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A CALCIUM OXIDE SORBENT PROCESS
FOR BULK SEPARATION OF CARBON DIOXIDE

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Executive Summary

This research project is investigating the technical feasibility of a high-temperature, high-pressure (HTHP) process for the bulk separation of CO₂ 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 CO₂ 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 CO₂ 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 CO₂. The concentrated CO₂ stream could be quite significant if, in the future, environmental regulations restrict atmospheric CO₂ emissions.

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. Parameters being studied in Phase II are essentially the same as in Phase I. The reactor response is being studied as a function of calcination and carbonation temperature and pressure, composition of the calcination and carbonation feed gas, and space velocity during the carbonation cycle. Multicycle tests are also being conducted to extend the information on sorbent durability.

Previous quarterly reports have described the design, construction, and commissioning of the fixed-bed reactor, development of analytical procedures, and results of a number of single-cycle tests using dolomite sorbent precursor. During the current quarter, reactor modifications to permit easier addition and removal of sorbent to and from the reactor were accomplished. It is now possible to remove sorbent after a run in discrete axial sections which will permit characterization of the sorbent as a function of axial position. Tracer response tests in which the chromatograph response to step function injections of hydrogen to flowing nitrogen under non-reactive conditions were carried out to evaluate the lag time between feeding reactive gases to the reactor and their appearance in the product gas sample. Fourteen additional calcination/carbonation reaction tests were completed this quarter, and the effects of carbonation background gas composition, sorbent particle size, calcination temperature, calcination gas flow rate, and calcination gas composition were studied. In addition, the first multicycle test involving five complete calcination/carbonation cycles was carried out.

Prebreakthrough concentrations of CO as low as 10 ppmv and CO₂ in the range of 150 ppmv have been routinely achieved, and the simultaneous occurrence of the shift

reaction and carbon dioxide removal has been proven. The experimental effort has been plagued on a number of occasions by failure of the high pressure mass flow controllers. Near the end of the present quarter silica gel dryers were installed between all the gas cylinders and the mass flow controllers. In addition, we have switched to higher purity CO since the most persistent problems were associated with the CO controller. These changes have not been in place for a sufficiently long period to determine if the flow controller problem has been solved.

Reactor Modifications

With the original reactor design, loading the sorbent precursor into the reactor was difficult and controlled removal of the sorbent following a reaction test was impossible. Because the sorbent was so tightly compressed within the reactor, a great deal of force was required to dislodge the sorbent, and the entire mass tended to come loose at one time. This prevented us from being able to obtain discrete samples from various axial positions.

The modified reactor is shown in Figure 1. The length of the reactor insert was reduced by six inches and the pins holding the porous stainless steel discs in place were moved from the top to the bottom of the sorbent bed. This change allows us to eliminate the split support tubing which was previously used to hold the bottom porous steel disc in place. Previously the reactor was loaded and unloaded in an upside down position; now the reactor is loaded and unloaded right side up.

Loading the reactor is now very straightforward. The bottom stainless steel disc is placed over the thermowell and its position within the reactor insert is determined by

Figure 1. Diagram of the Modified Reactor

the pins permanently fixed inside the insert. The disc is followed by a layer of quartz wool, another porous stainless steel disk, and then four layers of sorbent with each layer separated by another disc. The overall position is such that one of the axially spaced thermocouples is at approximately the mid point of each sorbent layer.

The following procedure is used to unload the reactor. First, the thermowell is pulled down so that the top of the thermowell is below the top disc. A tool resembling reverse acting tweezers has been fabricated which fits within the insert and permits removal of the top disc. The top layer of sorbent can then be poured from the reactor insert without disturbing the lower layers. The thermowell is then repositioned so that its top is below the second disc. This disc is then removed as before, permitting the second layer of sorbent to be removed. This procedure is repeated until each axial section of sorbent has been removed from the reactor insert.

Because the reactor insert was shortened by six inches to provide access for the tweezers-like tool, we were concerned that temperature distributions within the reactor might be altered. However, in subsequent tests the variation in temperatures between the old and new configurations was only 2 or 3 °C, well within the temperature limits. All tests conducted this quarter except one, test 24, utilized the new reactor configuration.

