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THE MAGSORB PROCESS FOR BULK SEPARATION OF CARBON DIOXIDE

Progress Report for the Period November 28, 1989-February 27, 1990

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Morgantown Energy Technology Center
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SUMMARY

The work performed during the first quarterly reporting period (November 28, 1989 through February 27, 1990) on the research program, "The MAGSORB Process for Bulk Separation of Carbon Dioxide," is presented in this report. This research program 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 is to investigate the removal of carbon dioxide from a fuel gas produced by a coal gasifier with a K_2CO_3 -modified MgO sorbent. The work consists of the measurement of the capacity and rates of absorption of the sorbent 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 will be studied.

During the first quarter of this program, the Test Plan was prepared and presented for discussion at the Morgantown Energy Technology Center. After modifications, the Test Plan was approved and is presented as an Appendix in this report.

Also this quarter, the thermobalance was prepared for the experimental program, the first batch of sorbent was formulated and subjected to preliminary CO_2 absorption/desorption thermobalance tests. These tests showed significant CO_2 absorption at 800°F at pressures above 400 psi.

Bechtel National, Inc. has begun the systems analysis of an overall coal-to-methanol process incorporating the MAGSORB Process. Their initial findings indicate that the rate of the highly exothermic CO_2 absorption by MgO may be heat-transfer limited. This will necessitate special methods to remove heat

from the CO₂ absorption step. These findings are being considered in relationship to the design of the reactor for the cycle testing to be performed in this program.

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INTRODUCTION

Gasification of coal for synthesis gas production yields a mixture of CO , CO_2 , H_2 , H_2O , H_2S , and NH_3 . 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 H_2 content with respect to CO , removal of the bulk of the CO_2 and H_2O , and complete removal of the H_2S . This program deals with the bulk separation of carbon dioxide by application of the novel MAGSORB process.

In the MAGSORB process, the CO_2 is removed from raw fuel gases by a $\text{MgO}/\text{K}_2\text{CO}_3$ sorbent at elevated temperature (650° to 1000°F) and pressure (300 to 850 psi) to match with pressurized coal gasification and high-temperature water-gas shift operations. The CO_2 removal is conducted in a swing-bed absorption/desorption cycle in which MgO absorbs the CO_2 and the MgCO_3 -containing spent sorbent is regenerated either by decreasing the pressure or by elevating the temperature to convert the MgCO_3 to MgO and CO_2 .

The overall objective of this program is to evaluate and develop a high-temperature process for CO_2 separation using a $\text{MgO}/\text{K}_2\text{CO}_3$ sorbent, which has the potential to significantly reduce the capital and operating costs for converting raw fuel gas to synthesis gas.

The specific objectives of this study will address the following topics:

- Preparation of a CO_2 sorbent material composed of MgO modified with K_2CO_3
- Investigation of the CO_2 absorption and desorption rates of the $\text{MgO}/\text{K}_2\text{CO}_3$ sorbent as a function of the system temperature and pressure
- Determination of the effects of H_2S and NH_3 on the absorption characteristics of the $\text{MgO}/\text{K}_2\text{CO}_3$ 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 result of the absorption/desorption cycles
- Analysis of the experimental data to determine the optimal operating conditions for the CO_2 removal system
- A systems analysis to develop an optimum scheme for integrating the MAGSORB bulk gas separation with selected gasification and gas-upgrading processes

- A technoeconomic analysis and comparison of the novel CO₂ separation scheme with conventional alternatives, performed in conjunction with Bechtel National, Inc.

The objectives of the program tasks, their technical progress during the first quarter (November 28, 1989 through February 27, 1990), and the plans for the next quarter are presented in this report.

TECHNICAL DISCUSSION

Task 1. Test Plan PreparationObjective

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

Summary

The Test Plan for this project, which details 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 program-month. The Test Plan was presented and discussed at the Morgantown Energy Technology Center and it was modified at the request of the Contracting Officer's Representative (COR). The implementation of the modified Test Plan, which is presented in Appendix A, was begun in January 1990.

Task 2. Facility Preparation and Equipment ModificationObjective

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

Summary

The minor modifications of existing IGT equipment that are required to perform the test program were completed. All of the initial testing will be performed using an existing thermobalance. This unit was tested this quarter by measuring the weight loss versus time of the decomposition of a sample of MgCO_3 . The system operated satisfactorily with the weight loss as measured by the thermobalance agreeing with the value determined using an analytical balance within $\pm 2\%$.

Construction of the packed-bed has not begun due to the necessity of possible modification of the design as will be discussed under Task 8.

