Removal and Recovery of Compressed CO_2 from Flue Gas by a Novel Thermal Swing Chemisorption Process

K. B. Lee and S. Sircar
Dept. of Chemical Engineering, Lehigh University, Bethlehem, PA 18015

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A synopsis of the published literature on removal of CO_2 from a flue gas is given. A novel thermal swing chemisorption (TSC) process concept is proposed for removal and recovery of compressed CO_2 from a flue gas without precompression, predrying, or precooling. The process uses Na_2O promoted alumina as a reversible CO_2 selective chemisorbent in conjunction with the principles of rapid thermal swing adsorption for direct production of compressed CO_2 from a flue gas. Several complementary process steps are used in the design to compress the product CO_2 and to achieve high CO_2 recovery and sorbent capacity utilization. Judicious steam purge steps are used for highly efficient sorbent regeneration and to minimize the steam requirement. The CO_2 chemisorption characteristics of the sorbent are reviewed and a model simulation of the TSC process performance is reported.
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Introduction

Carbon dioxide emission to the atmosphere is one of the main causes of global warming. Approximately 6.0 billion metric tons (bmt) of CO_2 was released into the air in the USA alone during the year of 2005, and it is estimated to reach 8.0 bmt per year by 2030.[1] CO_2 constitutes about 83.8% of total US greenhouse gas emission, others include CH_4 (9.3%), N_2O (5.2%), and HFCs (1.7%). Nearly 98% of all CO_2 emission sources in the USA are energy related. They include (1) the residential sector (e.g. combustion of natural gas for home heating), (2) the commercial sector (e.g. combustion of coal and natural gas for electricity production), (3) the industrial sector (e.g. chemical production of cement, lime, iron and steel, etc.), and (4) the transportation sector (e.g. combustion of gasoline and diesel).[1,2] Figure 1 shows the relative amounts of CO_2 emissions by these sectors. It is likely that CO_2 will continue to be emitted from the fossil fuel based energy infrastructure for the next several decades.[3]

The electric power generation industry (EPGI) approximately produces 40% of the total CO_2 in the USA. The shares of the electric power consumption by the above-described sectors are, respectively, 37.1, 34.5, 27.8, and 0.7%, and the primary sources of CO_2 for the EPGI are coal (~82.2%), natural gas (~13.5%), and petroleum (~4.2%).[1] The CO_2 is currently vented into the atmosphere as a waste (flue) gas after the necessary scrubbing and removal of acid gas contaminations (SO_x and NO_x). However, the CO_2 management goals by EPGI call for removal and sequestration of ~15, 30, and 80% CO_2 by the years 2015, 2025, and 2050, respectively.

Table 1 shows the CO_2 concentration of typical flue gases from various sources.[2–4] The balance is N_2, dilute O_2 (1–3%), and traces of the acid gases at a near ambient pressure and a temperature of 130–180°C.[2–4] The gas is generally saturated with water. The need for developing an efficient and economic method for recovering the CO_2 from a waste gas and its subsequent compression and sequestration

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Correspondence concerning this article should be addressed to S. Sircar at sircar@aol.com.

Current address of K. B. Lee: Alternative Fuels Research Center, Korea Institute of Energy Research, Daejeon, 305-343 Korea.

Figure 1. Annual CO_2 emissions by various sectors in the U.S.

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in geological formations (e.g. under ground caverns, fossil fuel reservoirs) or water bodies (e.g. lakes, oceans) has been a subject of much debate and discussions during the last decade. This has resulted in numerous studies and reviews on the subject.[3,5–8]

Some of the crucial technical issues for removal of CO_2 from a flue gas are that:

- The flue gas is generally produced at a near ambient pressure, and the volumetric flow rate is large. The separation process must not require much or any compression of the gas to be economically viable.
- The CO_2 partial pressure of the flue gas is low (0.05–0.3 atm). The separation process must be efficient under that low CO_2 driving force condition.
- The gas is saturated with water. Use of a separate drier prior to CO_2 removal from that gas (other than simple condensation of water) may be costly.
- The gas is generally produced at an elevated temperature of 130–180°C. It may be beneficial to treat the gas at its source temperature.

Three different generic separation technologies have been extensively studied for capture and recovery of CO_2 from flue gases during the past 15 years.[4] They include:

- Absorption of CO_2 in a physical or chemical solvent followed by regeneration of the solvent for production of CO_2.
- Physical or chemical adsorption of CO_2 on a solid adsorbent followed by regeneration of the sorbent to produce CO_2.
- Selective permeation of CO_2 through a porous or nonporous membrane.

Some of these technologies are fairly well developed for the application of interest and they continue to be further developed. The following sections highlight the key features.

Absorption of CO_2

Continuous absorption systems (scrubbers) use physical, chemical, or hybrid solvents for CO_2 removal. The flue gas is cooled to near ambient temperature and passed through a wet scrubber system (limestone or gypsum process) for removal of SO_x, and then passed through an absorber. The CO_2 free gas is vented. The solvent is counter-currently passed through the absorber and continuously regenerated in a stripping tower. Physical solvents like selexol or rectisol, which can be easily regenerated by pressure reduction without additional heat energy, are used when the partial pressure of CO_2 is moderately high. However, that often requires expensive compression of the flue gas.[4] Chemical solvents like alkanol-amines [e.g. monoethanolamine (MEA)], which are thermally regenerated by heating with steam, are preferred solvents for low partial pressure CO_2 removal. High heat of CO_2 reaction, limited CO_2 absorption capacity by the solvent, additional removal of the trace chemical solvents from the CO_2 free effluent gas and the waste water generated by condensation of the regenerating steam, and significant corrosion problems are some of the key design and cost issues.[3] Presence of O_2 in the flue gas can cause degradation of these amines during the thermal regeneration process,[3] and chemical inhibitors are added to the amine solution to counter this effect.[9,10] Removal of O_2 from the amine solution prior to its thermal regeneration by heating the solution and passing it through a flash tank under vacuum is also proposed.[3]