Tracer-Response Tests

A series of tests in which hydrogen was introduced as a step function into nitrogen flowing through the reactor was carried out to measure the lag time between the introduction of reactive gases and their appearance in the reactor product gas. The response curve corresponding to the introduction of 10% H₂ at a total flow rate of 100

sccm at 550 °C and 15 atmospheres is shown in Figure 2. Hydrogen flow was initiated at $t_0 = 4.0$ minutes, and no hydrogen was detected in the first three product gas samples taken after 9, 18, and 27 minutes. After 36 minutes the hydrogen mol fraction was approximately 0.04 and the concentration continued to increase as shown in the figure. By way of comparison, a lag time of 40 minutes was calculated using the estimated reactor volume between the feed and chromatograph sampling valves, the gas volumetric flow rate, and assuming plug flow. The fact that hydrogen was observed prior to 40 minutes along with the gradual increase in hydrogen concentration indicates that axial mixing is important and that plug flow is not a good assumption.

After examining this and other response curves under different conditions, we have concluded that the time required for the hydrogen concentration to reach 80% of its steady-state value is the proper definition of the reactor lag time. In the Figure 2 example, the resulting lag time is 52 minutes. Figure 3 shows a plot of lag time versus volumetric flow rate from a series of tracer-response tests at 550 °C and 15 atm. As shown in the figure, the lag time decreases to 20 minutes at the "standard" reactor flow rate of 250 sccm.

With the value of the lag time known at various reaction conditions, it is possible to calculate dimensionless breakthrough curves based upon the following equations:

$$t^* = \frac{F^0 (y_{CO_2}^0 + y_{CO}^0) (t - t_D)}{N_{CO}^0} \quad (1)$$

$$FCOX = \frac{(y_{CO_2} + y_{CO})F}{(y_{CO_2}^0 + y_{CO}^0)F^0} \quad (2)$$

Figure 2. Hydrogen Response Curve

Figure 3. Reactor Time Delay as a Function of Volumetric Flow Rate

$$X^* = \frac{1}{N_{CaO}^0} \sum_i [F^0(y_{CO_2}^0 + y_{CO}^0) - F(y_{CO_2} + y_{CO})] \Delta t_i \quad (3)$$

Where...

$F^0 =$ molar rate of total reactor feed (wet basis)

$F =$ molar rate of total reactor product (wet basis)

$y_{CO_2}^0, y_{CO}^0 =$ mol fractions of CO_2 and CO in feed gas (wet basis)

$y_{CO_2}, y_{CO} =$ mol fractions of CO_2 and CO in reactor product (wet basis) as a function of time

$N_{CaO}^0 =$ initial mols of CaO in the reactor

$t =$ time from initiation of the carbonation cycle

$t_D =$ dead volume correction time

$\Delta t_i =$ time increment between chromatograph samples

$t^* =$ dimensionless carbonation cycle time

$FCOX =$ dimensionless breakthrough concentration of total carbon oxides

$X^* =$ axial average fraction of CaO converted to $CaCO_3$

The characteristics of these equations are such that $X^* = t^*$ as long as complete removal of carbon oxides is accomplished, i.e., as long as $FCOX=0$. Once carbon oxide breakthrough begins, $X^* < t^*$. If both the shift and carbonation reactions were infinitely fast and complete sorbent conversion could be achieved, the reaction would be complete at $X^* = t^* = 1.0$, and $FCOX$ would change in a step function with $FCOX = 0$ for $t^* < 1.0$

and $\text{FCOX} = 1.0$ for $t^* \geq 1.0$. The idealized dimensionless response curve is shown in Figure 4a and compared to the typical response curve in Figure 4b.

In Figure 4b, the value of FCOX should approach the thermodynamic equilibrium limit for small t^* , which for practical purposes is zero for the shift and carbonation reactions of interest. As t^* increases, the value of FCOX will increase because of the finite rate of the global reactions and the traditional S-shaped breakthrough curve will result. For large t^* , FCOX will approach 1.0 as the total carbon oxide concentration in the product approaches the total carbon oxide concentration in the feed. Note that $\text{FCOX} = 1.0$ does not imply that both reaction rates are zero. The shift reaction may still occur but if the carbonation reaction rate is zero, no carbon dioxide is removed from the gas phase and the total carbon oxide concentration is constant. After carbon oxide breakthrough occurs, the slope of the X^* versus t^* curve will decrease and X^* will asymptotically approach its final value, typically in the range of $0.80 \leq X_f^* \leq 0.95$.

Mass Flow Controllers

Problems with the high-pressure mass flow controllers have plagued the project since its beginning. In May, three controllers failed and had to be returned to the factory. A similar problem with the CO controller occurred during September and this controller was returned to the factory a second time.

We have been told that an oily (?) build-up was found on the sensing elements of the controller. As a consequence, we are installing silica gel driers between all high pressure cylinders and the particulate filters. In addition, we will switch to a higher purity

a) Idealized Reactor Response

b) Actual Reactor Response

Figure 4. Dimensionless Breakthrough and Calcium Conversion Response Curves for a Fixed-Bed Reactor.