Plans for Next Quarter

The modifications to the thermobalance have been completed and preliminary checks indicate that the apparatus is working satisfactorily. The scheduled construction of the packed-bed reactor has been postponed until the preliminary design work in Task 8 and initial data from the thermobalance tests are available to finalize the design. Therefore, no further work on this task is required at this time.

Task 3. Preparation of Sorbent Material

Objective

The purpose of this task is to prepare the primary reference sorbent to be tested as well as compositional variations of this sorbent and a standard sorbent material, consisting of unmodified MgO pellets, to be used for comparison. The sorbents to be used in the experimental tests include the following:

- A MgO standard - 3.2 mm pellets of magnesia from Alpha Chemicals
- A K_2CO_3 modified MgO reference sorbent with an approximate Mg:K molar ratio of 29/1
- A K_2CO_3 modified MgO sorbent with an approximate Mg:K molar ratio of 26/1
- A K_2CO_3 modified MgO sorbent with an approximate Mg:K molar ratio of 32/1

Summary

This quarter, the material required to prepare the sorbent was received and the first batch of sorbent pellets was prepared. The materials used were:

- $4MgCO_3 \cdot 3Mg(OH)_2 \cdot 34H_2O$ - ALPHA Chemical No. 305950, Reagent Grade
- KOH - ALPHA Chemical No. 87798, Ultra-Pure Grade

A solution of 50 wt% KOH was prepared with distilled water, and 500 g of $4MgCO_3 \cdot 3Mg(OH)_2 \cdot 34H_2O$ was added to 84 g of the KOH solution. Additional distilled water was added to obtain a consistency that allowed good extrusion. This mixture was extruded into 1/8 in. pellets that were air dried before they were calcined at 900°F for 30 min. The resulting pellets were analyzed by x-ray diffraction and found to be composed of K_2CO_3 and MgO; there

was no evidence of water of hydration as was found in the material prepared in the previous program. Based on the amounts of material used, the calculated molar composition is one mole of K_2CO_3 per 14.3 moles of MgO .

Two absorption/desorption tests using pure CO_2 were conducted with the sorbent. These shakedown tests were performed mainly to test the functioning of the thermobalance. The results from these tests are shown in Figures 1 through 3.

In Test 61097-1-06, the sample of sorbent pellets was exposed to CO_2 at a temperature of 800°F and pressures between 150 and 300 psig. As shown in Figure 1, there was little or no gain in weight of the sorbent pellets. However, when the temperature was raised to 1000°F at 150 psig, the sorbent showed a rapid gain in weight. As the pressure of the CO_2 was increased to a maximum of 600 psig, the sorbent continued to gain weight until the weight gain equalled approximately 80% of the theoretical maximum. The weight loss curve for the desorption of this material is shown in Figure 2. This desorption was conducted in nitrogen at atmospheric pressure. At a temperature of 800°F, during the first 10 min of the test, no desorption was observed. When the temperature was raised to 1000°F, the sorbent weight decreased to a level that indicated only about 10% of the MgO remained as the carbonate.

The absorption portion of Test No. 61097-1-07 was conducted in pure CO_2 at 800°F with the pressure varying between 150 and 700 psig. At pressures below 400 psig, there was little absorption of the CO_2 . As the pressure was increased to 400 psig at approximately 35 min into the test, rapid absorption was observed. As shown in Figure 3, the weight of the sorbent increased with increasing CO_2 pressure to a maximum of 107% of the calculated theoretical value. The theoretical value was calculated from the composition of the reactants used in the formulation and does not account for possible nonhomogeneity of the sorbent. An exact theoretical value will be found from the chemical analysis of the sorbent pellets that is currently being performed. The carbonated sorbent sample was removed from reaction zone of the thermobalance at this point and the thermobalance was depressurized and purged with nitrogen. During this period, the material desorbed considerable CO_2 as shown by the data at the 80 min period of Figure 3. After the carbonated sorbent was reinserted into the reaction zone of the thermobalance

TEST NO. 61097-1-06
ABSORPTION

Figure 1. CO₂ ABSORPTION CURVE AS A FUNCTION OF TIME (AT 800°F AND 1000°F)

TEST NO. 61097-1-06 DESORPTION

Figure 2. CO₂ DESORPTION CURVE AS A FUNCTION OF TIME
(AMBIENT PRESSURE AND 800°F AND 1000°F)

TEST NO. 61097-1-07 ABSORPTION/DESORPTION

Figure 3. CO₂ ABSORPTION/DESORPTION CURVE AS A FUNCTION OF TIME
(150-750 PSIG CO₂, 800°F AND 1000°F)

at 800°F in nitrogen, there was no measurable weight loss. However, when the temperature was raised to 1000°F at the 100 min period, the weight of the sample decreased to the original sorbent weight within approximately 35 min.