The typical energy consumption for thermal regeneration of MEA is $\sim$4–5 MM BTU (4200–5300 MJ) per ton of CO_2 recovered[3] and the typical amine consumption is $\sim$4.5 lbs (2.05 kg) per ton of CO_2.[11] Use of formulated amines (new structures, mixed amines, amine additives, etc) and improving process efficiency are active R&D areas.[11–14] A proprietary formulation, [aqueous solution of $R_1R_2N(CHR_3)_nCH_2NH_2$, where R_1 and R_3 = H or alkyl; R_2 = OH-substituted alkyl; and n = 1, 2], to reduce the amine loss to $\sim$0.8 lb (0.36 kg) per ton of CO_2 from a steam reformer flue gas has been pilot tested in recent years.[11,12] The CO_2 product purity is better than 99.9% and its recovery is $\sim$90%. An economic evaluation of the CO_2 removal and recovery from a flue gas by the MEA absorption process can be found in Ref. 15.

Adsorption of CO_2

Several pressure swing adsorption (PSA), thermal swing adsorption (TSA), and combined PSA-TSA processes have been designed for removal and recovery of CO_2 from a CO_2 containing gas.[16–21] They generally use a CO_2 selective physical adsorbent like an activated carbon or a zeolite, and consist of a sequence of cyclic unsteady-state process steps. A number of parallel adsorbers are employed to achieve continuous operation. These adsorbents require that water and other highly polar compounds be removed from the feed gas prior

Table 1. Typical Examples of CO_2 Content of Flue Gases from Various Sources

Source of Flue Gas	CO_2 Concentration (mole %)
Pulverized coal fired power plant	13–15
Natural gas fired combined cycle power plant	3–9
Integrated gasification combined cycle power plant using coal slurry	7
Steam reformer	8
Petrochemical plant	7
Steel mill	25
Cement plant	30

to selective adsorption of CO_2. A layer of a desiccant material, such as alumina, is generally used for this purpose.

A four-step pressure-vacuum swing adsorption process using NaX zeolite was commercialized for removal of CO_2 from a landfill gas containing ~57% CH_4 + 43% CO_2.[16] Using a feed gas pressure of 5.8 atm (588 kPa) and a final evacuation pressure level of 50–200 torr (6.7–26.7 kPa), the process could produce a ~99% pure CO_2 product with a recovery of ~98%.[16] The same process was used to recover CO_2 (~99% purity at a recovery of ~63%) from a steel mill flue gas at ~1.12 atm (113.5 kPa) by using zeolite X as the adsorbent.[17] The CO_2 recovery could be raised to above 80% by modifying the process.[17] Simultaneous use of pressure reduction and heating of the adsorbent (CaX zeolite) to facilitate CO_2 desorption have also been used to produce 99% CO_2 with a recovery of 90% from a thermal power station flue gas.[18]

Research on improved adsorbents for CO_2 is ongoing. Examples include zeolites impregnated with azides (NaN_3) for use at elevated temperatures,[22] and hydrophobic, molecular sieve carbon (MSC) made by carbonizing poly-vinyl-alcohol/phenol resin.[23]

More recently, a novel pressure swing chemisorption (PSC) concept was developed for removal and recovery of CO_2 from a hot waste gas without cooling or predrying the feed gas.[24] The concept used a CO_2 selective chemisorbent (Na_2O promoted alumina) and a five-step cyclic PSA process consisting of (a) adsorption at feed gas pressure and temperature to produce a CO_2 depleted gas, (b) cocurrent CO_2 rinse with recycling of the effluent gas as feed, (c) counter-current depressurization to produce a CO_2 rich stream for use in step (b) after recompression, (d) counter-current evacuation and purging the adsorber with super-heated steam at feed temperature, and (e) repressurization of the adsorber to feed pressure using a part of the gas from step (a). The cycle is then repeated. The high purity CO_2 product is obtained by condensing out steam from the effluent of step (d). Using a feed pressure of ~8.6 atm (871 kPa) at a temperature of 200°C, and a steam purge at a pressure of ~130 torr (17.3 kPa) at the same temperature, the process could produce a CO_2 stream of 99+% purity with a recovery of ~78% when a feed gas mixture containing 10% CO_2 + 90% N_2 was used.[24] This process can potentially be tailored to recover CO_2 from flue gases.

All of the above described adsorptive processes can be adjusted to deliver a ~99% CO_2 product gas with high CO_2 recovery from a flue gas. They have the advantage of being dry processes (no solvent) without any corrosion problems. However, they will require additional equipments like compressors and vacuum pumps.