(and higher cost) carbon monoxide. These changes are being implemented at the end of the quarter, and it will be some time before it is known if these changes will solve the problem.

Reaction Tests

Fourteen calcination/carbonation tests were completed during the quarter; reaction conditions are summarized in Table I. In these tests, the following reaction parameters were varied: carbonation background gas composition (tests 24 and 27-1); sorbent particle size (tests 25, 26 and 27-1); calcination temperature (tests 27-1, 28 and 29); calcination gas flow rate (tests 27-1 and 30); and calcination gas composition (tests 30, 31 and 32-1). In addition, tests 27-1 through 27-5 represented a multicycle test at standard reaction conditions. The effects of these parameter variations are discussed below.

Background Gas Composition: The carbonation feed gas in test 24 contained all of the major components of coal gas (CO , CO_2 , H_2 , H_2O , and N_2) so that both the shift and carbonation reactions were free to occur simultaneously. In test 27-1, the carbonation feed gas contained only CO , H_2O , and N_2 so that no carbonation could occur and no hydrogen could appear in the product gas unless the shift reaction occurred first.

Results in the form of component breakthrough curves versus time for these runs are presented in Figures 5 and 6. The results are qualitatively similar in both cases. CO and CO_2 concentrations (as measured by the thermal conductivity detector) were zero for an extended time period. Hydrogen concentration in both tests began to increase after

TABLE 1. SUMMARY OF REACTION TEST CONDITIONS

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Figure 5. Reactor Response. Product Gas Composition. Test 24

Figure 6. Reactor Response. Product Composition. Test 27-1.

approximately 20 minutes and reached a plateau after about 40 minutes. The time required for the hydrogen concentration to reach the plateau is associated with the previously discussed reactor lag time. In test 24, the maximum hydrogen mol fraction of 0.27 (dry basis) was due to the hydrogen in the feed gas plus hydrogen formed by a shift reaction. In test 27-1, all of the hydrogen in the product was formed as a result of the shift reaction since there was no hydrogen in the feed gas.

Initial breakthrough of CO and CO₂ occurred as the sorbent approached complete carbonation, and was accompanied by a decrease in the hydrogen concentration. Near the end of the runs, only the shift reaction occurred, and the H₂, CO₂, and CO concentrations reached a second steady-state. In test 27-1 (Figure 6) the final concentrations of CO₂ and H₂ were equal as required by the shift reaction stoichiometry when neither CO₂ or H₂ is present in the feed. In test 24 (Figure 5) the final concentration of CO₂ was lower because of the high concentration of H₂ in the feed gas.

Sorbent Particle Size: Three different sorbent particle sizes were tested in runs 25, 26, and 27-1. Prebreakthrough concentrations of H₂, CO and CO₂ were similar in all cases, with CO and CO₂ concentrations below the detection limit of the thermal conductivity detector. Key performance parameters for the tests are summarized in Table 2. In addition to prebreakthrough CO and CO₂ concentrations being below the detection limit, prebreakthrough H₂ concentrations were similar in each test. Fractional sorbent conversion, X^* , at $t^* = 1$ and $t^* = t_f^*$ (final time) were also similar in each run. However, the smallest particles (test 26) produced a shorter prebreakthrough time and the breakthrough curve had a smaller slope. These features are emphasized in Figure 7

**Table 2. Performance Parameters for
Series of Tests Showing the Effect of Sorbent
Particle Size**

Test	25	26	27-1
Particle Size Range, μm	250-300	74-149	149-210
Prebreakthrough Concentrations			
% H_2	6.9	6.9	6.8
% CO	(1)	(1)	(1)
% CO_2	(1)	(1)	(1)
Postbreakthrough Concentrations			
% H_2	4.2	3.8	4.0
% CO	2.3	2.8	2.5
% CO_2	4.0	3.7	3.9
Dimensionless Breakthrough			
Time, t_b^*	0.68	0.62	0.69
Fractional Sorbent Conversion, X^*			
at $t^* = 1$	0.85	0.85	0.83
at $t^* = t_f^*$ (final)	0.86	0.86	0.84

(1)-concentration below TCD detection limit

Figure 7. Comparison of Dimensionless Breakthrough Curves as a Function of Sorbent Particle Size

where dimensionless breakthrough curves for tests 25 (largest particle size) and 26 (smallest particle size) are compared. In addition, the postbreakthrough concentrations appear to depend on sorbent particle size. Postbreakthrough H_2 concentration increased from 3.8 % with the smallest particles to 4.2 % with the largest particles. As a corollary, the postbreakthrough ratio of CO_2 to CO increased with increasing particle size, from 1.32 to 1.56 to 1.74. While the reason for this dependence on particle size is not clear, the results are consistent.

