Study of Regenerable Sorbents for CO$_2$ Capture

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Introduction

Carbon dioxide (CO$_2$) is a greenhouse gas that is customarily released to the environment during the usage of fossil fuels, including electric power generation. With the projected increase in consumption and demand for fossil fuels, CO$_2$ emissions will correspondingly increase in the absence of any capture/sequestration strategy. In view that CO$_2$ is a greenhouse gas with the potential to contribute to global climate warming, existing and improved technologies to mitigate the release of CO$_2$ to the environment are being considered as a prudent precaution against global warming. Industry, if mandated to remove CO$_2$ from gases emitted to the atmosphere, will certainly require improved and novel technologies for the removal of CO$_2$.

Carbon dioxide can be removed from flue gas and waste gas streams produced from carbon usage by various methods, that include absorption with a solvent, membrane separation, cryogenic fractionation, and adsorption using molecular sieves [Herzog et al., 1997]. Capture of CO$_2$ from each of these processes is costly. Another technique for removal of carbon dioxide is dry scrubbing or chemical absorption of CO$_2$ with a solid sorbent. The development of dry, regenerable scrubbing processes for CO$_2$ capture is the focus of the current study.

Objective

The objective of the study is to identify and evaluate novel sorbents that potentially could be utilized in a dry, regenerable scrubbing process for the capture of CO$_2$ from gaseous streams. Of particular interest are sorbents containing alkali- and alkaline-earth metals distributed onto a substrate support. Specifically, potassium carbonate and calcium oxide are the subjects of the experimental investigations. The chemical reactions for CO$_2$ capture using these compounds are shown in reactions 1 and 2. The forward reaction path depicts absorption of CO$_2$, whereas regeneration is expressed as the reverse reaction path.

$$K_2CO_3 + CO_2 + H_2O \Leftrightarrow 2KHCO_3 \qquad (1)$$

$$CaO + CO_2 \Leftrightarrow CaCO_3 \qquad (2)$$

The use of alkali- or alkaline-earth metals for CO$_2$ capture has been previously reported in the literature. Work by Japanese researchers encompassed the potential use of potassium, sodium, and

lithium compounds as CO_2 sorbents [Hayashi et al., 1998]. Potassium carbonate was emphasized as a good candidate while utilizing an activated carbon as the substrate material. Earlier studies by the same researchers [Hayashi et al., 1995; Hirano et al., 1995] examined the use of other substrate materials, including silica gel and alumina.

The use of potassium carbonate, in addition to other alkali-metal materials, was studied by the space agency (NASA) as a regenerative means by which to absorb CO_2 and H_2O [Onischak et al., 1978]. The intent was to develop portable life support systems to scrub breathing air during human space travel. Japan, in conjunction with development of the space station with NASA, also pursued regenerable solid sorbents for space travel using a solid amine [Otsuji et al., 1987]. Some of the yet earlier space work considered molecular sieves, clathrates, and zeolites for regenerable solid sorbents for CO_2 capture [Martin, 1969; Trusch, 1967; Remus et al., 1969].

In other work, silver was used to capture CO_2 [Nalette et al., 1992]. The unsupported solid sorbent was composed of silver carbonate in a combination of alkali metal silicate (sodium and/or potassium), alkali metal carbonate (cesium, potassium and/or sodium), and an alkaline earth metal salt (nitrates and chlorides of calcium, magnesium, and/or barium). An example was cited for a sorbent comprised of calcium nitrate, sodium silicate, potassium carbonate, and silver carbonate. The same authors also investigated amine compounds on solid supports for CO_2 sorbents [Bibara et al., 1999].

The use of calcium, an alkaline earth metal, for CO_2 capture in a dry, regenerable sorbent process, has been proposed in prior studies. The carbonation reaction is employed in the CO_2 Acceptor Process developed several decades ago for coal gasification [Curran et al., 1967]. A summary of the process [Elliott, 1981] describes the gasification of coal by steam. The energy required for gasification is partially supplied by the exothermic carbonation reaction of dolomitic lime.

