Technical Report

Carbon Capture Unit (C2U) Design and Experimental Results Using Polyethylenimene (PEI) Immobilized on Mesoporous Silicas

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Executive Summary

Campaign Objectives/Background

A Carbon Capture Unit (C2U) was created to test the effectiveness of sorbents composed of amines on a solid substrate to remove CO_2 from flue gas. The unit, which utilizes fluidized beds for both absorbtion and regeneration, was designed and constructed at the National Energy Technology Laboratory in Morgantown West Virginia. It was operated at NETL for approximately three years where two types of sorbents were tested in both circulating and batch modes under a variety of conditions. Both sorbents (AX, 32D) were comprised of polyethylenimine on a silica substrate. Mean Sauter diameters of both sorbents were roughly 100 µm. The particle density of AX was 0.88 g/cc and 0.48 g/cc for 32D.

This unit was moved to the National Carbon Capture Center (NCCC) in Wilsonville, Alabama in January 2014 to take advantage of the PC4 flue gas slipstream. The focus of these tests was exploring for accumulation of heavy metals, such as selenium, on the 32D sorbent from flue gas. Experiments were conducted in two phases: circulating and batch.

Description of Test Campaign

Circulating tests

The circulating tests were to be conducted over a period of a few weeks with an accumulated testing time of 100 hours of steady-state circulation; however only 43.5 hours of testing were obtained.

Fresh 32D sorbent (7.5 kg) was used for the test. The unit consisted of four reactors: adsorber, regenerator and two loop seals. Flue gas from the slipstream was directed to the adsorber plenum using vacuum pumps and the flow was measured with a rotameter. The flue gas then passed through a porous metal distributor plate into the adsorber where sorbent within this reactor collected CO_2 from the flue gas. The CO_2-laden sorbent migrated up the adsorber to a riser where it was swept up along with the now CO_2-deficient flue gas. Both the sorbent and flue gas entered a cyclone located past the riser where the particles and flue gas were separated. The sorbent fell to the upper loopseal below the cyclone, the flue gas exited the system from the cyclone top. The sorbent was transferred through the upper loopseal and into the regenerator. Heat was added to the regenerator bed, liberating the CO_2. The regenerator bed was fluidized with N_2 which swept the CO_2 into a separate stream (steam would normally be used as a sweep gas in an actual process if carbon sequestration were the goal). CO_2-lean particles were then transported to a second loopseal and ultimately back to the adsorber to begin the cycle anew.

Batch tests

The C2U was reconfigured to perform batch testing. CO_2 capture was not a priority during batch testing, only heavy metal accumulation. The regenerator was configured as the contacting vessel for the batch testing. Therefore, all heating was discontinued; the absorber and both loopseals were removed. The sorbent was not circulated or regenerated. Fresh sorbent was added to the regenerator where flue gas flow was maintained at approximately 15 slpm throughout the test. In this test, the only instrumentation in use was a vacuum pump, rotameter and magnehelic pressure gauge across the bed.

The batch testing occurred from June through August, but several leaks on the unit and plant delays limited the accumulated testing time. Over 346 hours of exposure were completed under simulated natural gas conditions. After transitioning to regular coal-fired flue gas, 282 hours were completed before the planned plant outage.

Primary results

Circulating tests

Data was acquired for approximately six-hours per day during circulating tests. The unit was first brought to the proper thermal conditions (heating of the regenerator) using nitrogen as a substitute for flue gas. When the regenerator reached the proper temperature, flue gas flow was initiated and the N_2 flow to the adsorber terminated. After circulating the sorbent for about six hours, the flue gas flow was substituted with N_2. The oil was allowed to cool while circulating through the regenerator bed to reduce the sorbent and regenerator temperatures to an acceptable level (70^oC). On the next day of operation the procedure was repeated.

Initially, the sorbent adsorbed most of the CO_2 presented to it; however, as hours of operation progressed the adsorption rate declined dramatically. Although detailed analysis of the degradation in performance of the system was not performed, incomplete regeneration of the sorbent is thought to be the cause of the reduced performance, resulting in an elevated lean CO_2 loading and a concomitant lower working capacity. Post-test thermo-gravimetric analysis (TGA) of sorbent samples from the NCCC circulation tests shows no permanent loss of CO_2 capture capacity. Complete regeneration of the sorbent would allow the system to attain the performance initially observed during the first few hours of testing with a fresh inventory of sorbent.

Batch tests

After the conclusion of the circulating tests, the C2U was reconfigured to perform a continuous batch test. During this batch test all heating and cooling was discontinued. New sorbent (2.4 kg) was added to the regenerator. The adsorber and both loopseals were removed from the system. The goal of this test was to supply flue gas to a single bed of sorbent for an extended period of time (1000 hours) and subsequently analyze the sorbent composition. The only instrumentation in use was a vacuum pump, a rotameter and a magnehelic pressure gauge across the bed.

The slipstream did not have sufficient pressure to operate within the test unit, thus the pressure was boosted using vacuum pumps. Two vacuum pumps were used in parallel to deliver a flow rate of approximately 30 slpm of flue gas through the system.

The flue gas initially supplied to the unit for the batch tests was diluted with air to simulate natural gas combustion products to accommodate other NCCC users. Although the sorbent was exposed to the diluted flue gas for 346 hours, the equivalent amount of flue gas exposure was 115 hours, due to dilution. After transitioning to regular coal-fired flue gas composition, an additional 282 hours of testing were completed before a planned plant outage for a total equivalent flue gas exposure of 397 hours. The end result was that 2.4 kg of sorbent was exposed to the equivalent 357,000 standard liters (12,600 scf) of coal-fired flue gas.

Samples of the sorbent from these tests (after the diluted flue gas and after full strength flue gas), unused samples taken before and after all NCCC testing and samples taken after circulation tests (described below) were analyzed for trace elements. The amount of arsenic, chromium, lead, mercury and selenium for these samples was compared to the amount required to be considered a hazardous waste by the EPA. In all cases, the trace element concentrations were significantly lower than the hazardous waste standards. As an example, if all of the selenium in the coal which supplied the flue gas to the sorbent bed was assumed to reach the skid and be deposited onto the sorbent bed, the resulting weight fraction of selenium on the bed would be 23 ppm. This value is well in excess of that measured (<1 ppm). However, to better gauge selenium accumulation on the sorbent, chemical analysis of the inlet flue gas slip stream to the skid should be conducted, due to the probable partitioning of selenium dropping out of the flue gas (i.e., fly ash collection device, FGD scrubber, etc.) and thus not reaching the skid.

Similar to the results in the circulating tests, post-test thermo-gravimetric analysis (TGA) of sorbent samples from the NCCC batch tests shows no permanent loss of CO_2 capture capacity.

Part 1

Experimental Apparatus

Introduction

A small scale circulating fluidized bed (Carbon Capture Unit or C2U) was designed to test the effectiveness of solid amine based sorbents for use in the capture of CO_2 from flue gas. Two types of sorbents, 32D and AX were ultimately tested in the Carbon Capture Unit. Both sorbents were comprised of polyethylenimine (PEI) on a simulated amorphous silica substrate and were tested by varying several independent variables at the National Energy Technology Laboratory (NETL) in Morgantown, West Virginia. Final tests were conducted at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama. Tests at NETL were conducted using a synthetic flue gas produced by mixing streams of N_2, CO_2 and H_2O vapor. The NCCC tests involved the use of flue gas produced from a coal fired steam generating power plant. The primary focus of the NCCC test was to examine for any possible adsorption of heavy metal contaminates, such as selenium, by the 32D sorbent.

The C2U consisted of four main vessels: fluid bed adsorber, moving bed regenerator regenerator, upper and lower loop seals. Flue gas would enter the adsorber plenum and rise through a bed of sorbent where CO_2 capture would occur. A reduction in pipe diameter at the top of the adsorber acted as a riser allowing transport of the CO_2 laden sorbent. Initially, the sorbent enters at the bottom of the adsorber and adsorbs CO_2 as it migrates upward. At the top of the adsorber, the sorbent particle is swept up the riser section. The sorbent, with adsorbed CO_2, and the flue gas, with reduced CO_2 concentration, is transported up the riser. At the top of the riser the particles and remaining flue gas pass through a crossover and into a cyclone which separates the solid particles from the flue gas. Solid particles fall through the cyclone bottom and the remaining flue gas exits the cyclone top and vents atmosphere.

The spent sorbent travels through the cyclone down comer and enters the bottom of the upper loopseal. As additional particles enter the bottom of the loopseal, particles that had previously entered, migrate toward the top. Previously cycled particles, now at the top of this loopseal, fall into the top of a regenerator

Particles at the top of the regenerator gradually move downward as particles at the bottom are removed. The regenerator contains internal coils where heated oil circulates. The CO_2 adsorption reaction is exothermic and desorption (regeneration) is endothermic. Heat addition is required in the regenerator to raise the sorbent temperature from the adsorption temperature (typically near 60°C to the regeneration temperature near 120°C. The addition of heat releases CO_2 from the sorbent which exits the top of the regenerator. Particles are drained from the bottom of the regenerator at the same rate they enter the top. As the moving bed of sorbent reaches the bottom of the regenerator, free of CO_2, they fall through a standpipe and enter an L-valve. At the L-valve the particles are transported through a horizontal pipe section and eventually arrive at a second loopseal (lower). As with the upper loopseal, the sorbent is fed into the bottom of the lower loopseal and migrates upward until they reach the top. From the top of the lower loopseal the sorbent falls to the bottom of the adsorber, completing the sorbent circulation loop.

When the system was originally designed the footprint of the C2U was considered. The overall height of the system needed to be less than 12 ft (3.7 m) due to the anticipated location of the apparatus. Likewise, the diameter of the vessels needed to be about 6 inches (0.15 m) due to the availability of gases. Flows were originally based on a sorbent with a bentonite substrate (density = 2.0 g/cc, particle diameter = 200 μm); however, the sorbents that were ultimately tested consisted of synthetic amorphous silica substrate with densities and diameters less than half that of the bentonite, thus reducing the required gas flows.

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^oC anticipated in the regeneration process. Ultimately, it was determined that the amines reacted with the polycarbonate causing it to crack. The system was rebuilt using high-density polyethylene. This material, while opaque, could withstand the temperatures and amine reactions.

As experiments progressed, several changes in geometry were made as knowledge was gained. Some of the modifications include: reduction of riser diameter, lowering vertical position of lower loopseal and extending the regenerator height. The final version of the C2U modifications is shown in Figure1.

