Carbon Capture Test Unit Design and Development Using Amine-Based Solid Sorbent

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Abstract:

This paper presents the design and development of a reactor system and the subsequent modifications to evaluate an integrated process to scrub carbon dioxide (CO₂) from synthetic flue gas using amine based solid sorbents. The paper presents the initial system design and then discusses the various changes implemented to address the change in sorbent from a 180 µm Geldart group B material to a 115 µm Geldart Group A material as well as issues discovered during experimental trials where the major obstacle in system operation was the ability to maintain a constant circulation of a solid sorbent stemming from this change in sorbent material.

The system primarily consisted of four fluid beds, through which an amine impregnated solid sorbent was circulated and adsorption, pre-heat, regeneration, and cooling processes occurred. Instrumentation was assembled to characterize thermal, hydrodynamic, and gas adsorption performance in this integrated unit. A series of shakedown tests were performed and the configuration altered to meet the needs of the sorbent performance and achieve desired target capture efficiencies. Methods were identified, tested, and applied to continuously monitor critical operating parameters including solids circulation rate, adsorbed and desorbed CO₂, solids inventories, and pressures.

Keywords: CO₂ adsorption, Carbon capture, Fluidization, Moving bed, Regenerator

1. Introduction

The United States emits more CO₂ than any other country, except China, with nearly 40% from fossil fuel-fired power plants (U.S. DOE, 2012). Successful carbon management relies on the development of cost effective methods to capture CO₂ from the flue gas of existing power plants (Ciferno, 2008; Pires et al, 2011; Susarla et al, 2015). Baseline studies for adding CO₂ capture and sequestration to existing power plants indicate that, using conventional technology, the cost of electricity would nearly double from coal fired pulverized coal power plants (Black, 2010). CO₂ capture can be realized in a two-step sequestration process where CO₂ is first separated from product gases and then stored in geological locations within the earth. Chemical solvent based absorption systems have been utilized and studied for nearly a century and have not shown the ability to limit significant cost or loss in efficiency below target values (Burchell et al, 1997; Yong et al, 2002).

Chemical adsorption using solid sorbents has been widely investigated and considered to be a promising alternative to liquid solvents for CO₂ capture. The use of light weight and selective solid sorbents coated with polyamines offer potential cost savings over conventional liquid based systems (Fisher and Keller, 2011; Yang and Hoffman, 2009). Solid sorbents have the potential to be used over a wide range of

temperatures up to 700°C and have been shown to be less environmentally impactful, when compared to liquid adsorbents. The use of solid sorbents has the potential to reduce process costs as compared to conventional liquid based systems by reducing evaporative heat losses (Frimpong et al, 2013; Zhenissova et al, 2014). Solid sorbents with high CO₂ capacity and readily adsorb and release CO₂ can improve the cost competitiveness of these processes.

Amine sorbents have a high capacity for CO₂, can be hydrophobic, and can readily adsorb and release CO₂ (Gray et al, 2008; Gray et al, 2003; Gray et al, 2005; Gray et al, 2004; Heydari-Gorji et al, 2011; Monazam et al, 2012; Samanta et al, 2012; Siriwardane, 2005). These sorbents adsorb CO₂ at low temperatures and release it at elevated temperatures. Scale up to utility applications requires that the solids are transported or conveyed between the adsorber and the regenerator. Fluidized bed technology appeared to be well suited for this type of thermal swing process because gas-solids suspensions can be readily transported between different reactors. Unfortunately, recent attempts to demonstrate integrated adsorption and regeneration were unable to achieve significant CO₂ capture during continuous flow process with an amine based sorbents. Sjostroma et. al. (2012) identified multiple potential causes such as deficiencies in sorbent and operating conditions. Long term stable operation and continuous solids circulation between two fluidized beds has been reported to demonstrate a system design that allows for high CO₂ capture efficiency but is still limited to an efficiency lower than 90%. Factors affecting the working capacity of the sorbents, which limits the capture efficiency, are mainly due to high adsorption temperatures and short absorber residence times (Zhao et al, 2013). Recently, a system study done by Proll et. al. (2016) with a double loop fluidized bed, showed reduction in sorbent circulation rates resulting in lower energy demand for the capture process. The study showed the potential of high carbon capture rates as well as low overall heat requirements through a temperature or thermal swing process. Temperature swing adsorption technology has previously shown reduction in thermal energy requirement while maintaining continuous CO₂ capture in circulating fluidized bed systems and bubbling fluidized beds. (Veneman et al, 2012; Zhang et al, 2014).

A small scale system was designed and constructed to evaluate various solid sorbents operated in a circulating fluid bed system using a thermal swing process. The original design incorporated the hydrodynamic characteristics of a certain class of particles; however, the sorbent that was ultimately available deviated from these. Other factors were also discovered that required modification of the system. The evolution of the experimental system is traced from concept through shakedown to final configuration. The design basis is described and causes for major modifications identified. Critical process measurement and control systems were developed to improve process stability and provide real-time measurement of process performance.

Sjostroma et. al. (2012) demonstrated that CO₂ adsorption occurs within a short section (less than 0.7 m) in the entrance of the riser. Ryan et al, (2013) and Breault and Huckaby (2013) present CFD simulations showing the CO₂ removal all taking place within the 0.7 m riser entrance region. As a result, the focus of this research was to further elucidate regeneration of the sorbent in a closed loop system since adsorption had been experimentally demonstrated.

2. Unit Design and Development

A small scale circulating fluidized bed system (Carbon Capture Unit or C2U) was designed to test the effectiveness of solid amine based sorbents for use in the capture of CO₂ from flue gas. The original C2U design can be seen in Figure 1 below where each component is identified along with fluidization gas inlet locations marked numerically. The C2U consisted of four fluidized bed vessels: the adsorber, the regenerator, plus the upper and lower loop seals. Nitrogen was supplied at all fluidization locations and would act as a synthetic flue gas. Note that in a commercial unit, steam will replace the N₂ used in this test units for fluidization of the regenerator. The regenerator product gas will then consist of steam and CO₂, the steam will be condensed and the remaining high purity CO₂ would then be compressed to be utilized or sequestered. Nitrogen and CO₂ were introduced to the adsorber plenum (1) and passed through a distributor plate into a fluidized bed of CO₂ free sorbent where CO₂ was captured from the flue gas in an exothermic process. A reduction in pipe diameter at the adsorber top increased exiting gas velocity and acted as a riser transporting the CO₂ laden sorbent. Within the adsorber, the sorbent captured CO₂ as particles migrated upward toward the riser inlet. Sorbent particles, with adsorbed CO₂, and flue gas with reduced CO₂ concentration, were subsequently transported via the riser to the crossover. Particles and remaining flue gas passed through a crossover and into a cyclone where solids and gas were separated. Solid particles exited the cyclone bottom and the remaining flue gas exited the cyclone top and was vented to atmosphere. CO₂ carrying sorbent filled the cyclone dip-leg. Aeration (N₂) near the base of the cyclone dip-leg (8) was used to move sorbent into the upper loopseal that was fluidized with N₂ (7). Particles then moved through the loopseal, overflowing into the regenerator.