Membrane Separation of CO_2

Removal of greenhouse gases (e.g. CO_2) by using membranes has been the subject of many works because of their dry and continuous operation.[4,25–27] Polymers exhibiting promising properties for this application include phenylene oxide, trimethylsilylpropine, and polycarbonates.[4] Nanoporous adsorbent membranes (zeolites and carbons) have also been produced for selective permeation of CO_2.[28–31] MSC membranes, which selectively permeate the smaller molecules of a gas mixture, exhibited fairly high permeance and permselectivity for removal of CO_2 from mixtures with CH_4.[29] Another nanoporous carbon membrane called selective surface flow (SSF) membrane, which selectively permeates more polar CO_2 from non or weakly polar gases by selective adsorption on the pore walls, has also been made and pilot tested.[30,31]

The feed gas containing low concentrations of CO_2, however, needs to be compressed for membrane separation, which can be very costly. In addition, the CO_2 permselectivities of these membranes are not high enough to achieve the desired CO_2 purity and recovery in the permeate side of the membrane in one stage. Multistage membranes with or without gas recycles of permeate gases after recompression will significantly add to cost.[4]

A more promising application of membrane technology for CO_2 removal is the so-called gas absorption membrane which uses the conventional membrane architecture such as the hollow fiber membrane as an efficient gas–liquid contactor. The separation mechanism is essentially absorption. The gas flows through one side of the membrane while a CO_2 selective solvent like an amine solution flows through the other side.[4,32,33] The CO_2-laden solvent leaving the membrane is thermally regenerated in a separate unit to produce the high purity CO_2 gas. The solvent is then recirculated.

The above sections provide a glimpse of the state of the art for CO_2 separation from a gas using absorption, adsorption, and membrane technologies. Some of these technologies have been tested in bench, pilot, or semicommercial scale units. Thus, removal and recovery of CO_2 from a flue gas is at least technically feasible and several choices exist. The recovered CO_2 must then be compressed to a very high pressure (~2000 psig, 13.9 MPa) for sequestration or delivery to the pipe lines.

The cost of CO_2 separation and sequestration is a crucial issue. Some of the published comments on this topic, such as, "Doubling of the cost of power generation and more than a 30% reduction in net power output,"[7] "Cost of power generation can increase by ~60% due to CO_2 removal from the flue gas,"[5] "Capture of CO_2 adds substantially to the cost of power generation and reduces plant efficiency,"[6] and "Storage of CO_2 in deep aquifers, the oceans, or in exhausted oil and gas fields is unproven but would be relatively inexpensive. There are major uncertainties about disposal in terms of environmental impact and long term security of storage,"[6] etc, are worth mentioning.

Novel Thermal Swing Chemisorption Process for Removal and Recovery of Compressed CO_2 from Flue Gas

The objective of this work is to propose a novel thermal swing chemisorption (TSC) concept for removal and recovery of compressed CO_2 from a flue gas without precooling, predrying, and precompressing the gas. It employs the previously mentioned Na_2O promoted alumina as a CO_2 selective chemisorbent for removal of CO_2 from the flue gas.[24] The material offers reversible and extremely high selectivity of chemisorption of CO_2 from an inert gas such as N_2 in presence of steam at a temperature of 200–450°C.[34] The TSC process uses a shell and tube arrangement of a CO_2 chemisorbent column where the tubes are packed with Na_2O promoted alumina particles (diameter = d_p) and the shell side is used for indirect heating and cooling of the tubes using a crossflow of super-heated steam at different temperatures and ambient pressure. The tubes undergo the following five-step cyclic process in a sequential manner:

(a) Sorption step where the CO_2 contaminated flue gas (mole fraction of CO_2 = y_F^o) is passed through the packed tubes at near ambient pressure (P_F ~1.1 atm, 111.4 kPa) and a temperature of T_F (>150°C). The CO_2 is selectively chemisorbed on the promoted alumina and a sharp CO_2 mass transfer zone is formed inside the tube which progressively moves toward the exit-end of the column as more feed gas is passed. A CO_2 depleted gas is produced during this step which is vented after heat recovery. The step is continued until the CO_2 concentration in the effluent gas rises to a preset level so that the average CO_2 concentration of the vented gas is ~1%.

(b) CO_2 rinse step where an essentially pure CO_2 stream (dry basis) is cocurrently passed through the packed tube at pressure P_F and temperature T_F to remove the interparticle void gas. Another sharp CO_2 mass transfer zone is formed inside the tube which progressively moves toward the exit-end of the column. The mole fraction of CO_2 in the effluent gas during this is $\sim y_F^o$, and it is optionally recycled as feed gas to step (a) or vented to the atmosphere. The column is saturated with essentially pure CO_2 (dry basis) at the end of this step.

(c) Heating step where the tubes are indirectly heated in a batch-wise fashion to a temperature of T_H when some of the chemisorbed CO_2 is thermally desorbed. The void gas pressure rises from P_F to P_H ($\gg P_F$) at the end of this step.

(d) High pressure steam purge step where the tubes are counter-currently purged with super-heated steam at temperature T_H and pressure P_H while indirectly heating the tubes at T_H. The step causes isobaric and isothermal desorption of chemisorbed CO_2 from the tubes at a total gas pressure P_H and temperature T_H.[35] The effluent gas consists of CO_2 + steam. The CO_2 is initially pure then the mole fraction of CO_2 progressively decreases. Heat is partly recovered from the effluent gas by heat exchange and then the steam is condensed out in a constant pressure device to produce a compressed CO_2 product at pressure P_H. The step is continued until the CO_2 mole fraction in the desorbed gas reaches a preset value. A portion of the chemisorbent at the steam inlet end is freed of CO_2 at the end of this step.

