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A CALCIUM OXIDE SORBENT PROCESS
FOR BULK SEPARATION OF CARBON DIOXIDE

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Phase II research involves a scale-up from microgram to gram quantities of sorbent and a switch from the electrobalance reactor to a fixed-bed reactor with capability for feed and product gas analysis. At the end of the previous quarter, a tentative method of product gas analysis involving only the thermal conductivity detector had been developed and the chromatograph had been calibrated using standard gas mixtures of known composition. The fixed-bed reactor system had been completed and a single reaction test involving the calcination of dolomite had been completed.

This report discusses our continuing effort to refine the chromatograph analytical technique. A simpler analytical method requiring two columns (instead of three) and one sampling valve (instead of two) is currently being used. The nickel-catalyzed methanizer has been replaced by a ruthenium-catalyzed methanizer. Because of its lower operating temperature the ruthenium system is less prone to fouling due to carbon deposition. With the methanizer, the flame ionization detector can be used for CO and CO₂ analysis, thus providing improved sensitivity for these compounds.

A number of reaction tests involving one complete calcination/carbonation cycle were completed during the quarter. The feed gas for these tests consisted of CO₂ in N₂. Standard CO₂ breakthrough curves were obtained, thereby proving the ability of the calcined dolomite to remove CO₂ at the temperatures and pressure of interest. Near the end of the quarter, three tests in which the feed gas contained water (steam) as well as CO₂ and N₂ were completed. While no quantitative data was obtained from the tests because of gas leaks, we did confirm that steam injection was feasible. In addition, small quantities of H₂

EXECUTIVE SUMMARY

This research project is investigating the technical feasibility of a high-temperature, high-pressure (HTHP) process for the bulk separation of CO_2 from coal-derived gas. The original contract for two years was awarded in September 1989 as a result of solicitation number DE-RA21-89MC26040 entitled "Novel Concepts for Bulk Separation of Gases in Coal Gasification Systems." Two no-cost extensions without a change in the statement of work extended the performance period by six months to March 1992. At that time a two-year contract extension with an enlarged scope of work and additional funding was approved so that the research is now scheduled to end in March 1994.

Phase I research, in which an electrobalance reactor was used to establish the technical feasibility of the regenerable sorbent process, was completed in March 1992 and results have been fully described in earlier quarterly reports. In Phase I, the calcination and carbonation characteristics of three calcium sorbents were studied as a function of calcination and carbonation temperature and pressure, mol fraction CO_2 in the carbonation gas, and carbonation background gas composition. Desirable reaction conditions required for high reactivity and good sorbent durability were determined. Multicycle tests consisting of as many as ten complete calcination and carbonation cycles were completed. Indirect evidence which suggested that the water-gas shift reaction occurred simultaneously with CO_2 removal was found. Occurrence of the simultaneous reactions created the possibility of a direct one-step process for the manufacture of hydrogen from coal-gas while at the same time separating a concentrated stream of CO_2 . The concentrated CO_2 stream could be quite significant if, in the future, environmental regulations restrict atmospheric CO_2 emissions.

were detected in the reactor product. Presumably the H_2 was formed as a result of the following pair of reactions

Small concentrations of CO had been detected in earlier tests involving CO_2/N_2 feed. The presence of product H_2 therefore confirmed that the water-gas shift reaction would occur at the conditions of interest.

ANALYTICAL PROCEDURE

At the beginning of the present quarter, the method used for product gas analysis required three chromatograph columns, two automated multi-port gas sampling valves, and the thermal conductivity detector (TCD). Use of the flame ionization detector (FID) had been temporarily suspended because of the extreme sensitivity of the nickel-catalyzed methanizer which converted CO and CO_2 to CH_4 for subsequent FID analysis. Although the method appeared to be quite reliable, it did not have the desired sensitivity for low concentrations of CO and CO_2 . A complete description of the analytical method being used at the beginning of the quarter was presented in the previous quarterly report.