The results of these shakedown tests are being analyzed to determine why there is little absorption of CO₂ at 800°F at pressures below 400 psig. However, the tests demonstrated that the existing thermobalance is in working order and that the procedure for preparation of sorbent pellets is satisfactory for absorption/desorption of CO₂.

Plans for Next Quarter

Next quarter, the chemical composition and surface area of the prepared sorbent will be determined to decide if it should be chosen as the reference sorbent for the thermobalance tests. In addition, the compositional variations, one with lower K₂CO₃ and one with higher K₂CO₃ content, will be prepared.

Tasks 4 Through 7

No work on these tasks was scheduled for this quarter.

Task 8. Systems Analysis and Technoeconomic Evaluation

Objective

The objective of this task is 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 will entail 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.

Summary

This quarter, Bechtel began an analysis of an overall coal-to-methanol process incorporating the MAGSORB Process. This preliminary assessment indicates that heat transfer may be the controlling factor in the MAGSORB process due to the high exothermicity of the absorption reaction. Bechtel has developed a preliminary design for the MAGSORB reactor that can maximize the heat transfer and minimize the heat input requirements for the regeneration reaction.

Technical Discussion

The absorption reaction of the MAGSORB Process, $\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3$, will be driven so long as the partial pressure of CO_2 in the gas phase exceeds the dissociation pressure of the solid carbonate. Based on published equilibrium data, acceptable levels of CO_2 can be removed from a high-pressure synthesis gas (300 to 800 psig) at temperatures as high as 700° to 800°F. For desorption of the CO_2 , either the temperature must be elevated to raise the dissociation pressure, or the CO_2 partial pressure must be lowered by dilution with a sweep gas or the absolute pressure must be lowered to bring the CO_2 partial pressure below the dissociation pressure of the carbonate.

A critical factor in the process design of the regenerative system is the very high heat of the absorption reaction (~1,000 Btu/lb of CO_2). To maintain absorption, the reaction heat must be dispersed by conduction through the solid or by gas phase convection. Otherwise, localized thermal excursions may stop or tend to reverse the reaction.

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. In both absorption and desorption, the system performance is then totally governed by heat management provided by heat transfer or by thermal accumulation. Accumulation requires that the absorbent be grossly diluted with a thermally conductive heat sink material to maintain the system temperature between the narrow limits (~50°F) imposed by the dissociation pressure/temperature relationship.

The heat transfer requirements of the system are inconsistent with the nature and physical form of the sorbent required for effective absorption. In addition, 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 holdup of treated gas. These opposing requirements will impact the physical form of the absorbent and thus its formulation and development.

The proposed absorption reactor configuration and absorbent form are illustrated in Figures 4 and 5. This configuration relies on continuous transfer of the heat of absorption to supply endothermic energy to a simultaneously occurring desorption. The vessel 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 internal fins imbedded in the absorbent matrix. Thermal conductivity of the absorbent mass may be enhanced if necessary by incorporating metallic or graphite fibers within the cast absorbent. Gas flows through an axial channel formed during the casting of the absorbent. CO_2 transfer into the absorbent is by gas diffusion from the channel through the pore structure of the absorbent matrix. The area of the gas path will be minimized consistent with pressure drop or velocity limitations to reduce treated-gas holdup.

The tubular array is manifolded as illustrated in Figure 5 by the use of a double tube sheet head construction. The cyclic absorption and desorption is conducted entirely within adjoining tubes in the array. In assembling the reactor, the finned inserts will first be formed from thin sheet metal, rolled and glued to form a cylinder diameter less than the inside tube diameter. The elements are then inserted within the tube, heated to destroy the glue and provide a spring fit and then solder-bonded with the tube wall.

The absorbent in paste form is then 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 calcine the absorbent. The mandrel is then removed. The absorbent can be removed by forming a soluble acid salt and flushing the material from the tubes.

The operating process configuration is illustrated in Figure 6 for a single element. In practice, a number of parallel elements would be employed to maintain steady operation of the cyclic system. The hot, clean CO_2 -rich synthesis gas passes upward through one half of the tubular array. CO_2 diffuses into the absorbent to form MgCO_3 and release heat. In the desorption half of the tubular array, residual treated synthesis gas from the absorption cycle is first withdrawn by a compressor. As the pressure is reduced, MgCO_3 decomposes, releasing CO_2 which displaces the treated synthesis gas from the tubes. The reaction cools the absorbent which then withdraws heat from the adjacent absorption tubes. When most of the residual synthesis gas has been displaced, the CO_2 is discharged to atmospheric pressure through a CO_2 letdown power recovery turbine. The pressure and rate at which the CO_2 is withdrawn will depend on the rate of heat transfer from the absorption side of the reactor and may vary throughout the cycle. Turbine performance may be stabilized by phasing a number of parallel absorption/desorption trains.