Calcination Temperature: In tests 28 and 29, the calcination temperature was reduced to 650 °C and then increased to 800 °C. Calcination at 650 °C was not acceptable as the reaction was still incomplete six hours after the cycle was initiated. As indicated in Table I, the calcination temperature was subsequently increased to 750 °C to complete the reaction.

A calcination temperature of 800 °C reduced the time required for calcination and increased the CO_2 composition of the product gas during the CaCO_3 decomposition period, both desirable results. Figure 8 compares the CO_2 product gas compositions and reactor temperatures for tests 27-1 and 29, corresponding to final calcination temperatures of 750 °C and 800 °C, respectively. MgCO_3 decomposition occurred during the heating period and was, as expected, approximately the same in both tests. The duration of the overall calcination cycle was reduced by about 30 minutes and the CO_2 mol fraction during CaCO_3 decomposition increased from about 0.05 to 0.09.

Results from Phase I of this study indicated that improved sorbent durability was associated with lower calcination temperature. However, there was little, if any, difference

Figure 8. CO₂ Composition of the Calcination Product Gas as a Function of Time and Temperature

in the first cycle carbonation performance of tests 27-1 and 29 as shown by the dimensionless response curves in Figure 9. CO and CO₂ concentration were below the TCD detection limit during the prebreakthrough period of both tests. Initial breakthrough occurred at approximately the same dimensionless time and the slope of the breakthrough curves was effectively equal. The only possible negative factor associated with the higher calcination temperature was the fact that the final fractional calcium conversion of $X_f^* = 0.81$ following 800 °C calcination was somewhat less than the value of $X_f^* = 0.84$ following 750 °C calcination. Additional tests will be required to determine if this difference is real or the result of random experimental variation.

Calcination Gas Flow Rate. Reducing the flow rate of the calcination gas provides an alternate means of increasing the CO₂ composition of the calcination product gas. In test 30, the N₂ flow rate was reduced from the standard 700 sccm to 250 sccm, and the CO₂ content as a function of time is given in Figure 10. During the MgCO₃ decomposition period the CO₂ content increased from approximately 13 % to 24 %; a smaller increase from 5 % to 7 % was observed during CaCO₃ decomposition. An increase in the total time required for calcination of about 50 minutes also accompanied the decreased flow rate.

Calcination Using H₂O/N₂ Mixtures. If future environmental regulations limit the discharge of CO₂ to the atmosphere, it will be necessary to maximize the CO₂ content of the calcination gas to facilitate ultimate disposal. Increasing the calcination temperature and decreasing the calcination gas flow rate provide two methods of increasing the CO₂

Figure 9. Dimensionless Carbonation Breakthrough Curves Following Calcination at 750°C (Test 27-1) and 800°C (Test 29)

Figure 10. Calcination Product Composition as a Function of N₂ Flow Rate

content and the effect of these changes was described in the previous sections. The addition of steam (or another condensible vapor) to the calcination gas provides another option. Separation of steam from the product gas could be accomplished by condensation, thereby increasing the CO₂ content of the final noncondensable gases.

The use of high concentrations of steam necessitated the use of a lower total flow rate because of the limited capacity of the high-pressure syringe pump. A flow rate of 250 sccm was chosen. Tests 30, 31, and 32-1 were carried out to compare calcination and carbonation performance with 0, 20, and 40 % steam in the calcination gas. An additional test using 60 % steam is planned for early in the next quarter.

Figure 11 compares the CO₂ content of the calcination product for tests 30 and 31 (0 % and 20% steam). Data for test 32-1, in which the calcination gas contained 40% steam, are not included in the figure because of an inadvertent change in the calcination heating rate. As expected, the addition of steam resulted in an increase in the CO₂ content, particularly during the CaCO₃ decomposition phase. The CO₂ mol fraction was essentially doubled, from 0.05 to 0.10, during this time. Not expected, however, was earlier onset of MgCO₃ calcination and the reduced time required for complete calcination. The maximum CO₂ composition was observed after 131 minutes in test 31 compared to 148 minutes in test 30. Similarly, complete calcination was achieved after 227 minutes in test 31 compared to about 270 minutes in test 30.