Several changes were made in the analytical method during the quarter. A new column, Carboxen 1000 (CBX), capable of separating H_2 , N_2 , CO, and CO_2 was installed. This single column replaced the previous Hayesep Q and mol sieve columns, and also eliminated the need for the six-port gas sampling valve. The original nickel-catalyzed methanizer was replaced with a more robust ruthenium-catalyzed methanizer. Since ruthenium catalyzes the methanation reaction at a lower temperature, the problem of catalyst fouling due to carbon deposition was lessened.

Availability of the methanizer permitted us to use the FID, and improve the analytical sensitivity for low concentrations of CO and CO₂. Finally a three-way valve was installed between the TCD and the methanizer. This valve permits us to bypass the methanizer and FID when the product gas contains high concentrations of CO and CO₂, and then switch the methanizer and FID into the analytical train when low CO and CO₂ concentrations are expected.

The new sampling and separation arrangement is shown in Figure 1. Valve VO determines whether the reactor feed or product gas is being sampled. With VO in the position shown, reactor product is sampled. In step 1, reactor product enters the ten-port sampling valve (V1), flows through the sample loop, and to vent. Primary argon carrier gas (C1) enters V1 and flows, in turn, through the carboxen 1000 column (CBX), the thermal conductivity detector (TCD) and then either through the methanizer and flame ionization detector (FID) to vent, or directly to vent from the TCD. Secondary argon carrier gas enters V1 and flows through the Hayesep N (HSN) column and to vent.

Sampling is initiated by switching V1 to the position indicated in step 2. Reactor product now flows directly into and out off V1 to vent. Primary carrier C1 picks up the sample from the sample loop and flows into HSN where trace H₂O which escaped condensation is trapped. Argon plus H₂, N₂, CO and CO₂ pass through HSN to CBX where separation of the four reactor products occurs. Reactor products are eluted in the order H₂, N₂, CO, and CO₂ and transported by C1 to the analytical train. Analysis of H₂, N₂, and high concentrations of CO and CO₂ is accomplished using the TCD. Low concentrations of CO and CO₂ are analyzed using the more sensitive FID. Secondary carrier gas C2 flows into and out of V1 to vent during this step.

GC OPERATION — STEP TWO

GC OPERATION — STEP ONE

GC OPERATION — STEP THREE

Figure 1. Revised GC Sampling Sequence.

After H_2 , N_2 , CO, and CO_2 have eluted from HSN but before H_2O is eluted, V1 is switched to the position shown in step 3. Note that valve positions in steps 1 and 3 are identical. Reactor product again flows into V1, through the sample loop, and to vent. C1 flows into V1 and then through CBX where separation of H_2 , N_2 , CO and CO_2 occurs. As these components are eluted from CBX, they pass individually through the appropriate configuration of the sample train. During this period C2 flows through HSN to backflush H_2O to vent. When backflushing is complete and when reactor products have been analyzed, V1 is switched back to the step 2 position to begin analysis of the next sample.

GC operating conditions currently being used are summarized below:

1. Temperature of V1 and sample loop	55°C
2. Column temperature	85°C
3. TCD temperature	80°C
4. Methanizer temperature	300°C
5. FID temperature	250°C

The overall time between samples can be as short as 8 minutes. V1 is programmed to remain in the step 2 position for 3.2 minutes, thus providing at least 4.8 minutes to complete backflushing H_2O from HSN. Retention times for the four components using the above operating conditions are:

H_2	0.69 min
N_2	1.26 min
CO	1.53 min
CO_2	6.05 min

This new valve and column arrangement is simpler than the previous configuration. If the ruthenium methanizer proves to be reliable over

the long term so that the FID can be used to provide the desired low concentration sensitivity, then this new method should improve the accuracy and reliability of the analysis.