Two types of sorbent were investigated: AX and 32D. Both have amines immobilized onto an amorphous silica substrate. The sorbents were tested by varying parameters such as regeneration temperature, gas flow rates in adsorber and regenerator reactors, and sorbent circulation rate as well as other minor parameters. Two main modes of experimentation were conducted: circulating and batch.

A variety of instrumentation was employed to measure relevant parameters. Thermocouples measured temperature and pressure transducers measured pressure differentials at many locations within the system. Continuous emission monitors (gas analyzers) were used to measure CO_2 and O_2 concentrations at the exit of the adsorber and regenerator. Heat flux gauges were employed to determine heat loss through vessel walls. Mass flow controllers were used to meter gas flows at various positions and to manufacture simulated flue gas. Heating and cooling were performed using a circulating oil heater and a water chiller respectively.

Parameters were controlled and data recorded using laptops with a LabVIEW based control program. The program allowed the operator to adjust the various gas flow rates and heating temperatures while monitoring exit gas composition and sorbent efficiency.

In succeeding sections details of the overall design is given as well as the criteria for selection of flow rates in various portions of the C2U. The location and purpose of each instrument is given. The LabVIEW operator interface is shown and described. A detailed analysis of the methods used for heat transfer will be presented. Finally, the results of experiments conducted using both AX and 32D sorbent are detailed.

Figure1. Final version of the C2U unit

Overall Geometry

A small scale circulating fluidized bed unit was designed to characterize sorbents used in the capture of CO_2 from flue gas. The unit was comprised of four reactors (adsorber, regenerator, two loopseals) plus other ancillary parts (

Figure 2).

Each reactor was composed of the reactor body with a plenum underneath. The reactor bodies were comprised of high-density polyethylene (ID = 5.375", OD =6.375"). Plenums were comprised of aluminum with a 6 inch ID and 0.25 inch wall. Between each reactor body and plenum, a porous metal distributor plate was located. The distributor plates were 6" diameter disks cut from a sheet of 316 stainless steel (Mott corporation media grade 40, thickness 0.078").

Gas with a CO_2 component (simulated flue gas) was introduced into the adsorber plenum (3A) where the gas passed through a sintered metal distributor plate and fluidized the sorbent within. The gas flow needed to be sufficient to produce a turbulent bed in the adsorber section (3) and exceed the particle terminal velocity in the riser section (5 and 6).

The circulation rate of the sorbent needed to be sufficiently large so that the adsorption capacity of the sorbent was not exceeded. Within the adsorber, when the sorbent adsorbed CO_2, an exothermic reaction occurred, heating the sorbent. If the sorbent is heated above a certain temperature then adsorption ceases and desorption dominates. Therefore, in some cases, heat was removed in the adsorber to an external sink.

As the sorbent entered the adsorber (3) from the lower loopseal (1) it was intended to be free of CO_2. Upon entering the adsorber the sorbent adsorbed CO_2. The bed level within the adsorber was maintained at sufficient height so that some particles were close enough to the adsorber transition (4) to be swept into that region where the gas velocity increases and entrainment into the riser was possible. In the polycarbonate version, the transition reduced the adsorber inner diameter from 5.5" to 2" ID of the riser (5,6). The final version of the HDPE configuration was an abrupt transition to a 1" ID riser.

The particles and gas with reduced CO_2 concentration passed through the crossover (7) and into the cyclone (8), where the sorbent was separated from the gas stream. The particles settled from the cyclone into the bottom of the upper loopseal and the reduced CO_2 gas exited the top of the cyclone vent.

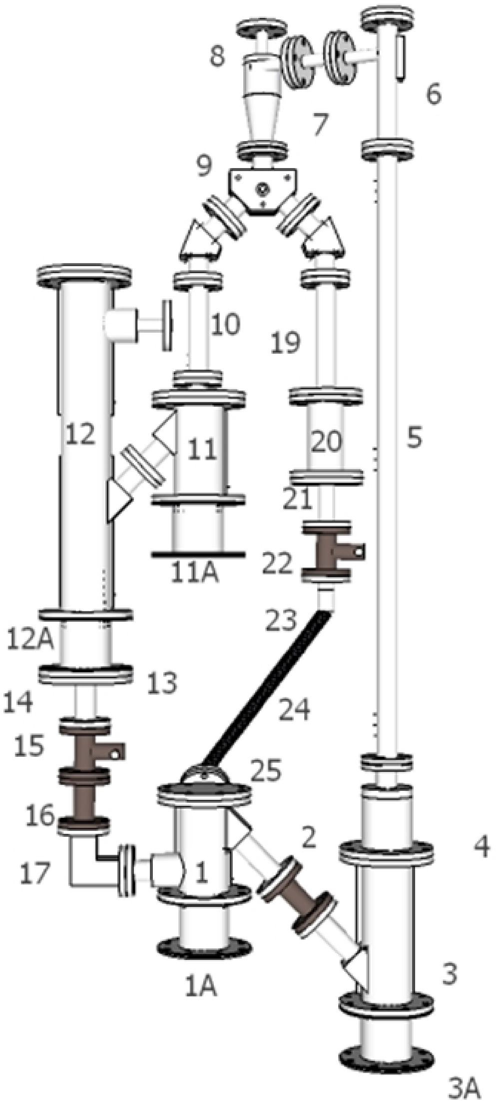
Sorbent particles migrated from the bottom to the top of the minimally fluidized upper loopseal (11). Sorbent particles at the top of the loopseal fell into the top of the regenerator (12). The particles formed a fluidized bed in the regenerator where sorbent entering the top migrates to the bottom. The particles in the regenerator were heated with internal coils as they pass to the bottom releasing captured CO_2. In an actual carbon capture process the regenerator would be fluidized with superheated steam which would sweep away the CO_2 through the gas exit at the top of the regenerator freeboard. The steam would then be condensed and a concentrated stream of CO_2 would remain for subsequent compression and sequestration. However, for this case, N_2 was used to fluidize the regenerator.

The particles passed through a tube that is inserted through the regenerator plenum (12A) then through the regenerator transition (14), butterfly valve (15) and down to the L-valve (17). Here the particles were pushed through the horizontal section using motive gas to the bottom of the lower loopseal (1). The horizontal section was also fluidized with a sparger. As with the upper loopseal, the particles migrated from the bottom to the top under minimally fluidized conditions and eventually fall back into the adsorber where the sorbent circulation cycle begins again.

Some geometrical changes were implemented between the initial polycarbonate version and the final version of the C2U comprised of HDPE. When the polycarbonate version failed due to the degradation of the polycarbonate, the HDPE version was constructed with approximately the same geometry. Subsequent versions of the HDPE configuration elevated the regenerator higher relative to the adsorber, lowered the lower loopseal, reduced the riser diameter from 2” to 1” and extended the regenerator bed by adding a 12” spool to the bottom. Also, the diameter of the reactor sections was slightly reduced between polycarbonate (5.5”) and HDPE (5.375”). Aluminum plenums were retained for all versions.

Table 1. Dimensions of selected components (inches)

		HDPE version		
	#	ID	OD	Length
		(in)	(in)	(in)
Lower loopseal	1	5.375	6.375	12
Lower loopseal plenum	1A	5.5	6	6
Flexible connector	2	2		
Adsorber	3	5.375	6.375	18
Adsorber transition	4	-	-	-
Riser long section	5	1	1.5	72
Riser short section	6	1	1.5	21
Crossover	7	1	1.5	13
Upperloopseal	11	5.375	6.375	12
Upperloopseal plenum	11A			
Regenerator	12	5.375	6.375	54
Regenerator plenum	12A	5.5	6	6
Regenerator insert	13	2	2.5	7.5
Standpipe transition	14	2	2.5	6
Butterfly valve	15	2		6
Flexible connector	16			6



Parts:
1.	Lower loopseal
1A.	Lower loopsealplenum
2.	Flexible connector
3.	Adsorber
4.	Adsorber transition
5.	Small dia. riser long section
6.	Small dia. riser short section
7.	Crossover
8.	Cyclone
9.	Diversion valve
10.	Diversion valve to lower loopseal
11.	Upper loopseal
11A.	Upperloopseal plenum
12.	Regenerator
12A.	Regenerator plenum
13.	Regenerator insert
14.	Standpipe transition
15.	Gate valve
16.	Flexible connector
17.	L-valve
19.	Diverter valve to collector
20.	Collector
21.	Collector to Loopseal #1 transition
22.	Valve for solids sampling
23.	Connection for flexible tube
24.	Flexible tube
25	Connection for flexible tube

Figure 2. C2U unit design

Flow rate calculations and circulation rates

The initial selection of mass flow controllers was based on a bentonite substrate with a density of 2 g/cc and a diameter of 200 um. However, the sorbents that were ultimately used were on a silica substrate. Therefore, modifications were made to accommodate the change in material, the change in riser diameter being the most obvious.

Two types of sorbent were ultimately tested which will be referred to as AX and 32D. The AX sorbent had a mean Sauter diameter of 115 um and an intrinsic density of 0.9 g/cc. The mean Sauter diameter was 90 um and particle density 0.48 g/cc for the 32 D.

A typical case of a circulation condition will be described below using sorbent 32D. Typically 7.5 kg of the sorbent is added to the system with a volume of 22,000 cc

Assume a flue gas with a composition of 76% N_2, 12% CO_2, 6% O_2 and 2% H_2O (vapor) entering at 20°C. The viscosity of the mixture at this temperature is $1.68\text{x}10^{-5}$ kg/m-s. Operating pressure is atmospheric.

Minimum fluidization velocity

According to Wen and Yu, [4][1] a simplified form of the Ergun equation, in terms of Reynolds and Archimedes numbers can be reduced to

$$\mathrm{Re}_{mf} = \sqrt{C_1^2 + C_2 * Ar} - C_1$$

The coefficients C_1 and C_2 were modified by Grace [4] where $C_1 = 27.2$ and $C_2 = 0.0408$.

$$Ar = \frac{d_p^3 \rho_g (\rho_p - \rho_g) g}{\mu^2}, \quad \mathrm{Re}_{mf} = \frac{d_p U_{mf} \rho_g}{\mu}, \quad U_{mf} = \frac{\mathrm{Re}_{mf}\, \mu}{d_p \rho_g}$$

Gas density calculated at operating pressure

$$\rho_g = \frac{p * MW}{R^* T} = \frac{1.01325x10^5 * 28.84}{8314.3 * (25 + 273)} = 1.18 \text{ kg/m}^3$$

Archimedes' number is calculated:

$$Ar = \frac{d_p^3 \rho_g (\rho_p - \rho_g) g}{\mu^2} = \frac{(9x10^{-5})^3 * 1.18 * (480 - 1.23) * 9.8}{(1.68x10^{-5})^2} = 14.3$$

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[1] Handbook of Fluidization and Fluid Particle Systems (Yang) p. 63

The minimum fluidization Reynolds' number is calculated:

$$\mathrm{Re}_{mf} = \sqrt{C_1^2 + C_2 * Ar} - C_1 = \sqrt{27.2 + 0.0408 * 15} - 27.2 = 0.011$$

From this Reynolds' number the minimum fluidization velocity is calculated:

$$U_{mf} = \frac{\mathrm{Re}_{mf}\,\mu}{d_p \rho_g} = \frac{0.011 * 1.68x10^{-5}}{9.0x10^{-5} * 1.18} = 0.0017 \text{ m/s}$$

This value compares well with the experimentally determined value of 0.23 cm/s for 32D sorbent.

