have about the same surface area (Table 5) as the more porous Batch 23 pellets, but, based on average pore diameter, the pores are smaller. This may account for the large difference in reactivity on a weight basis, because initial chemisorption of CO₂ in the pores may inhibit further diffusion of CO₂ through the narrow pores.

Table 7. SORBENT CAPACITY COMPARISON ON WEIGHT AND VOLUMETRIC BASIS --
WEIGHT GAIN FOR 30 MINUTES ABSORPTION

	g CO ₂ absorbed	
	per gram	per cm ³
Batch 19 (no NH ₄ HCO ₃)	0.370	0.353
Batch 23 (with NH ₄ HCO ₃)	0.700	0.419

Sorbents recovered from packed-bed tests performed under Task 6 were analyzed for physical properties (density, pore properties) and crush strength. Crush strength -- specifically, diametrical compression tensile strength -- was measured in an Instron Model 1011 tensile strength tester. The results of these analyses are shown in Table 8. The values shown for 3 cycles and 7 cycles are the averages from pellets recovered from duplicate tests. The values shown for 20 cycles are from a single test.

The physical property data reflect the decrease in reactivity by showing an increased density, decreased pore volume, and sharply decreased surface area for the reacted pellets. There is no apparent change in these properties

beyond 3 cycles. Pellet strengths, on the other hand, did not change significantly after 3 cycles, although this is difficult to assess because of large random variations in strength among pellets from the same sample. The pellet strength decreased significantly upon further cycling, from an average value of 0.77 lb for the unreacted material to 0.70 lb (9% decrease) after 3 cycles and 0.48 lb (38% decrease) after 7 cycles. There was no further decline in strength after 20 cycles.

Table 8. PHYSICAL PROPERTIES OF SORBENTS FROM CYCLE TESTS

Cycles	Mercury Porosimeter				N ₂ Porosimeter	Crush strength, lb ^a
	Particle density, g/cm ³	True density, g/cm ³	Pore volume, cm ³ /g	Mean pore diameter, μ m	Surface area, m ² /g	
None	0.584	2.64	1.33	0.154	20.7	0.77±0.30
3	0.703	2.83	1.09	0.244	6.3	0.70±0.64
7	0.669	2.72	1.15	0.249	7.3	0.48±0.25
20	NA	NA	NA	NA	NA	0.48±0.27

^a Test conditions: 10-lb spring, 2.0-lb load range, flat table; error limits shown are 95% confidence limits

Task 7. Test Data Analysis and Interpretation

Analysis and interpretation of the data obtained in the project are included in the discussion of the tasks in which the data were collected.

Task 8. Systems Analysis and Technoeconomic Evaluation

Objective

The objective of this task was to develop an optimum scheme for integrating the MAGSORB Process for CO₂ absorption with selected gasification and gas-upgrading processes for a technoeconomic analysis and comparison with conventional alternatives. In particular, this entailed a comparison of the estimated economics of the MAGSORB process with removal of CO₂ by conventional Rectisol technology using refrigerated methanol scrubbing, in the production of a synthesis gas for methanol production. Bechtel National, Inc. performed this task as a subcontractor to IGT. The specific Task objectives were to:

- Compare the process configuration and the capital and operating costs of a low-temperature gas-treating system (Rectisol) with and without the introduction of MAGSORB for separate CO₂ removal. This cost differential is to be later compared with an estimated cost for the MAGSORB facilities
- Develop a conceptual design for the MAGSORB process and define its process and mechanical operating characteristics
- Reconcile the above MAGSORB conceptual design requirements with the preliminary data from the bench-scale absorbent tests and identify targets for absorbent development and testing

Summary

Bechtel National, Inc. has completed a preliminary MAGSORB reactor and system design and a preliminary comparison of the estimated economics of CO₂ removal from methanol synthesis gas by conventional Rectisol technology with and without MAGSORB. A comprehensive report was submitted in the third quarter of the project. At the end of the experimental program, the design economic assessment was updated by integrating technical information about sorbent properties which were obtained in the IGT experimental program. This section consists of an updated version of the earlier report.

Synthesis gas (syngas) from a coal gasifier can be used as a feedstock for methanol synthesis, but before this processing can take place, the CO₂ must be removed. In conventional CO₂ removal processes (e.g., Rectisol or Selexol), the syngas is cooled substantially, CO₂ and sulfur gases are removed, and the resulting syngas is reheated to a temperature suitable for subsequent processing. In the MAGSORB process, the CO₂ is separately removed at an elevated temperature, after which the reduced volume of the resultant syngas is cooled and desulfurized in a conventional low-temperature process.

The use of the MAGSORB process for bulk separation of CO₂ offers three potential major advantages over conventional processes:

- A lower heat loss associated with gas cooling and reheating
- A conventional desulfurization process that is simplified and reduced in cost and energy consumption by prior CO₂ removal
- A potential for integration with advanced hot gas desulfurization

The application scenario selected for this process assessment is the production of syngas for methanol production. The evaluation basis is confined to the gas treatment after the water gas shift (required to adjust the H_2/CO ratio of the gas) and prior to the final sulfur scavenging required for the methanol plant feed.

Desulfurization Cost Comparison: Two cases of coal-derived syngas desulfurization were compared. Each case was based on Texaco coal gasification at a scale equivalent to 11,000 bbl/day of methanol. Both cases employed Rectisol refrigerated methanol absorption/stripping for H_2S removal.

Case 1 provided a Rectisol unit for both selective CO_2 recovery and separate H_2S recovery in a concentrated stream for Claus plant sulfur production. Case 2 was based on bulk removal of CO_2 by MAGSORB and provided only H_2S removal in the Rectisol plant.

The capital cost for Case 2 was estimated at \$91.5 million less than that of Case 1. The annual operating cost for Case 2 was estimated at \$9.1 million less than that of Case 1.