Of more recent notable interest is a series of papers by several investigators [Siliban et al., 1995; Siliban et al., 1996; Han et al., 1997]. The effects of temperature, pressure, and reactive gas composition on the gas-solid reaction was examined in an electrobalance reactor. Multicyle tests were conducted to demonstrate the durability of the material. Some degradation of the material was observed during multicycle tests. Calcined dolomite, a mixture of $CaCO_3$ and $MgCO_3$, proved to be superior in performance to calcined $CaCO_3$. It should be noted that these studies were conducted using fine, unsupported, powdered materials and are therefore much smaller than the sorbents under consideration in the current study.

Approach

Prior to the experimentation, a thermodynamic analysis was conducted for some proposed alkali- and alkaline-earth sorbents of interest. Enthalpy and free energy changes were calculated for both absorption and regeneration reactions. Equilibrium constants were formulated over a range of temperatures. Results for alkali-based sorbents are generally favorable in that the forward (CO_2 absorption) reaction rate is typically much larger than the reverse reaction. Thermodynamic analysis identified ranges of temperature for absorption and regeneration to be thermodynamically feasible.

The approach undertaken in the study was to investigate sorbents using two reactor systems; a thermogravimetric analyzer (TGA) and a packed-bed reactor. For the TGA system, change in sample weight was recorded as the sorbent was exposed to gases under conditions representative of absorption and regeneration. The extent of chemical reaction was linked to sample weight change, from which kinetic rate parameters could be estimated. In the packed-bed reactor system, process gases were flowed through a stationary bed of sorbent. The effluent from the reactor was fed to continuous emission monitors (CEM), facilitating on-line measurement of gas composition, including CO_2, and thus the breakthrough curve.

Project Description

Experiments were performed using a microbalance assembly consisting of a Cahn TG-131 Thermogravimetric Analyzer (TGA). Gas composition that approximately simulates flue gas was created by blending high purity gases using mass flow controllers (Brooks model 5850E controller and Brooks model 5878 instrument readout). Carbon dioxide of stock gas grade (99.99%) was supplied by gas cylinder and pressure regulator, and a house supply of dry nitrogen was utilized. The gas stream was humidified using a sparger vessel. Gas relative humidity was verified using a Vaisala HMP-36 humidity/temperature probe and a Vaisala HMI-32 instrument readout. Moisture-laden gas streams were heat-traced with electrical heating tapes and controlled by variable autotransformers (Variac). A heated section had one heating tape with one thermocouple mounted on the external surface. The electrical power to the tape was manually governed by Variac setting to achieve a temperature readout in excess of the dew point to prevent condensation. A circulating bath (Haake) of ethylene glycol/water was used to provide fine temperature control of the gas mixture prior to the gas entering the reactor.

Approximately 200 mg of sample was placed in a quartz cylindrical sample pan. Slotted apertures in the bottom and side wall of the sample pan help mitigate gas diffusional resistance. Sample temperature was measured and controlled with a type K thermocouple placed immediately below the suspended sample pan. Total gas flow rate was held constant at 140 cc/min. For the typical baseline condition during CO_2 absorption, the gas inlet composition (vol%) was typically 10% CO_2, 10% H_2O, and 80% N_2, at a TGA reactor temperature of 60°C.

After charging the sorbent to the TGA, the sample was preconditioned and dried in nitrogen by elevating the reactor temperature to 150°C for approximately 4 hours. This preheating near the thermal regeneration temperature assured that the initial chemical state of the sample contained only reactant material (potassium carbonate) and no product material (potassium bicarbonate). The sample was then cooled to the desired absorption temperature and allowed to come to steady state, both thermally and gravimetrically.

The sample was then preconditioned with humidified gas by switching the sparger in-line, whereby nitrogen was flowed through the heated reservoir of water in the sparger. The ability of the sparger to achieve saturation of the nitrogen gas was verified with a sampling probe measuring relative humidity and gas temperature. The humidity probe was independently calibrated against several standards including saturated salt solutions.

Once the sample achieved steady state under humidified conditions, carbon dioxide was added to the water/nitrogen mixture. Nitrogen gas flows were adjusted so that the sample was exposed to the same level of moisture (10%) and total flow rate (140 cc/min) prior to the introduction of CO_2. The CO_2 absorption stage was allowed to proceed until a steady-state weight gain was achieved.