Within the fluidized regenerator (6), solids at the regenerator top gradually moved downward as particles at the bottom were removed through the underflow. During this process, the sorbent was heated by contact with internal coils through which heated oil was circulated, releasing captured CO₂ in an endothermic reaction. The CO₂, now in concentrated form, exited the regenerator. Particles were drained from the bottom of the regenerator at the same rate they entered the top. As the moving bed of CO₂ stripped sorbent reached the bottom of the regenerator it passed into the standpipe. The standpipe was aerated with stripping gas (5) and move air (4). At the L-valve, particles were transported through a horizontal pipe section fluidized with sparger gas (3) and eventually arrived at a second loopseal. As with

the upper loopseal, sorbent was fed into the bottom and migrated upward to the top. Sorbent fell from the top of the lower loopseal (2) to the bottom of the adsorber, completing the sorbent circulation loop. Streams 2-4 enter the adsorber as well.

Figure 1 Schematic of primary components of the C2U (Mod-0 geometric configuration) along with fluidizing gas inlet locations.

Alterations were made to the system to improve operability and solids transport as experiments progress (Figure 2). Glass beads were successfully circulated in the original geometric design (Mod 0), however, lighter sorbent would not successfully circulate. The lower loopseal was dropped to the adsorber level and the 90° L-valve was replaced with a sweeping arc (Mod 1). Additionally, the cyclone dip-leg was shortened, effectively increasing the overall height between the bottom of the regenerator and the bottom of the lower loopseal. There was continuing difficulty in maintaining consistent solids circulation rates so the L-valve was reintroduced, this time with a sparger to fluidize the horizontal section of the L-valve (Mod 2). A third modification entailed replacing the 5 cm ID riser with a 2.5 cm pipe and later heating coils were placed in the upper loopseal to preheat sorbent entering the regenerator (Mod 3-4). The final modification extended the regenerator approximately 0.3 m (Mod 5). A detailed explanation of each modification and its effects are provided later.

Modification Steps	Alterations
1	Lowered the lower loop seal and shortened dip-leg. L-valve replaced with swinging arc.
2	L-valve reinstalled with sparger.
3-4	5cm riser reduced to 2.5cm. Heating coils replaced in upper loop seal.
5	Regenerator lengthened 0.3m

Figure 2 Evolution of C2U system through modification steps.

Figure 3 illustrates a typical pressure profile during operation across the system circulating AX sorbent. Pressure relative to atmosphere was measured at the L-valve on the regenerator side and in the plenum on the adsorber side. Incremental pressures were measured between the L-valve and solids valve (a), solids valve to regenerator bottom (b), regenerator solids region (c) and regenerator freeboard (d) on the regenerator side. On the adsorber side, incremental pressures across the distributor plate (e), adsorber bed (f), transition (g), riser (h), crossover (i) and filter (j).

Figure 3 Typical pressure drops across system components (Mod 4)

2.1 Original System Design

The design of the C2U system was subject to a number of constraints and design parameters which are listed in Table 1. The footprint of the C2U system was of primary concern during the initial design phase. The overall height of the system needed to be less than 3.7 m due to the anticipated location of the apparatus. Likewise, the diameter of the vessels could not exceed about 0.152 m due to the availability of CO₂. The CO₂ was to be provided by pressurized cylinders, thus a reasonable volumetric flow rate was required. Since the purpose of the system was to analyze various types of solid sorbent and a particular sorbent was unavailable at the time, the system was designed based on a proxy sorbent. The substrate was based on the characteristics of a glass beads (density = 2.5 g/cc, particle diameter = 180 μ m, U_{mf} = 2.7 cm/s) with an assumed working capacity of 1.5 gmol CO₂/kg sorbent.

Table 1 Design Basis for C2U

PARAMETER	UNITS	VALUE/CONSTRAINT
MAXIMUM HEIGHT	m	3.7
CO2 AVAILABILITY	slpm	24.2
CO2 IN FEED	Vol %	15
VOLUMETRIC FLOW	slpm	161
RISER DIAMETER	m	0.152
PARTICLE INFORMATION		
DIAMETER	μ m	180
DENSITY	kg/m ³	2500
U_{MF}	m/s	0.027
GELDART CLASSIFICATION	-	B
WORKING CAPACITY	gmol CO ₂ /kg	1.5
SORBENT FLOW RATE	kg/hr	42
EXOTHERMIC HEAT GENERATION	kW	1.51

This material should behave as a Geldart group B material. A flow rate producing a superficial gas velocity of 6.5 x U_{mf} was envisioned as a moderate case for adsorber inlet flow. Vessel diameters, using the original polycarbonate were 0.14 m, yielding an internal floor area of 0.0154 m² (disregarding the

presence of internal coils). Therefore, the adsorber baseline total volumetric flow was 161 slpm of simulated flue gas with a 15% volume concentration of CO₂. The sorbent was required to adsorb 24.2 slpm CO₂ (0.91 gmol/min, 0.67 g/s) setting the solids circulation rate at 0.72 kg/min. As a baseline for initial calculations, the heat of reaction of MEA sorbent (1.91 x10⁶ J/kg CO₂ adsorbed) (Amines and Plasticizers, 2004) was used so the heat produced by the exothermic adsorption would be 1.51 kW. This heat is to be removed via internal cooling coils if a constant bed temperature is to be maintained. The characteristics of the coils will be addressed in a succeeding section.