MAGSORB Process Description: In the MAGSORB process, CO_2 is removed from a hot high-pressure gas stream with an activated form of MgO to form $MgCO_3$.

The carbonation reaction is reversible, and its direction is dependent on the absorbent temperature and the partial pressure of the CO_2 in the gas. Because the heat of reaction is also very high, heat must be removed from the absorbent during absorption to maintain the forward reaction and similarly be added during desorption to obtain complete regeneration.

Absorber Concept: In the envisioned process, fixed beds of the KOH-modified $MgO/MgCO_3$ sorbent are alternately cycled between absorption and desorption. During absorption, the MgO is exposed to the high-pressure CO_2 -rich gas and must be simultaneously cooled to remove the heat released during the production of the $MgCO_3$. During desorption, the saturated bed ($MgCO_3$) is reduced in pressure and simultaneously heated to release the absorbed CO_2 . The absorption/desorption beds are configured so that heat

released during absorption is employed as heat input during regeneration. To transfer this heat, the beds are contained in thin parallel tubes arranged for heat transfer between tubes.

Absorber Model: A simplified mathematical model of the absorber concept was developed to verify that direct heat transfer between absorption and desorption reactions was feasible. The modeling indicated that the temperature approach between absorption and desorption is about 50° to 75°F. The absorbent must contain closely spaced conductive fins to achieve the required heat transfer. The choice of gas inlet temperature is important, and the desorption requires a deep pressure reduction. It also indicated that the absorbent should be formed with minimum void volume to permit the maximum amount of active absorbent to be contained in a minimum absorber volume.

Assessment of Absorbent Test Data: Absorption and desorption data developed by IGT have been compared with the absorption/desorption model described above. The calculated CO₂ absorption and desorption rates, assuming heat transfer is limiting, were found to be higher than those observed in thermobalance tests. This indicates that other limitations, such as pore diffusion or chemical reaction kinetics, may be factors.

The sorbent formulation used for the final design evaluation was Batch 23. Table 9 shows calculated properties and kinetic data based on a regression curve derived from thermobalance Tests 02-25 through 02-27. These data were used in the calculation of breakthrough lines shown later in Figures 36 through 38. As expected, the reaction rate is highest at the beginning of the reaction. The maximum rate was calculated to be 0.0156 kmol CO₂ per second per m³ of sorbent volume.

Technical Discussion

To prepare a coal-derived synthesis gas (syngas) for methanol production, a large portion of CO and CO₂ must be removed so that it meets the chemical requirements of the methanol synthesis reactor. The C:H ratio is adjusted by a water-gas shift conversion of CO to CO₂ with subsequent production of H₂. Along with the main constituents of a fossil-fuel-derived

Table 9. CO₂ ABSORPTION RATE BASIS FOR REACTOR DESIGN

Time, min	Extent of reaction, %	Absorption, kg CO ₂ /kg sorbent		Rate, kmol CO ₂ /(s ² ·m ³)
		Measured data	Regression curve	
0	0.0000	0.0000	0.0048	0.0156
3	0.2797	0.1905	0.1785	0.0108
6	0.4312	0.2937	0.2979	0.0074
9	0.5478	0.3731	0.3794	0.0051
12	0.6410	0.4366	0.4360	0.0036
15	0.6993	0.4763	0.4776	0.0028
18	0.7576	0.5159	0.5109	0.0023
21	0.7984	0.5437	0.5395	0.0020
24	0.8217	0.5596	0.5639	0.0016
27	0.8485	0.5779	0.5810	0.0009
30	0.8625	0.5874	0.5851	0.0000

synthesis gas (CO, H₂, CH₄, CO₂), the sulfur present in the syngas in the form of H₂S and COS must also be removed.

Conventionally, the separation of CO₂ and sulfur compounds is achieved by means of a selective sour gas removal process. As shown schematically in Figure 26A, the syngas is separated into three gas streams: The adjusted clean syngas ready for the methanol synthesis; The sour gas stream carrying the sulfur; And a CO₂ stream. This gas separation process is most efficient at elevated pressures and low temperatures, where physical absorption in the solvent is enhanced. This implies that hot syngas exiting the shift reactor has to be cooled to very low temperatures for efficient gas separation. Extensive cooling and subsequent reheating impose significant capital and energy costs.

The MAGSORB process for bulk CO₂ removal recovers CO₂ at elevated temperatures. The CO₂ removal is conducted in a swing-bed absorption/desorption cycle in which the spent sorbent is regenerated either by decreasing the pressure or elevating the temperature to decompose MgCO₃ to MgO and CO₂. A modified conventional sour gas removal operation subsequently retrieves the sulfur from the syngas. Figure 26B shows the basic arrangement.

A) Conventional Sour Gas Removal Flow Diagram

B) MAGSORB Sour Gas Removal Flow Diagram

Figure 26. CONVENTIONAL AND MAGSORB SOUR GAS REMOVAL FLOW DIAGRAMS

Bulk CO₂ removal at elevated temperature has the potential to simplify the heat recovery and syngas preparation process, both upstream and downstream of the CO₂ removal process. Syngas cooling for sulfur recovery is still required, but because of the reduced gas volume to be treated, the loading and heat cycling are greatly reduced. Because of increased sulfur concentration in the syngas, the equipment in the sulfur recovery process becomes smaller and less cooling is required.