The above changes required that the analytical system be recalibrated. Additional calibration mixtures were purchased to provide a wider range of concentrations than previously available. The compositions of seven calibration gas mixture are summarized in Table I. Combinations of these standard mixtures shown in Table II were used to develop new calibrations for both detectors. Higher concentrations were used for TCD calibration while lower concentrations were used for FID calibration. Both detectors were calibrated using intermediate concentrations to provide overlap. Quadratic constants for the new calibrations are summarized in Table III. Each calibration is based on a minimum of three concentration levels. Correlation coefficients for the new TCD calibrations are similar to those previously reported using the previous analytical method.

Three instances of calibration overlap occurred. That is, CO₂ concentrations of 0.5 mol per cent and 0.999 mol percent, and a CO concentration of 0.999 mol per cent were used to calibrate both detectors. The calibrated CO₂ concentrations were within 2.5% of the actual concentration in both cases using both detectors. However, there was considerable difference between the CO mol per cent calculated from the TCD calibration and the actual CO concentration of the calibration gas. The CO concentration calculated using the FID calibration was quite close to the actual CO concentration. This illustrates the importance of the more sensitive FID at low concentrations.

Table I. Calibration Gas Compositions

(mol percent)

Original

Standard	CO	CO ₂	H ₂	N ₂
O1	9.98	9.99	9.98	balance
	±0.20	±0.20	±0.20	
O2	0.050	0.100	15.04	balance
	±0.001	±0.002	±0.30	
O3	1.00	4.00	20.00	balance
	±0.02	±0.10	±0.40	

New

Standard

N1	0.099	0.099	2.99	balance
	±0.002	±0.002	±0.06	
N2	0.501	0.500	5.99	balance
	±0.010	±0.010	±0.10	
N3	0.999	0.999	11.90	balance
	±0.020	±0.02	±0.20	
N4	5.02	5.03	20.00	balance
	±0.10	±0.10	±0.40	

Table II. Standard Gas Compositions Used for GC Calibration

Compound	Detector	Calibration Mixture
CO	FID	O2, N1, N2, N3
	TCD	O1, N3, N4
CO ₂	FID	N1, N2, N3
	TCD	N2, N3, N4
H ₂	TCD	O2, N1, N2, N3, N4
N ₂	TCD	O2, N1, N2, N3, N4

Table III. Quadratic Constants for GC Calibration

$$y_i = a_i A_i + b_i A_i^2$$

y_i = mol percent i

a_i, b_i = calibration constants

A_i = chromatograph peak area

R_i^2 = correlation coefficient

Component	Detector	a_i	b_i	R_i^2
CO	FID	1.551×10^{-7}	1.658×10^{-15}	1.0071
	TCD	1.19×10^{-4}	-8.009×10^{-11}	1.0264
CO ₂	FID	1.010×10^{-6}	-1.225×10^{-13}	0.9865
	TCD	1.356×10^{-4}	3.371×10^{-11}	1.0012
H ₂	TCD	7.617×10^{-6}	3.476×10^{-13}	1.0075
N ₂	TCD	8.390×10^{-5}	1.008×10^{-11}	0.9997

REACTION TEST RESULTS

Near the end of the previous quarter, the initial reaction test involving sorbent calcination (one-half cycle) was completed. Eight preliminary reaction tests involving one complete calcination-carbonation cycle were carried out during the present quarter and a summary of test conditions is presented in Table IV.

The original sorbent charge in all tests was in the carbonate form. Dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$) was used in all tests except 06 where marble chips were used. The marble chips were high in CaCO_3 and contained no MgCO_3 . The initial sorbent mass ranged from 15.8 to 20.4 g and three different particle size ranges were tested. A new charge of sorbent was used in all tests except 09 where the test 08 charge was subjected to a second calcination/carbonation cycle. There was no particular effort to keep tight control over these parameters since these tests were considered to be preliminary.

