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THE MAGSORB PROCESS FOR BULK SEPARATION OF CARBON DIOXIDE

Progress Report for the Period February 28-May 27, 1991

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MASTER

SUMMARY

The work performed during the sixth quarterly reporting period (February 28 - May 27, 1991) 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 sixth quarter of this program, work continued on the preparation of homogeneous batches of sorbent. It had previously been found that there was not consistent agreement between the Mg/K ratios calculated from the amounts of reagents used and the ratios determined by chemical analysis using atomic absorption spectrometry. In our investigation of the causes of these inconsistencies, we also found that there was an unacceptably high variation in the Mg/K ratio among the individual sorbent pellets.

This quarter, sorbent pellets that had shown excessive variation in the Mg/K ratio were ground and the powder mixed to produce a uniform material. This material was then pelletized with a compaction device and the pellets checked for composition and reactivity. Although this procedure produced pellets with consistent Mg/K ratios, thermobalance tests showed reduced

reactivity. This reduction in reactivity is thought to be due to a reduction in pore size during the pelletization. However, because most of the previous reactivity measurements were conducted with pellets that had a nominal Mg/K ratio of 7 rather than 6 which is the value for these pellets, the change in Mg/K ratio cannot be ruled out as a possible cause of the reduced reactivity. Next quarter, previously prepared pellets with a nominal Mg/K ratio of 7 will be finely ground and the powder mixed prior to pelletizing in a compaction device. Reactivity tests of these pellets should decide whether the Mg/K ratio or closing of pores due to the compaction is the cause for the reduced reactivity. If the pellets show closing of pores due to the compaction operation is the cause of the reduced reactivity, pellets will be prepared with a blowing agent such as ammonium carbonate to increase the porosity and increase reactivity.

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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 MgO/K_2CO_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 MgO/K_2CO_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 MgO/K_2CO_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 MgO/K_2CO_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
- A technoeconomic analysis and comparison of the novel CO_2 separation scheme with conventional alternatives, performed in conjunction with Bechtel National, Inc.

The objectives of the program tasks, their technical progress during the sixth quarter (February 28 through May 27, 1991), and the plans for the next quarter are presented in this report.

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

Summary

The construction of the packed-bed reactor was delayed pending solution of the problem of sorbent inhomogeneity.

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

Following preparation of previous batches of sorbent, we found that the Mg/K ratios calculated from the amounts of reagents used and the ratios determined by chemical analysis using atomic absorption spectrometry were not consistently in agreement. Analyses of multiple pellets from each batch also revealed a gross inhomogeneity in the material with respect to potassium content. Because of this we have investigated alternative methods of mixing the ingredients to achieve chemical homogeneity at the desired Mg/K ratio. The results of these efforts are summarized in Table 1.

At this point, a determination was made to prepare pellets by crushing, remixing, and repelletizing previously calcined batches, in order to ensure a uniform MAGSORB material for resumed 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 ten-pellet sample of this batch of sorbent was analyzed and found to be acceptably uniform with respect to Mg/K ratio. The Mg/K ratio was 6.68, and the relative standard deviation in Mg/K ratio among ten randomly selected pellets was 3.7%. This degree of variation is well within the error limits of the analytical technique. The CO_2 content of the batch was 11.1%, which, after accounting for K_2CO_3, indicated that about 8% of the magnesium was present as $MgCO_3$.

Table 1. VARIATION IN MG/K MOLE RATIO AMONG SORBENT BATCHES

		Mg/K Ratio			
Batch	Comments	Calc	Meas	Meas/ Calc	% Rel Std Dev[a]
13	Added powder to KOH solution in homogenizer; analyzed before calcining	6.0	6.6	1.1	9.7
"	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
"	After calcining in tube furnace in 75% H_2/25% CO_2	7.0	9.3	1.3	21.0
"	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
"	Extruded paste	6.0	8.9	1.5	21.7
"	Pellets air-dried overnight; not calcined	6.0	5.7	0.95	27.9
16	Revised mixing order: slurry $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ in water, then add KOH solution; unthickened paste	6.0	6.2	1.03	1.9
"	After thickening and extrusion	6.0	7.1	1.2	7.7
"	After overnight air-drying of pellets	6.0	7.8	1.3	32.6
"	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
"	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., cont. VARIATION IN MG/K MOLE RATIO AMONG SORBENT BATCHES