Although time comparisons between tests 30, 31, and 32-1 are not valid because of the different heating rate used in test 32-1, comparisons of the maximum CO₂ mol fractions should be meaningful. In test 32-1 the CO₂ maxima increased to 30% (dry basis) during MgCO₃ decomposition and to 13% (dry basis) during CaCO₃ decomposition.

Figure 11. Calcination Product Composition as a Function of Steam Content of the Calcination Gas

Despite the differences in calcination conditions, carbonation results from tests 30 and 31 were quite similar as shown in Figure 12. The higher H_2 concentration during the prebreakthrough period and the earlier breakthrough of CO and CO_2 may be attributed to the higher concentration of CO in the test 31 feed gas.

Multicycle Durability. In tests 27-1 through 27-5, the sorbent was exposed to five calcination/carbonation cycles at effectively the same reaction conditions. While there are a number of ways of evaluation durability, all show a gradual decrease in sorbent reactivity with cycle number. Figure 13 compares the CO and CO_2 breakthrough curves for the first and fifth cycles. Data from the thermal conductivity and flame ionization detectors are combined on this semi-log plot to show the complete breakthrough curve with concentrations ranging from 10 to 100,000 ppm (0.001% to 10.0%). Flame ionization detector results were used for all concentrations below 5000 ppm (0.5%) with thermal conductivity results used at the higher concentrations. CO concentrations during the prebreakthrough period are shown as 10 ppm, although in some samples no CO was detected even by the sensitive flame ionization detector.

In the first cycle, CO concentration was at or below the 10 ppm level for the first 72 minutes. Thereafter the traditional S-shaped breakthrough curve was observed and the CO concentration increased to 26,000 ppm (2.6%) at the end of the test. Initial CO concentrations in cycle 5 were also at or below the 10 ppm level, but initial breakthrough occurred after 30 minutes. The slope of the breakthrough curve decreased indicating a somewhat slower global reaction rate and the final CO concentration was 33,000 ppm (3.3%), considerably higher than in the first cycle. At the end of the run only the shift

Figure 12. Carbonation Breakthrough Curves Following Calcination in N₂ and in 80% N₂/20% H₂O

Figure 13. Comparison of CO and CO₂ Breakthrough Curves in First and Fifth Cycles of Multi-Cycle Test

reaction was occurring, and this result suggests that sorbent aging has a negative effect on the kinetics of the shift reaction at conditions where carbonation does not occur.

Prebreakthrough CO_2 concentrations were similar in both the first and fifth cycles, and were in the general range of 90 to 220 ppm (0.009 to 0.022 %). However, CO_2 breakthrough in the fifth cycle clearly occurred at an earlier time. Final CO_2 concentration in the fifth cycle was also lower than in the first cycle, in agreement with the previously described reduction in the global kinetics of the shift reaction.

An alternate way of comparing sorbent durability is shown in Figure 14 where CO and CO_2 breakthrough time is plotted versus cycle number. The breakthrough times in this figure are arbitrarily defined as the times required for the CO product gas composition to reach 100 ppm and for the CO_2 product gas composition to reach 500 ppm. Over the five cycles the CO_2 breakthrough time decrease from 94 to 75 minutes while the CO breakthrough time decreased from 85 to 55 minutes. These numbers represent an average decrease in breakthrough time of from 4% to 7% per cycle.

Still another means of evaluating multicycle durability is provided by Figure 15 where fractional calcium conversion, X^* , is plotted versus cycle number at two dimensionless times, $t^* = 0.5$ and $t^* = 1.0$. The fact that $X^* = 0.5$ at $t^* = 0.5$ indicates that effectively complete carbon oxide removal was achieved during the early reaction stages of all cycles. At $t^* = 1.0$, the values of X^* increased from 0.83 in cycle 1 to a maximum of 0.84 in cycle 3 and then decreased to 0.79 in cycle 5. Thus the average sorbent capacity decrease was only about 1% per cycle. For practical purposes, the carbonation reaction was complete at $t^* = 1.0$ since final values of X^* ranged from 0.84 in cycles 1 and 3 to 0.80 in cycle 5.

Figure 14. CO and CO₂ Breakthrough Times as a Function of Cycle Number

Figure 15. Fractional Calcium Conversion at Selected Dimensionless Times as a Function of Cycle Number

Some performance deterioration in multicycle operation is expected at the extreme conditions of the reactions. However, this first multicycle run confirmed that the rate of deterioration was modest through five cycles. A preliminary economic evaluation will be required to obtain an estimate of the economically allowable deterioration rate. The low cost of the sorbent precursor (dolomite) is an important factor in the process economics.

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