The sequence of gas switching was then reversed. First CO_2 was turned off, eventually followed by a termination of the humidification. The motivation for observing the sample during CO_2 isolation was to verify what fraction of the weight gain during absorption was indeed permanent weight gain by chemical reaction to form bicarbonate. Some of the weight gain was due to physical sorption of CO_2, most likely onto the alumina substrate. Once the sample was exposed to a gas lacking carbon dioxide (i.e., moist N_2), sorbed CO_2 would then desorb from the substrate, resulting in sample weight loss. This difference in the initial and final sample weight under humidified conditions represented chemical CO_2 uptake by the sorbent, from which an overall sorbent utilization was calculated based on the metal loading and theoretical weight gain due to bicarbonate formation.

Experiments were conducted at larger scale in a packed-bed reactor to supplement the information obtained during TGA testing. The reactor is comprised of a quartz tube measuring 40 mm internal diameter by 450 mm length. Sorbent sample was placed on a fritted filter in the center of the quartz tube, and then positioned at the center of a 400 mm clam-shell furnace. The furnace has a heating zone of 300 mm length and is controlled by a linear programmable controller. Bed temperature was measured and controlled through the use of a dual type J thermocouple located in the sample bed. A sample charge of 75 grams of sorbent resulted in a bed height of about 3 inches, and the thermocouple was positioned at approximately the 1-inch bed height, corresponding to the bottom third of the inventory. Secondary temperature controls for heater tapes along the gas inlet path served to control the temperatures of several gas mixing chambers and a water humidification chamber. A superficial gas contact time of 3.7 seconds was provided based on total gas flowrate (1.5 liter/min at STP) and sample bulk density. Gas composition was blended from gas cylinders using thermal mass flow controllers, and water was metered using a variable flow dispensing pump. The packed-bed system is configured with gas analyzers for continuous monitoring of flue gas components (SO_2, NO_2, O_2, hydrocarbons, etc.), but for the current study, only a CO_2 gas analyzer was required to monitor gas composition. The process gas is passed through a Perma Pure drying tube to remove moisture prior to the stream entering the gas analysis train.

The experimental procedure and test conditions employed for the packed-bed tests were similar to those used for the TGA tests. Gas composition and reactor temperatures were chosen to replicate the TGA test conditions. For the typical baseline condition during CO_2 absorption, the gas inlet composition (vol%) was typically 10% CO_2, 10% H_2O, and 80% N_2, at a reactor temperature of 60°C. Once the sample was charged to the system, it was dried under nitrogen, then humidified, and then exposed to CO_2 during the absorption step. Once CO_2 breakthrough was complete and the exit gas reached the inlet CO_2 level, the reactor was isolated (i.e., gas bypass) and the gas analyzer was recalibrated. The reactor was then brought back on-line and thermal regeneration was initiated by raising the bed temperature. However, the rate of temperature ramping was much slower in the packed-bed tests, due to larger thermal inertia, as compared to the TGA tests. Therefore, it is difficult to assign a singular temperature for the condition of regeneration, although a target

regeneration temperature of 150°C was eventually achieved. Due to limited sample quantity, the same sample was used repetitively and was not removed from the reactor after each test, but instead remained within the reactor as the sample was cycled between absorption and regeneration for various test conditions. Baseline conditions were re-tested periodically to check for degradation in system performance.

Results

Results using a potassium carbonate sorbent have been previously reported [Hoffman and Pennline, 2000], and major findings are summarized here. The experimental description for the current study, with few minor exceptions, remains unchanged from the previous investigation.

Thermodynamic analysis identified ranges of temperature for absorption and regeneration to be thermodynamically feasible. Potassium carbonate is applicable for CO_2 capture at low absorption temperatures (less than 145°C), while calcium oxide is applicable for much higher absorption temperatures (less than 860°C).

Experiments were conducted in both a TGA reactor and a packed-bed reactor using sorbent fabricated from potassium carbonate supported on a high surface area activated alumina. Sorbent batches with potassium loadings (as potassium carbonate) of 12.2 and 17.1 weight percent were prepared for experimental evaluation. Chemical analyses indicated approximately one-third of the surface area was lost upon impregnation of the metal, but the potassium loading is uniform across the cross-section of the sorbent sample as determined by XPS analysis.