(e) Multitasking regeneration step where the tubes are counter-currently depressurized from P_H to P_F and purged with steam initially at temperature T_H and pressure P_F and thereafter at temperature T_F, while simultaneously cooling the tubes (indirectly) from T_H to T_F. The purge steam flow rate is initially large and then it is significantly reduced. The effluent gas (CO_2 + steam) containing a progressively decreasing concentration of CO_2 is recycled as rinse gas to step (b) after cooling and condensing out the steam, and then reheating the gas. The chemisorbent in the tubes is cooled down to T_F and a significant amount of the chemisorbent at the steam inlet end is freed of CO_2 at the end of this step. The cycle then repeats itself starting from step (a).

Figure 2 schematically depicts an example of the operational sequence of the five-step TSC cycle described above. It corresponds to a case where P_F = 1.1 atm (111.4 kPa), T_F = 200°C, y_F^o = 0.15, T_H = 500°C, and P_H = 13.5 atm (1.37 MPa). The key benefits of this process design are (a) removal of CO_2 from the flue gas at near ambient pressure without predrying or precooling the gas, (b) direct production of a compressed CO_2 product gas, (c) high recovery of compressed CO_2, (d) high utilization of the CO_2 sorption capacity of the chemisorbent, and (e) use of steam as the purge gas for desorption of chemisorbed CO_2. Many of these advantages were generated by the application of the principles of TSA in the TSC process in conjunction with the complementary process steps like (b), (c), and (d).

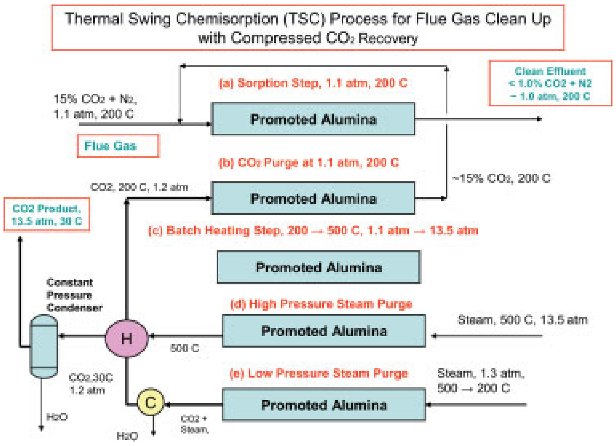

Figure 2. Schematic drawing of the operational sequence of the TSC process concept.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Examples of TSC process embodiments

Figure 3 shows the arrangement of multiple sorbers to introduce the poly-bed concept in the TSC process where three parallel sorbers simultaneously receive the feed flue gas and undergo other steps of the process to substantially reduce the size of each adsorber. The poly-bed concept is a commercially successful option for the design of (PSA) processes when a very large feed gas rate is involved.[36] Figure 4 describes an operational plan for the poly-bed TSC system of Figure 3. Each process step is operated in a continuous fashion. The cleaned effluent gas and the high pressure CO_2 product gas are withdrawn continuously from the system. All recycle streams are also continuous.

CO_2 Chemisorption on Na_2O Promoted Alumina

The recently measured CO_2 chemisorption characteristics[34] on Na_2O promoted alumina are briefly summarized below because they were used in the model simulation of the TSC process.

CO_2 chemisorption isotherm

A novel, analytical, chemisorption-surface complexation reaction model can be used to describe the equilibrium sorp-

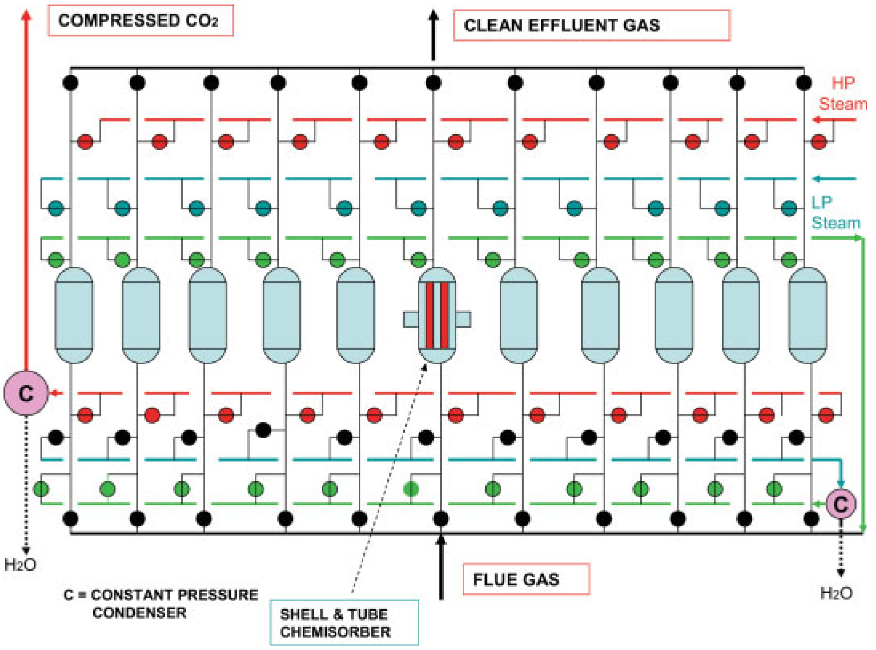

Figure 3. Schematic flow sheet of a poly-bed TSC system.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion of CO_2 on the chemisorbent in the temperature range of 200–500°C[34]:

$$n^*(P,T) = \frac{mK_C P[1 + (a+1)K_R P^a]}{[1 + K_C P + K_C K_R P^{(a+1)}]} \tag{1}$$