Terminal velocity

$$\mathrm{V_{term}} = \sqrt{\frac{2\mathrm{W}}{\mathrm{C_D} * \rho_{\mathrm{gas}} * \mathrm{A}_{face}}}$$

Where W is the particle weight in Newtons (1.8 x 10^{-9}) assuming a 90 µm particle with a density of 0.48 g/cc (32D). The drag coefficient (C_D) is determined from a correlation [4]

$C_{D=}\frac{24}{Re} * (1 + 0.1935 * Re^{0.6305})$ when 0.01 < Re < 20

$C_{D=}\frac{24}{Re} * (1 + 0.1315 * Re^{0.82-0.05z})$ when 20 < Re < 250

Where $z = \log_{10}\mathrm{Re}$

Also:

$D = ½*\rho_g*V^2*A*C_D$

The velocity where the drag force D equals the weight W is the terminal velocity and where A is the face area of the particle ($\pi/4 * d^2$) = 6.36x10^{-9} m^2

The equation is implicit so one must assume a velocity to calculate Re. This value is used in the V_{term} equation. When V_{Term} equals the assumed velocity then the correct value has been solved for.

Assume V = 0.12 m/s

$$\mathrm{Re} = \frac{\rho_g \mathrm{Vd}}{\mu} = \frac{1.18 * 0.12 * 9 \text{ x}10^{-5}}{1.68 \text{ x } 10^{-5}} = 0.76$$

Since Re < 20

$$C_{D=}\frac{24}{0.72}*(1+0.1935*(0.72)^{0.6305})=31.65$$

$$\mathrm{V_{term}}=\sqrt{\frac{\mathrm{2W}}{\mathrm{C_D}*\rho_{\mathrm{gas}}*\mathrm{A}}}=\sqrt{\frac{2*1.8\mathrm{x}10^{-9}}{31.65*1.18*6.36\mathrm{x}10^{-9}}}=0.12\ \mathrm{m}/s$$

Adsorber

The adsorber normally contained 3500 cc of 32D sorbent bringing the bed level up to about 0.35 m (14 inches). This placed the bed level near enough to the transition to allow particles to be entrained.

A nominal flue gas inlet flow rate to the adsorber plenum can be assumed to be 35 slpm. The 5.375" ID adsorber had a flow area of 1.46 x10^{-2} m^2. At 35 slpm the superficial velocity would be 0.04 m/s and U/U_{mf} = 23.5.

$$V=\frac{\dot{Q}}{A}=\frac{35}{1.46x10^{-2}*1000*60}=0.04\ m/s$$

Volumetric flow of CO_2 is 4.2 slpm with 12% CO_2 concentration, therefore, the mass flow rate of CO_2 is 1.26x10^{-4} kg/s. Assuming 90% of the CO_2 is removed then 1.13 x10^{-4} kg/s (9.28 gmol/hr) would be removed and 1.26 x10^{-5} kg/s would remain in the flue gas.

Riser

Assuming 90%, by volume, of the CO_2 is removed from the flue gas (3.78 slpm CO_2 out of 35 slpm) then the remaining 31.22 slpm of flue gas must have a sufficient velocity to transport the material through the 1 inch ID riser. This velocity must be substantially greater than the terminal velocity of a single particle to have adequate solids transport.

The riser has a flow area of 5.07x10^{-4} m^2 and the volumetric flow of the remaining flue gas is 5.2 x10^{-4} m^3/s; therefore the gas velocity is 1.0 m/s. The terminal velocity has been calculated to be 0.11 m/s. Since the actual gas velocity far exceeds the terminal velocity there should be adequate flow to transport particles up the riser.

$$\mathrm{A}=\frac{\pi {D_i}^2}{4}=\frac{\pi*2.54^2}{4*100^2}=5.07x10^{-4}\ m^2$$

$$\dot{\mathrm{Q}}=\frac{31.22}{1000*60}=5.20x10^{-4}\ \frac{m^3}{s}$$

$$\mathrm{V} = \frac{\dot{Q}}{A} = \frac{5.20x10^{-4}}{5.07x10^{-4}} = 1.0\ \frac{m}{s}$$

Sorbent circulation rate

The 32D sorbent has an estimated working capacity of about 1.8 gmol CO_2 per kg sorbent. From the adsorber calculations above the adsorption rate should be 9.28 gmol/hr therefore a sorbent circulation rate of at least 5.15 kg/hr is prescribed.

$$\dot{m}_{sorbent} = \frac{\dot{m}_{CO2}}{capacity} = \frac{9.28}{1.8} = 5.15\ \frac{kg}{hr}$$

Loopseal(s) fluidization

Both loopseals require that the particle bed within be fluidized at or slightly above the minimum fluidization velocity. The minimum fluidization velocity of the 32 D sorbent was previously determined to be about 0.17 cm/s. The flow area of both loopseals is equivalent to that of the adsorber (1.46 $x10^{-2}$ m^2). Therefore a volumetric flow rate of at least $2.48x10^{-5}$ m^3/s (1.5 slpm) is required. From experimental evidence the required flow rate was actually about twice U_{mf} (3 slpm) to achieve full fluidization. The solids depth in each loopseal was approximately 9” (0.23 m).

$$\dot{\mathrm{Q}} = AV = 1.46x10^{-2} * 1.7x10^{-3} * 1000 * 60 = 1.49\ slpm$$

Cyclone standpipe to upper loopseal fluidization

The 2” pipe carrying solids from the cyclone to the bottom of the upper loopseal required fluidization to assure the movement of sorbent particles. This was normally fluidized near the minimum fluidization velocity with 1 – 2 slpm N_2.

Regenerator fluidization

The regenerator fluidization was also maintained at some low multiple of the minimum fluidization level. The overall gas flows were larger than those of the loopseals since some sweep gas is required. Typically, 10 slpm of N_2 was used which was near 11x U_{mf} for 32D sorbent. Heated coils were used in the regenerator to heat the bed and aid in regeneration. The regenerator would normally contain sorbent up to the level of the solids inlet from the upper loopseal. In the original configuration, this level would be 14” (0.36 m) and the extended regenerator solids depth was 26” (0.67 m)

Regenerator standpipe fluidization

Solids descend through a 2” tube which was passed through the center of the regenerator plenum. A flow of approximately 0.5 slpm was maintained to fluidize the column of solids and allow solids flow down to the L-valve.

Sparger and motive gas

A sparger runs the length between the L-valve and the lower loopseal allowing fluidization of the horizontal section. Also, move gas was inputted about 3” above the L-valve to control circulation rate.

Heat transfer

The adsorption of CO_2 by the sorbent is an exothermic reaction which causes the sorbent particle temperature to increase if heat is not removed. When a sorbent particle exceeds a certain temperature, adsorption ceases, and desorption can begin. Therefore, heat was removed to cool the sorbent either prior to and/or during adsorption. Likewise, heat must be added prior to and/or during regeneration to facilitate CO_2 removal

Instrumentation

Mass flow controllers

Alicat MC series mass flow controllers were used for gas flow control. The input and output control for the instruments were based on standard volumetric flow where P_{std} = 101324 Pa and T_{std} = 25°C (298 K). Ranges and purposes of the controllers in the last configuration of the C2U can be found in Table 2.

Adsorber plenum

There were four mass flow controllers used in the plenum of the adsorber allowing a simulated flue gas to be produced. N_2 flow was controlled by using either FTC1100 for low volume flows (0 – 50 slpm) or FTC1150 for high volume flows (50 – 500 slpm). FTC1150 was rarely used with the AX or 32D sorbents. FTC 1200 was used to add CO_2 to the N_2 to simulate a flue gas. Likewise FTC 1101 was used to deliver a quantity of liquid water to a humidification system that ultimately sent water vapor to the adsorber plenum.

A typical total flue gas flow to the adsorber plenum was nominally 30 to 35 slpm for 32D sorbent and 45 – 50 slpmfor AX sorbent. The median CO_2 concentration was 12% volume; water vapor wasapproximately 2% of the total flow.

The amount of humidification in g/hr was determined from the mass derived assuming the ideal gas equation. If the total flue gas flow rate was 35 slpm and 2% of this was water vapor then 0.70 slpm ($1.167\text{x}10^{-5}$ m^3/s) water vapor flow was required. From the ideal gas equation the mass flow of H_2O is found to be 30.9 g/hr. CO_2 flow is 4.2 slpm and the remaining 86% of the flow is N_2 at 30.1 slpm. However, not all of this flow was delivered by FTC1100. Also, included in the total N_2 flow within the riser was motive air (FTC4150), sparger (FTC3100) and lower loopseal fluidization (FTC 4100) flows.

$$\dot{m}_{H2O} = \frac{P_{std}\dot{V}(MW)}{R^{*}T_{std}} = \frac{101324 * 1.167x10^{-5} * 18 * 3600 * 1000}{8314 * 298} = 30.9\ \frac{g}{hr}$$

Cyclone standpipe

The tube used for solids flow between the upper loopseal solids entrance and the cyclone bottom (cyclone standpipe) was fluidized at about twice minimum fluidization using flow controller FTC2100. The 2 inch ($2\ \text{x}10^{-3}$ m) diameter pipe was normally fluidized with 0.5 slpm of N_2. This flow was assumed to rise up the cyclone standpipe and exit the cyclone top where it merged with gases exiting the riser. This flow contributed to the total flow when calculating exit gas composition using gas analyzers located at the adsorber side exit.

Loopseal plenums

Both loopseal plenums were normally fluidized at approximately twice $U_{mf.}$ Loopseal flow areas were identical to the adsorber and riser flow areas. Therefore, both loopseals were normally fluidized at approximately 3.0 slpm N_2. The upper loopseal used FTC 2150 and the lower loopseal used FTC 4100. Gases from the lower loopseal combined with flue gas and exited the top of the cyclone to be counted as adsorber side exit gas while gases from the upper loopseal were assumed to enter the regenerator and werecounted as regenerator side exit gas.