Batch	Comments	Mg/K Ratio Calc	Meas	Meas/Calc	% Rel Std Dev[a]
18	Calcined pellets from Batch 16 were crushed, the powder blended and pellets reconstituted in a compressive pelletizer	6.0	6.7	1.1	3.7
19	Crushed uncalcined pellets from Batch 11, powder pelletized as for Batch 18 and then pellets were calcined	6.0	6.6	1.1	5.7
20	Paste prepared from reagents, slurry air dried, ground, and mixed; powder was rewetted and paste extruded into pellets	6.0	9.1	1.5	24.7

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

To prepare Batch 19, pellets from a previous batch (Batch 11A) which had not yet been calcined were crushed, homogenized, and pelletized in the pellet press used to prepare the previous batch 18. 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. Ten batch 19 pellets were randomly selected and analyzed, showing an average Mg/K mole ratio of 6.64 with a relative standard deviation of 5.7%. This confirmed acceptable uniformity of composition for the batch.

To prepare more reactive but uniform composition pellets, a new MAGSORB (Batch 20) was prepared from reagents and dried in air. 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 of carbon dioxide absorption, and the composition of the ten-pellet sample showed an average Mg/K ratio of 9.1 with a standard deviation of 24.7%.

Plans for Next Quarter

Prepare batches of sorbent by: grinding previously prepared pellets to produce a uniform composition powder, pelletizing this material (with and without a blowing agent such as ammonium carbonate) using a compaction pelletizing device, and calcining the resultant pellets slowly in air.

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 will be determined. All of the tests in this task are conducted in a high-pressure thermobalance.

Summary

Five thermobalance tests were performed during the quarter. Three were conducted using the Batch 18 pellets. Figures 1-3 show the weight gain-vs-time plots for these tests. All of the tests were conducted on the absorption cycle at 800°F and 300 psig using a gas atmosphere of 41.5% CO_2/41.5% He/17% steam. Test 0214 resulted in a 39% weight gain over 32.3 minutes, which represented 59% of the theoretical limiting weight gain. Test 0215 was a duplicate of Test 0214, and showed a similar weight gain of 37% absolute, or 56% of the theoretical limit, but at a 50% slower rate. The rate of weight gain in both of these tests was low compared with previous tests using MAGSORB prepared from extruded slurry batches with a 7:1 Mg-to-K ratio. In order to determine whether this may have been due to decreased surface porosity caused by compressive pelletization, Test 0217 was made with batch 18 pellets broken into pieces approximately the size of the original pellets to increase surface area and expose fresh surface. However, the results of Test 0217 actually showed further decreased reactivity, with a weight gain of only about 22% in