where n^* is the amount of CO_2 sorbed (mol/kg) at a partial pressure of P (atm) and temperature T (K). The model parameters are the saturation CO_2 chemisorption capacity of the chemisorbent surface, m (mol/kg); the equilibrium constant for surface chemisorption of CO_2, K_C (atm^{-1}); the equilibrium constant for the additional surface complexation reaction between the gaseous and chemisorbed CO_2, K_R (atm^{-a}); and the stoichiometric coefficient for the complexation reaction, a. The parameter m is independent of temperature while the other model parameters are exponential functions of T. Table 2 reports the values of the model parameters at three different temperatures. The isosteric heat of chemisorption and the heat of surface reaction of CO_2 were estimated to be, respectively, 64.9 and 37.5 kJ/mol.[34] The relatively low heats are unique properties of this chemisorbent. They permit reversible chemisorption and easy desorption of CO_2.

<table>
<tr><th colspan="23">Operational Scheme of Poly bed System for CO₂ Removal & Recovery from Flue Gas</th></tr>
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Figure 4. Plan for operation of poly-bed TSC scheme, cyclic steps: S = sorption of flue gas; R = cocurrent CO_2 rinse; BH = indirect batch heating; HPSP = counter-current high pressure steam purge; MTR = multitasking regeneration.

CO_2 chemisorption kinetics

The kinetics of chemisorption and desorption of CO_2 on the promoted alumina could be described by the conventional linear driving force (LDF) model[37]:

$$\frac{dn(t)}{dt} = k[n^*(t) - n(t)] \tag{2}$$

where $n(t)$ is the specific amount (mol/kg) of CO_2 chemisorbed at time t and $n^*(t)$ is the specific equilibrium adsorp-

Table 2. Model Parameters for Equilibria and Kinetics of Chemisorption of CO_2 on Na_2O Promoted Alumina at Various Temperatures

T (°C)	m (mol/kg)	a	K_c (atm^{-1})	K_R (atm^{-a})	k_{LDF} (min^{-1})
250	0.295	2.0	536	8	4.0
350	0.295	1.7	48.3	2	5.0
450	0.295	1.5	8.47	0.73	5.8

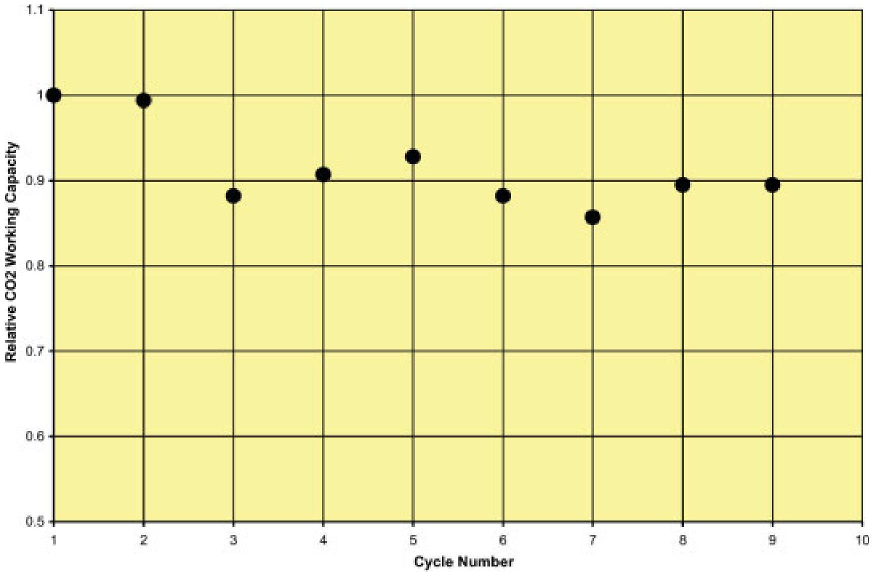

Figure 5. Cyclic thermal stability of Na_2O promoted alumina measured by TGA at 250°C adsorption and 500°C regeneration.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion capacity of CO_2 (given by Eq. 1) at the prevailing gas phase conditions. The parameter k (time^{-1}) is the LDF mass transfer coefficient for CO_2 ad(de)sorption. Their values at different temperatures are reported in Table 2.[34]

Cyclic thermal stability of promoted alumina

We tested the thermal stability of the Na_2O promoted alumina in a commercial thermogravimetric apparatus (TGA) by cyclically measuring the pure CO_2 sorption capacity at ~1.0 atm (101.3 kPa) pressure and 250°C (4 h contact) and then completely desorbing the CO_2 by flowing pure N_2 at ~ambient pressure and 500°C (10 h contact) over a few particles of the promoted alumina placed on the pan of the microbalance. Figure 5 plots the relative cyclic CO_2 capacity of the material over a period of nine cycles. It may be seen that there was an initial ~10% lowering of the CO_2 cyclic capacity followed by a fairly stable cyclic capacity after three cycles of thermal swing regeneration at 500°C. Thermal stability of the material in presence of wet CO_2 was also tested in past at 200°C during the cyclic operation of the PSA process mentioned earlier.[24] Nevertheless, it should be emphasized that more extensive testing of the thermal stability of the chemisorbent in presence of CO_2 and H_2O at a temperature of ~550°C will be necessary.

