

CARBON DIOXIDE CAPTURE FROM FLUE GAS USING DRY REGENERABLE SORBENTS

QUARTERLY TECHNICAL PROGRESS REPORT

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ABSTRACT

This report describes research conducted between April 1, 2004 and June 30, 2004 on the preparation and use of dry regenerable sorbents for removal of carbon dioxide from flue gas. Support materials and supported sorbents were prepared by spray drying. Sorbents consisting of 20 to 50% sodium carbonate on a ceramic support were prepared by spray drying in batches of approximately 300 grams. The supported sorbents exhibited greater carbon dioxide capture rates than unsupported calcined sodium bicarbonate in laboratory tests.

Preliminary process design and cost estimation for a retrofit application suggested that costs of a dry regenerable sodium carbonate-based process could be lower than those of a monoethanolamine absorption system. In both cases, the greatest part of the process costs come from power plant output reductions due to parasitic consumption of steam for recovery of carbon dioxide from the capture medium.

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1.0 EXECUTIVE SUMMARY

The objective of this project is to develop a simple and inexpensive process to separate CO₂ as an essentially pure stream from a fossil fuel combustion system using a regenerable sorbent. The sorbents being investigated in this project are alkali carbonates, and particularly sodium carbonate, which is converted to bicarbonate or an intermediate salt through reaction with carbon dioxide and water vapor. Bicarbonate is regenerated to carbonate when heated, producing a nearly pure CO₂ stream after condensation of water vapor.

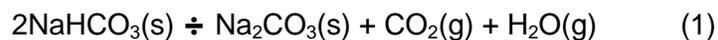
This quarter, 16 supported sorbents composed of 20 to 50% sodium carbonate on a support were prepared by spray drying. The supported sorbents had greater surface areas and activities than calcined Grade 3 sodium bicarbonate (SBC#3). Activity was based on sorbent weight gain during a 20-minute period of exposure to a simulated flue gas in a thermogravimetric analyzer (TGA). Six different spray dried support formulations (without active sorbent material) were also prepared.

Preliminary process design and cost estimation for a retrofit application consistent with an EPRI baseline case, suggested that costs of a dry regenerable sodium carbonate-based process could be lower than those of a monoethanolamine absorption system. In both cases the greatest part of the process costs come from power plant output reductions due to parasitic consumption of steam for recovery of carbon dioxide from the capture medium.

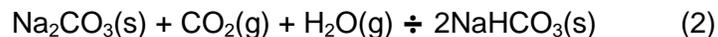
2.0 INTRODUCTION

Fossil fuels used for power generation, transportation, and by industry are the primary source of anthropogenic CO₂ emissions to the atmosphere. Much of the CO₂ emission reduction effort will focus on large point sources, with fossil fuel fired power plants being a prime target. The CO₂ content of power plant flue gas varies from 4% to 20% (vol), depending on the type of fossil fuel used and on operating conditions. Although new power generation concepts that may result in CO₂ control with minimal economic penalty are under development, these concepts are not generally applicable to the large number of existing power plants.

This study is based on the use of a dry, regenerable sorbent to remove CO₂ from flue gases. Sorbent regeneration produces a gas stream containing only CO₂ and H₂O. The H₂O may be separated by condensation to produce a pure CO₂ stream for subsequent use or sequestration. The primary reactions, based upon the use of sodium bicarbonate (SBC) as the sorbent precursor and sodium carbonate as the reaction product are:



and



Reaction (1) releases CO₂ and regenerates the sorbent, while Reaction (2) is used to capture CO₂. Other solid products, intermediate between sodium carbonate and sodium bicarbonate, may also be produced under the anticipated reaction conditions. An intermediate compound, Na₂CO₃·3NaHCO₃, known as Wegscheider's salt, forms at the reaction conditions of interest.

The carbon dioxide capture reaction is exothermic and the sorbent regeneration reaction (calcination) is endothermic, and takes place at a slightly higher temperature. The sorbent can

be recycled numerous times. Traces of SO₂ and HCl, which may be present in desulfurized flue gas from coal-fired power plants, will react irreversibly with the sorbent.