The steps involved in the study were as follows:

- A simulation model was developed for a conventional low-temperature methanol-based physical absorption process for H₂S removal. Establish the process configuration, equipment size, and utility requirements both with and without MAGSORB fuel gas processing
- The capital and operating cost differential between the two low-temperature methanol solvent systems was estimated
- The physical parameters of the conceptual MAGSORB reactor were defined and a mathematical model to simulate its performance was developed
- The desirable characteristics of the absorbent and the design parameters for experimental development and testing were defined

To be economically advantageous, the cost savings for the sulfur removal process that are due to the MAGSORB bulk CO₂ removal must exceed the cost of the MAGSORB process. The cost savings have been estimated assuming a low-temperature methanol (LTM) absorption process. In the conventional design, the process removes both H₂S and CO₂. With the MAGSORB system, a simpler and less costly LTM process removes sulfur (and smaller amounts of residual CO₂).

The process integration of the CO₂ and sulfur removal facilities for both cases to be compared are illustrated in block diagrams in Figures 27 and 28. More detailed illustrations of the process configurations are shown in Figures 29 and 30.

Syngas Preparation for Methanol Synthesis: The methanol synthesis reactions with syngas are $2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}$ and $3\text{H}_2 + \text{CO}_2 = \text{CH}_3\text{OH}$. The combined stoichiometry can be expressed in terms of the mole ratio $\text{H}_2:(2\text{CO}+3\text{CO}_2)$, which should be equal to 1.0. Texaco-coal-gasification-derived syngas results in a

Figure 27. BLOCK FLOW DIAGRAM FOR THE REMOVAL OF CO₂ AND SULFUR BY A CONVENTIONAL PROCESS

Figure 28. BLOCK FLOW DIAGRAM FOR THE REMOVAL OF CO₂ AND SULFUR BY THE MAGSORB PROCESS

Figure 29. COAL-GASIFICATION-BASED SYNGAS PRODUCTION USING A CONVENTIONAL LOW-TEMPERATURE METHANOL (LTH) PROCESS FOR SYNGAS PREPARATION

Figure 30. COAL-GASIFICATION-BASED SYNGAS PRODUCTION USING THE MAGSORB CO₂ REMOVAL AND MODIFIED LTM PROCESS FOR SYNGAS PREPARATION

ratio of about 0.27. This ratio needs to be adjusted by enhancing the concentration of H_2 with respect to the concentration of CO. A shift conversion operation and the removal of the bulk CO_2 and H_2O provide this adjustment. Quenching part of the raw syngas exiting the coal gasification reactor adds enough water to satisfy the shift conversion's chemical needs. The amount of water needed determines the flow rate of the gas to be quenched. The remainder of the raw gas is mixed to the shifted portion prior to the CO_2 and H_2S removal operation.

Conventional Low-Temperature Methanol (LTM) Process: The CO_2 and H_2S acid gases are conventionally removed by liquid scrubbing employing either a physical solvent, such as methanol, or a chemisorption solvent, such as an amine. High-pressure gas treatment, as envisioned here for methanol feed preparation, favors physical absorption at low (refrigerated) temperatures.

Figure 31 illustrates a typical configuration for the conventional LTM process. In this arrangement, a portion of the hot gas from the gasifier is cooled by direct water quench to supply the water needed for the water gas shift conversion. This water-saturated stream is combined with hot unquenched gas, resulting in a stream with a temperature still suitable for high-temperature heat recovery, but well below the slag softening temperature. This solidifies the entrained liquid slag carried with the unquenched raw gas so that ordinary convective cooling equipment can be applied for high-temperature heat recovery to produce high-pressure steam for other process uses. This raw gas, after a COS hydrolysis reaction operation, is then mixed at a temperature of about 100° to $130^\circ C$ with cooled syngas from the shift conversion unit and passed to the subsequent LTM process. The syngas cooling simultaneously knocks out the bulk H_2O by condensation.

The LTM process considered involves a three-step methanol regeneration operation using pressure letdown, thermal stripping, and nitrogen stripping. This regeneration yields two CO_2 -containing offgas streams and an H_2S -rich acid gas stream suitable for sulfur recovery in a Claus plant. One CO_2 offgas stream contains a considerable amount of CO and H_2 suitable for further use as a fuel gas. The other CO_2 -containing offgas stream, diluted with N_2 , is suitable for discharge to the atmosphere or other optional processing to isolate CO_2 .

MAGSORB CO₂ Removal and Modified LTM Process: The integration of the MAGSORB process and the accompanying simplification of the LTM process are illustrated in Figure 32. This design also requires syngas cooling to very low temperatures since the modified LTM process for only H₂S separation works at the same temperature level as the conventional LTM process. However, the MAGSORB process operates at elevated temperatures, and experimental data available indicate that the reactor inlet temperature needs to be as high as 430°C. The MAGSORB system must be placed at the proper temperature level in the course of syngas cooling. Particulate removal preceding the MAGSORB system is necessary to prevent clogging of the absorbent's pores.

The MAGSORB system employs a number of reactors, each operating in a cyclic mode using pressure-swing regeneration to produce a relatively pure but low pressure CO₂ product. The hot, clean, CO₂-rich syngas passes upward through one half of a tubular array. CO₂ diffuses into the absorbent to form MgCO₃. The heat released by absorption provides the necessary heat for desorption. In the desorption half of the tubular array, residual treated syngas from the absorption cycle is withdrawn by a compressor. As the pressure is reduced, MgCO₃ decomposes, releasing CO₂, which displaces the treated syngas from the tubes. When most of the residual syngas has been displaced, the CO₂ is discharged through a compressor, evacuating the desorbing tubes. In practice, a number of parallel units will be employed to maintain steady operation of the cyclic system.

A COS-hydrolysis operation to convert COS to H₂S ensures proper desulfurization in the subsequent modified LTM process because of methanol's higher affinity for H₂S. The cooling section after the MAGSORB system produces steam for other process uses.