Simulation of the TSC Process

The above described thermodynamic and kinetic models for describing the chemisorption of CO_2 on the promoted alumina were used in conjunction with a "CSTR in series model" to simulate each individual steps of the TSC process. It was assumed that the effluent gas from the column during step (b) of the process was not recycled because the amount of CO_2 in that gas was relatively small. Details about the model framework and methods of solution can be found elsewhere.[38] The model was adapted for dynamic simulation of (a) sorption and desorption of CO_2 from a packed bed of promoted alumina and (b) thermal regeneration steps of the TSC process. The model simultaneously solved the algebraic and ordinary differential equations describing the component and overall mass balances and the energy balance for each tank in series. The model could simulate isothermal or adiabatic operation. It could also account for heat exchange between the packed bed and the surroundings using an overall wall-heat transfer coefficient. The Matlab function ODE15s, which is a variable-order solver based on the numerical differential formulas, was used for the mathematical integration process. It was found that 250 tanks in series were adequate to simulate the sharp sorption-column breakthrough data for sorption of CO_2 on promoted alumina.

Simulation results

The simulations were carried out using a shell and tube configuration of the sorber column [tube inside diameter (d) = 1.73 cm, tube length (L_c) = 184 cm]. This length was chosen to guarantee a total pressure drop of ~1 psi (6.9 kPa) during the step (a) of the process. The bulk density of the chemisorbent was 0.697 g/cm^3 and the helium void fraction in the column was 0.70. The feed gas was a mixture of 15% $CO_2 + N_2$ at a pressure of 1.1 atm. The feed gas and sorber temperatures for step (a) were 200°C. The feed gas flow rate for step (a) was ~20.4 mol/m^2/s (~15 lbmoles/ft^2/h).

Figure 6 shows the simulated CO_2 loading (mol/kg) profiles on the promoted alumina inside the column as functions of the distance from the feed gas end (L) at the end of each step of the TSC process. The CO_2 mass transfer zone partially breaks through the exit end of the column at the end of the step (a) so that the average mole fraction of CO_2 in the column effluent gas during this step is ~1%. About 70% of the column at the feed gas end is equilibrated with CO_2 at

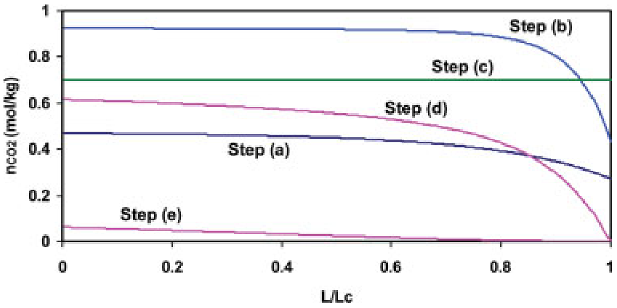

Figure 6. CO_2 loading profiles inside the sorber at the end of each step of the TSC cycle.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

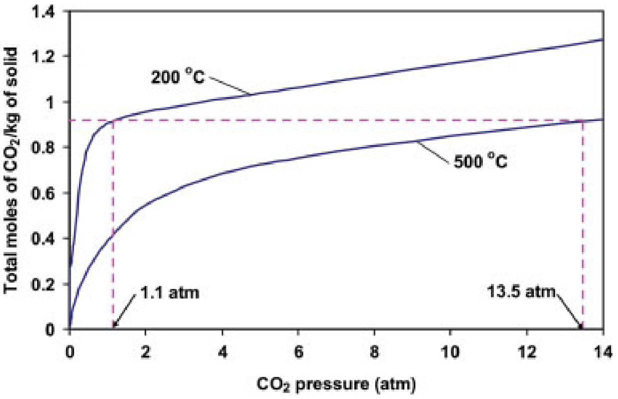

Figure 7. Total specific equilibrium amount (void gas + sorbed) of pure CO_2 in the column at different temperatures and pressures.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the feed gas conditions (CO_2 partial pressure = 0.165 atm, temperature = 200°C) when step (a) stops. About 90% of the column at the feed gas end is equilibrated with CO_2 at the rinse gas conditions (CO_2 partial pressure = 1.1 atm, temperature = 200°C) at the end of step (b). The CO_2 loading in the column rises above the loading at feed gas conditions and the interparticle void space in the column is filled with pure CO_2 during step (b). The CO_2 loading on the sorbent in the entire column uniformly decreases during the batch-wise thermal desorption step (c) but the gas phase pressure increases substantially to ~13.5 atm from the starting pressure of ~1.1 atm. The CO_2 loadings in the entire column decrease during the desorption steps (d) and (e) by steam purge. About 44% of CO_2 present in the column at the end of step (c) is desorbed during step (d), and about 97% of CO_2 present in the column is removed by the end of step (e). The residual CO_2 in the column at the end of step (e) is pushed toward the feed end of the column, thereby creating a substantially CO_2 free zone (~30% of the column at the exit end) before the next cycle begins. The total integrated amount of residual CO_2 in the column at the end of step (e) is only ~0.0275 mol/kg.

The gas phase pressure rise in the column during the batch heating step (c) of the process is explained by Figure 7 which plots the total specific equilibrium amount of pure CO_2 in the column (void gas + sorbed) as a function of CO_2 pressure at 200 and 500°C. They were estimated by using the CO_2 chemisorption isotherm model (Eq. 1) and the physical properties of the packed column. Batch heating causes thermal desorption of CO_2 from the sorbent and its accumulation in the gas phase, thereby raising the gas pressure, while the system remains in thermodynamic equilibrium during the process.

