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THE MAGSORB PROCESS FOR BULK SEPARATION OF CARBON DIOXIDE

Progress Report for the Period November 27, 1991 - February 27, 1992

DOE/MC/26364--3231

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

For

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June 1992

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Printed in the United States of America

**Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161**

**NTIS price codes
Printed copy: A01
Microfiche copy: A01**

SUMMARY

The work performed during the ninth quarterly reporting period (August 28 - November 27, 1991) on the research program, "The MAGSORB Process for Bulk Separation of Carbon Dioxide," is reported in detail in the Final Report, submitted on February 27, 1992. A summary of the quarterly work 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 are being studied.

During the ninth quarter of this program, the construction, shakedown, and operation of the packed-bed reactor system for cycle testing of MAGSORB was completed. MAGSORB batch 24 was prepared for cycle tests according to the same procedure as batches 22 and 23. In this procedure, a slurry was prepared from $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ and aqueous KOH , the slurry was extruded and dried, the dried extrudate was crushed and blended with NH_4HCO_3 as a pore structure control agent, the powder was pelletized, and the pellets were calcined at $500^\circ C$ for 30 minutes. Based on shakedown operations, the selected test procedure consisted of the following steps:

- MAGSORB bed is captured between plugs of glass wool in reactor; swept volumes above and below bed are filled with Kimax beads
- Reactor is heated to 800°F under N₂ at 300 psig for leak-testing
- Reactor is depressurized to atmospheric pressure and isolated (bypass mode)
- CO₂-containing reactant gas is flowed in bypass until CO₂ concentration indicated on infrared monitor is steady.
- Gas flow is diverted to reactor at atmospheric pressure; MAGSORB absorbs CO₂ while pressure rises to 300 psig
- Gas flow is maintained at constant input rate until CO₂ output concentration indicates 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

Six packed-bed absorption/desorption cycle tests were conducted, three with three absorption/desorption cycles, two with seven cycles, and one with 20 cycles. All of the tests were operated at 300 psig system pressure, which corresponded to a CO₂ partial pressure of 155 psi.

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.

Thermobalance testing was completed during this quarter. Two MAGSORB batches (25 and 26) were prepared and tested. Batch 25 was prepared with a Mg:K atomic ratio of 5.7:1, and batch 26 with a Mg:K ratio of 7.5:1. Duplicate tests were performed with each sorbent at 800°F and 300 psig, using

the standard gas (42% CO₂, 42% He, 16% H₂O). The results did not differ significantly from those obtained with Batch 23 (Mg:K ratio of 6.8:1).

Updated experimental data were provided to Bechtel National, Inc., for completion of the preliminary technoeconomic analysis. Bechtel completed a cost estimate for the MAGSORB unit in a coal gasification/methanol synthesis plant, and comparison of the economics of gas conditioning with and without MAGSORB. 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 annual 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.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
TECHNICAL DISCUSSION	2
Task 1. Test Plan Preparation	2
Objective	2
Summary	2
Task 2. Facility Preparation and Equipment Modification	2
Objective	2
Summary	2
Task 3. Preparation of Sorbent Material	3
Objective	3
Summary	3
Task 4. Thermobalance Sorbent Tests	3
Objective	3
Summary	4
Task 5. Cycle Tests of Sorbent in Packed-Bed Reactors	4
Objective	4
Summary	4
Task 6. Analysis of Chemical and Physical Properties of Sorbent	4
Objective	4
Summary	4
Task 7. Test Data Analysis and Interpretation	4
Task 8. Systems Analysis and Technoeconomic Evaluation	5
Objective	5
Summary	5

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 deals with the bulk separation of carbon dioxide by application of the novel MAGSORB process.

In the MAGSORB process, the CO₂ is removed from raw fuel gases by a MgO/K₂CO₃ 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 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 overall objective of this program is to 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.

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

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

TECHNICAL DISCUSSION

Task 1. Test Plan Preparation

Objective

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 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 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 laboratory packed-bed reactor for the cycle tests to be performed in Task 5.

Summary

Modifications of existing equipment to accommodate a packed-bed reactor were completed. Details are provided in the Final Report.

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
- A K_2CO_3 -modified MgO reference sorbent with an approximate Mg:K molar ratio of 7:1
- A K_2CO_3 -modified MgO sorbent with an approximate Mg:K molar ratio of 6:1
- A K_2CO_3 -modified MgO sorbent with an approximate Mg:K molar ratio of 8:1

Summary

This quarter, three sorbent batches (24, 25 and 26) were prepared. Batch 24 was a large batch prepared for packed-bed tests. Batch 25 was prepared with an Mg:K ratio of 5.7:1, and Batch 26 with an Mg:K ratio of 7.5:1. Details are provided in the Final Report.

Task 4. Thermobalance Sorbent Tests

Objective

The objectives of this task are to determine the operating conditions of temperature and pressure to be used in the absorption and desorption of CO_2 by the sorbent and to investigate the effect of variation of the K_2CO_3 content of the MgO sorbent. Once the operating conditions and sorbent composition are fixed, the rates of absorption and desorption are determined. All of the tests in this task are conducted in a high-pressure thermobalance containing the sorbent in a fixed bed exposed to excess flowing gas.

Summary

This quarter, four successful thermobalance tests were performed, two each with batches 25 and 26, at 800°F and 300 psig, in standard gas. Details are provided in the Final Report.

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

Objective

The objective of this task is to perform absorption/desorption cycle tests in a laboratory packed-bed reactor to determine the effects of cycling on the reactivity and physical integrity of the sorbent. Tests of 3, 7, and 20 cycles are to be performed in duplicate with a simulated syngas atmosphere, for a total of 6 tests.

Summary

The packed-bed reactor was completed and shaken down. Six packed-bed tests were performed on MAGSORB Batch 24. Packed-bed cycle testing has been completed, and details are provided in the Final Report.

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

Analyses were performed on MAGSORB batches before and after testing in the thermobalance and packed-bed reactor. Details on this task are provided in the Final Report.

Task 7. Test Data Analysis and Interpretation

Analysis and interpretation of the data obtained this quarter have been 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 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 entails 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 task was completed during the quarter. Bechtel National, Inc. completed a cost estimation of the MAGSORB operations, and projected savings of \$91.5 million in capital cost, and \$9.1 million in annual operating cost for the methanol plant using MAGSORB and a small Rectisol plant for H₂S removal, compared to a plant using Rectisol only. Details are provided in the Final Report.

END

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