This report describes activities conducted between April 1, 2004 and June 30, 2004 by RTI and its subcontractor Church and Dwight (C&D). Activities conducted this quarter include development of improved spray dried supported sorbents, mathematical modeling of equipment design and cost estimation.

3.0 EXPERIMENTAL

3.1 Sorbent Preparation

A total of 23 different materials were produced this quarter. This materials included 17 supported sodium carbonate sorbents prepared in slightly different ways, and five plain supports for determination of mechanical properties in the absence of active sorbent. Small batches were made by co-precipitation, followed by pressure filtration. The materials were spray dried, and then calcined at 450EC for two hours. Spray dryer parameters, including slurry moisture content, additive composition, nozzle size and nozzle projection were varied in an attempt to produce high surface area, high density (attrition-resistant) particles. Analytical grades of sodium carbonate from two different suppliers were used. The BET surface areas, compact bulk densities and Davison attrition indexes of these sorbents were determined. The carbonation activities were evaluated by monitoring short term weight gain in a TGA.

3.2 Thermogravimetric Testing of Supported Sorbents

The supported sorbents were screened by thermogravimetric analysis to determine their relative carbonation activity. These tests were conducted at 60EC in an atmosphere of 7.5% carbon dioxide and 5.9% water vapor. Weight gain over the initial 20 minute period of exposure to the carbonation gas was used to compare the activities of the sorbents.

4.0 RESULTS AND DISCUSSION

4.1 Properties of Supported Materials

Seventeen supported sodium carbonate sorbents were prepared this quarter. The compositions and selected properties of these materials are shown in Table 1. This table also includes the properties of plain support materials, without incorporation of Na₂CO₃, as well as a commercial fluidized catalytic cracking catalyst, and the previously reported RTI-5 material which was produced by a commercial catalyst manufacturer in a batch of several hundred pounds.

Table 1. Sorbent Properties

Sample #	Na ₂ CO ₃ content of sorbent (%)	Compact Bulk Density (g/mL)	BET Surface Area (m ² /g)	TGA Weight Gain, 20 min. (%)	Attrition (Davison Index)
041604-1a	0	0.68	96.6	3.8	71.34
042004-1a	0	0.74	120.8	4.6	68.67
051304-1a	0	0.95	135.8	nt	nt
050504-1	0	0.66	139	nt	nt
050504-2	0	0.63	126.3	nt	nt
0513041a	0	0.95	135.8	nt	nt
040204-1a	20	0.51	28.43	7	nt
040504-1a	40	0.64	12.91	10	nt
040804-1a	20	0.5	33.7	6.2	nt
040904-1a	40	0.64	14.29	9	nt
041204-1a	20	0.5	31.4	6.6	nt
041604-2a	40	0.64	13.5	8.7	nt
041604-3a	50	0.71	10.7	9.2	nt
042104-1a	40	0.74	7.9	8.9	nt
042104-2a	40	0.74	7.0	7.9	nt
042804-1a	20	0.43	34.8	6.7	nt
042804-2a	40	0.51	10.9	8.9	nt
042904-1a	40	0.49	9.84	9.1	nt
050504-3	40	0.89	6.96	5.2	20.01
050704-1a	40	0.54	14.3	nt	53.39
050704-2a	40	0.53	15.4	nt	nt
050704-3a	40	0.54	11.4	nt	30.06
051404-1a	40	0.57	14.8	nt	nt
051604-1a	16	1.00	84.1	nt	nt
Calcined SBC 3	---	0.99	2.41	4.2	nt
FCC+	---	0.96	nt	nt	23.37
RTI-5	40	1.61	1.85	1.5	12

nt = not tested

+ = Commercial fluid cracking catalyst

The objective of the sorbent development work is to produce an active (as indicated by high BET surface area and rapid conversion to Wegscheider's salt) material which is mechanically stable (as indicated by high compact bulk density and Davison attrition index). Sorbent composition and spray dryer operation were varied to identify important parameters. The details of the sorbent preparation are proprietary to RTI, as the methods and techniques are potentially patentable.