In the LTM process, methanol at low temperatures, contacted with the syngas, absorbs the sulfur compounds H₂S and COS. A two-step regeneration operation involving pressure letdown and thermal stripping generates an H₂S-rich stream suitable for sulfur recovery in a Claus plant. The offgas, flashed from the spent methanol at the pressure letdown step, contains not only CO and H₂ but also some sulfur compounds, and is therefore recompressed and recycled to the absorber. Because of the prior removal of the bulk of the CO₂, the result is a much simpler process configuration that uses only two absorption/distillation columns with some heat exchange equipment. The

comparative conventional system consists of four columns, a number of pressure letdown drums, and extensive heat exchange equipment.

Capital and utility costs for a conventional LTM process for bulk CO₂ and H₂S removal were compared with capital and utility costs for a modified LTM process for H₂S removal only. The differences in the costs of these two procedures were then compared with the capital and operating costs of the MAGSORB process developed after the conclusion of Task 4. For all these processes, it is assumed that the syngas is supplied by Texaco gasification of an Illinois No.6 coal and that the prepared syngas is used as a feedstock for methanol production of 11,000 ton/day.

Table 10 presents the results of the comparison between the conventional LTM process and the modified LTM process. For the conventional process, some Bechtel in-house data were used. For the modified LTM process, the system was designed and sized to produce the same amount of syngas as the conventional process, and costs were determined using standard estimation methods. Capital costs include the cost of the absorption process as well as the refrigeration equipment. Utility costs are split into costs for electricity, cooling water, and steam. For the sake of simplicity, the refrigeration compressor's power demand, which is usually satisfied with process steam turbines, is included as part of electrical power demand.

Because of the reduced volume of gas treated and the resulting increased concentration of the sulfur-containing constituents, the modified LTM process is considerably less complex (smaller refrigeration units, fewer absorption/distillation columns, and less heat exchange equipment) than the conventional process. Hence, its capital and utility costs are considerably lower than those of the conventional process.

Because the capital and utility costs of the MAGSORB process are less than the capital cost differential and the total utility cost differential, respectively, in Table 10, the MAGSORB process is economically attractive.

Table 10. CAPITAL AND UTILITY COST COMPARISON OF CONVENTIONAL AND MODIFIED LTM PROCESSES (\$ BASIS: OCT 89)

Item	Capital Cost (\$1,000)	Utility			
		Electricity (\$/hr)	Steam (\$/hr)	Cooling Water (\$/hr)	Total Utility (\$/hr)
Conventional LTM process for bulk CO ₂ and H ₂ S removal	156,218	1,432	691	43	2,166
Modified LTM process for H ₂ S removal only	19,058	731	198	36	965
Estimated MAGSORB process cost	34,872	46	0	2	49
20% allowance for unproven technology	10,786				
Total MAGSORB process for bulk CO ₂ and H ₂ S removal	64,716	777	198	38	1,014
Overall cost savings for system with MAGSORB CO ₂ removal	91,502				
					1,152

Critical Absorbent Requirements: The MAGSORB process makes use of the reversible reaction of CO₂ with MgO to form MgCO₃. The absorption reaction is driven as long as the partial pressure of CO₂ in the gas phase exceeds the dissociation pressure of the solid carbonate. At CO₂ partial pressures 30 to 300 psia, CO₂ absorption at acceptable rates takes place at temperatures as high as 750° to 805°F. For desorption of the CO₂, the temperature must be elevated to raise the dissociation pressure above the system pressure, the CO₂ partial pressure must be lowered by dilution with a sweep gas, or the absolute pressure must be lowered below the dissociation pressure of the carbonate.

A critical factor in the process design of the regenerative system is the very high heat of reaction (≈ 100 MJ/kmol CO₂, $\approx 1,000$ Btu/lb CO₂). The heat of absorption tends to raise the temperature of the reaction site to the dissociation temperature and hence reduces the driving force for the reaction.

To maintain an acceptable rate of absorption, the reaction heat must be dispersed by conduction through the solid or by gas phase convection. Ultimately, the heat must be removed by heat transfer. The effect of the heat of desorption is similar: for desorption to continue, heat must be supplied to the reactive solid either by conduction or by gas convection.

Thus, in both absorption and desorption, system performance is governed by heat transfer. The absorbent may be diluted with a thermally conductive heat sink material to maintain system temperature within the 30°C range imposed by the dissociation pressure-temperature relationship. A compromise is necessary between optimum properties to satisfy heat transfer requirements and properties required for effective absorption. A porous matrix is required for gas access to the reactive MgO solid. At the same time, minimum porosity is desirable prior to desorption to minimize absorber volume and holdup of the treated gas.

Reactor Configuration: The MAGSORB reactor configuration under consideration is illustrated in Figure 31. This configuration theoretically provides continuous transfer of the heat of absorption to the simultaneously occurring desorption. The retort consists of an array of small-diameter steel tubes joined together for good thermal contact. Heat transfer from the absorbent to the tube walls is enhanced by conductive metallic fins embedded in the absorbent matrix. Gas flows through an axial channel formed during the casting of the absorbent. CO₂ transfer into the absorbent is by gas diffusion from the channel through the pore structure of the absorbent matrix.

As shown in Figure 31, the tubular array is manifolded through the use of a double-tube sheet head construction. A separate pressure shell is not required because the cyclic absorption and desorption take place entirely within adjoining tubes in the array.

Absorbent Form, Design Variation 1, Longitudinal Fins: In assembling the reactor, the finned inserts are first formed from thin sheet metal which are rolled and glued to form a cylinder whose diameter is less than the inside tube diameter. The elements are then inserted within the tube, and heated to destroy the glue and provide a spring fit contact with the tube wall. This design variation is shown in Figure 32A.

Figure 31. MAGSORB REACTOR CONFIGURATION AND TUBULAR ARRAY

A) Longitudinal Fins, Spring Fit Design

B) Radial Fins, Compression Mold Design

Figure 32. MAGSORB REACTOR FIN DESIGN

Next, the absorbent in paste form is injected into each tube around a porous mandrel used to form the gas path. The bundle is then heated by electrical resistance (or inductance) to dry and form the absorbent, and the mandrel is removed. Absorbent can be removed for replacement by means of high-pressure water jetting commonly used for heat exchanger cleaning.