Figure 4. MAGSORB REACTOR HEAT EXCHANGE CONFIGURATION

Figure 5. MAGSORB REACTOR PRESSURE HEADS

Figure 6. MAGSORB PROCESS

The competitiveness of the MAGSORB Process with solvent-based acid gas removal systems will be determined by its CO₂ removal performance and its thermal efficiency. Both are critically influenced by heat transfer considerations, which in turn strongly influence capital cost. For this reason, the absorbent development must be directed toward meeting the heat transfer needs at minimum cost. The process scheme and reactor configuration described above appears to be a potentially attractive approach.

The high exothermicity of the CO₂ absorption reaction should have little effect on the results of the thermobalance tests due to the high convective heat transfer to the gas from the small quantity of solid sorbent used. However, to determine any possible effects of heat transfer, preliminary experiments will be conducted in two different configurations, one in which the sorbent is contained in a small packed bed inside a wire mesh basket and one in which metal wires are inserted into the powdered sorbent for maximum heat transfer. Heat transfer could have a significant effect in the packed-bed cycle testing that will be performed in the later stages of this program. Therefore, the design of the packed-bed reactors will be deferred until further data are available from the thermobalance tests.

Plans for Next Quarter

In the next quarter the initial comparison of the estimated economics of the MAGSORB process with removal of CO₂ by conventional Rectisol technology, in the production of a synthesis gas for methanol production will be completed. This analysis will then be modified as required by the results of the experimental tests to form the final systems analysis and technoeconomic evaluation of the MAGSORB Process.

APPENDIX A

TASK 1. TEST PLAN PREPARATION

12/89

61097

THE MAGSORB PROCESS FOR BULK SEPARATION
OF CARBON DIOXIDE

TASK 1. TEST PLAN

December 1989

Contract No.: DE-AC21-90MC26364

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INTRODUCTION

Gasification of coal yields a mixture of CO , CO_2 , H_2 , H_2O , H_2S , and NH_3 . 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 H_2 content with respect to CO , removal of the bulk of the CO_2 and H_2O , and removal of substantially all of the H_2S . This program deals with the bulk separation of carbon dioxide by application of a novel MAGSORB process.

Historically, uses for synthesis gas requiring the separation of CO_2 have required that the gas be dehydrated and also delivered at higher pressure than that of the gasification. Since both of these operations entail cooling the gas, scrubbing systems employing liquid solvent absorption at low temperature have been used. It is known that most chemically reactive solvents distinguish only weakly between CO_2 and H_2S ; thus, non-reactive solvents operating under refrigerated conditions are conventionally used for H_2S removal. Subsequent CO_2 rejection may employ either a reactive or non-reactive solvent. The deep cooling and subsequent reheating of the treated gas, along with the requirements of the absorption, impose a significant capital and energy cost.

In the MAGSORB process, the CO_2 is absorbed, before H_2S removal, at elevated temperature (650° to 800°F) and pressure (300 to 850 psia) to match with pressurized coal gasification and high-temperature water-gas shift operations. The CO_2 removal is conducted in a swing-bed absorption/desorption cycle in which the MgCO_3 -containing spent sorbent is regenerated either by decreasing the pressure or by elevating the temperature to decompose the MgCO_3 to MgO and CO_2 . In this sequence of gas separation, MAGSORB has the advantage of greatly reducing the loading, and thus the heat cycles involved in conventional solvent absorptions of H_2S . The MAGSORB process offers significant potential economic advantages over a conventional CO_2 -removal process.

In this program, the work will consist of the preparation of absorbent materials composed of mixtures of MgO and K_2CO_3 and measurement of their rates and capacities for absorption and desorption of CO_2 . The effects of the absorption and desorption processes on the chemical and physical properties of the sorbent will be investigated to determine the cause of any change in the

absorptive/desorptive properties of the material. The bench-scale experiments will be completed by conducting repeated absorption/desorption cycles (at least 20 cycles) on the material, using a gas mixture typical of the effluent of a water-gas shift reactor. At the beginning of the program, Bechtel National, Inc. (BNI) will conduct a systems analysis which is expected to suggest the optimal conditions for integrating the MAGSORB process with selected conventional gasification and gas-upgrading process steps. The results of the systems analysis will be reviewed by IGT to revise, if necessary, the experimental test plan. The experimental data will be used to propose improved absorptive materials and/or methods for their preparation, and to determine absorber operating conditions for maximum absorption with minimum deterioration of the sorbent. In addition, BNI will conduct a systems analysis and a technoeconomic assessment of the MAGSORB process showing its benefits over conventional alternatives, and also identifying the critical design and operating parameters.