Calcination was carried out by heating the sorbent to 750°C (800°C in test 02) under flowing nitrogen at pressures ranging from 3.2 to 3.7 atm. Two nitrogen flow rates were used with the higher flow rate of 500 sccm used in the later tests. Complete calcination, as indicated by zero CO_2 concentration in the reactor product, was achieved in all tests. The higher N_2 flow rate was used to speed the calcination process and reduce the time required to complete the lengthy one-cycle reaction test. For example, 12.5 hours were required to complete test 03.

Carbonation test conditions were chosen on the basis of electro-balance results from Phase I of this study. The reactor pressure was 1.5 atm except during the early stages of test 02, while temperature ranged

Table IV. Summary of Reaction Test Conditions

Run	02	03	04	05	06	07	08	09
Sorbent	D*	D*	D*	D*	M*	D*	D*	D**
Mass, g	18.5	20.4	19.1	19.8	19.9	17.6	15.8	-
Particle Size Range, μm	149-210	149-210	149-210	210-250	149-210	149-210	74-149	-
Calcination Cycle								
Temp., $^{\circ}\text{C}$	800	750	750	750	750	750	750	750
Press, atm	3.2	3.2	3.4	3.2	3.2	3.7	3.3	3.3
Gas Composition	100% N_2	100% N_2	100% N_2	100 N_2	100% N_2	100% N_2	100% N_2	100% N_2
Flow Rate, sccm	250	250	500	500	500	500	500	500
Space Velocity (stp), hr	1138	1138	2275	2275	2275	2275	2275	2275
Carbonation Cycle								
Temp., $^{\circ}\text{C}$	800	750	650	550	550	650/550	550	550
Press, atm	3.2/15	15	15	15	15	15	15	15
Nominal Feed Gas	15% CO_2	15% CO_2	15% CO_2	15% CO_2	15% CO_2	15% CO_2	15% CO_2	15% CO_2
Composition	in N_2	in N_2	in N_2	in N_2	N_2	20% H_2O in N_2	20% H_2O in N_2	20% H_2O in N_2
Flow Rate, sccm	250	150	100	100	100	100/120	100	100
Space Velocity (stp), hr	1138	683	455	455	455	455/546	455	455

* - dolomite

M - marble chips

(2) - indicates second calcination cycle of sorbent first used in test 08.

from 800°C to 550°C. High fractional CO₂ removal is favored at low temperature while 800°C is near the maximum possible carbonation temperature allowed by thermodynamics. The simplest possible gas mixture consisting of 15% CO₂ in N₂ was used in tests 02 through 06. In test 07, 20% H₂O (steam) was added to the carbonation feed gas to verify our ability to inject steam into the high pressure reactor. Carbonation volumetric feed rate ranged from 250 to 100 sccm, with the lower value used in most tests to provide maximum residence time in the reactor in order to achieve high fractional CO₂ removal.

Selected results from these tests are described below.

Calcination Results

The sorbent was loaded into the reactor at room temperature and the reactor was heated at a nominal 5°C per minute to the desired final calcination temperature. Heating was carried out under flowing N₂ at the pressure and flow rate indicated in Table IV. Reactor product during the calcination cycle was sampled at 8 or 10 minute intervals and analyzed using the gas chromatograph. Results for tests 02 through 06 referred to in the following discussion utilized the original analytical sequence involving three GC columns and two multiport sampling valves with only the TCD used for analysis. The new analytical method was implemented between tests 06 and 07.

Reactor temperature profiles during the heating and calcination periods of test 03 are shown in Figure 2. During the early heating stages, the large mass of the reactor caused a considerable thermal lag between the set-point temperature, T_f , and the temperatures at various positions in the reactor. T_1 represents the temperature of the preheated gas just before contacting the sorbent. T_2 through T_5

FB-03

Figure 2. Reactor Temperature History During the Heating and Calcination Phases of Test 03.

represent temperatures at various axial positions within the sorbent, with T_2 near the top of the sorbent and T_5 near the bottom. T_6 represents the product gas temperature after it has been partially cooled just before it exits the reactor. A figure in the previous quarterly report shows the axial location of the thermocouples in more detail. After an initial period of about 30 minutes the reactor temperature begins to catch up with the set-point temperature and the temperature lag is about 70°C after 100 minutes. By 200 minutes when the set-point temperature was 750°C, the reactor feed had been preheated to $T_1 \sim 740^\circ\text{C}$, while the temperatures within the sorbent were approximately 750°C range (T_2 through T_5). The product gas temperature was approximately 325°C at this time which provides an ample margin of safety for the high-pressure O-ring seals.