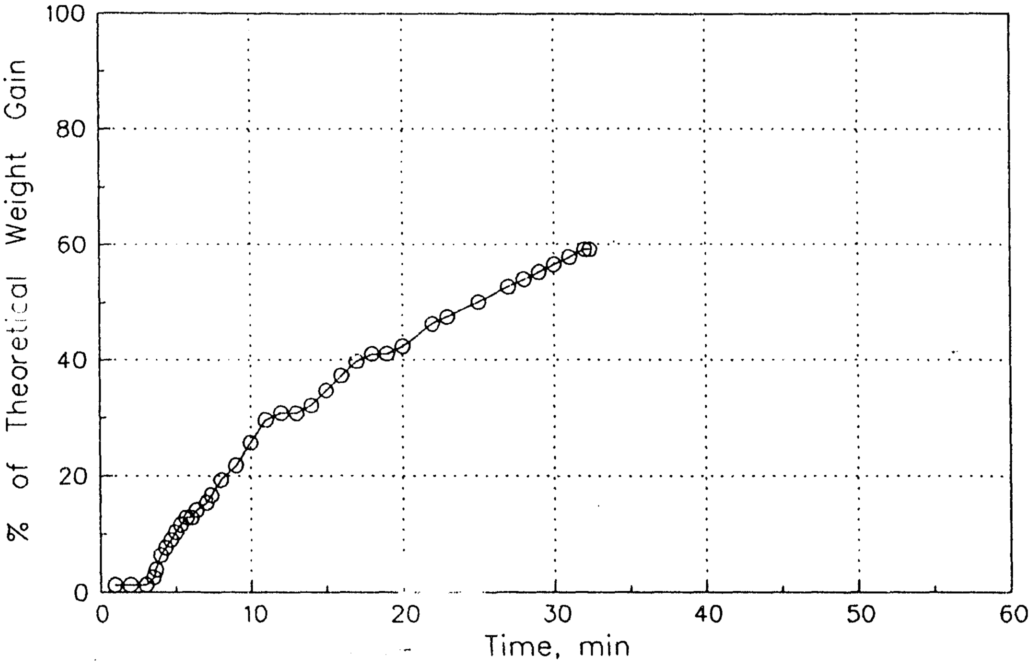

Figure 1. CO_2 ABSORPTION IN THERMOBALANCE TEST 0214 (BATCH 18)

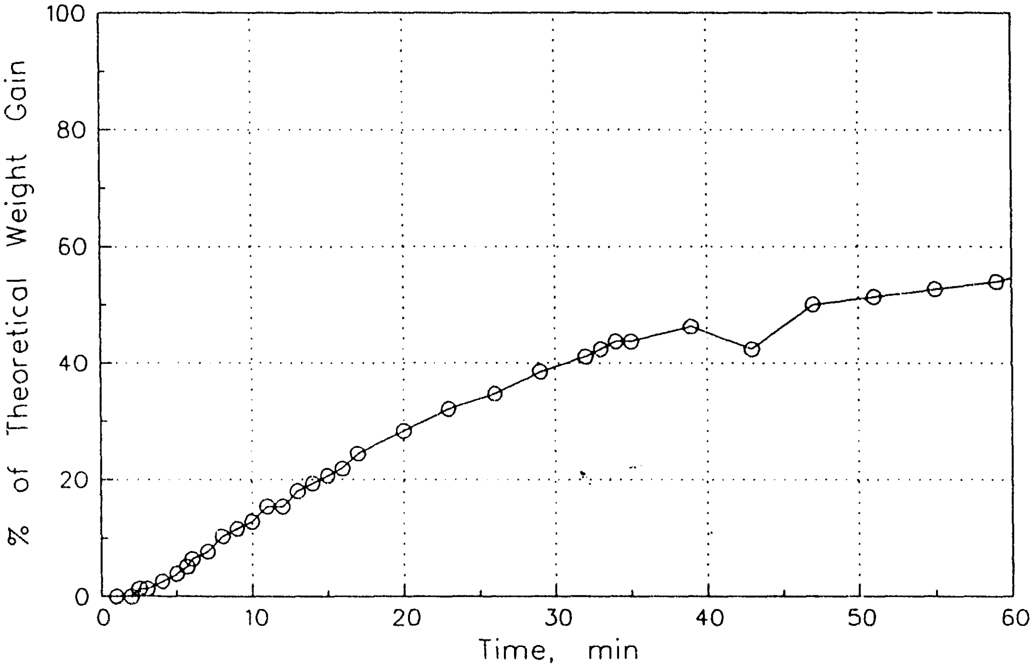

Figure 2. CO_2 ABSORPTION IN THERMOBALANCE TEST 0215 (BATCH 18)