The total program approach will include a detailed systems analysis by BNI to suggest optimal conditions for integrating the MAGSORB process with selected gasification and gas-upgrading process subdivisions. The results of the systems analysis will be reviewed by IGT to revise, if necessary, the experimental test plan. The IGT test program will include the formulation and investigation of $\text{MgO}/\text{K}_2\text{CO}_3$ sorbent in existing bench-scale thermobalance and packed-bed apparatus. The test program will study in detail the role of promoters for MgO , rates of CO_2 absorption and desorption, the effect of H_2S and NH_3 , and the performance of the sorbent, including the changes in physical and chemical processes during cyclic operation. The experimental program will conclude with an analysis of the test results, along with a review of the systems analysis and the technoeconomic evaluation. These will show the benefits of the MAGSORB process over conventional alternatives, identify critical design and operating parameters, and recommend research and development topics for further development and commercialization.

TECHNICAL DISCUSSION

The equilibrium partial pressure of CO_2 over a binary mixture of MgO (magnesia) and MgCO_3 , calculated as a function of temperature from thermodynamic data, shows that the equilibrium CO_2 pressure at 800°F is approximately 25 psia. Ideally, the system is reversible, according to the following reaction:

At temperatures above 600°F , the rates of both forward and reverse reactions are expected to be rapid. Furthermore, based on thermodynamic calculations, MgO undergoes no significant degree of reaction with steam, H_2S , NH_3 , or hydrocarbons at the anticipated temperature of 800°F . This is important, because such components will invariably be present in coal-gasification product gases.

With a magnesia-based sorbent, the temperature of maximum CO_2 absorption should lie between 750° and 950°F .^{1,2} The operating pressure should be as high as practicable to offer a partial pressure of CO_2 that provides a driving force for the absorption reaction. Regeneration of the sorbent can be approached by either a thermal-swing or pressure-swing method.

The reactivity of MgO for gas absorption is dependent on the method of preparation. Magnesia is commercially available (in descending order of reactivity) as caustic-calcined magnesia, dead-burned magnesia, and fused magnesia. Caustic-calcined magnesia is produced by thermal decomposition of the basic carbonate, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, at temperatures below 1650°F (900°C), with a temperature range of 932° to 1022°F (500° to 550°C) giving the highest reactivity.³

In the work of Colombo and Mills,² MgO pelletized with 20 wt % KOH was found to yield higher rates and capacities for carbon dioxide absorption than pure MgO . The investigators also noted that the presence of water vapor increased the absorption efficiency at ambient temperature and pressure. The highest CO_2 absorption capacity determined experimentally was about 40% of the theoretical maximum at the point of CO_2 breakthrough.

In a prior IGT study,⁴ the rates of absorption and desorption of CO₂ with MgO-containing materials were determined under conditions simulating both thermal-swing and pressure-swing cycles. This experimental work was performed in a thermobalance with He/CO₂ mixtures and with gas mixtures designed to simulate synthesis gas. Three sorbent formulations were tested, including commercially obtained MgO pellets, a pelletized mixture of MgO with Al(OH)₃, and an activated magnesia made from mixing commercial magnesium carbonate, 4MgCO₃·Mg(OH)₂·4H₂O, with aqueous KOH, followed by calcination at 932°F (500°C). The third method was found to be most effective.

The CO₂ absorption/desorption experiments with this material at the selected conditions (50% CO₂/He, 850°F, 300 psig total pressure) revealed a maximum rate of absorption weight gain equivalent to approximately 0.07 s⁻¹. The rate of desorption weight loss was lower by an order of magnitude.

OBJECTIVES

The overall objective of this program is to further evaluate and develop a high-temperature process for CO₂ separation using a MgO/K₂CO₃ sorbent, which has the potential to significantly reduce the capital and operating costs for converting raw fuel gas to synthesis gas for methanol production.

The specific objectives of the study will address the following technical topics:

- Investigation of the CO₂ absorption and desorption rates of a 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 result of the absorption/desorption cycles
- Analysis of the experimental data to determine the optimal operating conditions for the CO₂ removal system

- A systems analysis to develop optimum schemes for integrating the MAGSORB bulk gas separation with selected gasification and gas-upgrading processes
- A technoeconomic analysis and comparison of the novel CO₂ separation scheme with conventional alternatives.

TEST PLAN

Task 1 of this program is preparation of the test plan and Task 8 is the technoeconomic analysis and comparison of the MAGSORB Process with conventional alternatives. The experimental work and the data analysis and interpretation of results will be performed in Tasks 2 through 7.