Absorbent Form, Design Variation 2, Radial Fins: In this design, shown in Figure 32B, the absorbent elements are formed in a compression mold (11/16-in.-OD x 1/4-in. element height x 1/4-in.-ID center hole) to produce high-density ring pellets. Wrapping the pellets with corrugated aluminum foil provides radial fins which increase thermal conductivity in the radial direction. The result is improved heat transport to the corresponding desorbing elements within the tubular array.

In assembling the reactor, the ring pellets, lined up on a center rod mandrel, are pressed into the tubes and compacted. The corrugations between the pellets flatten, and the corrugations between tube wall and pellets provide good thermal contact. Hot gas is used to calcine the pellets after assembling. The absorbent can be removed for replacement by pushing or drilling out the pellets.

MAGSORB Reactor Modeling

An attempt was made to model the cyclic absorption and desorption of a tubular absorber configuration as described above and illustrated in Figure 32A. The details of the model are given in the Appendix. Only the results are described below and compared with absorbent test data reported in Tasks 3-5. Three factors control the performance of the MAGSORB process: *reaction kinetics* (heat transfer and reaction rates), *reaction equilibrium* (dissociation temperature-pressure relation), and *absorbent porosity*. The model was simplified to reflect only the specific limitations of heat transfer, gas-solid equilibrium, and absorbent porosity and thermal conductivity. Limitations imposed by chemical reaction rate or gaseous diffusion were not included.

Reaction Kinetics: The chemical reaction forming MgCO_3 from CO_2 and MgO proceeds in four steps:

- Diffusion of a CO_2 molecule from the bulk of the gas to the outer absorbent surface (film diffusion)
- Diffusion of a CO_2 molecule through the pores to the solid surface (pore diffusion)
- Diffusion of a CO_2 molecule through a layer of formed product (product layer diffusion)
- Chemical reaction of a CO_2 molecule with the MgO absorbent (chemical resistance)

With highly exothermic or endothermic heterogeneous chemical reactions, limited heat transport can also govern the rate of reaction. This effect is not related to the transport of CO_2 , but becomes significant as the temperature at the reaction site approaches the dissociation temperature, where formed product starts to decompose and reverses the reaction. Further absorption/desorption proceeds only at the rate of heat transport corresponding to the heat release due to the reaction.

The simulations of the proposed tubular contactor indicate that simultaneous heat transfer between absorbing and desorbing zones adequately handles the heat transport necessary to sustain absorption and desorption.

The model examines a defined segment of two adjoining tubes. One tube is undergoing absorption, the other desorption. The point absorption rate determined from the element model is then integrated to the limiting absorption capacity of the volume of absorbent. This establishes the total absorber volume required to absorb a given quantity of CO_2 and the rate at which it is absorbed. The quantity of CO_2 absorbed is determined by the gas flow rate and the selected cycle time for the full absorption/desorption cycle.

The reaction rate becomes zero if the dissociation pressure of the absorbent equals the partial pressure of the CO_2 in the gas phase. If the reaction rate is assumed to be heat-transfer-limited, the resulting temperature profile is illustrated in Figure 33. This figure clearly shows the sharp increase in temperature that occurs within the absorbent during absorption, the heat transfer to the cooler tube wall and the embedded metallic fins, the heat transfer through the tube walls, and the transfer of heat from the tube walls and fins to the heat-absorbing (desorption) solid.

**Figure 33. ABSORBENT TEMPERATURE DISTRIBUTION IN TUBE PAIR
WITH REACTION RATE LIMITED BY HEAT TRANSFER**

Heat is transferred from the absorbing sorbent to the CO₂-rich gas. consequently, to maintain the heat balance for equivalent desorption rate, some heat has to be supplied by the sweep gas. Figure 34 shows the dilution gas being fed at about 842°F. With this arrangement, the reaction rate was calculated to be 0.8 kmol CO₂/(s·m³). This is a considerably higher rate than the rate indicated by the thermobalance experiments. Conclusively, the featured design suffices the heat transfer requirements, including heat conduction through thermal coupling and convective gas-to-sorbent heat transfer. However, reaction rates under the above limitations will never be reached for two reasons: (1) thermobalance test data show lower reaction rates, and (2) a very sharp drop in temperature at the desorbing side is necessary to drive the heat to the place of reaction. The lowest temperature is about 536°F, corresponding to dissociation equilibrium and CO₂ partial pressure. Desorption experiments indicate that desorption does not proceed at a significant rate at temperatures below about 790°F. A simulation run under the assumption of reaction rates equal to those achieved in thermobalance tests resulted in the temperature profile shown in Figure 34. Temperatures on both sides, absorption and desorption, are high enough for sufficient reactions rates to occur.

Table 11 summarizes the geometrical and physical parameters used for reactor simulation runs, using the dissociation temperature/pressure relation calculated by IGT from thermodynamic data.^{3,4} The equilibrium curve was shown earlier in Figure 1. Thermodynamic data published in the International Critical Tables (ICT) were found to be in conflict with the thermodynamic calculations, and the thermobalance data reported in Task 4 confirmed the validity of the calculated equilibria.