Figures 3 and 4 show CO_2 concentration in the calcination product gas as a function of time from tests 05 and 06, respectively. The most striking difference in the two figures is the sharp spike in the CO_2 concentration in Figure 3 at about 150 minutes. This peak is attributed to decomposition of MgCO_3 prior to decomposition of CaCO_3 . The sharp peak is not present in Figure 4 where the sorbent did not contain of MgCO_3 . Similarly, the peak was not present during the calcination phase of test 09 in which the composition of the sorbent at the beginning of the second calcination cycle was a mixture of MgO and CaCO_3 .

During the calcination of dolomite (Figure 3), the first traces of CO_2 appeared after 80 minutes at $T \sim 325^\circ\text{C}$, and the calcination rate became significant after 104 minutes with $T \sim 475^\circ\text{C}$. The maximum CO_2 concentration of 17.9 mol% appeared in the sample taken at 144 minutes

FB-05

(TCD Response)

Figure 3. Mol Percent CO₂ Versus Time During the Calcination Phase of Test 05.

FB-06

(TCD Response)

Figure 4. Mol Percent CO₂ Versus Time During the Calcination Phase of Test 06.

($T \sim 700^{\circ}\text{C}$). Decomposition of MgCO_3 is responsible for the peak and much of the early CO_2 . After 144 minutes the CO_2 concentration decreased rapidly and leveled out at about 5 mol % CO_2 over the time interval 168 to 232 minutes ($T \sim 750^{\circ}\text{C}$). Thereafter, the CO_2 concentration decreased once again and was below the TCD detection limit after 280 minutes.

In addition to the absence of the sharp CO_2 peak in Figure 4, the first appearance of CO_2 was delayed by about 30 minutes until the temperature was above 500°C . Thereafter, the CO_2 concentration rose to just over 5% after 190 minutes and remained at that level for about 60 minutes before decreasing to below the TCD detection limit at about 300 minutes. Calcination performance during the latter stages of the calcination cycle was similar in both tests 05 and 06.

Complete calcination of the 19.8 g of dolomite used in test 05 should produce 0.215 mol of CO_2 . Numerical integration of the CO_2 concentration-time curve in Figure 3 accounts for 0.209 mol of CO_2 , corresponding to greater than 97% CO_2 material balance closure. In test 06, the 19.9 grams of sorbent should produce 0.199 mol of CO_2 (assuming that the original sorbent is pure CaCO_3). Integration of the CO_2 concentration-time curve of Figure 4 accounts for 0.146 mol of CO_2 , which represents only about 73% CO_2 material balance closure. However, it should be recognized that the composition of the marble chips is not known.

Calcination results from tests 02, 03, 04, 07, and 08 were qualitatively similar to the results from test 05 shown in Figure 3. Small differences were attributed to differences in the calcination pressure and/or flow rate. The calcination results from test 09 were qualitatively similar to the Figure 4 results from test 06. Even though

the original sorbent was dolomite (used in test 08), no MgCO_3 was reformed during the carbonation portion of test 08. Therefore, in the test 09 calcination, only CaCO_3 was decomposed.