Task 2. Facility Preparation and Equipment Modification

After receiving DOE's approval of the test plan, IGT will begin the minor modifications of existing IGT equipment that will be required to perform the test program. The equipment includes the thermobalance shown in Figure 1 and the packed-bed reactor system shown in Figure 2. The thermobalance will be used to investigate the effects of temperature and pressure on the rates of absorption and desorption of CO₂, and the packed-bed reactor will be used to conduct the cyclic absorption/desorption studies.

Although no major modifications are required for the thermobalance, the packed-bed reactor apparatus shown in Figure 2, consisting of a tube furnace containing a 1-in.-ID high-pressure stainless steel reactor tube, will be modified to contain the sorbent bed and provide a uniform gas flow across the inlet to the bed. A new valving system will be added to allow cyclic absorption/desorption operation of the system. The reactor shell for this system will be constructed of 316 stainless steel tubing (0.083-in.-wall-thickness). For those tests in which the feed gas contains H₂S, 446 stainless steel, either in tubing or pipe form, will be used.

Task 3. Preparation of Sorbent Material

IGT will examine two distinct sorbent materials in the experimental program: an MgO standard to be purchased from a commercial supplier, and an activated MgO/K₂CO₃ sorbent prepared at IGT. The MgO standard will consist of 2-mm-diameter pellets of magnesia from Alpha Chemicals (No. 11853).

Figure 1. SCHEMATIC DIAGRAM OF THERMOBALANCE

Figure 2. SCHEMATIC DIAGRAM OF PACKED-BED REACTOR SYSTEM

IGT will prepare the $\text{MgO/K}_2\text{CO}_3$ sorbent to be used in the testing program using the following steps:

1. A solution of 50 wt % aqueous KOH in deionized water will be prepared, using Alfa No. 87798 ultrapure-grade KOH.
2. 100 parts by weight of basic magnesium carbonate, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (Alfa No. 305950 reagent-grade, approximately -325 mesh) will be mixed with 16.8 parts by weight of 50 wt % aqueous KOH, as prepared in step 1.
3. The resulting slurry, which has a KOH:MgO weight ratio of 0.2, will be allowed to equilibrate for 1 hour, then extruded into 1/8-inch pellets.
4. The pellets from step 3 will be calcined in a muffle furnace at 932°F (500°C) for 30 minutes to yield a solid sorbent that is a physical mixture of MgO and $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$. This is designated as the reference mixture.

For comparison with the reference mixture, two additional sorbent mixtures will be prepared; one at a 10% higher concentration of KOH and one at a 10% lower concentration. These sorbents will be tested in initial thermobalance tests at 800°F with the absorption at 850 psia and desorption at 15 psia. These tests are listed in the thermobalance test matrix given in Table 1 as Test Nos. A-10 to A-13. The results of these tests will indicate the dependence of the sorbent properties on the formulation. The formulation of the sorbent to be tested in the complete series of thermobalance and packed-bed cycle tests will be changed only if the comparison of sorbent properties with KOH concentration indicate a radical improvement from the reference formulation.

The composition of the sorbent pellets will be analyzed using X-ray diffraction and by SEM elemental mapping for Mg and K to determine uniformity of distribution before they are used in the test program.

Task 4. Thermobalance Sorbent Tests

The effects of temperature and pressure on the absorption of CO_2 by the $\text{MgO/K}_2\text{CO}_3$ sorbent material prepared in Task 3 will be investigated by

measuring the absorption and desorption rates using a thermobalance apparatus. The temperatures and pressures for conducting these tests are given in the Test Matrix for Task 4 of Table 1. In addition to the tests performed on the sorbent materials prepared in Task 3, the MgO standard will also be tested at the baseline temperature and pressure conditions (Tests Nos. A-6 and A-7).

As shown in Table 1, Tests Nos. A-1 to A-5 will be used to investigate the effect of temperature and pressure variation on the CO₂ absorption rate with no corresponding desorption test. The results of these tests will be used to determine the temperature and pressure of the remainder of the thermobalance tests. Duplicates of the 19 thermobalance tests outlined in the test matrix will be performed for a total of 38 tests.

Once the standard temperature and pressure have been determined, the absorption and desorption tests (Tests Nos. A-6 to A-19) will be performed as pairs to simulate, as nearly as possible, actual system operating conditions. Therefore, in Table 1, the odd-numbered tests A-7, A-9, A-11, A-13, A-15, A-17, and A-19 are desorption tests, using N₂ as a sweep gas, that will be performed immediately after the previous corresponding absorption tests. In Tests Nos. A-10 and A-11, the sorbent used will have a 10% higher concentration of KOH than the reference mixture while in Tests Nos. A-12 and A-13 the sorbent used will have a 10% lower concentration of KOH than the standard sorbent. Most of the absorption tests will be performed using a CO₂/He/H₂O gas mixture. In absorption Tests Nos. A-16 and A-18, H₂S and NH₃, respectively, will be added to the the CO₂/He/H₂O to investigate their effects, if any, on the sorbent performance. In Test No. A-14, a synthesis gas of H₂/CO/CO₂/H₂O at the equilibrium composition for the temperature of the test will be used to measure the effects of H₂ and CO on the sorbent properties.