The volumetric flow rate of the syngas, the pressure drop allowance, and the tube dimensions determine the size of one reactor module. The outer dimensions and the number of tubes of each reactor are listed under "Results" in Table 11. The volume of the absorbent placed according to the longitudinal fin design amounts to 38.82 m³ per reactor module (77.64 m³ counting elements in both absorption and desorption mode). In the simulation runs, the CO₂ absorption rate assumed was derived from thermobalance experiments (see Table 9). Because the absorption rate is slower than the desorption rate,

**Figure 34. ABSORBENT TEMPERATURE DISTRIBUTION IN TUBE PAIR
WITH REACTION RATES BASED ON THERMOBALANCE DATA**

Table 11. PRELIMINARY REACTOR DESIGN

<u>Item</u>	<u>Values</u>
ASSUMPTIONS	
Sorbent	
Thermal conductivity, W/m-K	1.45
Density, kg/m ³	598
Porosity	0.7714
Process syngas data	
Volumetric flow rate, m ³ /h	67,210
Rate of CO ₂ to remove, kmol/h	16,800
Gas velocity, m/s	10.0
Desorption pressure, bar	0.015
Geometry, longitudinal fin design	
Element height, mm	1.02
Fin thickness, mm	0.4064
Fin sheet thickness, mm	0.1524
Thermal coupling OD, mm	22.78
Absorbent ID, mm	9.09
Absorbent OD, mm	15.44
Number of radial elements	4
Delta R, mm	0.79
Element angle, deg	10
Number of fins	9
Reactor tube	
Tube OD, mm	19.05
Tube ID, mm	9.09
Gas path ID, mm	6.35
Tube length, m	12.19
Free area, m ²	6.49×10 ⁻⁵
Active reaction volume, m ³	0.00135
Total void fraction	0.856
RESULTS	
Reactor module	
Number of tubes (absorbing + desorbing)	57,496
Diameter, m	5.66
Length, m	14.00
Active volume, m ³ (absorbing + desorbing)	77.64

absorption requires a larger reaction zone volume to take up the amount of CO_2 to be removed. Figure 18 verifies that desorption occurs faster than absorption. The results of simulation runs are shown in Figures 35 and 36. These figures show the CO_2 molar flow rate through a series of reactors for two time intervals. The flow direction is shown in terms of active reactor volume passes on the way through the reactor units. Because of the system's cyclic operation, a split into two parallel trains was chosen. Phased operation of the two trains minimizes flow variation during switching periods.

In Figure 35, the number of units in series was chosen such that at the selected cycle time (6 minutes), the flow at the end of the last unit goes to zero. To meet this constraint, 7 units in series were required. The calculations do not take into account a possible decline in reaction rate because of declining CO_2 partial pressure. This may not be of significance, based on thermobalance data which have shown a considerable sensitivity to temperature, but not to variations in CO_2 partial pressure. However, if an assumption of declining reaction rate is made for the 6-minute cycle time, the resulting estimated total active reactor volume would increase from 543 m^3 to 776 m^3 , requiring 2 parallel trains of 10 reactors each. A simulation run was also made for a 20-minute cycle time using the same assumptions as the run shown in Figure 35. The results of this simulation are shown in Figure 36.

Reaction Equilibrium: The gas-solid equilibrium as described by the MgCO_3 dissociation pressure is a critical factor in determining the performance of the absorption/desorption system. Figure 1 showed the pressure-temperature relationship calculated by IGT from thermodynamic data, and Figure 34 illustrated the model element temperature profile. Because the gas-solid reaction rates are suppressed at temperatures below 750°F , even though the equilibrium would favor rapid reaction, the desorption temperature rises as required for the desorption to occur, and the decreased temperature difference limits the heat transfer and the CO_2 reaction rates.

Reactor Train Design: The findings above result in the following process design concept, outlined in Figure 37. The MAGSORB reactor (a single unit is shown) contains a set of 20 units, 2 parallel trains, 10 in serial arrangement. Within each train one set of tubes is in absorption mode and one in desorption mode. Phased operation and additional buffer tanks should

Cycle Time 6 [min]
 Number of reactor units in series 7 [-]
 Active Reactor Volume per train 272 [m3]
 Number of trains in parallel 2
 Total number of reactors 14
 Total active reactor volume 543 [m3]

Figure 35. SIMULATION BREAKTHROUGH LINES FOR 6-MINUTE CYCLE

Cycle Time 20 [min]
 Number of reactor units in series 14 [-]
 Active Reactor Volume per train 543 [m3]
 Number of trains in parallel 2
 Total number of reactors 28
 Total active reactor volume 1087 [m3]

Figure 36. SIMULATION BREAKTHROUGH LINES FOR 20-MINUTE CYCLE

Figure 37. SCHEMATIC DIAGRAM OF MAGSORB PROCESS UNIT

minimize flow rate variations from switching between absorption and desorption modes.

A fired heater and a feed/product heat exchanger supply the balance of heat to achieve desorption at an equivalent rate and sufficient sorbent regeneration. The recycle compressor minimizes synthesis gas losses while switching one train from absorption mode to desorption mode. The dilution gas booster is necessary to drive hot sweep gas through the desorbing tube set.

Proper pipe connection and valve equipment would allow for optimum auxiliary equipment utilization. The dilution gas booster may operate at almost constant rate, only being connected to different sections of the reactor module over time. The recycle compressor serves intermittently either train of the arrangement because of the phased operation.

CONCLUSIONS AND RECOMMENDATIONS

The experimental work performed in this program has revealed the impact of formulation procedure on MAGSORB properties, and has shown that the sorbent has adequate potential as a CO_2 sorbent for synthesis gas production. MAGSORB is a highly selective CO_2 sorbent that does not react with other synthesis gas components (H_2 , CO , H_2O , H_2S , or NH_3), nor is its performance adversely affected by these components. A technoeconomic analysis has shown that the integration of MAGSORB into a syngas conditioning train can result in significant capital and operating cost benefits when compared with conventional technology.

Several areas of further development are still needed. The laboratory preparation method used in this program may not be optimal in terms of sorbent properties and practicality on a commercial scale. Alternative methods involving co-precipitation or co-crystallization of MgCO_3 and K_2CO_3 should be investigated. The life-cycle tests have shown that the sorbent as made in this study loses reactivity after absorption/desorption cycling. A fundamental study of surface properties should be made to determine the cause of deactivation.