Figure 8 shows the simulated midpoint temperature-time profiles inside the sorbent column during the nonisothermal steps (c) and (e) of the process where the shell side was heated and cooled by crossflow of super-heated, ambient pressure steam at, respectively, 520 and 155°C. A period of 3 min was used for these steps. The tubes were heated during the entire period of step (c). The tubes were maintained at 500°C for the first minute, and then cooled down to 200°C in 2 min during step (e). A realistic shell to tube side heat transfer coefficient of ~50 watts/m^2/°C was used for the design. Thus, Figure 8 shows that steps (c) and (e) can each be realistically carried out within 3 min. Shorter times may be feasible if different shell side steam temperatures are used during these steps. This concept of rapid thermal swing adsorption (RTSA) for bulk gas purification has recently been proposed.[39]

Indirect heating and cooling of the sorbent permits the TSC concept to be operated with a cycle time of several minutes as opposed to a cycle time of several hours for a conventional TSA process, where the sorbent is directly heated or cooled by flowing a gas over the sorbent. Consequently, the TSC concept having a cycle time comparable to that of a PSA process, can be scaled-up to a very large size since the net cyclic CO_2 removal capacity of the TSC process can be much larger than that of a PSA process. This point is illustrated later by example given in Table 4.

Figure 9 shows the simulated CO_2 concentrations of the column effluent gas during the regeneration steps (d) and (e) of the TSC cycle. The effluent gas is pure CO_2 during the initial part of the high pressure steam purge step (d). The CO_2 mole fraction then progressively decreases to ~0.3 at the end of this step. The gas temperature is 500°C and the average mole fraction of CO_2 is ~0.59. This mixture of CO_2 and steam is produced at a pressure of 13.5 atm (1.37 MPa). The steam can be condensed out in a constant pressure

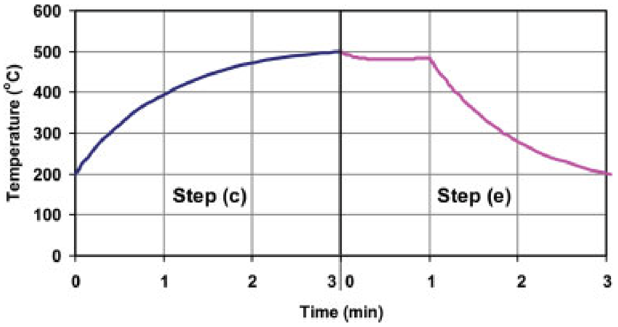

Figure 8. Heating and cooling profiles of sorber tubes.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

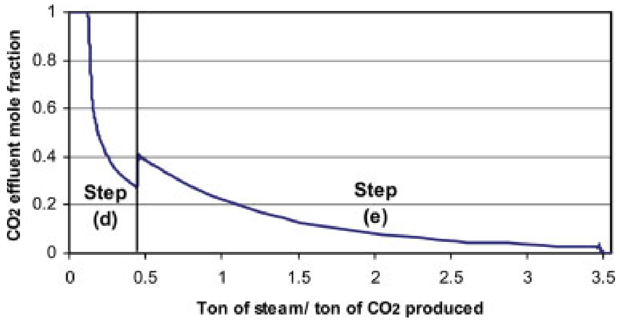

Figure 9. CO_2 mole fractions in the effluent gases of steps (d) and (e) of the TSC process.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

condenser to directly produce a pure, compressed CO_2 gas at ~13.5 atm (1.37 MPa). The CO_2 mole fraction of the effluent gas during step (e) is initially ~0.4, and then it progressively decreases as the ambient pressure steam purge step is continued. This gas is also a mixture of steam and CO_2 and it is produced at nearly ambient pressure at a temperature varying between 500 and 200°C. The average CO_2 mole fraction of the effluent gas during step (e) is ~0.13. This gas is used as the rinse gas in step (b) after condensation of steam by cooling to 30°C and then reheating to 200°C.

Figure 10 describes the integrated CO_2 desorption characteristics from the sorber by the TSC concept. It plots the fraction of CO_2 remaining inside the column at the end of step (c) that is removed during steps (d) and (e) of the process as functions of steam purge quantities expressed as tons of steam per ton of CO_2 produced as high pressure product gas during step (d). It may be seen that desorption of CO_2 from the column consumes a relatively smaller amount of high pressure steam (<0.5 tons/ton of CO_2 product) during step (d). The amount of low pressure steam needed to remove most of the CO_2 (upto 90% of total residual amount) during step (e) is also relatively small (~1.5 tons/ton of CO_2 product). However, a relatively larger amount of low pressure steam (~1.5 tons/ton of CO_2 product) is used to achieve ~97% desorption of the residual CO_2. Thus, the total amount of steam required to obtain 97% desorption of the residual CO_2 under the conditions of operation of the TSC concept is ~3.5 tons of steam/ton of compressed CO_2 product. The recovery of compressed CO_2 from the feed flue gas is ~93.5%.