Regenerator plenum

The regenerator plenum gas was supplied using FTC3150 with flows between 5 and 10 slpm. This gas flowed through an annular porous plate. A 2 inch diameter pipe extended through the center of the plate, through which solids were transported.

Regenerator standpipe (Underflow)

The 2 inch diameter pipe through which solids were conveyed from the regenerator bottom to the L-valve was fluidized using FTC4150 usually at 0.25 to 0.5 slpm. This flow was thought to contribute to regenerator exit flow.

Sparger

A sparger which extends the length of the horizontal tube between the L-valve and lower loopseal solids entrance was used to fluidize the material within. Flow controller FTC3100 normally delivered about 2 slpm of N_2. This flow contributed to total adsorber flow

Motive

A move gas port was located about 3 diameters above the L-valve bend. This flow was supplied by FTC 3170 at low flow rates from 0 – 2 slpm and also contributed to total adsorber flow.

Table 2. Flow controllers

Tag #	Description	Units	Range
1100	Adsorber plenum (N2 low flow)	SLPM	50
1150	Adsorber plenum(N2 high flow)	SLPM	500
1200	Adsorber plenum CO2	SLPM	50
1011	Adsorber humidification	gram/hr	150
2100	Dipleg	SLPM	20
2150	Upper loopseal plenum	SLPM	50
3100	Sparger	SLPM	5
3150	Regen plenum	SLPM	20
3170	Move	SLPM	10
3200	Regenerator plenum CO2	SLPM	250
3300	Dilution air	SLPM	250
4100	Lower loopseal plenum	SLPM	50
4150	Underflow	SLPM	10
4300	Air	SLPM	500

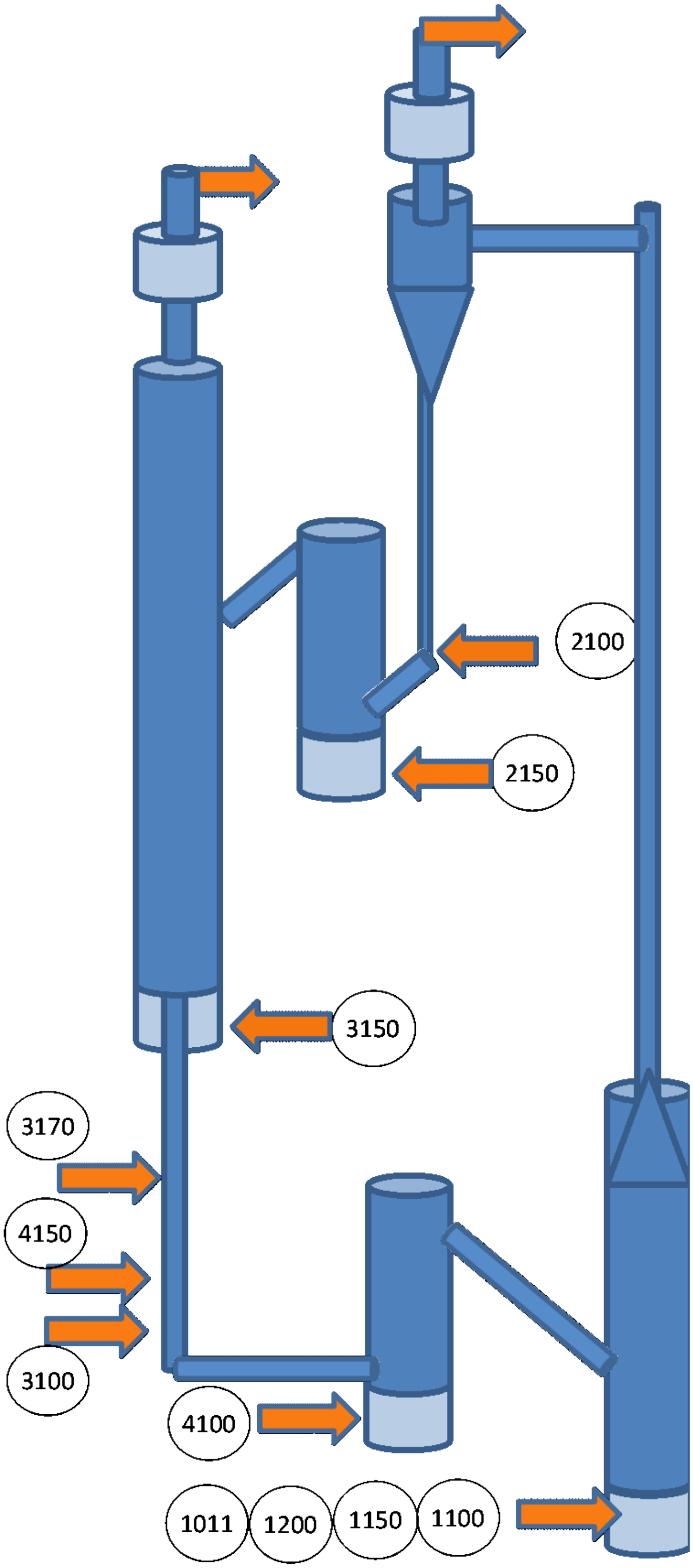


Figure 3. **Final position of Mass flow controllers**

Pressure measurements

Differential pressure measurements were made using Rosemont pressure transducers at various locations within the system (Table 3, Figure 4). Barometric pressure was also recorded. Total system pressure on both the regenerator and adsorber sides was determined using PT 3805 and PT 1810. PT 3805 was located at the L-valve and PT1810 was located at the adsorber plenum.

Table 3. Pressure locations

Tag Number	Description
1810	Bottom adsorber to atm
3805	Regenerator standpipe to atm
0801	Barometric Pressure
1801	Top lopseal #1 to bottom adsorber
1812	Across adsorber distributor plate
1820	Across adsorber 5.5 ID section
1830	Across adsorber transition
1840	Across adsorber 2" ID pipe
1841	Across crossover
1853	Across adsorber filter
1854	Loopseal #2 standpipe to solids inlet loopseal #2
1860	Cyclone to atm
2801	Solids inlet loopseal #2 to bottom loopseal #2
2812	Across loopseal #2 distributor plate
2820	Across loopseal #2
3801	Top of loopseal #2 to solids inlet regenerator
3812	Across regenerator distributor plate
3820	Regenerator bottom to solids inlet
3830	Bottom of regenerator and across solids control valve
3853	Solids control valve to L-valve
3860	Across upper half of regenerator
3870	Across regenerator gas exit filter
4801	Across L-valve
4812	Across loopseal #1 distributor plate
4820	Across loopseal #1

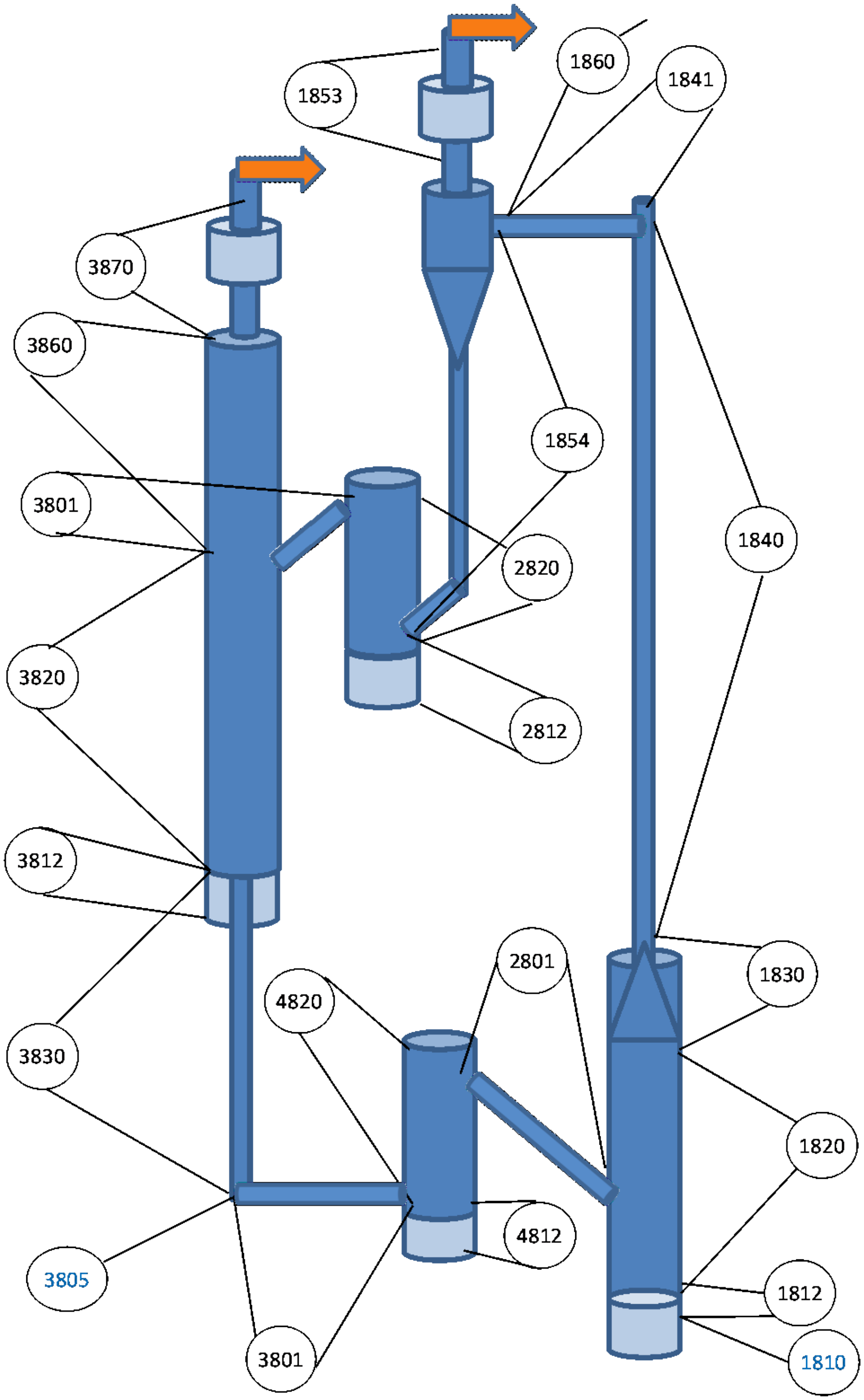


Figure 4. Pressure transducer locations

Temperature measurements

Temperatures at various points within the system were determined using output from type K thermocouples. Table 4 and Figure 5 illustrate their locations. Heating control was managed by output from either TE3964 (coil entrance oil temperature) or TE3965 (regenerator mid-bed temperature).