Terminal velocity of an individual glass sphere was determined to be about 1.1 m/s. Terminal velocity was calculated in its simplest form assuming monodisperse distribution of spherical particles where drag equals weight, A_{pp} is the projected area of the sphere and $C_D = 24/Re_p * (1 + 0.1935 * Re_p^{0.6305})$ and $Re_p = \rho_{gas} V_{term} d_p / \mu_{gas}$ (Yang, 2003).

$$V_{term} = \sqrt{\frac{2W}{C_D * \rho_{gas} * A_{pp}}} \quad \text{Eq. 1}$$

More accurate methods of terminal velocity calculation are available, however the solids are not expected to be completely spherical or monodisperse, nor will only a single particle be involved. However, only a general indication of an adequate riser diameter is required so the method employed will serve its purpose. The pipe diameter of the riser section was originally chosen to be 5.1 cm. The volumetric flue gas flow through the riser has been reduced to 137 slpm, in the base case, since the CO₂ component was adsorbed. Therefore, riser gas velocity is 1.13 m/s which exceed the terminal velocity making particle transport possible.

CO₂ laden particles along with the CO₂ reduced flue gas, transported up the riser, now proceed into the cyclone for separation. The flue gas exits the cyclone vortex finder then through an external filter and finally to the atmosphere. Solids fall from the cyclone down comer into the bottom of the upper loopseal. The upper loopseal, with a diameter identical to that of the adsorber, is fluidized near the minimum fluidization velocity with approximately 25 slpm N₂. Eventually, the CO₂ laden sorbent particles migrate to the regenerator where CO₂ is to be desorbed. The regenerator is also fluidized with N₂, now at approximately twice U_{mf} (50 slpm). Within the regenerator it is necessary to add the approximately 1.5 kW of energy liberated in the adsorber to the regeneration process. Additional sensible energy must also be added to increase the sorbent to the regeneration temperature. A specific heat of 1000 J/kg-K was assumed for the proxy sorbent, initial temperature of 70°C and final temperature of 110°C. The circulation rate was previously determined to be 0.72 kg/min, and sensible heat required is 0.48 kW. Total heat required is 2.0 kW supplied by internal coils with heated circulating oil for testing purposes A

real world application would likely utilize superheated steam for fluidization rather than the N_2 used in the test unit. The steam will have the added benefit that it can supply the heat addition rather than internal coils. The use of steam will improve the product CO_2 as it will not be diluted with N_2 . Steam requirements have been estimated previously for various reactor configurations and represented less than 50% of the steam requirements and approximately 1/3 of the power loss as compared to a conventional MEA carbon capture system (Hoffman et. al. 2008).

2.2 Instrumentation

The C2U facility consisted of regular process instruments for measuring gas flow rate, pressure, temperature, heat flux and weight of solids. Other instrumentation was used to measure relative humidity and CO_2 concentration; control heating of the granular beds (regenerator and upper loopseal) and cooling in the (adsorber and/or lower loopseal) and protected the unit from high pressure or high temperature excursions.

Plenum, sparger, motive, dilution and standpipe fluidization gas flows were metered with Alicat mass flow controllers. Standard conditions were taken as 25 °C and 1 atmosphere as per Alicat mass flow controller specifications.

Thirteen Alicat mass flow controllers with flow ranges from 0-20 up to 0-500 slpm and preprogrammed for gas composition were used. Process gases used in the C2U were limited to nitrogen, air and CO_2 . Alicat mass flow controllers provided an accuracy calculated by $\pm (0.8\% \text{ Reading} + 0.1\% \text{ Full Scale (FS)})$, repeatability of $\pm 0.2\% \text{ FS}$, response time of $< 10 \text{ ms}$ to setpoint changes and valve control time of less than 100 ms. The built in actuator Proportional-Derivative (PD) controller controls actual gas flows within $\pm 1\%$ of the setpoint.

Twenty-one Rosemount differential pressure transmitters with ranges of 0-6.9 to 0-186 kPa and an accuracy of $\pm 0.075\% \text{ FS}$ were installed in the C2U facility. Two were configured for the absolute pressure measurements at the bottom of the adsorber and the regenerator relative to ambient barometric pressure, the rest measured differential pressures across various locations in the process unit. Local barometric pressure was determined using a Mensor pressure transducer.

Five dual headed type K thermocouples were inserted at the location of the C2U where temperature measurement was the most critical and fifteen single headed thermocouples were used for additional temperature information. All thermocouples were grounded to protect data acquisition (DAQ) card from static discharge. Two heat flux sensors (thermopiles) were attached to the wall of the regenerator to evaluate heat losses during sorbent regeneration.

A combination of N_2 and CO_2 was humidified before feeding into the absorber plenum. Humidification was provided by a Controlled Evaporation Mixture (CEM) system which maintained a 2% by vol. moisture content to avoid degradation of the amine based sorbent. Water was drawn from a pressurized tank and measured by a liquid flow meter where it was mixed with the incoming gas and fed into a heated evaporator section controlled at 88 °C.

CO_2 and H_2O exit concentrations in both the adsorber and regenerator exit streams were monitored using PP Systems WMA-4 CO_2 analyzers (range – 0 – 10,000 ppm CO_2 , 0 – 1000 mb H_2O). O_2 and high CO_2 concentration measurements were made with Quantek model 902P analyzers (range 0 – 100% O_2 , 0 – 100% CO_2 , accuracy 1% FS).

The regenerator bed was heated using custom made heat exchanger coils installed within the regenerator bed. A heat exchange fluid, mineral oil, was pumped through a Chromalox electric heater controlled at a target temperature and then through the heat exchange coils. The process temperatures in the middle of the regenerator were used to control the heat input to the electric heaters using a cascaded proportional/integral (PI) controller. Controlling the temperature of the regenerator bed proved more difficult than controlling the oil temperature because there were additional disturbances such as variable gas and solids flow rates, solids temperature, and heat consumption during CO_2 regeneration. Cascaded PI controllers were used to compensate for these disturbances. The bed temperature was chosen as primary control variable and the oil temperature was the secondary variable. The primary loop sends the operator input set-point to the secondary loop (typically 125°C). Accordingly, the PI controller adjusts the current to maintain the required oil temperature. The bed temperature can be controlled within 5% of the set-point.

