

CARBON DIOXIDE CAPTURE FROM FLUE GAS USING DRY REGENERABLE SORBENTS

QUARTERLY TECHNICAL PROGRESS REPORT

Reporting Period: July 1, 2004 to September 30, 2004

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ABSTRACT

This report is being submitted as the Quarterly Technical Progress Report covering the period July 1, 2004 through September 30, 2004. During this period a Topical Report was prepared that includes research conducted. The cover sheet, abstract, list of figures, tables and executive summary of that report is attached.

CARBON DIOXIDE CAPTURE FROM FLUE GAS USING DRY REGENERABLE SORBENTS

TOPICAL REPORT

DOE Cooperative Agreement No. DE-FC26-00NT40923

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ABSTRACT

Laboratory studies were conducted to investigate dry, regenerable, alkali carbonate-based sorbents for the capture of CO_2 from power plant flue gas. Electrobalance, fixed-bed and fluid-bed reactors were used to examine both the CO_2 capture and sorbent regeneration phases of the process. Sodium carbonate-based sorbents (calcined sodium bicarbonate and calcined trona) were the primary focus of the testing. Supported sodium carbonate and potassium carbonate sorbents were also tested.

Sodium carbonate reacts with CO_2 and water vapor contained in flue gas at temperatures between 60 and 80°C to form sodium bicarbonate, or an intermediate salt (Wegscheider's salt). Thermal regeneration of this sorbent produces an off-gas containing equal molar quantities of CO_2 and H_2O . The low temperature range in which the carbonation reaction takes place is suited to treatment of coal-derived flue gases following wet flue gas desulfurization processes, but limits the concentration of water vapor which is an essential reactant in the carbonation reaction. Sorbent regeneration in an atmosphere of CO_2 and water vapor can be carried out at a temperature of 160°C or higher. Pure CO_2 suitable for use or sequestration is available after condensation of the H_2O . Flue gas contaminants such as SO_2 react irreversibly with the sorbent so that upstream desulfurization will be required when sulfur-containing fossil fuels are used.

Approximately 90% CO_2 capture from a simulated flue gas was achieved during the early stages of fixed-bed reactor tests using a nominal carbonation temperature of 60°C. Effectively complete sorbent carbonation is possible when the fixed-bed test is carried out to completion. No decrease in sorbent activity was noted in a 15-cycle test using the above carbonation conditions coupled with regeneration in pure CO_2 at 160°C.

Fluidized-bed reactor tests of up to five cycles were conducted. Carbonation of sodium carbonate in these tests is initially very rapid and high degrees of removal are possible. The exothermic nature of the carbonation reaction resulted in a rise in bed temperature and subsequent decline in removal rate. Good temperature control, possibly through addition of supplemental water and evaporative cooling, appears to be the key to getting consistent carbon dioxide removal in a full-scale reactor system.

The tendency of the alkali carbonate sorbents to cake on contact with liquid water complicates laboratory investigations as well as the design of larger scale systems. Also their low attrition

resistance appears unsuitable for their use in dilute-phase transport reactor systems. Sodium and potassium carbonate have been incorporated in ceramic supports to obtain greater surface area and attrition resistance, using a laboratory spray dryer. The caking tendency is reduced and attrition resistance increased by supporting the sorbent. Supported sorbents with loading of up to 40 wt% sodium and potassium carbonate have been prepared and tested. These materials may improve the feasibility of large-scale CO₂ capture systems based on short residence time dilute-phase transport reactor systems.

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LIST OF ACRONYMS AND ABBREVIATIONS

AR	Attrition Ration
BET	Brunauer-Emmett-Teller
FID	flame ionization detector
HPLC	high-pressure liquid chromatography
LSU	Louisiana State University
MFC	mass flow controllers
SBC	sodium bicarbonate
TCD	thermal conductivity detector
PTFE	polytetrafluoroethane
PC	personal computer
ppm	parts per million
sccm	standard cubic centimeters per minute

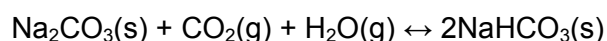
EXECUTIVE SUMMARY

This report contains information relating to research on the capture of CO₂ from flue gas using dry, regenerable, alkali carbonate–based sorbents. The research was sponsored by the U.S. Department of Energy, National Energy Technology Laboratory. RTI International¹ (RTI) was the prime contractor and Louisiana State University (LSU) served as subcontractor. Church and Dwight, Inc. was the industrial partner for the project.

Combustion of fossil fuels since the beginning of the industrial revolution is believed to be a major cause of the increased concentration of CO₂ in the atmosphere. It is becoming clear that improved energy efficiency and substitution of low-carbon fuels, while important, will not be sufficient to limit the growth of atmospheric CO₂ concentrations. New technologies for the capture and sequestration of CO₂ are needed.