Table 4. Thermocouple locations

Tag #	Description
1910	Adsorber entrance
1912	Heat Trace
1914	Adsorber bottom
1920	Adsorber at top of chiller coils
1930A	Crossover entrance - dual head
1961	Middle of 5.5" ID adsorber
1962A	Top of 5.5" adsorber section - dual head
2914A	Bottom of loopseal #2 - dual head
2930	Upper loopseal top
2963	Lpsl#2 coil exit
2964	Lpsl#2 coil entry
3914	Bottom of regenerator
3920	Gas entering regenerator plenum
3922	Regenerator outlet
3930	Top of regenerator
3962A	Midpoint of regenerator column/top coils
3963	Heater exit
3964	Heater entry
3965	Midway of coils
4910	Gas entering loopseal #1 plenum
4914A	Mid of loopseal #1 - dual head
4918	Loopseal #1 entry
4930	Chiller entry
4935	Regenerator solids valve
4940	Chiller exit
4950	Solids exiting loopseal #1

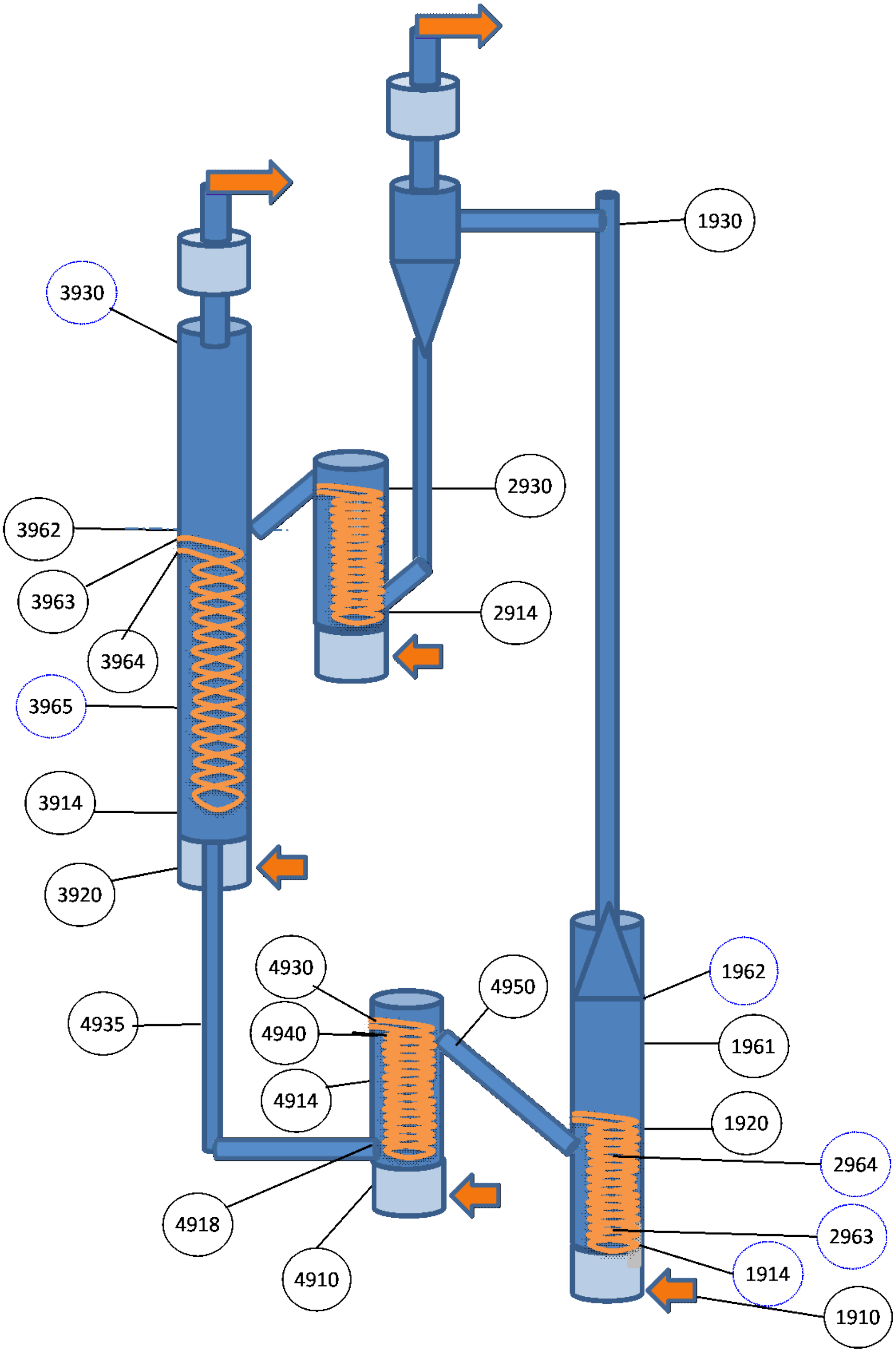


Figure 5. Thermocouple placement

Exit gas composition

The concentration of CO_2 and O_2 was measured at the exit of both the regenerator side and adsorbed side using Quantex Model 902P CO_2 /O_2 gas analyzer with ranges of 0 – 100% CO_2 and 0 – 20% O_2. The adsorber CO_2 measurement was designated as AIT1531, O_2 measurement as AIT1532. On the regenerator side, the designations were AIT3531 and AIT3532 for CO_2 and O_2 respectively.

Originally two PP Systems analyzers were used, however, the ranges of 1% and 10% CO_2 concentration was too low. Prior to obtaining the Quantex analyzers, it was necessary to dilute the exit gases to lower CO_2 concentration within the range of the 10% PP analyzer. The designations were AIT1530 on the adsorber side and AIT3530 on the regenerator side. These analyzers also reported humidity, thus they were left installed on the system.

The volumetric exit gas flow rate was unknown, thus to determine the quantity of CO_2 adsorbed on the adsorber side and liberated on the regenerator side, the inlet gas flows were used to implicitly determine the exit CO_2 flow. When using this equation a negative value for CO_2 adsorbed indicates CO_2 regeneration.

The analyzer provides the following information:

$CO_2^{\text{ fraction at exit}} = CO_2^{\text{ exit}}/\ \text{Total flow}^{\text{ exit}}$

The CO_2 reaching the exit is less than that inputted during the adsorption process and greater if the process is regeneration:

$CO_2^{\text{exit}} = CO_2^{\text{ inlet}} - CO_2^{\text{ adsorbed}}$

The total flow at the exit includes the addition or subtraction of CO_2:

$\text{Total flow}^{\text{ exit}} = CO_2^{\text{ inlet}} + \text{Other flows}^{\text{ inlet}} – CO_2^{\text{ adsorbed}}$

$\text{Total flow}^{\text{ inlet}} = CO_2^{\text{ inlet}} + \text{Other flows}^{\text{ inlet}}$

Substituting into the initial equation:

$$CO_2^{fraction\ at\ exit} = \frac{CO_2^{inlet} - CO_2^{adsorbed}}{Total\ flow^{inlet} - CO_2^{adsorbed}}$$

Rearranging

$$\mathrm{CO_2}^{\mathrm{adsorbed}} = \frac{\mathrm{CO_2}^{\mathrm{inlet}} - Total\ flow^{inlet} * CO_2^{fraction\ at\ exit}}{\left(1 - CO_2^{fraction\ at\ exit}\right)}$$

Heat flux sensor

Heat flux gauges were placed on the regenerator wall to estimate the amount of heat loss to the environment through the vessel wall. The sensors were thin film self-generating thermopile transducers.

Distributor pressure drop

The plenum of each reactor has a 6 inch diameter distributor plate formed from 316 SS sintered metal. Pressure drop as function of gas flow is shown on Figure 6

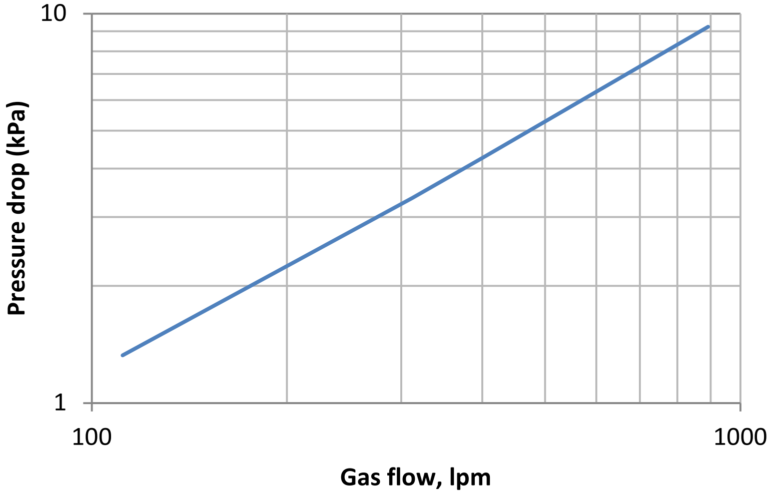


Figure 6. Pressure drop across distributor plates

For internal flows:

$$\dot{Q} = \frac{-\kappa A \Delta P}{\mu L}$$

Software control

Flows and oil heating were controlled via virtual control panels written on a LabVIEW platform. Two laptop computers were used simultaneously, one with the LabVIEW platform, the other monitored data via an EXCEL spreadsheet.

Main panel

The main panel (Figure 7) allowed the operator to start/stop the program, call up the sub panels and display temperature and pressure trends. Temperature trends were useful in the control of regenerator heating whereas the pressure trends allowed the operator to determine if sorbent circulation was constant or a particular reactor was accumulating solids.