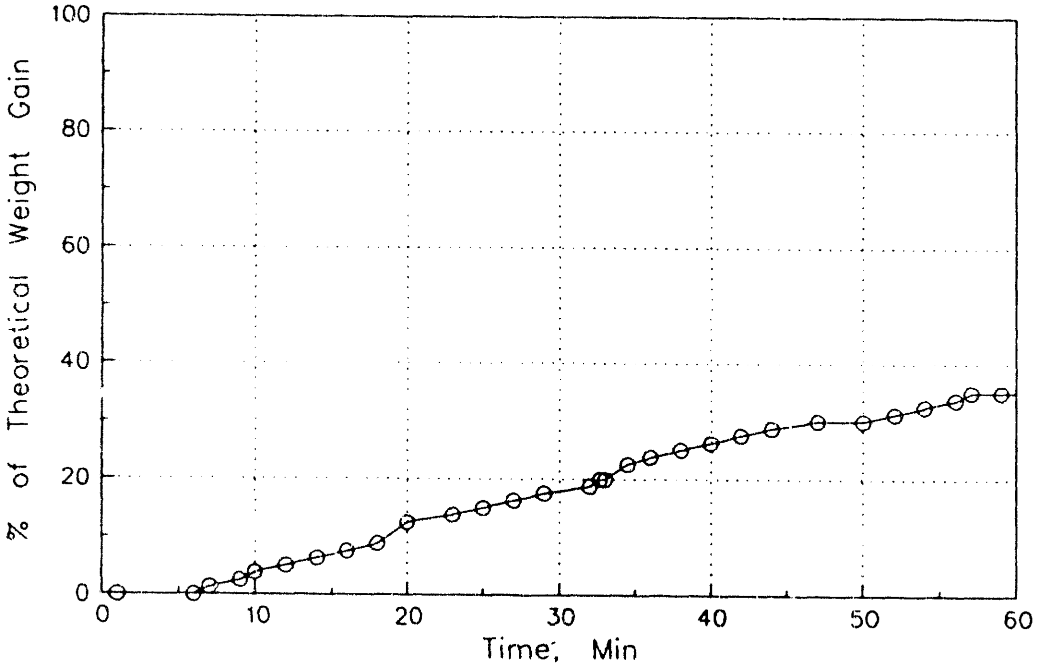

Figure 3. CO_2 **ABSORPTION IN THERMOBALANCE TEST 0218 (BATCH 19)**

30 minutes, as shown in Figure 3. The reason for this deterioration of reactivity is not clear.

One thermobalance adsorption test (Test 0218) was conducted with Batch 19, which resulted in the weight gain-vs-time curve shown in Figure 4. The test conditions were 50% CO_2/He at 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, may destroy the reactivity of the MAGSORB. The compression of the material may be collapsing the pore structure and inhibiting the access of reactants to the inside of the pellet.

One thermobalance adsorption test (Test 0218) was conducted with Batch 20, which resulted in the weight gain-vs-time curve shown in Figure 5. The test conditions were 50% CO_2/He at 800°F and 300 psig. The results indicate a reactivity similar to that previously observed for Batch 18, higher than that of Batch 19 but much lower than that of earlier batches such as Batches 1 and 2. The common factor in Batches 18-20 is the Mg/K ratio of 6:1,