TGA experiments were typically conducted using a gas composition (vol%) of 10% CO_2, 10% H_2O, with balance N_2. TGA results indicate CO_2 capture is favored at low absorption temperature (50-60°C), with sorbent utilization strongly decreasing with higher absorption temperature (80-100°C). Higher potassium loading on the sorbent did not provide additional benefit for CO_2 capture, as evidenced by lower sorbent utilization for the higher loaded sorbent. The sorbent was thermally regenerated at 150°C, which is consistent with the predicted temperature based on thermodynamic analysis.

Packed-bed results provided the additional benefit of measuring changes in exit gas composition (CO_2) as well as changes in bed temperature due to exothermic reaction. Breakthrough of CO_2 through the bed was strongly influenced by higher inlet CO_2 levels. The onset of bed temperature rise was noted to coincide with the breakthrough of CO_2, with earlier CO_2 breakthrough characterized by earlier temperature rise within the bed. Minor differences in the breakthrough curve were noted for absorption temperatures ranging between 60-100°C. Moisture difference was found to have little influence on the breakthrough curve. Sorption of moisture onto the sample, in the absence of CO_2, did not result in bed temperature rise. Absorption after multi-cycling of the sorbent between absorption and regeneration results in equivalent CO_2 breakthrough curves and thus indicates that negligible sorbent degradation is occurring.

The alumina substrate, when tested individually, does exhibit an affinity to sorb CO_2. In the TGA tests, some of the CO_2 is presumably desorbed (as observed as sample weight loss) as the sample is

exposed to nitrogen following CO_2 absorption. In the packed-bed tests, the CO_2 breakthrough curve for the substrate occurs in approximately half the time as for the sorbent (alumina plus potassium carbonate). In addition, a temperature rise does occur for the substrate when exposed to CO_2, indicating that the substrate does participate in the capture of CO_2.

More recently, the TGA data was analyzed in greater detail in an attempt to extract kinetic rate information. The effect of temperature on the reaction rate was studied, and an apparent activation energy was determined. Chemical reaction is assumed to be the rate limiting step, and diffusion is assumed to be a minor resistance. Derivatives of the weight/time data were calculated, from which the maximum and average derivatives were then related to reaction rate law expressions. Data was fitted to a first order Arrhenius rate law, and the regression line coefficients were used to calculate the overall activation energy and preexponential term. It must be noted that some limitations in the data did periodically make interpretation of the results difficult. For the reaction of CO_2 absorption using potassium carbonate, the activation energy was estimated at approximately 4 kcal/mole and the preexponential term was approximately 10^{-3}/hr. A comparison was made to an analogous gas-solid absorption reaction that has previously been investigated at NETL [Yeh et al., 1987]. The reaction of SO_2 with an alumina supported copper oxide sorbent has been used in regenerable processes to remove SO_2 from flue gas. The copper oxide absorption reaction has a similar activation energy (approximately 5 kcal/mole), but the preexponential term (approximately 10^{+4}/hr) is vastly larger by many orders of magnitude than the CO_2 absorption reaction. Hence the CO_2 absorption reaction appears considerably slow in comparison to an SO_2 removal system. Although the reactions have different optimal reaction temperatures and process conditions, concentration levels, etc., the comparison does yield qualitative insight into the slow nature of the CO_2 absorption reaction using the potassium carbonate sorbent.

For the next phase of the investigation, sorbents composed of calcium deposited on silica were prepared. For the substrate support, silica was selected based on the thermodynamically-predicted high operating temperatures required for absorption and regeneration. Sintering expected to occur for activated alumina at elevated temperature would be eliminated with silica.

The silica, Type XS 16080 from Norton Chemical [Koradia, 2000], consists of 1/8" diameter cylindrical pellets. The original extrudates were cleaved with a razor blade to yield pellets whose length approximated its diameter, and thus a similar aspect ratio. The silica has a medium surface area (117 m^2/g) with a packing density of 40.5 lbs/ft^3 and a crush strength of 14.4 lbs. The total pore volume was 0.8 cc/g and the median pore diameter was 393 Angstroms.