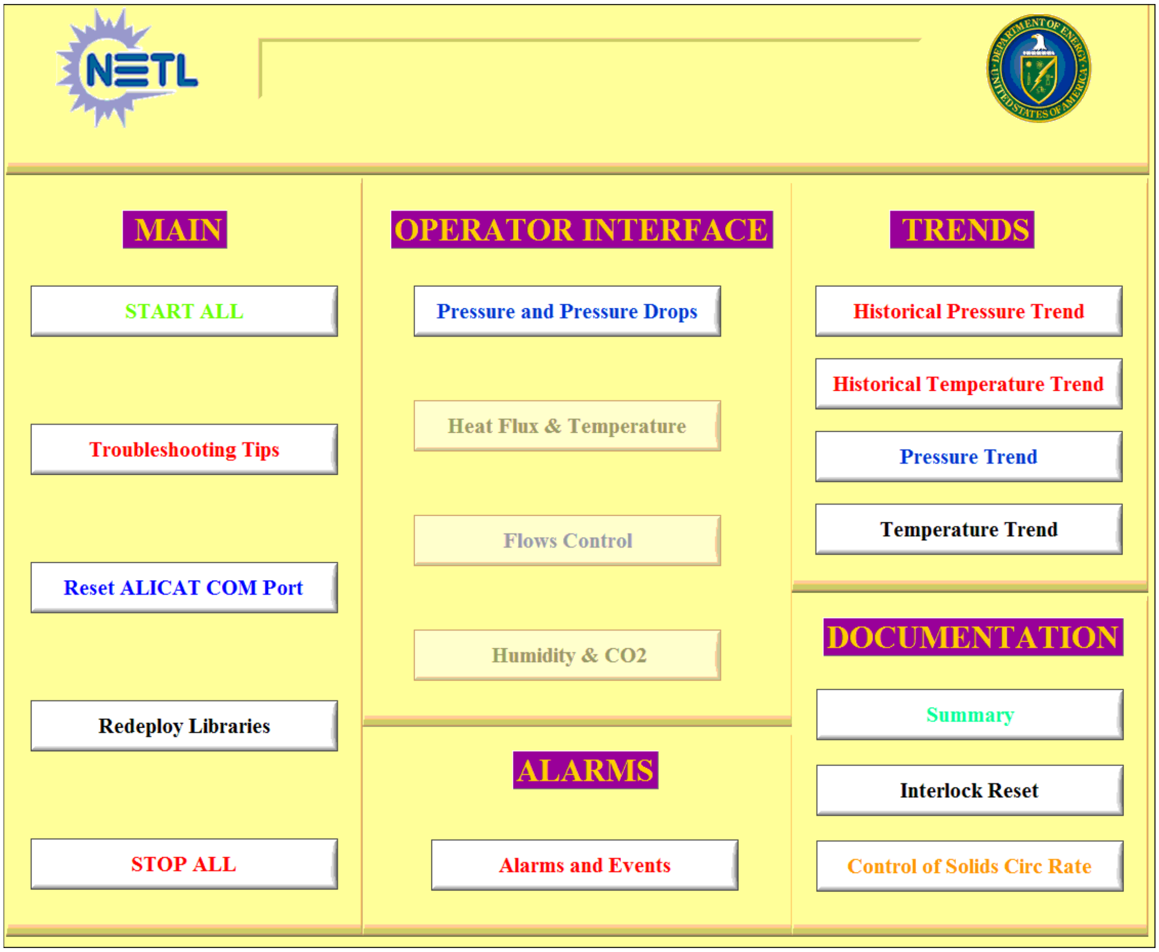


Figure 7. LabVIEW main control panel

Flow rate control panel

The flow rate control panel allowed the operator to set the proper flows on each of the Alicat mass flow controllers. The panel also displayed a return signal from each mass flow controller to confirm that the desired flow was achieved (Figure 8). The panel is separated by gas type: N_2, CO_2, air.

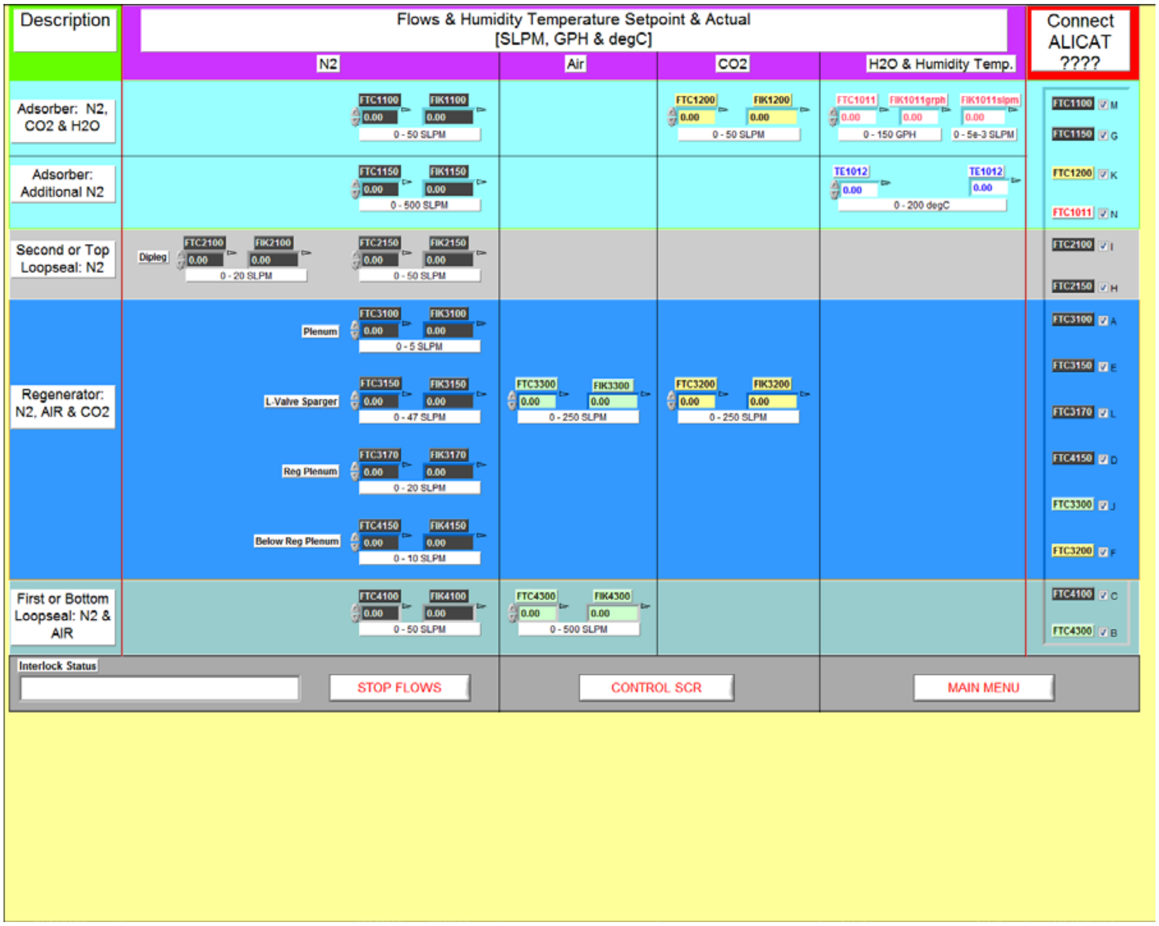


Figure 8 LabVIEW. flow rate control panel

Heater control panel

The heater control panel allowed the operator to turn on/off both the oil heater and oil circulating pump. The oil temperature could be controlled by response from one of three thermocouples TE3964 (oil temperature at coil inlet), TE3965 (sorbent temperature in the middle of the regenerator bed) or TE3962A (sorbent temperature at the top of the regenerator bed). The control current between 4 – 20 mA could also be set directly controlling the proportional output of the heater. This panel also displayed safety interlocks that guarded against overheating (Figure 9).

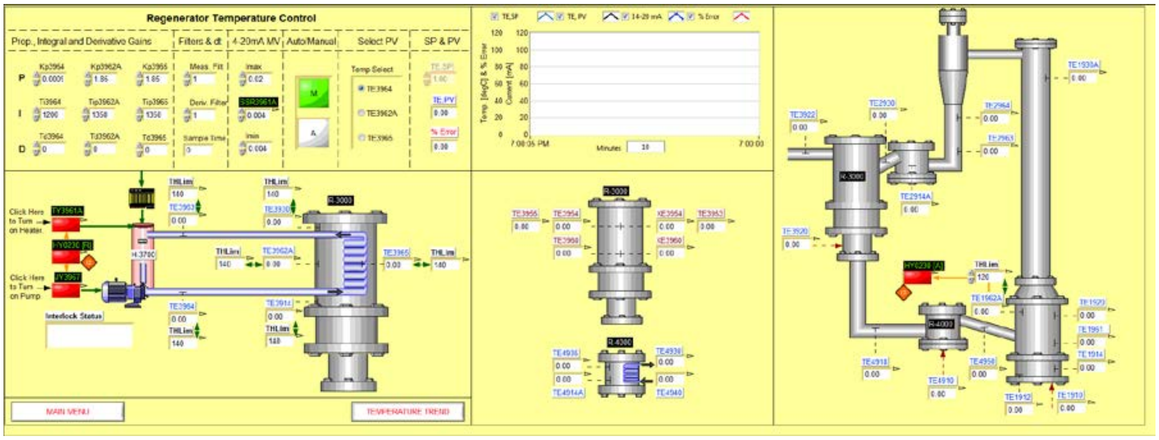


Figure 9 LabVIEW. heater control panel

Pressure panel

This panel displayed pressures throughout the system and safety interlocks corresponding to overpressure conditions (Figure 10).