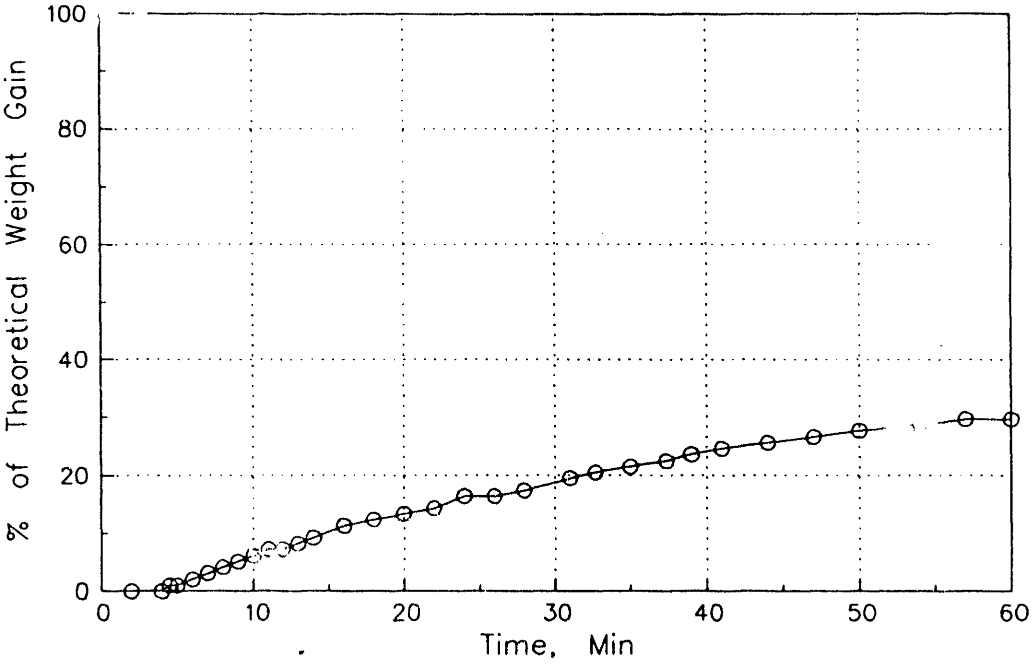

Figure 4. CO_2 ABSORPTION IN THERMOBALANCE TEST 0217 (BATCH 18)

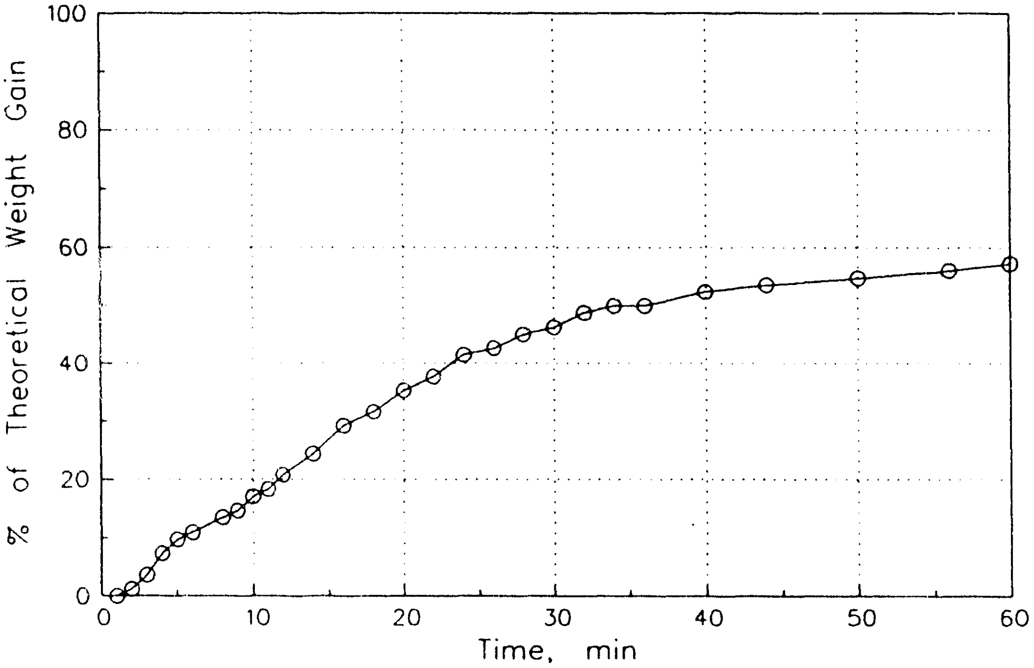

Figure 5. CO_2 ABSORPTION IN THERMOBALANCE TEST 0219 (BATCH 20)

and the results indicate that the Mg/K ratio, rather than the method of pelletization, may be the cause in the decrease in reactivity and capacity.

Plans for Next Quarter

Conduct thermobalance tests to determine the cause of reduced reactivity.

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

No work was scheduled for this task during the quarter.

Task 6. Analysis of Chemical and Physical Properties of Sorbent

The only analyses performed this quarter were the magnesium and potassium contents of the modified sorbents. These results are reported in connection with the results of the testing of these sorbents.

Task 7. Test Data Analysis and Interpretation

The 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 CO_2 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 CO_2 by conventional Rectisol technology using refrigerated methanol scrubbing, in the production of a synthesis gas for methanol production.

Summary

No work was scheduled on this task for this quarter.

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