The initial design for the cooling exchange coil called for installation in the adsorber because of the high amount of energy released when the bentonite material was to be employed (nominal 1.28 kW). With the change to the silica based sorbents, energy production within the adsorber was greatly reduced (nominal 0.18 kW), therefore, the need to remove heat within the adsorber was lessened. The cooling coils were moved to the lower loopseal to only cool the sorbent exiting the regenerator prior to reentry into the adsorber. Cooling was accomplished by passing chilled water through the heat transfer tubes. Water was cooled using a Lytron chiller Model RC045J03BG.

2.3 Data acquisition

Data acquisition was performed using National Instruments (NI) LabVIEW software and NI DAQ modules contained in an 8 Channel NI Compact DAQ Chassis. Two analog input cards acquired signals

from pressure transmitters and CO₂ analyzers, three temperature DAQ cards acquiring both thermocouple and heat flux sensor readings. A single Analog Output card transmitted 4-20 mA current to the solid state relay (SSR) for heater temperature control and a Digital Output card controlled the on/off state of the heater and pump relays and the solenoid valves. Also, two 4 Channel NI RS232 – ENET modules were used to communicate with the RS232 devices (flow controllers). Data regarding gas flows, temperatures, CO₂ concentrations and other pertinent conditions were acquired at one second intervals throughout the duration of the experiments.

3. Operation of Original Design

Operation was initiated by first introducing minimal flows ($2U_{mf}$) of humidified nitrogen to the regenerator, adsorber and each loop seal. Humidification was controlled at 2% vol which is near saturation under ambient conditions. The experiments were run with a synthetic flue-gas that contained a CO₂ concentration of 6-21% and a 2% by volume of moisture. The remaining was nitrogen. These experiments did not consider the effects of trace components such as SO₂, O₂ or ash.

Sorbent within the regenerator and upper loopseal was heated using the internal coils until the desired operating temperature was reached. Once this was accomplished move air was introduced and adsorber fluidization flow increased to allow solids circulation. Particles were circulated without introduction of CO₂ until the desired adsorber temperature was achieved. Once thermal equilibrium was attained, move and lance flows were adjusted to yield the desired circulation rate and the required mixture of N₂/CO₂ was introduced to the adsorber. If the temperature of the solids entering the lower loopseal exceeded the desired temperature for solids entering the adsorber then cooling water flow would be pumped through the heat transfer coils in the lower loopseal. Conditions were maintained until the CO₂ outlet concentrations, temperatures, circulation rate and pressures were invariant.

3.1 Circulation rate

Sorbent circulation rate during operation could be inferred by the pressure drop across the crossover and confirmed using the diversion valve. Previously, during operations at a given test condition the solids flow below the cyclone separator was diverted into a container for a short period of time (15 – 30 sec) where approximately 100 to 200 g of material was extracted. The extracted material was weighed and rate of discharge was determined. Correlating these measurements with the pressure drop across the crossover yielded a method of continuous realization of circulation rate (Figure 4) for AX sorbent. Circulation rate could be varied by varying motive air (introduced two pipe diameters above the bend in the L-valve) and sparger air (which ran the length of the L-valve horizontal section).

Figure 4 Correlation between sorbent circulation rate and crossover dp.

3.2 Sorbent and vessel material change

The first version of the C2U was transparent and constructed primarily of polycarbonate. This material was chosen because it was clear and allowed visual observation inside the system. Acrylic, while clear, could not withstand the temperatures of nearly 130°C anticipated in the regeneration process. The proxy sorbent (glass beads) was circulated within the C2U to test hydrodynamic performance and results were as expected (Clay et al, 2013). However, the particle characteristics of the first available sorbent were different than those of the original concept. This sorbent, designated AX with properties displayed in Figure 2, had a smaller diameter, lower density and comprised of polyethylenimine (PEI) immobilized on mesoporous silica (Gray et al, 2008; Gray et al, 2005; Gray et al, 2004; Monazam et al, 2012). The minimum fluidization velocity of AX ($U_{mf} = 0.52$ cm/s) is about 20% that of glass beads, with all flows reduced accordingly. Initial testing of the AX sorbent using the C2U system revealed a flaw in the materials used for construction. The amines within the sorbent reacted with the polycarbonate components causing brittle failure. The system was rebuilt using high-density polyethylene. This material, while opaque, could withstand the temperatures and amine reactions. The lengths of each reactor were maintained but the internal diameter was reduced to 0.137 m due to increased wall thickness. Another PEI sorbent was also tested (32D), similar to AX but with approximately half the particle density (0.48 g/cc).

Table 2 – Particle Properties for AX sorbent

PROPERTY	UNIT	AX SORBENT
DIAMETER	μm	115
DENSITY	kg/m^3	910
U_{MF}	m/s	0.0052
GELDART CLASSIFICATION	-	A
WORKING CAPACITY	$\text{gmol CO}_2/\text{kg}$	1.5

The change in physical characteristics had a dramatic effect on system hydrodynamics. The sorbent behaves more as a Geldart group A material. Also, flows are greatly reduced. If the flue gas flow to the adsorber is maintained on the basis of ratio of minimum fluidization velocity ($6.5 \times U_{\text{mf}}$), the new total volumetric flow to the adsorber is now 30 slpm with a CO_2 flow of 4.5 slpm and a riser gas flow of 25.2 slpm. Terminal velocity has been calculated to be 0.28 m/s, whereas the riser gas velocity is only 0.21 m/s; therefore the flow is now insufficient to carry the sorbent to the cyclone. There were two alternatives available to solve this dilemma: increase flue gas rate or decrease riser diameter. The riser diameter was eventually decreased to 2.54 cm, reducing the flow area by one fourth and increasing the riser velocity to 0.83 m/s (in this case), well above terminal velocity.

Assuming a comparable working capacity, 1.5 gmol CO_2/kg sorbent and CO_2 is introduced at 0.2 gmol/min, the required solids circulation rate has been reduced to 0.13 kg/min (8.0 kg/hr). AX sorbent heat of adsorption is 65.8 kJ/mol CO_2 (Spenik et al, 2015) and therefore 0.22 kW of energy is continuously released during adsorption. Within the regenerator, the required heat addition has also been dramatically reduced. Sorbent specific heat was estimated at 1600 J/kg-K (Spenik et al, 2015). Assuming a 40°C temperature increase in the regenerator, an additional 75 W is required. Total heat required for regeneration purposes is now 293W using AX sorbent.