The only currently available process for the capture of CO₂ from flue gas streams is based on amine scrubbing, a costly and energy-intensive process. The regenerable sorbent-based process being developed in this project provides an alternate to amine scrubbing. This process is applicable to the capture of CO₂ from existing fossil fuel–fired power plants and is potentially applicable to CO₂ capture from all stationary fossil fuel combustion sources.

The important reactions involved in the capture of CO₂ using sodium carbonate (Na₂CO₃) sorbents result in the reversible formation of sodium bicarbonate (NaHCO₃) and Wegscheider's salt (Na₂CO₃•3NaHCO₃):



and



Both forward reactions are exothermic. CO₂ capture is accomplished by the forward reactions while equal molar quantities of CO₂ and H₂O are produced by the reverse, or sorbent regeneration, reactions. Condensation of H₂O from the regeneration product gas results in a pure CO₂ product suitable for use or sequestration.

Laboratory studies of the CO₂ capture and regeneration reactions have been conducted in an electrobalance (thermogravimetric analyzer) and in bench-scale fixed-bed and fluidized-bed

¹ RTI International is a trade name of Research Triangle Institute.

reactor systems. Physical properties of sorbents including several grades of calcined sodium bicarbonate (SBC), calcined trona, and potassium carbonate have been determined.

Multicycle tests have been conducted to provide preliminary information on sorbent durability. The carbonation reaction was studied in the electrobalance between 60°C and 80°C using, in most cases, a feed gas containing 8% CO₂ and 16% H₂O, with the balance made up of an inert gas (either He or N₂). These CO₂ and H₂O contents simulate the flue gas formed from the complete combustion of CH₄ using 10% excess air. Calcination was studied between 120°C and 200°C in an atmosphere ranging from 0% CO₂ (100% inert) to 100% CO₂. Low-temperature calcination in an inert atmosphere, while not commercially feasible, was chosen to minimize the severity of the sorbent exposure during the calcination phase. If pure CO₂ is to be produced in a commercial process, a high-CO₂ calcination atmosphere must be used along with a higher calcination temperature. These tests confirmed that the optimal carbonation temperature was in the 60°C to 70°C range. The minimum temperature is established by the dew point of the feed gas while the maximum temperature is limited by the thermodynamics of the reversible carbonation reaction. The carbonation rate was found to increase with increases in both the H₂O and CO₂ concentrations.

The addition of SO₂ (0.1% to 0.4%) to the carbonation feed gas to simulate the flue gas composition from combustion of a sulfur-containing fuel produced a rapid decrease in CO₂ removal capacity due to the formation of Na₂SO₃. For example, when 0.1% SO₂ was added to the feed gas, the sorbent capacity for CO₂ removal decreased by about 76% during five-cycle tests. The Na₂SO₃ was stable in an inert atmosphere at temperatures as high as 200°C. When sulfur-containing fossil fuels are used, the CO₂ sorbent capture step must be downstream of a desulfurization step.

Fixed-bed reactor tests with product gas analysis as a function of time using gas chromatography were used to study the extent of CO₂ removal as a function of time. Nominal carbonation temperatures of 60°C and 70°C were studied, along with calcination in N₂ at 120°C and in CO₂ at both 160°C and 200°C. Five-cycle tests and one 15-cycle test were used to obtain additional information on sorbent durability. When the fixed-bed tests were carried to completion, the final percentage conversion of Na₂CO₃ to Wegscheider's salt was approximately 100% in the 60°C tests and about 90% in the tests at 70°C.

Fluidized-bed reactor tests of up to five cycles were conducted. Carbonation of sodium carbonate in these tests was initially very rapid and high degrees of removal were obtained. The exothermic nature of the carbonation reaction resulted in a rise in bed temperature and subsequent decline in removal rate. Good temperature control, possibly through water addition and subsequent evaporative cooling, appears to be the key to getting consistent carbon dioxide removal in a full-scale reactor system.

The tendency of the alkali carbonate sorbents to cake on contact with liquid water complicates laboratory investigations as well as the design of larger scale systems. The low temperature range in which the carbonation reaction takes place is suited to treatment of coal-derived flue gases following wet flue gas desulfurization processes, but limits the concentration of water vapor which is an essential reactant in the carbonation reaction. Also these sorbents have low attrition resistance and cannot be used without modification in dilute-phase transport reactor systems.

Sodium and potassium carbonate have been incorporated in high surface area ceramic supports to obtain greater surface area and attrition resistance, using a laboratory spray dryer. The caking tendency is reduced and attrition resistance increased by supporting the sorbent. Supported sorbents with loadings of up to 40 wt% sodium and potassium carbonates have been prepared and tested. These materials may improve the feasibility of large-scale CO₂ capture systems based on short residence time dilute-phase transport reactor systems.