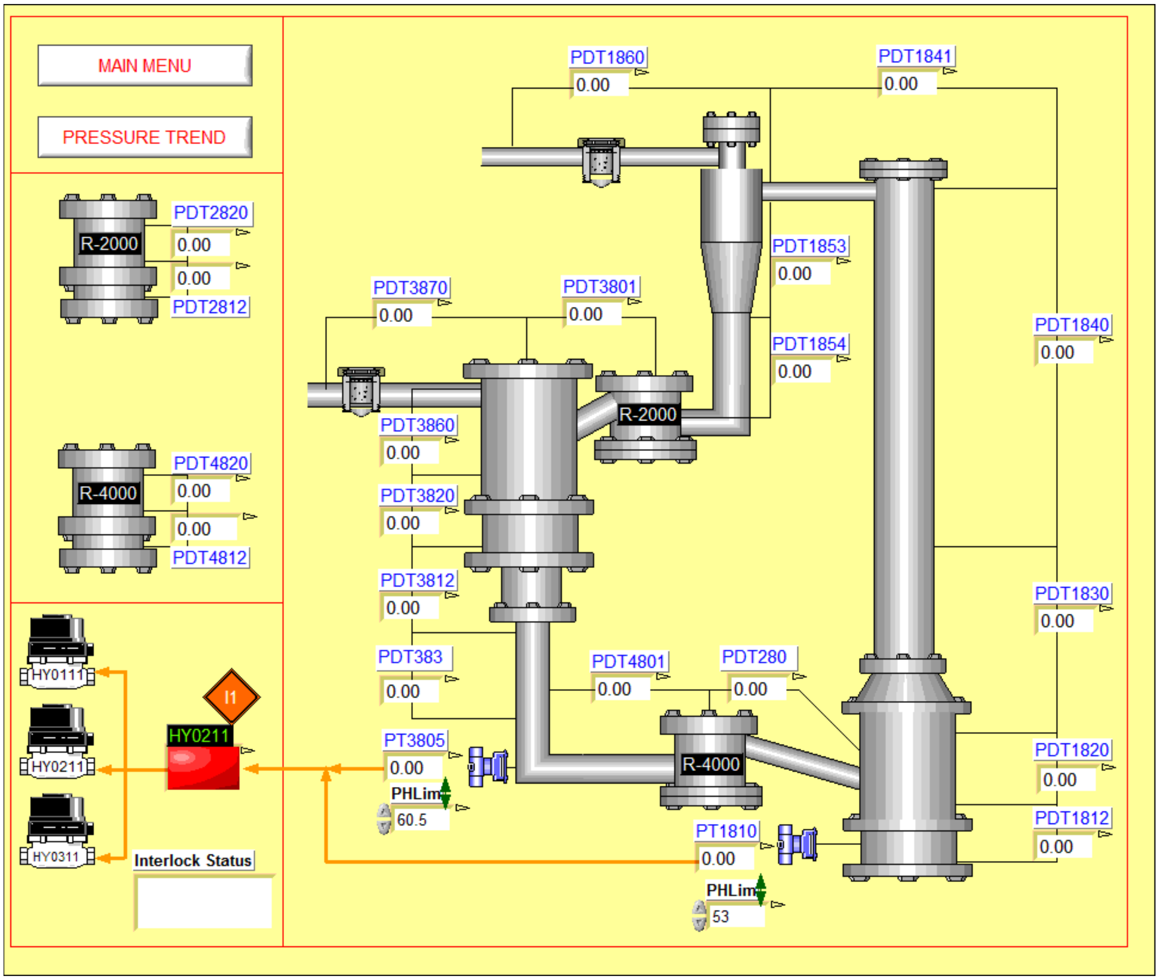


Figure 10 LabVIEW. pressure panel

Gas analyzer panel

This panel displayed outputs from the four gas analyzers. The left side of the panel represents the regenerator and the Quantex analyzer output for CO_2 (AIT3531), O_2 (AIT3532) also PP systems CO_2 (AIT3530), humidity (XE3019). Adsorber concentrations are on the right hand side Quantex analyzer output for CO_2 (AIT1531), O_2 (AIT1532) also PP systems CO_2 (AIT1530), humidity (XE1529).

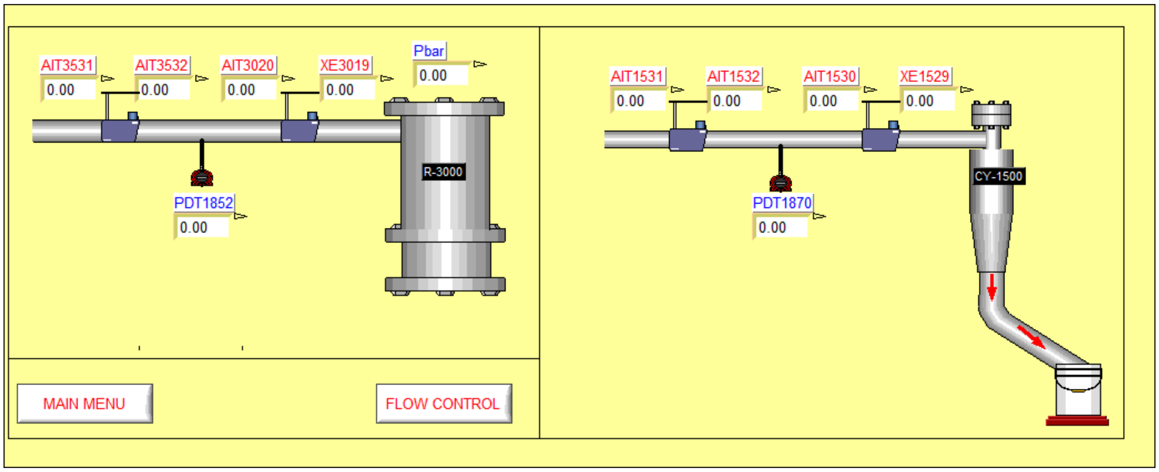
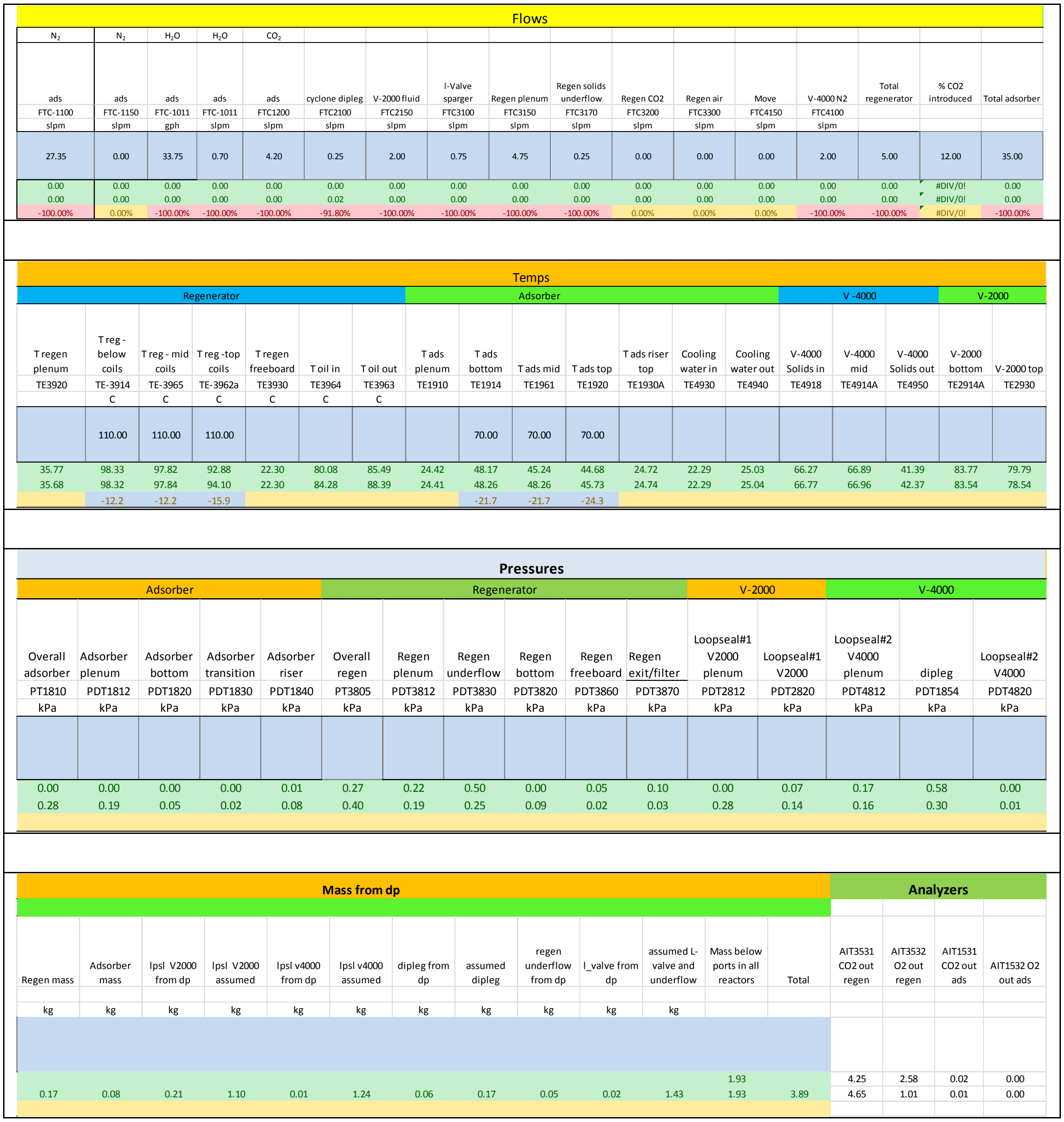


Figure 11. LabVIEW gas analyzer panel

Excel panel

A separate panel displays an Excel spreadsheet. In this panel the instrument outputs are displayed both instantaneous and one minute average (green fields). In the blue field, the target values are displayed. The bottom field displays the error between desired and actual values. Figure 12 illustrates the spreadsheet. In the actual spreadsheet the four panels below are lined up horizontally. In some cases a calculated value is displayed using a combination of instrument outputs.



Flows

N_2	N_2	H_2O	H_2O	CO_2												
ads	ads	ads	ads	ads	cyclone dipleg	V-2000 fluid	l-Valve sparger	Regen plenum	Regen solids underflow	Regen CO2	Regen air	Move	V-4000 N2	Total regenerator	% CO2 introduced	Total adsorber
FTC-1100	FTC-1150	FTC-1011	FTC-1011	FTC1200	FTC2100	FTC2150	FTC3100	FTC3150	FTC3170	FTC3200	FTC3300	FTC4150	FTC4100			
slpm	slpm	gph	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm			
27.35	0.00	33.75	0.70	4.20	0.25	2.00	0.75	4.75	0.25	0.00	0.00	0.00	2.00	5.00	12.00	35.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	#DIV/0!	0.00
0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	#DIV/0!	0.00
-100.00%	0.00%	-100.00%	-100.00%	-100.00%	-91.80%	-100.00%	-100.00%	-100.00%	-100.00%	0.00%	0.00%	0.00%	-100.00%	-100.00%	#DIV/0!	-100.00%

Temps

Regenerator							Adsorber							V -4000			V-2000	
T regen plenum	T reg - below coils	T reg - mid coils	T reg -top coils	T regen freeboard	T oil in	T oil out	T ads plenum	T ads bottom	T ads mid	T ads top	T ads riser top	Cooling water in	Cooling water out	V-4000 Solids in	V-4000 mid	V-4000 Solids out	V-2000 bottom	V-2000 top
TE3920	TE-3914	TE-3965	TE-3962a	TE3930	TE3964	TE3963	TE1910	TE1914	TE1961	TE1920	TE1930A	TE4930	TE4940	TE4918	TE4914A	TE4950	TE2914A	TE2930
	C	C	C	C	C	C												
	110.00	110.00	110.00					70.00	70.00	70.00								
35.77	98.33	97.82	92.88	22.30	80.08	85.49	24.42	48.17	45.24	44.68	24.72	22.29	25.03	66.27	66.89	41.39	83.77	79.79
35.68	98.32	97.84	94.10	22.30	84.28	88.39	24.41	48.26	48.26	45.73	24.74	22.29	25.04	66.77	66.96	42.37	83.54	78.54
	-12.2	-12.2	-15.9					-21.7	-21.7	-24.3								