Calcium nitrate tetrahydrate [ACS reagent grade, 99% $Ca(NO_3)_2 \bullet 4H_2O$] from Aldrich Chemical was used to deposit the calcium onto the silica. Acetone [ACS reagent grade, 99.6%] from Mallinckrodt Chemical was the solution medium in which the wet impregnation occurred. Calcination of the impregnated silica at 400°C under nitrogen for 48 hours converted the calcium nitrate tetrahydrate into calcium oxide on the silica.

Six batches of sorbent were prepared for use in this study. For a batch, silica was added to a specific solution, soaked for 18 hours, dried at 100-110°C for approximately three hours, and then calcined. Properties of the sorbent batches and of the silica substrate itself, are listed in Table 1.

Samples were routinely dried at temperatures in excess of 100°C prior to performing the chemical analysis. In Table 1, samples not calcined are designated as "uncal", whereas calcined samples are denoted as "cal". Silica substrate (with no calcium impregnation) is designated as "Sub", and impregnated sorbent batches as "B#". Analysis for metals were conducted using two sample preparation methods. For the microwave digestion technique, high-temperature fusion of the sample matrix with a low-melting salt is conducted followed by dissolution with a dilute acid. The hot plate digestion technique follows ASTM Method PS 52-96. For both methods, the resulting solution is analyzed using ICP emission spectroscopy on a Perkin Elmer Optima 3000 spectrometer. The former preparation method allows both calcium and silicon to be dissolved from the sample matrix for analysis. The latter method assures better dissolution of the calcium from the matrix, but silicon is not recovered.

Results in Table 1 are given in terms of pure metal content as determined by analysis, as well as the calculated loading of each metal compound assumed in its oxidized state. A check on the material balance of analysis for the sample is calculated by summing the levels of the calcium oxide and silica loadings, the only two predominant compounds assumed present. Higher levels of impregnated calcium (up to 9 wt% Ca) were achieved by raising the calcium nitrate tetrahydrate concentration in the starting absorbing solution, but a point of diminishing return was obvious in the trend of the data. There is generally good agreement in calcium content when the results of the two sample preparation techniques are compared, lending confidence to the calcium determination. For most of the samples, the material balance is within 10% for the summed total analysis.

Materials will be additionally characterized for BET surface area, pore volume, and average pore radius. To check on the uniformity of the impregnation of calcium within the pellet, representative samples will be analyzed with x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). In order to image the cross section of the calcium-containing pellet, the pellets will be cleaved both radially and longitudinally in half with a razor blade to produce a relatively smooth cross section to image.

Preliminary SEM photos taken of the sorbent cross sections have yielded favorable results with respect to calcium distribution. The inner region of the pellet definitely contains calcium, and therefore internal calcium voids are not present. The distribution of calcium is fairly uniform across the majority of the cross section, both longitudinally and radially. For some of the samples, particularly those having higher overall calcium deposition, an outer shell of high calcium loading can be observed, suggesting an impedance to experimentally attaining even higher calcium deposition uniformly throughout the entire pellet. When comparing uncalcined and calcined samples, no apparent differences are noted due to the calcination step. In some of the samples, hairline fractures are evident throughout the cross section of the pellet.

Application

For a dry, regenerable sorbent system, the process consists of two major steps: an absorption step where CO_2 is removed from a gaseous stream by the action of the sorbent; and a regeneration step where the sorbent is rejuvenated and a concentrated stream of CO_2 is off-gased. In the first step, the reaction of the active chemical by itself or on a support occurs in the gas phase to form a

bicarbonate/carbonate that is the product of the CO_2 removal reaction. In the second step, the sorbent is regenerated by chemically treating it or by heating it to the decomposition temperature so that CO_2 is produced in a concentrated stream. The sorbent is then recycled back to begin another cycle

For a conceptual commercial system employing continuous integrated absorption and regeneration operation, the process is cyclic but different than switching between two static reactors in tandem or parallel. It is envisioned that in the first step, carbon dioxide is captured by a moving-bed of sorbent. The absorption reactor design is unique in that a cross-flow moving-bed configuration is utilized. Carbon dioxide-laden gas flows horizontally through the reactor where the sorbent removes CO_2. Similarly, the sorbent flows continuously vertically through the reactor. The sorbent is then transported to the regenerator. In the regenerator, the sorbent is thermally or chemically regenerated in a moving-bed or fluidized-bed mode. The sorbent flows continuously through the reactor and is transported back to the absorber where another sorbent cycle begins.