3.3 Solids inventory and residence times

Each loopseal can be filled with AX sorbent to a height of 23 cm (volume ≈ 3300 cc), the adsorber and regenerator (short version) to 36 cm (volume ≈ 5200 cc), the L-valve contains an extra volume of 2100 cc; thus the full system holds over 19100 cc AX sorbent. The total inventory of AX sorbent, in this case, is about 12 kg. With a solids circulation rate of 8.0 kg/hr, a sorbent particle completes a circuit in 91 minutes. The regenerator was to contain material up to the level of the heat transfer coils which is also the level where solids enter from the upper loopseal at 0.36 m above the distributor plate. Using AX, the

regenerator contained 3.28 kg at any given instant; therefore the residence time of a particle would be 24.7 minutes in which time the CO₂ must be released. Later, to extend regeneration time, this height was increased to 0.67m with the addition of a spool piece.

3.4 Heat transfer

During a particles residence within the regenerator sufficient energy must be imparted to it to liberate the captured CO₂. Energy is supplied by heated mineral oil circulating at a rate of approximately 4.5 lpm through copper coils immersed in the bed. Specific heat and density of the oil is 1670 J/kg-K and 830 kg/m³ respectively. Normally during operation, the drop in temperature between inlet and outlet oil temperatures of approximately 3°C was seen, indicating a heat transfer rate between the sorbent bed and coils of 312 W. This energy transfer rate is sufficient to liberate CO₂ and account for additional parasitic losses to the environment. Desired bed temperatures were achieved by adjusting the oil inlet temperature accordingly.

The heat transfer coefficient between the immersed coils and sorbent bed was determined using a correlation for horizontal tubes in a bubbling bed (Yang, 2003) using separate equations for laminar and turbulent regimes.

For $\rho_p/\rho_g * Re_p > 2550$ (Turbulent regime)

$$h_c = 420 \left(\frac{k_g}{D_t} \right) \left(\frac{\rho_p}{\rho_g} * Pr * \frac{\mu_g^2}{g \rho_p^2 d_p^3} \right)^{0.3} Re_D^{0.3} \quad \text{Eq.2}$$

and for $\rho_p/\rho_g * Re_p < 2050$ (Laminar regime)

$$h_c = 0.66 \left(\frac{k_g}{D_t} \right) Pr^{0.3} \left(\frac{\rho_p(1-\epsilon)}{\rho_g \epsilon} \right)^{0.44} Re_D^{0.44} \quad \text{Eq. 3}$$

For $2050 < \rho_p/\rho_g * Re_p < 2550$ an average of the two can be used.

The void fraction (ϵ) can be estimated using King's formula with the superficial velocity U_g in m/s:

$$\epsilon = \frac{U_g + 1}{U_g + 2} \quad \text{Eq. 4}$$

With the small diameter particles being used and the superficial velocities near minimum fluidization, the value U_g (in m/s) is a small number so the void fraction can usually be estimated at 0.5.

The heating coils consisted of two nested coils: the outer coil was a 6 m long, 1.25 cm OD copper tube of wound in twelve, 10.2 cm diameter loops, each loop separated by a large OD tube thickness. The inner coil was a 4 m long 0.95 cm OD copper tube wound in sixteen 5.1 cm loops, each loop separated by a small OD tube thickness. The tubes were joined at one end within the reactor. Oil flowed through the reactor wall into the larger diameter tube through a fitting and exited the wall through a fitting attached to the smaller tube. Total surface areas of the outer and inner tubes were 0.15 and 0.12 m² respectively. Within the regenerator, the term $(\rho_p/\rho_g)Re_p = 56$ for the AX sorbent, fluidized at twice U_{mf} . Therefore, the condition was laminar and the heat transfer coefficients were calculated to be 56 and 66 W/m²-K for the larger and smaller tubes respectively with a combined heat transfer of 16 W/K given the surface area of both tubes.

It should be noted that if glass beads (proxy sorbent) were used and fluidization increased to 4.5x U_{mf} , then $(\rho_p/\rho_g)Re_p = 2761$ well within the turbulent regime. The heat transfer coefficients become 905 and 529 W/m²-K for the large and small diameter coils respectively and the combined heat transfer would be 203 W/K. In the original design it was shown that at least 2.0 kW would have been required for regeneration but this could have been supplied via the increased heat transfer.

The thermal potential required to transfer the 0.25 kW of heat required for regeneration is determined from $\Delta T = Q/hA$ where hA is the combined heat transfer (16 W/K), in the AX case $\Delta T = 15.4$ K. This value is used as the log mean temperature difference (LMTD) if the coils and bed can be considered as a parallel flow heat exchanger where $T_{h,i}$ and $T_{h,o}$ are the oil inlet and outlet temperatures and $T_{c,i}$ and $T_{c,o}$ are the sorbent inlet and outlet temperatures.

$$\Delta T = LMTD = \frac{(T_{h,i} - T_{c,i}) - (T_{h,o} - T_{c,o})}{\ln[(T_{h,i} - T_{c,i}) / (T_{h,o} - T_{c,o})]} \quad \text{Eq. 5}$$

Previously, it was determined that the difference between inlet and outlet oil temperatures would be limited to about 3°C. However, the sorbent temperature will vary about 30°. Therefore, the average of the inlet and outlet oil temperatures can be considered as single value, an approximation of the tube surface temperature (T_s). Assuming the sorbent enters at 80°C and exits at 110°C the average surface temperature required is 115°C. This is an achievable temperature that should not damage the sorbent with direct contact. The inlet oil temperature would be set to about 118 °C. In the bentonite case, the required surface temperature would be lower (112°C) due to the enhanced heat transfer.

$$T_s = \frac{T_{c,i} - T_{c,o} \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right]}{1 - \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right]} \quad \text{Eq. 6}$$

4.0 System Development

4.1 The Modifications

The C2U configuration was altered a number of times to obtain a controllable circulating system capable of operating on the Geldart group A material rather than the original Geldart group B material. The sorbent properties for the group A material were previously shown in Table 2. The original configuration, designated Mod 0, is depicted in Figure 1 where the underflow tube below the regenerator transitioned into the L-valve. The adsorber consisted of a 45 cm tall fluidized bed section situated below a conical transition. The transition reduced the 14 cm diameter adsorber to a 5 cm diameter riser. The regenerator underflow was relatively short so the lower loopseal (chiller) was mounted about 30 cm above the adsorber. Stable fully integrated operations were successful using glass beads (Clay et al, 2013); however, sorbent AX did not develop sufficient head pressure to avoid backflow of gases from the adsorber into the regenerator or allow controlled solids circulation.