4.2 TGA Testing of Supported Sorbents

The supported sorbents produced this quarter were screened for activity by TGA at 60°C in an atmosphere of 7.5% carbon dioxide and 5.9% water vapor. Prior to carbonation, the samples were heated to 150°C in helium to eliminate the effects of moisture gain and adsorption of atmospheric gases (including carbon dioxide). Weight gains resulting from conversion of sodium carbonate in the sorbent to sodium bicarbonate over an arbitrary 20-minute calcination time were used to compare sorbent activity. Supports prepared by spray drying without addition of sodium carbonate to the slurry were also tested. These supports displayed reversible weight gains that were smaller than the weight gains of the supported sorbents, presumably due to adsorption of moisture. Weight gains are listed in Table 1.

The supported sorbents show much greater reactivity over the arbitrary 20-minute period than calcined grade 3 sodium bicarbonate. In addition, the supported sorbents exhibit a much greater initial weight gain in the first minute of contact with the carbonation gas.

4.3 Process Modeling: Reactor Design and Cost Estimation

At present, one large scale carbon dioxide recovery process is in limited use at coal-fired electric utilities. The principle of operation of this process is liquid absorption in a solution of inhibited monoethanolamine (MEA). The operational experience with this process at a small number of generating plants, as well as its more extensive use in natural gas treatment make it a benchmark for other carbon dioxide recovery processes under development. RTI and Church and Dwight have conducted a comparative economic evaluation of this process and the dry regenerable sodium carbonate based sorbent process.

4.3.1 Basis for Economic Feasibility Analysis

The baseline comparison for this economic analysis is Case 7A in the December 2000 EPRI report (Holt, 2000). In this case, the economics of adding a conventional MEA-based CO₂ capture process designed for 90% removal of the CO₂ to a nominal 500-MW power plant was investigated. The capture technology was conceived of as an "end-of-pipe" process added to a conventional coal-fired plant. The EPRI report presents detailed heat and mass balances.

The key aspect of the EPRI conceptual model is that the energy for regenerating the MEA solution (and producing a concentrated CO₂ stream) is supplied by steam withdrawn from the steam cycle, upstream of the low-pressure (LP) turbine. The reduced steam flow to the LP turbine results in reduced power production - a derating of the plant.

For this feasibility study to be consistent with the EPRI basis, the RTI process was also configured to use steam withdrawn from the steam cycle as the source of the heat energy for the sorbent regeneration. Figure 1 is a schematic of the process modeled to provide a consistent basis for a comparative economic evaluation. It comprises two entrained bed reactors and supporting equipment including pumps, compressors and heat exchangers. The

dry regenerable sorbent is assumed to be an attrition-resistant, supported sodium carbonate in order to meet the performance requirements of an entrained-bed reactor system.