In a typical thermobalance test, the wire mesh basket will initially be located in the upper, cooled portion of the reactor, in which a downflow of inert gas will be maintained. During this time, the desired temperature and pressure conditions will be established in the lower, heated portion of the reactor in the presence of flowing reactant gases. The test will be initiated by lowering the basket into the heated reaction zone, a procedure that will take about 5 to 6 seconds. The sample will be kept in the heated portion of the reactor for the specified time while its weight is continuously

Table 1. TEST MATRIX FOR TASK 4

Test No.	Sorbent	Temp, °F	Pres, psia	Atmosphere	Objective of Test
A-1	MgO/K ₂ CO ₃	650	300	CO ₂ /He/H ₂ O	effect of temperature
A-2	MgO/K ₂ CO ₃	800	300	CO ₂ /He/H ₂ O	and pressure on
A-3	MgO/K ₂ CO ₃	650	600	CO ₂ /He/H ₂ O	absorption rates
A-4	MgO/K ₂ CO ₃	800	600	CO ₂ /He/H ₂ O	and capacities
A-5	MgO/K ₂ CO ₃	800	850	CO ₂ /He/H ₂ O	using reference KOH conc.
A-6	MgO std.	TBD*	TBD	CO ₂ /He/H ₂ O	absorption on commercial MgO
A-7	MgO std.	TBD	15	N ₂	desorption
A-8	MgO/K ₂ CO ₃	TBD	TBD	CO ₂ /He/H ₂ O	absorption on MgO/K ₂ CO ₃ , reference KOH concentration
A-9	MgO/K ₂ CO ₃	TBD	15	N ₂	desorption
A-10	MgO/K ₂ CO ₃	TBD	TBD	CO ₂ /He/H ₂ O	absorption on MgO/K ₂ CO ₃ , higher KOH concentration
A-11	MgO/K ₂ CO ₃	TBD	15	N ₂	desorption
A-12	MgO/K ₂ CO ₃	TBD	TBD	CO ₂ /He/H ₂ O	absorption on MgO/K ₂ CO ₃ , lower KOH concentration
A-13	MgO/K ₂ CO ₃	TBD	15	N ₂	desorption
A-14	MgO/K ₂ CO ₃	TBD	TBD	CO ₂ /CO/H ₂ /H ₂ O	effect of synthesis gas
A-15	MgO/K ₂ CO ₃	TBD	15	N ₂	desorption
A-16	MgO/K ₂ CO ₃	TBD	TBD	CO ₂ /He/H ₂ O/H ₂ S	effect of H ₂ S
A-17	MgO/K ₂ CO ₃	TBD	15	N ₂	desorption
A-18	MgO/K ₂ CO ₃	TBD	TBD	CO ₂ /He/H ₂ O/NH ₃	effect of NH ₃
A-19	MgO/K ₂ CO ₃	TBD	15	N ₂	desorption

*TBD = To be determined from the results of Tests Nos. A-1 to A-5.

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recorded. The test will be terminated either by raising the basket back to the upper, cooled portion of the reactor or, in the case of desorption, by changing the operating conditions.

At the conclusion of Tests Nos. A-7, A-9, A-15, A-17, and A-19, the solid sorbent will be analyzed as outlined in Task 6 to determine any change in the chemical or physical state of the sorbent due to the absorption/desorption cycle.

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

At the completion of Task 4, IGT will use the analyses of the thermobalance test results to choose the operating conditions for the cycle tests to be performed in the packed-bed reactor. The purpose of these tests is to study the effect of repeated absorption/desorption cycles on the reactivity and physical integrity of the sorbent. Duplicates of three tests that consist of 3, 7, and 20 absorption/desorption cycles will be performed in the packed-bed reactor, for a total of 6 tests. Two tests with up to 7 absorption/desorption cycles will be conducted using a selected concentration of H_2S in the gas mixture for the absorption test phase. All operating conditions of temperature, pressure, gas compositions, and gas flow rates for the cycle testing will be selected in consultation with the COR.