This dry, regenerable sorbent process can be installed on new facilities or retrofitted into an existing producer of CO_2-containing gas, for example, a utility or industrial boiler. Depending on the optimum temperature of CO_2 absorption with the sorbent, the absorber could be placed anywhere along the gas stream that may have been or will be treated with another scrubbing process to remove other pollutants. With respect to new advanced power systems, for example, Integrated Gasification Combined Cycle, High Performance Power Systems, Pressurized Fluid Bed Combustors, Vision 21 Systems, etc., the process can be installed at appropriate locations.

A dry, regenerable sorbent process can offer certain processing advantages. Utilization of a cross-flow, moving-bed absorber, as compared to fluidized bed or other reactor configurations, presents the potential advantages of high levels of CO_2 removals, high sorbent utilization, low pressure drop, and low sorbent attrition. Additional economic advantages over commercially available CO_2 wet scrubbing technologies [Bartoo, 1984] exist. The contacting of the CO_2-laden gas with a solid bed of material is better since less vessel volume is needed for the processing; temperature control could be better; a massive quantity of water is not required in the capture step; and overall energy consumption would be less since pressure drop would be less for gas/solid contact as compared to commercial gas/liquid contact design. Also, the land area required for installation of the proposed technology is less since wet scrubbing systems, if retrofitted onto existing power plants, would require land area almost as vast as the power plant itself [DOE, 1993].

Future Activities

Parametric experiments using a calcium-based sorbent will be continued in both the TGA and the packed-bed apparatus. Optimal process parameters for absorption and regeneration will be identified, and kinetic rate information extracted. An existing numerical model of a moving-bed absorber will be modified to incorporate the kinetic information of the alkali/alkaline earth sorbents tested to date. Additionally, a systems analysis will be pursued to help identify key parameters affecting performance as well as guide future research efforts to enhance technical performance and/or reduce costs.

Disclaimer

References in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Table 1. Elemental Analysis of Ca-Loaded Silica Samples

Sample	Solution Mix			Silica (g)	Ca (wt%)		Si (wt%)	CaO (wt%)		SiO$_2$ (wt%)	Total (wt%)
	Ca(NO$_3$)$_2$•4H$_2$O (g)	Acetone (ml)	Conc (g/ml)		Micro wave	Hot Plate	Micro wave	Micro wave	Hot Plate	Micro wave	Micro wave
uncal-Sub	-	-	-	12	0		47.4	0		101.4	101.4
uncal-B1	8	50	0.16	12	1.92		44.5	2.69		95.2	97.9
uncal-B2	16	50	0.32	12	3.07		42.1	4.29		90.0	94.3
uncal-B3	24	50	0.48	12	4.06		40.0	5.68		85.6	91.3
uncal-B4	32	50	0.64	12	4.83		37.4	6.76		80.0	86.8
uncal-Sub	-	-	-	12	0		46.4	0		99.2	99.2
uncal-B6	25	25	1.00	12	5.80		30.5	8.11		65.2	73.3
uncal-B5	40	25	1.60	12	7.33		29.5	10.3		63.1	73.4
cal-Sub	-	-	-	12	0	0	47.9	0	0	102.4	102.4
cal-B1	8	50	0.16	12	1.70	2.09	40.7	2.38	2.92	87.0	89.4
cal-B2	16	50	0.32	12	3.13	3.41	41.0	4.38	4.77	87.7	92.1
cal-B3	24	50	0.48	12	4.64	4.68	44.4	6.49	6.55	95.0	101.5
cal-B4	32	50	0.64	12	5.68	5.73	43.7	7.95	8.02	93.5	101.5
cal-Sub	-	-	-	12	0		47.5	0		101.6	101.6
cal-B6	25	25	1.00	12	7.49		39.9	10.5		85.3	95.8
cal-B5	40	25	1.60	12	8.92		37.1	12.5		79.3	91.8