In the first modification implemented for the C2U, Mod 1, the regenerator and upper loopseal were raised and the lower loopseal was dropped, placing its distributor plate at the same elevation as that of the adsorber. This provided the additional height needed for solids circulation and avoid gas back-flow into the regenerator from the adsorber. In the same modification, the L-valve was also replaced with a sweeping arc stand leg. Unfortunately, the aeration motive air in the sweeping arc configuration was limited to a single location near the loopseal end of the sweep. Varying the motive air introduced at this point did not allow control of circulation rate. This can be seen in Figure 5 as well as the results from Mod-2. For example, Figure 5a. indicates that for Mod-1 with a motive air flow of 6 slpm the circulation rate varied between 2 and 38 kg/hr. Experiments were conducted with motive air rates of 12 and 18 slpm with no improvement of the stability. Furthermore, there was a remarkable lack of CO₂ capture, less than 30% of the CO₂ introduced. In several cases the transitions between operating conditions lead to process instabilities such that the shifting in solids inventories from adsorber to regenerator led to pressure imbalances, stoppage in solids flows, and flow reversal.

Figure 5 Variations in the solids circulation rate for configuration with the long radius elbow (Mod-1) and the L-valve (Mod-2).

As a result of these instabilities (inventory swings between vessels) and the lack of solids flow control a second set of modifications (Mod 2) were performed. The long radius elbow below the regenerator was replaced with a more conventional L-valve which consisted of vertical and horizontal piping of 4.9 cm inner diameter located below the regenerator. A 6.35 mm outer diameter stainless steel lance was inserted along the bottom of the horizontal section running from the far wall of the underflow pipe to the entrance of the loopseal chiller as is normal for L-Valves with small height to length ratios. This change allowed greater control of the circulation rate as seen in Figure 5b. For example, at a move gas flow rate of 0.2 slpm, the solids flow rate was 20 ± 5 kg/hr. This was a significant improvement that allowed the research to move forward in developing an operating test unit. Even though repeatability was observed with the

solids flow rate, other process instabilities continued to plague operations with pressure imbalances. It was observed that solids would deplete from the regenerator and accumulate in the adsorber indicating insufficient riser gas velocity.

In order to reduce the buildup of solids in the adsorber, a third modification was implemented (Mod 3) where the riser diameter was reduced from 5 to 2.5 cm to increase riser gas velocity with identical adsorber volumetric gas flow. The 2.54 cm ID riser tube was extended further down into the adsorber reactor such that the solids entered this transport line 35.6 cm above the gas distributor. The reduced pressure at the base of the adsorber provided a smaller hurdle for the regenerator Δp to aid in solids transport to the adsorber. A second advantage was that the shorter height in the adsorber fluid bed altered the relative volumes of the regenerator and adsorber. The volume in fluid bed portion of the adsorber was reduced from 6.88 to 5.20 L, while the regenerator had only 4.43 L reactor volume in the bed below the solids inlet port and with heat transfer surface. The volume ratio, or residence time ratio, was reduced from 1.55 to 1.15 (V_{ads}/V_{reg}). Additionally, a heat exchange surface was added to the upper loopseal making this vessel a regenerator preheater (Mod-4). These modifications did not substantially aid in the ability to control circulation rate but there was a significant improvement in sorbent working capacity and CO₂ capture efficiency. Previous experiments indicated a capture efficiency of less than 30% however subsequent tests yielded efficiencies between 70 – 96%. Adsorption efficiency is a ratio of the amount of CO₂ adsorbed to the total CO₂ inputted. Regeneration efficiency is the ratio of CO₂ regenerated to the amount of CO₂ previously adsorbed. Regeneration efficiency can also be thought of as closure, an indication of CO₂ accumulation within the sorbent over repeated cycles.

A final modification (Mod 5) was incorporated in which the regenerator was extended by approximately 0.3 m by the addition of a spool piece between the existing regenerator and plenum. The coils within the regenerator were also lengthened by this amount.

4.2 Modified System Operation

Table 3 lists parameters from a series of tests in the Mod 4 configuration that were conducted in which some variables were held nearly constant: total adsorber bed flow ($\sim 10.9 \pm 0.4 U_g/U_{mf}$), regeneration temperature ($\sim 117 \pm 4$ °C), adsorption temperature ($\sim 72 \pm 5$ °C), and humidification ($1.8 \pm 0.01\%$ H₂O vol.). Controlled variables were adsorber CO₂ concentration (6 – 21%) and regenerator sweep gas flow ($1.3 - 7.9 U_g/U_{mf}$). Control of circulation rate was attempted initially with mixed results therefore motive and sparger flows were set to a minimum ($\sim 0.6 \pm 0.2$ slpm) letting the circulation rate depend on adsorber flow. Difficulties maintaining a consistent circulation rate was encountered for some points within this matrix. REG 5 was the extreme case of variable circulation (Figure 6). During this test, 8.0 slpm CO₂

was introduced to the adsorber plenum with a concentration of 16.6% where most was adsorbed while circulation was maintained. However, at approximately 1800 seconds, solids circulation abruptly ceased causing adsorption to cease some 200 seconds later but regeneration continued unabated. When circulation could be resumed then adsorption commenced almost immediately. During the period between 500 and 1500 seconds while solids were circulating at about 75 kg/hr, the adsorption efficiency was 87% of the 9.0 slpm inputted but the regeneration efficiency was merely 50% of the 7.8 slpm CO₂ adsorbed. Later, when circulation ceased adsorption rate declined however, regeneration continued. This can be contrasted with case REG8a (Figure 7) where circulation was maintained at a constant rate of approximately 25 kg/hr and 93.3% of the 6 slpm CO₂ inputted was adsorbed and 89.5 of that was regenerated.