The following are specific recommendations for future MAGSORB development activities.

Preparation techniques: Alternative sorbent preparation techniques are available to make MAGSORB with more intimately mixed MgO and K_2CO_3 . A literature survey should be performed to obtain a list of candidate methods. Some possible examples are:

- Precipitation from MgCl_2 -- $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{Mg}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ could be co-precipitated by bubbling CO_2 through a solution of soluble MgCl_2 and K_2CO_3 salts. The K salt would be in large enough excess to obtain the desired Mg/K mol ratio. The resulting precipitate would be filtered off, dried, and calcined.
- Precipitation from KHCO_3 -- aqueous potassium bicarbonate (KHCO_3) could be added to a saturated MgCO_3 solution to precipitate out a mixture of MgCO_3 and $\text{MgCO}_3 \cdot \text{KHCO}_3 \cdot 4\text{H}_2\text{O}$. The K content would be adjusted by the amount of KHCO_3 added, and the resulting precipitate filtered off, dried and calcined.
- Crystallization of $\text{MgCO}_3/\text{K}_2\text{CO}_3$ -- Saturated solutions of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ would be mixed at an elevated temperature, then cooled to room temperature to co-crystallize the two carbonates. The relative

quantities of the saturated solutions would be selected to obtain the desired Mg/K ratio in the solid phase, which could be filtered off, dried and calcined.

Alternate methods would be assessed to arrive at an optimum combination of strength, density, and reactivity. Testing of sorbents of different densities and porosities would show the influence of gas diffusion within the porous structure.

Programmed Gas Temperature Variations: There is evidence that some minimum temperature is required to initiate the absorption reaction. However, with the inherent heating accompanying the reaction, heat removal may be augmented by reducing the gas temperature after the reaction has been initiated. Experiments where the gas temperature is lowered after the reaction takeoff should show an increased reaction rate if heat transfer is limiting the rate of reaction. If there is no increase in the reaction rate after lowering the gas temperature, a significant resistance due to product layer diffusion must be considered instead. This means that diffusion of CO₂ through a layer of carbonate is limiting. If there are product layer diffusion limitations, heat transfer may no longer be the limiting factor.

Construction and Testing of a full-scale reactor tube pair: Because of the complex interaction of heat transfer, gas diffusion, and chemical reactivity, a confirmation test of the commercial concept of thermally coupled pairs of absorption and desorption tubes should be carried out using an experimental arrangement as illustrated in Figure 38. Such a scheme would employ multiple absorbent pellets made by an optimized technique. After the desired gas composition and pressure have been established in the recycle test loop, the following operating sequence is suggested:

- Set the feed gas flow rate to give about a 5-minute cycle time to CO₂ breakthrough
- Set the inlet gas temperature
- Set the desorption gas flow rate to depressure the desorbing tube to atmospheric pressure in about 4 minutes or less, as needed for optimum absorption
- Once stable cycle has been established, adjust the inlet feed gas temperature for optimum performance

Figure 38. SIMULATION OF THERMALLY COUPLED MAGSORB ABSORPTION/DESORPTION CYCLE

- Reset the feed gas flow and cycle time for maximum loading of absorbent per cycle
- During regeneration, decrease the pressure rapidly until the CO₂ content of the vent rises, and release the flow control gradually

REFERENCES CITED

1. Colombo, G.V., and Mills, E.S., "Regenerative Separation of Carbon Dioxide via Metallic Oxides," *CEP symposium Series*, 61, No. 63, pp. 88-94 (1966).
2. Colombo, G.V., and Mills, E.S., "CO₂ Sorption Material," U.S. Patent No. 3,557,011 (1971).
3. JANAF Thermochemical Tables, Second Edition, U.S. Department of Commerce, National Bureau of Standards, NSRDS-NBS 37
4. Robie, R.A., Hemingway, B.S., and Fisher, J.R., *Thermodynamic Properties of Minerals and Related Substances at 298.15K and 1 Bar (10⁵ Pascals) Pressure and at Higher Temperatures*, U.S. Geological Survey Bulletin 1452 (1978).

APPENDIX.
REACTOR SIMULATION MODEL

APPENDIX. REACTOR SIMULATION MODEL

The two-dimensional reactor model that was developed is based on heat conduction calculations through a porous solid with an internal heat source/sink. The control volume contains a thin cross-sectional slab of a pair of reactor tubes (one absorbing and one desorbing) and covers a single sector of absorbent material on each side. The calculations were carried out using a finite differential method applied to a grid of small elements within a control volume. The simulation run yielded a mean CO_2 absorption and desorption rate, the size of the active reaction zone volume on either side, and the temperature distribution. Trends may be calculated, using different data for the reaction equilibrium (dissociation pressure-temperature relationship), for the thermal conductivity of the materials and for absorbent density and porosity. The model is two-dimensional in the circumferential and radial directions; no longitudinal effects were considered.

Geometric Arrangement, Control Volume

Figure A-1 illustrates the geometric arrangement according to the reactor design described above (design 1; longitudinal fins). Each tube faces a quarter of each of the four neighboring tubes so that within this tubular array one tube in the absorption mode is exposed to one tube in the desorption mode for heat transfer. Because of this symmetry, the control volume chosen consists of a single sector of absorbents between two of the nine longitudinal fins inserted into a reactor tube on each side. Figure A-2 shows the applied control volume. The simulation calculation distinguishes between three main parts of the control volume: the absorbent matrix in the absorption mode, the thermal connection, and the absorbent matrix in the desorption mode.

Model Assumptions

The following assumptions were made in the development of the reactor simulation model:

- Heat transfer governs only the rate of reaction.
- The CO_2 absorption and desorption rates are the same throughout the absorbent matrix.