Table 3 summarizes the overall simulated performance of the proposed TSC process concept for removal and recovery of compressed CO_2 from the flue gas. The concept is capable

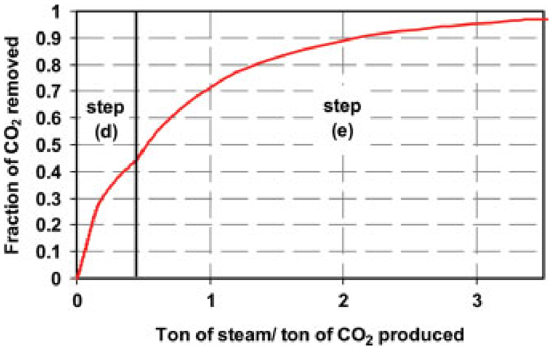

Figure 10. Simulated CO_2 desorption characteristics of the TSC concept.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of removing CO_2 from a flue gas without predrying and precompression of the gas, and directly producing a highly compressed, nearly pure CO_2 product gas with high recovery of CO_2. Consequently, some of the key advantages of the proposed concept over an existing MEA absorption system include (a) dry operation, (b) elimination of solvent loss, (c) direct production of compressed CO_2 product with high recovery from feed gas, (d) subsequent reduction of compression energy and compressor capital investment for CO_2 sequestration, and (e) relatively low steam duty for regeneration. It should be emphasized here that the object of this work was to describe a novel process concept for removal and direct recovery of compressed CO_2 from a flue gas at near ambient pressure without predrying, precooling, and precompressing using a TSC concept. No attempt is made to optimize the operation or to integrate heat recovery systems. They must be done to appreciate the full value of the proposed concept. Only one example of the model simulation of the concept is presented. For example, it should be obvious from Figure 10 that the low pressure steam purge quantity can be reduced at the cost of higher residual CO_2 in the column at the end of step (e), which will lower specific feed gas handling capacity of the system and CO_2 recovery.

Comparison Between Pressure and Thermal Swing Chemisorption Concepts

It may be interesting to compare the performance of the previously reported PSC process[24] and the currently proposed TSC process for removal and recovery of CO_2 from a flue

Table 3. Summary of Simulated Performance of the TSC Concept

		Effluent Waste Gases		Recovered CO_2 Product Gas	Steam Requirement	
	Feed Flue Gas	Step a	Step b		High Pressure	Low Pressure
Average CO_2 concentration	15.0%	~1.0%		99.9+%		
Pressure (atm)	1.1	1.1	1.1	13.5	13.5	1.3
Temperature (°C)	200	200	200	30	500	500–200
Quantity of CO_2 (mol/kg)	0.431	0.0263	0.0017	0.402		
Quantity (tons/ton of CO_2 product gas)					0.44	3.06
CO_2 recovery from feed gas				93.4%		

Table 4. Comparative Performance of PSC and TSC Concepts for CO_2 Recovery

	PSC Process[24]	TSC Process
Feed flue gas conditions		
CO_2 mole fraction	0.10	0.15
Pressure (atm)	8.6	1.1
Temperature (°C)	200	200
Quantity of CO_2 per cycle (mol/kg)	0.0536	0.458
Effluent vent gas conditions		
CO_2 concentration	~2.8%	~1.0%
Final regeneration conditions		
Temperature (°C)	200	500
Pressure (atm)	0.17	1.1
Recovered CO_2 product gas		
CO_2 mole fraction (dry basis)	0.99+	0.99+
Pressure (atm)	1.0	13.5
Recovery from feed (%)	78	93
Quantity per cycle (mol/kg)	0.041	0.402

gas using the same chemisorbent. Some of the striking differences in the performances of these concepts are summarized in Table 4. Both processes recover nearly pure CO_2 from the flue gas and both processes use steam as the desorbing gas. However, the TSC concept does not require an external vacuum pump and a compressor needed by the PSC process for CO_2 desorption and CO_2 rinse steps, respectively. Furthermore, the TSC concept offers (a) approximately an order of magnitude increase in the specific productivity of CO_2 on the chemisorbent, (b) a significantly higher CO_2 recovery, and (c) a remarkably increased CO_2 product pressure without external compression, compared to the PSC concept.

These striking advantages are achieved by employing more elaborate hardware like shell and tube type sorbers, heat recovery systems, rapid thermal swing concepts, etc. The TSC process also facilitates the subsequent sequestration of compressed CO_2 by substantially reducing the capital cost and the energy required for compression of the recovered CO_2 from the flue gas.

Summary

A novel TSC process concept is proposed for removal and production of pure, compressed CO_2 with high recovery from a flue gas without precompression and predrying. Na_2O promoted alumina, which is a reversible CO_2 chemisorbent, is employed in the TSC process. The chemisorbent selectively removes CO_2 from a wet gas at an elevated temperature. Cyclic process steps like CO_2 purge following the sorption step, batch-wise heating of the sorbent, and desorption of CO_2 by high and low pressure steam purges permit direct production of compressed CO_2 product with high recovery. The chemisorptive properties of CO_2 on the promoted alumina are reviewed and new data on its thermal stability at 500°C is reported. The performances of the individual steps of the TSC process are simulated using a "continuous stirred tank reactors in series model." Operating between a sorption temperature of 200°C and a final desorption temperature of 500°C, the TSC process simultaneously produces (a) an effluent vent gas stream containing ~1% CO_2 and (b) a 99+% CO_2 product stream at a pressure of 13.5 atm (1.37 MPa) from a wet flue gas containing 15% CO_2 at a pressure of 1.1 atm (111 kPa). The recovery of compressed CO_2 product from the flue gas is ~93%. The amounts of high (~13.5 atm, 500°C) and low (1.3 atm, 200–500°C) pressure steam consumed by the process are, respectively, 0.44 and 3.06 tons/ton of CO_2 product. A shell and tube heat exchanger type sorber design, where the shell side is cyclically heated or cooled by crossflow of steam, may be used to operate the rapid TSC cycle. A train of parallel sorbers operated in the fashion of the poly-bed sorber design may be used to reduce the sizes of the individual sorbers. The TSC concept offers significant performance advantages over a PSC concept. However it requires a more elaborate hardware design.

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