Table 3 Circulating carrier tests conducted with Mod 4 configuration

	CIRCULATION				SET POINTS		DEPENDENT VARIABLES		
	Duration (sec.)	Average (kg/hr.)	stdev (kg/hr.)	stdev/avg.	CO ₂ in (%)	Reg Flow (U/U _{mf})	Ads. Eff (%)	Reg. Eff (%)	Capacity (gmol/kg)
REG 2A	2640	25.22	3.49	0.14	5.9	1.3	86.0	53.5	0.26
REG 3	4920	28.00	5.35	0.19	5.9	3.5	89.9	90.3	0.27
REG 4	3600	20.87	6.67	0.32	11.9	3.5	86.2	67.9	0.68
REG 5	5760	33.88	20.08	0.59	16.6	3.5	65.1	73.6	0.54
REG 6	3600	17.26	1.47	0.09	11.8	3.5	88.6	78.4	0.82
REG 7	5400	16.32	1.04	0.06	11.8	6.8	91.5	86.9	0.88
REG 8	2700	22.38	1.24	0.06	11.8	5.2	96.4	77.2	0.70
REG 8A	21120	24.67	2.29	0.09	11.8	5.2	93.3	89.5	0.59
REG 9	14400	25.19	1.85	0.07	11.8	5.2	93.0	83.0	0.59
REG 10	3600	27.76	3.38	0.12	14.7	3.5	82.4	76.4	0.60
REG 11	1740	33.44	8.42	0.25	14.5	3.5	56.9	73.0	0.47
REG 12	1200	52.49	9.63	0.18	17.5	3.5	51.1	52.6	0.34
REG 13	3540	48.02	6.56	0.14	14.7	4.6	80.8	81.3	0.37
REG 13A	2700	35.20	2.78	0.08	15.6	4.6	85.6	76.3	0.48
REG 14	3600	21.12	1.70	0.08	15.8	7.9	85.1	100.6	0.87
REG 15	4500	22.95	8.19	0.36	15.8	1.3	70.0	76.8	0.64
REG 16	3600	20.24	1.63	0.08	15.7	4.6	83.1	94.5	0.86
REG 17	2700	22.33	1.89	0.08	15.8	4.6	85.9	89.8	0.75
REG 18	3600	23.46	3.38	0.14	10.5	4.6	99.0	100.2	0.54
REG 19	3600	24.29	3.26	0.13	21.0	4.6	81.6	72.5	1.04
REG 20	2700	17.05	4.96	0.29	15.8	4.6	58.4	73.5	0.64

Figure 6 Time series data during continuous operations of test REG5.

Figure 7 Time series data during continuous operations of test REG8a.

Table 4 lists parameters from a series of tests in the Mod 5 configuration which approximate those of the Mod 4 tests: total adsorber bed flow ($\sim 11.0 \pm 0.1 U_g/U_{mf}$), regeneration temperature ($\sim 114 \pm 3^\circ\text{C}$), adsorption temperature ($\sim 70 \pm 5^\circ\text{C}$), and humidification ($1.7 \pm 0.01\%$ H_2O vol.). Controlled variables were adsorber CO_2 concentration ($6 - 18\%$), regenerator sweep gas flow ($2.0 - 5.9 U_g/U_{mf}$) and motive and sparger flows ($\sim 1.0 \pm 0.2$ slpm). It should be noted that the values for the capacity in Table 4 are less than the reported working capacity in Table 1 of 1.5 mol/kg . The value in Table 1 is for “clean” or “fresh” sorbent. The values in Table 4 are less than this amount, ranging from a low of 0.34 mol/kg to a high of 1.36 mol/kg . In an earlier publication on the performance of this sorbent in batch tests, Spenik et al. (2015) point to overheating as a reason why the capacity might be lower than the theoretical value for a “fresh” sorbent. The main point made in that discussion was that the heating coils were at an elevated

temperature and that slow moving sorbent particles that were in direct contact with the heating coils were overheated, causing thermal degradation of the sorbent.

A second reason why sorbent capacity is lower in than the theoretical value is that the sorbent is not being fully regenerated back to a value of zero. It has residual CO₂ on it at or near the equilibrium value associated with the regenerator temperature and CO₂ content in the gas. In this regard, the sorbent performance cycles between the regenerator near equilibrium value (i. e.: lean or low loading) and fully carbonated (i.e.: high loading). For example, if the residual CO₂ on the sorbent is 0.5 mole/kg, the working capacity is reduced from 1.5 mole/kg to 1.0 mole/kg.

The Mod 4 modification increased the adsorption efficiency to nearly 100% for CO₂ concentrations around 6% but the efficiency decreased with increasing CO₂ concentration (Figure 8). The subsequent Mod 5 redesign to increase the regenerator residence time provided nearly 100% regeneration independent of circulation rate fluctuations as is shown in Figure 9.

Table 4 Circulating carrier tests conducted with Mod 5 configuration

	CIRCULATION				SET POINTS		DEPENDENT VARIABLES		
	Duration (sec.)	Average (kg/hr.)	stdev (kg/hr.)	stdev/avg.	CO ₂ in (%)	Reg Flow (U/U _{mt})	Ads. Eff (%)	Reg. Eff (%)	Capacity (gmol/kg)
AX 2	3306	15.4	1.15	0.07	12.3	2.2	78.7	103.6	0.82
AX 4	7993	20.9	5.48	0.26	12.3	2.1	67.0	85.0	0.51
AX 5	4993	8.7	2.71	0.31	12.2	2.6	58.6	99.2	1.36
AX 6	7992	14.1	3.38	0.24	12.0	3.3	70.6	100.1	0.67
AX 7	7093	15.4	0.88	0.06	6.0	2.2	96.4	100.8	0.45
AX 8	5991	16.9	2.17	0.13	18.0	2.2	55.8	102.5	0.73
AX 9	8548	14.4	7.24	0.50	11.9	2.8	78.6	97.0	1.03
AX 9B	6242	15.6	3.22	0.21	12.0	2.4	70.4	100.0	0.68
AX 10	1441	15.0	0.92	0.06	12.0	2.0	71.5	90.8	0.46
AX 11	4200	15.7	1.90	0.12	11.9	3.9	72.4	91.4	0.65
AX 12	7999	15.3	1.98	0.13	12.0	3.5	79.5	99.0	0.67
AX 13	3000	16.2	3.97	0.24	12.0	4.5	68.1	98.2	0.92
AX 14	4992	17.7	3.82	0.22	12.1	5.4	80.7	92.9	0.61
AX 15	5992	9.6	1.19	0.12	6.0	4.0	96.4	102.0	0.82
AX 16	2992	15.0	2.21	0.15	18.0	5.1	50.4	93.5	0.82
AX 17	6000	18.9	4.09	0.22	12.1	3.4	77.0	96.6	0.60
AX 18	9992	16.4	6.09	0.37	12.0	2.4	59.1	100.8	0.62
AX 20	7898	22.1	1.05	0.05	5.9	4.2	98.5	99.8	0.34
AX 21	10999	13.1	1.44	0.11	6.0	5.9	98.5	100.5	0.52
AX 22	7150	16.3	1.09	0.07	5.9	2.9	98.5	105.0	0.48