The Three Major Areas within the Control Volume

Figure A-2. CONTROL VOLUME

- Input gas properties
 - Temperature
 - Transport properties to calculate the film coefficient
- Pressure
 - CO₂ partial pressure
 - Desorption side pressure
- Absorbent properties
 - Porosity
 - Density
 - Thermal conductivity
- Chemical reaction
 - Dissociation temperature-pressure relation
 - The temperature dependence of heat of reaction
- Reactor geometry

The calculation sequence is as follows:

- Assume both a CO₂ absorption rate and a CO₂ desorption rate.
- Estimate the wall temperature at the desorption side.
- Given the CO₂ rates, the gas temperatures, and the pressures, calculate the temperature distribution throughout the absorbent in the absorption mode and the desorption mode as well as the heat transported to and from the thermal connection.
- Iterate the wall temperature at the desorption side as long as the heat emitted from the absorption side matches the heat absorbed by the desorption side.
- Iterate the CO₂ absorption and desorption rates as long as the highest absorbent temperature in the absorption mode equals the dissociation temperature corresponding to the partial pressure in the gas on the absorption side. At the same time, iterate the CO₂ rate at the absorption side until the lowest temperature in the absorbent matches the corresponding dissociation temperature.

The heat transfer and the temperature distribution in the absorbent matrices are calculated with the aid of a finite difference method applied to both the absorption side and the desorption side. The sector of the absorbent matrix is divided in 16 elements, as shown in Figure A-3. The adjoining fins (1/2 of the fin width on each side) are also divided into corresponding elements. Solving the heat balance for each of these elements gives the element temperature. The procedure is iterative since the temperature dependence of the heat of reaction is also taken into account. The heat

Figure A-3. ABSORBENT MATRIX SECTOR

transferred from one element to the other, to the fin, or to the gas depends on the temperature of the neighboring elements. Therefore, the calculation for the whole field also proceeds iteratively.

The heat transfer through the thermal connection of both absorbent areas via fin sheet, tube wall, and thermal coupling is numerically treated as heat conduction through composite cylindrical walls. For the purpose of this calculation, the rectangular volume, shown in Figure A-1, between the absorbent tube and the desorption tube has been replaced by a cylinder of equal volume.

The governing equations for the heat balance, the heat flux due to thermal conduction, and the element temperatures are described in the equations below.

The heat flux between two adjoining elements (absorbents-absorbents, absorbents-wall, fin-fin) in the radial direction:

$$q_{r+} = kA_{r+} \frac{T_i - T_{i+1}}{R_i - R_{i+1}}, \quad q_{r+} = K_{r+} (T_i - T_{i+1}), \quad K_{r+} = \frac{kA_{r+}}{R_i - R_{i+1}}$$

$$q_{r-} = kA_{r-} \frac{T_i - T_{i-1}}{R_i - R_{i-1}}, \quad q_{r-} = K_{r-} (T_i - T_{i-1}), \quad K_{r-} = \frac{kA_{r-}}{R_i - R_{i-1}}$$

The heat flux in the circumferential direction (absorbents-absorbents, absorbents-fin):

$$q_{\varphi+} = kA_{\varphi+} \frac{T_i - T_{i+1}}{\varphi_i - \varphi_{i+1}}, \quad q_{\varphi+} = K_{\varphi+} (T_i - T_{i+1}), \quad K_{\varphi+} = \frac{kA_{\varphi+}}{\varphi_i - \varphi_{i+1}}$$

$$q_{\varphi-} = kA_{\varphi-} \frac{T_i - T_{i-1}}{\varphi_i - \varphi_{i-1}}, \quad q_{\varphi-} = K_{\varphi-} (T_i - T_{i-1}), \quad K_{\varphi-} = \frac{kA_{\varphi-}}{\varphi_i - \varphi_{i-1}}$$

Heat flux between absorbent element and gas:

$$q_{r-} = K_{G-}(T_G - T_1), \quad K_G = \frac{kA_{I-}}{R_1 - R_1 + \frac{k}{h}}$$

Heat release per element:

$$q_{\text{source}} = CO_2\text{-Rate } V_{\text{elem}}(-\Delta H_R)$$

Heat balance for the ith element:

$$q_{r+} + q_{r-} + q_{\varphi+} + q_{\varphi-} + q_{\text{source}} = 0$$

The resulting element temperature is:

$$T_i = \frac{q_{\text{source}} + \sum K_n T_m}{\sum K_n}$$

with $n = r+, r-, \varphi+, \varphi-$, and correspondingly, $m = i+1, i-1, \varphi+1, \varphi-1$.

Heat flux through the walls and thermal coupling:

$$q_{TC} = UA_W(T_{W,Abs} - T_{W,Des}), \quad U = \frac{1}{2R_W \sum \frac{\ln(r_o/r_i)}{k_i}}$$

Nomenclature:

i	-	Fin sheet, tube wall, thermal coupling
T	-	Temperature, °C
q	-	Heat flux, W
k	-	Thermal conductivity, W/m-°K
h	-	Film coefficient, W/m ² -°K
r _o , r _i	-	Outer, inner radius of i, m
φ	-	Circumferential position, m

A	-	Area, perpendicular to the direction of the heat flux, m^2
U	-	Heat transfer coefficient, thermal connection (fin sheet, tube wall, thermal coupling), $W/m^2 \cdot ^\circ K$

Subscripts signify:

I	-	Inner absorbent surface
i	-	ith element
W	-	Tube wall
G	-	Gas
r+, r-	-	Positive and negative radial directions, respectively
$\varphi+$, $\varphi-$	-	Positive and negative circumferential directions, respectively
Abs, Des	-	Absorption, desorption side

END

**DATE
FILMED**

10 / 7 / 92