Each test will use a packed bed of the sorbent material contained in a 1-in.-ID tube reactor. As shown in Figure 2, a synthesis gas representing the equilibrium composition expected from a water-gas-shift reactor will be prepared by adding steam to a premixed $H_2/CO/CO_2$ mixture. An equilibrium gas composition will be used to minimize changes in gas composition due to gas phase reaction. The packed-bed reactor will be heated to the desired temperature, and the preheated synthesis gas mixture at the desired pressure will be introduced into the sorbent bed. The effluent CO_2 concentration will be monitored using an infrared gas analyzer, and the absorption phase will be concluded at the point when the CO_2 concentration increases rapidly as it approaches total CO_2 breakthrough. At the conclusion of the absorption phase, the reactor temperature and pressure will be reset as necessary for the desorption phase, and a stream of N_2 , representing low- CO_2 content purge gas, will be introduced into the packed bed. A drop of the CO_2 concentration in the effluent to approximately 10% of the initial value will signal the end of the desorption phase. A single absorption/desorption cycle will consist of

one absorption phase followed by the corresponding desorption phase. At the conclusion of each test, portions of the sorbent from the packed-bed reactor will be analyzed according to the methods outlined in Task 6.

It is recognized that the gas flow rates of both the feed and purge gases will be important in scale-up of the process but the scope of this program does not allow investigation of this parameter.

Task 6. Analysis of Chemical and Physical Properties of Sorbent

To obtain an understanding of the fundamental changes that occur in the sorbent and their impact on its absorption/desorption capability, IGT will analyze relevant chemical and physical properties of the initial $\text{MgO}/\text{K}_2\text{CO}_3$ sorbents prepared in Task 3, the reactive MgO standard, and the sorbent material from the tests indicated in Tasks 4 and 5. The properties to be investigated and the corresponding tests that will be performed are as follows:

- Morphology -- optical microscopy
- Surface Area -- BET analysis using N_2 and CO_2
- CO_2 Content -- chemical analysis
- Crystalline State -- X-ray diffraction

The physical changes that may occur in the sorbent material will be investigated by microscopic examination of the solid for changes in pore shape or size, changes in roundness of the particles and general observation of the physical integrity of the solid. Significant observation will be recorded with photomicrographs. The surface area, a critical parameter in any gas-solid interaction, will be determined from BET analyses of the sorbent with N_2 and CO_2 . The BET analysis with the two gases will be used to measure the pore volume and pore size distribution. X-ray diffraction analysis will be conducted to obtain information on the crystalline phase changes that the sorbent may have undergone and chemical reactions between the solid components of the sorbent.

Up to 7 sorbent samples will be characterized using scanning electron microscopy (SEM) methods. Characterization by SEM includes photomicrographs of external surfaces and internal particle cross sections, with elemental mapping or profiling if needed. Elemental mapping for Mg and K by SEM may be used to determine the uniformity of the distribution of the MgO and K_2CO_3 in the prepared sorbent samples. The samples to be characterized will include:

- Two freshly prepared sorbents from Task 3; one being the reference sorbent preparation and the other being either the commercial MgO or one of the variations on the reference sorbent
- Three sorbent samples from the cycle testing of Task 5
- Two sorbent samples from the cycle testing of Task 5 in which H_2S is added to the gas mixture for the absorption test phase

Crush strength tests will be conducted on freshly prepared sorbent pellets and pellets recovered from the packed-bed tests in Task 5.

Task 7. Test Data Analysis and Interpretation

IGT will correlate test conditions, consisting of the temperature, pressure, type of sorbent used, and gas composition, with the test results, consisting of the rate of absorption/desorption of CO_2 . In addition, the results of the tests performed in Tasks 4 and 5 will be interpreted in light of the analyses of the chemical and physical properties of the sorbent performed in Task 6. In all phases of the experimental testing, IGT will analyze the test data as soon as possible after completion of the test. Rapid analysis of tests results will be used to provide feedback regarding the sorbent preparation and design of the testing program, as well as for the subcontract systems analysis and technoeconomic evaluation work at BNI.

Task 8. Systems Analysis and Technoeconomic Evaluation

At the beginning of the program, BNI will conduct a systems analysis of an overall coal-to-methanol process incorporating the novel CO_2 separation scheme, to suggest the optimal conditions for testing the MgO/ K_2CO_3 sorbent. IGT will evaluate these suggestions and modify the test program, if necessary.

IGT will analyze the parametric test results showing the rates and capacities of absorption/desorption of CO_2 and, in conjunction with BNI, select the operating conditions of temperature and pressure that will yield the most favorable sorbent capacity, absorption/desorption rates, and sorbent

endurance for a commercial CO₂ removal system. These data will be used as the basis for preparing a technoeconomic analysis of the MAGSORB system and its comparison with conventional processes. This analysis will also include an assessment of future research and development leading to the scale-up and commercialization of the system.

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