Figure 8 Adsorption efficiencies in the Mod 4 and Mod 5 configurations

Figure 9 Regeneration efficiencies in the Mod 4 and Mod 5 configurations

Summary:

Significant CO₂ capture was demonstrated in a relatively simple, continuous fluidized bed processes. The adsorption of carbon dioxide (CO₂) by immobilized amine (PEI) on mesoporous silica was investigated using a series of coupled fluidized beds referred to as the C2U. This test unit employed fluidized bed technology to adsorb CO₂ from a simulated mixture of gases representing the flue gas from a pulverized coal power plant. The sorbent was then transferred using non-mechanical valve technology (upper loop seal) into a fluidized bed where it was regenerated by heating it to 120°C under a nitrogen flow where the solids moved down counter to the up flowing sweep gas. The nitrogen and CO₂ gas stream was then

released to the atmosphere. In a commercial system, steam would have been used for fluidization, the escaping gas would have been captured, the steam condensed and the remaining CO₂ would then be compressed to be utilized or sequestered. In depth characterization of amine-based sorbents enabled identification of the critical parameters necessary to demonstrate these performance advancements. Tests were completed to evaluate the optimum reactor throughput and maximum working capacity. Several additional reactor modifications have been identified which are expected to improve performance significantly. As a means to summarize the modification steps, Table 5 below outlines the changes made and the impact observed.

Table 5: Advancements made and problems solved through each stage of modification.

No.	Description of changes	Basis/Constraints	Performance/Effect of Modifications
Mod 0	Baseline design for Group B Material	Height of facility, and gas throughput defined. Transparent for visual observation.	Operated well in cold flow tests well on glass beads, but did not circulate reliably with sorbent. Gas flow reversal was observed. Acrylic vessels corroded, embrittled, and lost integrity upon exposure to PEI loaded sorbent.
Mod1	Replace acrylic with polyethylene vessels and reinforced rubber connecting tubes. Increase overall height in recycle leg (standleg below regenerator) by dropping the lower loopseal and raising the upper loopseal and regenerator. Replace L-valve at base of standleg with a sweeping arc.	Loss ability to visually observe performance. Reduced the height between cyclone and loopseal. Increased wall thickness and reduced inner diameter.	Circulation limited to very narrow range, with low solids flows and intermittent stoppages. Lack of solids flow control. Process upsets occasionally led to loss of sorbent inventory through cyclone, clogging the downstream barrier filters.
Mod2	Replaced sweeping arc with L-valve and sparger on horizontal.	Reduced the potential for gas bypassing standpipe solids to minimize pressure loss needed for solids circulation and reduce pressure upset events. Enabled more direct control of solids flow.	Continuous circulation of solids achieved with fewer upset events. Capture efficiency remained low for all cases below 80%. Solids would deplete from the regenerator and accumulate in the adsorber.
Mod3	Reduced the riser diameter from 5 to 2.5 cm.	Reduced the back pressure of the adsorber on the regenerator as well as the relative volume of the adsorber compared to the regenerator	Target capture efficiency achieved under select conditions. Operations continue to be limited to select adsorber flows but circulation rates can be varied somewhat. Capture efficiencies are achieved above

			target level 90%.
Mod4	Provide sorbent preheat in return leg upstream from regenerator	The design was to add heat transfer surface to regenerator, but the heat coils added to loopseal (V2000) were removed from the regenerator because additional length increased back pressure pumping the heat transfer fluid (oil).	Performance was consistent with Mod3.
Mod5	Add additional regenerator volume	An additional 0.3 m of height was added to the regenerator enabling operations with larger relative volume in the regenerator and higher height in the return leg.	Performance was consistent with Mods 3 and 4. Further analysis is required to establish the effect of regenerator volume and heat transfer surface on the overall performance.

5. Nomenclature:

A_{pp} – Projected particle area (m^2)

C_D – Drag coefficient

$CO_2\%$ - CO_2 volume concentration in adsorber flow (%)

d_p – Particle diameter (m)

D_t – Heat transfer tube diameter (m)

F_a – Total flow to adsorber plenum (slpm)

F_{ls} – Total flow to loopseal plenums (slpm)

F_{mv} – Total move air flow (slpm)

F_r – Total flow to regenerator plenum (slpm)

g – gravitational acceleration ($9.8 m/s^2$)

h_c – Heat transfer coefficient between immersed tube and bed ($W/m^2 \cdot ^\circ K$)

k_g – Gas conductive heat transfer coefficient ($W/m \cdot ^\circ K$)

LMTD – Log mean temperature difference ($^\circ K$)

M_{inv} – Sorbent mass inventory (kg)

Pr – Prandtl #

Re_p – Reynolds' # (particle)

$T_{c,i}$ – Solids inlet temperature (regenerator)

$T_{c,o}$ – Solids exit temperature (regenerator)

$T_{h,i}$ – Oil inlet temperature (regenerator)

$T_{h,o}$ – Oil inlet temperature (regenerator)

T_s – Coil average surface temperature

U_{mf} – Minimum fluidization velocity (m/s)

U_g – Superficial gas velocity (m/s)

V_{term} – Particle terminal velocity (m/s)

W – Particle weight (kg)

ε – Void fraction

η – Capture efficiency (%)

μ_{gas} – Gas viscosity (kg/ms)

ρ_g – Gas density (kg/m³)

ρ_p – Particle density (kg/m³)

6. Disclaimer

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