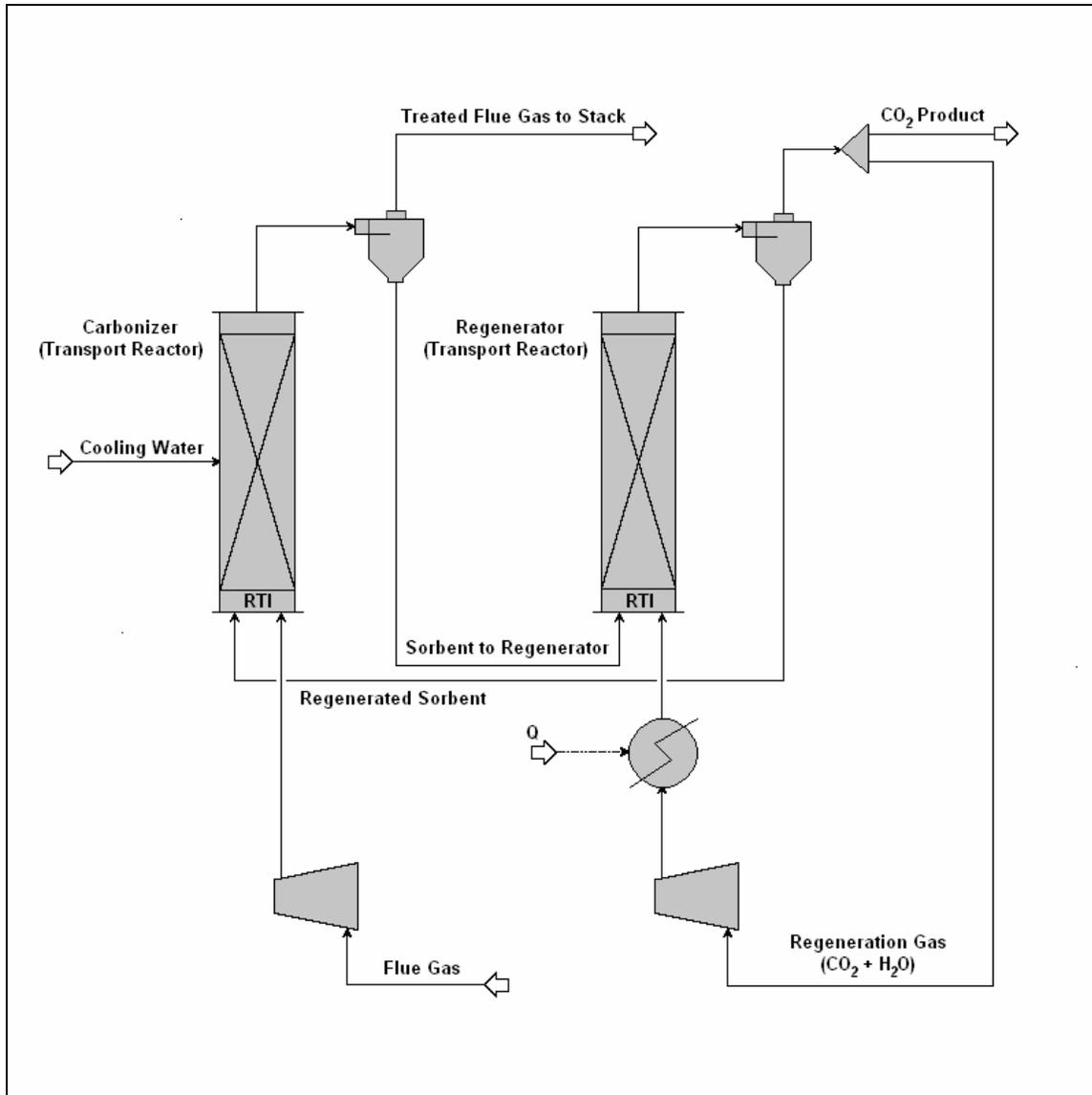


Figure 1. Schematic representation of the process concept that was modeled using ASPEN PLUS software. The results of this simulation were supplied to Church & Dwight as the basis for the economic feasibility study.

Flue gas, assumed to be coming from a wet scrubber-type flue gas desulfurization unit is boosted to the required pressure by a blower. This pressure varies depending on the assumed height of the carbonizer and the assumed gas velocity.

The flue gas contacts the regenerated sorbent in the vertical upflow carbonizer. Liquid water is added to the carbonizer which, through evaporation removes part of the heat of the carbonation

reaction. The carbonated sorbent is separated from the flue gas (using a cyclone as the primary separation device) at the top of the carbonizer, and passes to the regenerator.

A recycle stream of carbon dioxide and water vapor is used as the regeneration gas. In the process configuration used for this study, all of the heat required for regeneration (shown as "Q" in Figure 1) is transferred to the regeneration gas that in turn transfers the heat to the solid sorbent. The regenerated sorbent is separated from the flue gas in a cyclone (or other device) at the top of the regenerator, and passes back to the carbonizer. A portion of the regeneration gas flow is diverted to become the net CO₂ product stream, after condensation of water.

EPRI case 7A is based on withdrawal of steam from the generating plant at ~78 psia and 725°F. These conditions have been preserved for the comparative analysis. A mass and energy balance for the regenerable sorbent process was developed on this basis. The flow rate of steam to the regeneration gas heater was fixed at the same flow rate as Case 7A. Several key parameters were varied to close the energy and mass balances:

- Sorbent loading in the carbonizer (a function of assumed carbonation reaction rate and the entrained flow/fluidization characteristics)
- Regeneration gas flow rate (sufficient to fluidize and transport the sorbent in the regenerator)
- Regeneration gas inlet temperature (sufficient to keep the regeneration gas temperature above the equilibrium temperature of the regeneration reaction).