One additional topic pertaining to the calcination portion of the cycle was resolved during the quarter. As reported in the previous quarterly report, small concentrations of CO were found in the calcination product gas from test 01. The presence of CO was tentatively attributed to the reaction

with the reactor tube walls serving as the carbon source. Small concentrations of CO continued to appear in the calcination portion of the tests completed this quarter. CO is definitely tied to the presence of CO_2 in that no CO is found during the heating period before carbonate decomposition begins. Similarly, no CO is found after the CO_2 concentration returns to zero at the end of carbonate decomposition. The reaction between $\text{CO}_2(\text{g})$ and the tube walls was confirmed as the source of CO in a test in which CO_2 and N_2 were fed at high temperature to the reactor which contained no sorbent. CO was also found in the reactor product under these conditions.

Carbonation Results

The simplest carbonation gas composed of 15 mol% CO_2 in N_2 was used in tests 02 through 06. Carbonation temperature and feed rate were varied, and the carbonation reaction proceeded as expected. 20% steam was added to the feed gas beginning in test 07 to verify our ability to inject steam into the high pressure reactor. The tests were successful in that respect, but no quantitative reaction data was obtained because

of gas leaks in tests 07 through 09. In addition to proving our ability to inject steam at high pressure, it is important to note that small amounts of H_2 were found in the reactor product during the carbonation cycle. The only possible source of the H_2 is by the water-gas shift reaction with H_2O in the feed gas reacting with CO formed by the reaction of CO_2 with the reactor walls. This result, although preliminary and only qualitative, is significant in that it does prove that the water-gas shift reaction will occur at the reaction conditions of interest.

Quantitative results which were obtained from tests 02 through 06 are summarized below. Figure 5 and 6 show the CO_2 breakthrough curves from tests 05 and 06, respectively. In test 05 (Figure 5), the carbonation gas consisting of 15% CO_2 in N_2 (nominal) was fed to the reactor beginning at 390 minutes. The CO_2 concentration in the product gas remained below the TCD detection limit for 65 minutes. Thereafter, the CO_2 concentration increased rapidly and the traditional breakthrough curve was formed. The final CO_2 composition of the product gas was about 17 mol %, somewhat higher than the nominal 15 mol % fed. The total quantity of CO_2 removed from the gas phase during carbonation was 0.066 mols, which corresponds to 59% conversion of CaO.

The CO_2 breakthrough curve from test 06 (Figure 6) is qualitatively similar to that for test 05 (Figure 5). Carbonation gas was introduced after 380 minutes and CO_2 in the product gas was below the TCD detection limit for 68 minutes. The first significant amount of CO_2 appeared at about $t = 520$ minutes, and the concentration rapidly increased to about 18% after 560 minutes. The total quantity of CO_2 removed from

FB-05

(TCD Response)

Carbonation starts at $t=390$ min.

Figure 5. CO₂ Breakthrough Curve During the Carbonation Phase of Test 05.

FB-06

(TCD Response)

Carbonation starts at $t=380\text{min}$.

Figure 6. CO₂ Breakthrough Curve During the Carbonation Phase of Test 06.

the gas phase during carbonation was 0.116 mols which corresponds to replacement of 79% of the CO_2 produced during calcination.

Tests 02 through 05 represent a series in which the primary variable was carbonation temperature. Test 02 was begun at a carbonation pressure of 3.2 atmospheres but the pressure was soon increased to 15 atmospheres. In addition the volumetric feed rate was changed during the series. Neither of these changes, however, should have a significant effect on the prebreakthrough CO_2 concentration. The experimental prebreakthrough CO_2 partial pressure as a function of temperature is shown in Figure 7, along with the equilibrium CO_2 partial pressure. Because carbonation is exothermic and reversible, the CO_2 equilibrium partial pressure increases with temperature. The experimental results follow the same pattern, but the experimental values are three to four times larger than the equilibrium values. Failure to achieve equilibrium is due to finite rate of the reaction. In principle, the two values can be brought closer together by increasing the reactor volume and/or decreasing the volumetric flow rate.

Figure 7. Prebreakthrough Partial Pressure of CO₂ From the Fixed-Bed Reactor.

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