The mass and energy balance indicated that 32% of the CO₂ in the flue gas could be captured (converted to Wegscheider's salt) and subsequently released from the sorbent in concentrated form. In this balance, only the sensible heat (superheat) of the steam was used to provide the regeneration energy. The regeneration gas had to be at least 600°F at the inlet in order to provide sufficient sensible heat to regenerate the sorbent. This temperature is above the saturation temperature of 78 psia steam (310°F); thus, no latent heat of condensation could be recovered to drive the regeneration reaction, and the capacity of the system is constrained.

4.3.2 Summary of Church and Dwight Process Analysis

From the mass and energy balance supplied by RTI, Church & Dwight, working with a consultant, calculated that four or five 100-foot tall towers could be used to conduct the carbonation reaction, with a 15 ft/sec gas velocity (to result in a 7-second residence time). The reactor pressure drops were estimated to be 0.6 psia for carbonation and 0.9 psia for regeneration.

Under these assumptions, the retrofit process cost was estimated at \$6 to \$8/ton CO₂ for capital and operating costs and \$19 to \$21/ton CO₂ for the value of the lost power output. The total cost of \$25 to \$29/ton of CO₂ compared favorably to the EPRI case 7A/7B cost estimates of \$31 to \$32/ton CO₂. [It should be noted that the cost estimates for the EPRI cases with MEA absorption are more certain because equipment costs are based on actual operating experience.]

4.3.3 Additional Considerations

A potential advantage of the Dry Carbonate process over a MEA-based process is that the regeneration of dry sodium bicarbonate (more precisely, Wegscheider's salt) to sodium carbonate could be accomplished with lower quality steam than that used in the EPRI analysis.

With optimized heat integration (one possibility is by using indirect heat exchange in the regenerator) it is likely that parasitic power costs could be lowered, making the dry carbonate process more attractive.

Clearly, the capital cost of the dry carbonate process is strongly dependent on the reaction rates (particularly the carbonation rate) that can be achieved in a realistic reactor system. Sorbent testing in a fast fluidized-bed reactor system can provide information leading to more realistic rate predictions, better equipment sizing and a more accurate cost estimate. An additional uncertainty is expected sorbent life. Operation in a fast fluidized bed reactor system, particularly with a coal combustion flue gas will provide a better idea of the extent of sorbent makeup requirements, which may have a significant effect on process economics.

4.4 Other Project Activities

RTI presented a paper at the Global Climate and Energy Project Workshop on Carbon Capture and Sequestration at Stanford University in April, 2004. Also, RTI prepared a poster that was exhibited at the Third Annual Conference on Carbon Sequestration in Alexandria, Virginia, in May, 2004.

5.0 CONCLUSIONS

When the water content of the slurry from which spray dried sorbents were prepared was minimized, the resulting sorbents, after drying and calcination had inadequate attrition resistance. Varying the nozzle size and projection had minimal effect on the activity and attrition resistance of spray dried sorbents. Sorbents can be prepared by impregnating spray dried support materials that retain the attrition resistance of the support at the expense of some decrease in surface area.

A conceptual design of a dry regenerable sodium carbonate-based CO₂ capture process applied to a baseline retrofit power plant case suggested that 4 or 5 100-foot towers could be used for carbonation. As with MEA-based processes, lost power output, resulting from the use of steam for sorbent regeneration accounts for the bulk of the process cost.

6.0 FUTURE WORK

Design work for a pilot fluidized bed regenerable dry sodium carbonate sorbent module for use at the NETL modular carbon capture facility will continue. Optimization of the supported sorbent will continue. Activity and attrition testing of sorbents prepared in the current quarter will be completed in the upcoming quarter.

7.0 REFERENCES

1. Holt, N. A., Ed. "Evaluation of Innovative Fossil Fuel Power Plants with CO₂ Removal." Interim Report 1000316. EPRI, Palo Alto, California. December 2000.