Pressures

Adsorber					Regenerator						V-2000		V-4000		
Overall adsorber	Adsorber plenum	Adsorber bottom	Adsorber transition	Adsorber riser	Overall regen	Regen plenum	Regen underflow	Regen bottom	Regen freeboard	Regen exit/filter	Loopseal#1 V2000 plenum	Loopseal#1 V2000	Loopseal#2 V4000 plenum	dipleg	Loopseal#2 V4000
PT1810	PDT1812	PDT1820	PDT1830	PDT1840	PT3805	PDT3812	PDT3830	PDT3820	PDT3860	PDT3870	PDT2812	PDT2820	PDT4812	PDT1854	PDT4820
kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa
0.00	0.00	0.00	0.00	0.01	0.27	0.22	0.50	0.00	0.05	0.10	0.00	0.07	0.17	0.58	0.00
0.28	0.19	0.05	0.02	0.08	0.40	0.19	0.25	0.09	0.02	0.03	0.28	0.14	0.16	0.30	0.01

Mass from dp / **Analyzers**

Regen mass	Adsorber mass	lpsl V2000 from dp	lpsl V2000 assumed	lpsl v4000 from dp	lpsl v4000 assumed	dipleg from dp	assumed dipleg	regen underflow from dp	l_valve from dp	assumed L-valve and underflow	Mass below ports in all reactors	Total	AIT3531 CO2 out regen	AIT3532 O2 out regen	AIT1531 CO2 out ads	AIT1532 O2 out ads
kg	kg	kg	kg	kg	kg	kg	kg	kg	kg	kg						
											1.93		4.25	2.58	0.02	0.00
0.17	0.08	0.21	1.10	0.01	1.24	0.06	0.17	0.05	0.02	1.43	1.93	3.89	4.65	1.01	0.01	0.00

Figure 12. Excel spreadsheet

Heat transfer

Heat is either added to or removed from the bed through copper coils within the bed. Coils have been used in the regenerator, adsorber and both loopseals. Initially coils were used only in the regenerator (heat addition) and in the lower loopseal (heat subtraction). Later, additional heating coils were added to the upper loopseal. In the final arrangement (NCCC tests) the cooling coils were removed from the lower loopseal and placed in the adsorber.

The solution for cooling was more manageable than that of heating. A water chiller (Lytron Kodiac, RC045, 4500 watt) was employed for cooling where the water temperature could be adjusted from 3 – 25°C. This chiller was controlled independent of the rest of the system. Some water flow could be diverted through a bypass system, thus all flow did not necessarily pass through the internal coils. The large temperature differential between the cooling coils and sorbent bed (>60°C) allowed for significant heat transfer rates. In fact, in some cases the chiller could be turned off and the heat transfer between the stagnant water within the coils and the bed was sufficient to maintain desired bed temperature. However, for regeneration, the maximum temperature was determined by the desire to keep all temperatures below 130 C to prevent sorbent decomposition. Below is an explanation of the methodology used in regenerator heat transfer design.

Regenerator internal coils

The maximum temperature that the sorbent could be subjected to was approximately 130 °C and maximum regeneration temperature was 120 °C. Since the temperature differential is small, the convective heat transfer equation ($Q = hA\Delta T$) indicates that a large surface area was required.

There were two versions of the regenerator; the first smaller in height than the second. The initial version was 40” (1.02 m) tall; the second was 52” (1.32) with the addition of a 12” spool piece on the bottom. The first version employed nested coils with a total height of 12” (0.305 m), the second version used a single set of coils with a total height of 24” (0.61 m).

In both versions, the external coil is a 0.5” (0.0127 m) diameter copper tube with wound into 4 inch (0.102 m) diameter coils. These coils are spaced axially one inch (0.0254 m) apart, center to center (Figure 13). In the first version the total length is 12.56 ft (3.83 m), the second version was twice that length

A second set of smaller coils 0.375” (0.0096 m) diameter copper tube was wound into 2 inch (0.102 m) diameter coils in series (Figure 14). This set of coils is attached to the outer coils so that the same fluid flows through both sets (Figure 15) and was the version initially used. Figure 16 shows the single coil used in the extended regenerator

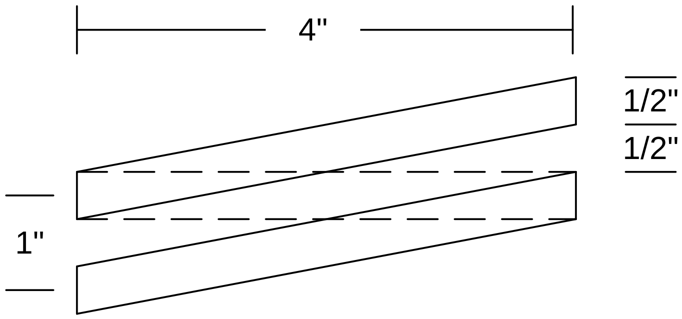


Figure 13. Outer coil spacing

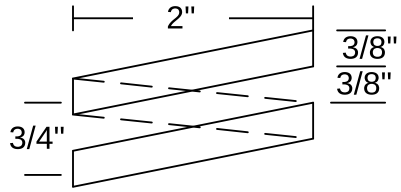


Figure 14. Inner coil spacing

Figure 15. Dual regenerator coils

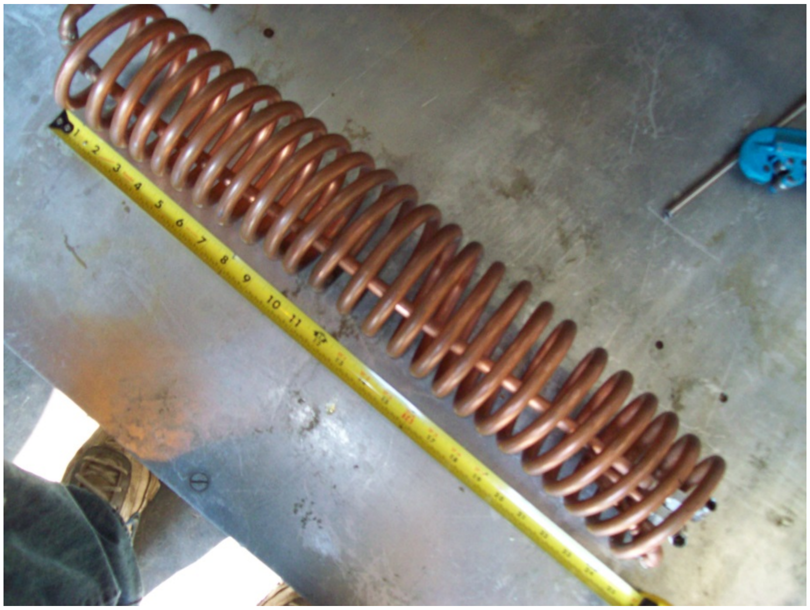


Figure 16. Regenerator coils - extended version

Table 5. Regenerator copper coil parameters

OD	0.5	in	1.27E-02	m
Wall	0.045	in	1.14E-03	m
loop dia	4	in	1.02E-01	m
coil spacing	1	in	2.54E-02	m
total height	12	in	3.05E-01	m
#coils =	12		12	
ID	0.41	in	1.04E-02	m
internal flow area	1.32E-01	in^2	8.52E-05	m^2
total length	150.8	in	3.83	m
total internal volume	19.91	in^3	3.26E-04	m^3
external surface area	236.9	in^2	0.153	m^2
external volume	29.61	in^3	4.85E-04	m^3
Face area	1.57	in^2	0.001	m^2
Inner coil				
OD	0.375	in	9.53E-03	m
Wall	0.035	in	8.89E-04	m
loop dia	2	in	5.08E-02	m
coil spacing	0.75	in	1.91E-02	m
total height	12	in	3.05E-01	m
#coils =	16.0		16.0	
ID	0.305	in	7.75E-03	m
flow area	7.31E-02	in^2	4.71E-05	m^2
total length	100.5	in	2.55	m
total internal volume	7.34	in^3	1.20E-04	m^3
external surface area	118.4	in^2	0.000	m^2
external volume	11.10	in^3	1.82E-04	m^3
Face area	1.18	in^2	0.001	m^2
total internal volume of both coils =			4.47E-04	m^3
total internal volume of both coils =			4.47E-01	liter
Total external surface area=			0.153	m^2
Total external volume	40.71	in^3	6.67E-04	m^3
Total face area =	2.75	in^2		

Energy required for desorption

Previously, an example was given where 32D sorbent circulating at a rate of 5.15 kg/hr would adsorb 9.28 gmol/hr of CO_2. This was for a 12% concentration of CO_2 flowing at 35 slpm with capture 90% efficiency.

The regenerator must liberate this CO_2. To do so, the energy to compensate for the heat of reaction must be supplied as well as the sensible energy to heat the sorbent substrate and amine to the regeneration temperature. In this example, the latter version of the regenerator will be considered which contains the single coil set.

The following is an example of the heat required for a steady state operation and does not include the energy required to initially heat the walls of the regenerator. There are four remaining streams that must be supplied energy: heat of reaction, sorbent temperature increase, fluidizing gas temperature increase and environmental losses.

Some sources [1] have estimated a heat of reaction (ΔH) of approximately 580 BTU/lb CO_2 (59.2 kJ per gmol CO_2 or (1.35 x10^6 J/kg CO_2 adsorbed). Therefore, 126 Watts must be added to the sorbent to desorb the CO_2

$$Q_{reaction} = \dot{m}_{CO2} * \Delta H_r = 1.13x10^{-4}\, kg/s * 1.35x10^6\, J/kgCO_2 = 152.6\_\,J/s$$

Additional energy must also be added to increase the sorbent to the desorption temperature. The sorbent specific heat (Cp) is estimated to be 1800 J/kg-K.

Assume the sorbent enters at 80 C and must be heated to 110°C.

$$Q_{sorbent} = \dot{m}_{sorbent} * C_{substrate} * \Delta T = 1.43x10^{-3}\, kg/s * 1800 J/kg - K * (110 - 80) = 77.3\_\,J/s$$

The regenerator fluidizing gas must also be heated. Typically the regenerator was fluidized with 10 slpm (1.91x10^{-4} kg/s) N_2 entering at 20°C. This gas must be heated to the regeneration temperature of 110 C. The specific heat of N_2 is 1040 J/kg-K.

$$Q_{fluidizinggas} = \dot{m}_{fluidizinggas} * C_{N2} * \Delta T = 1.91x10^{-4}\, kg/s * 1040 J/kg - K * (110 - 20) = 17.9\_\,J/s$$

There are additional losses such as convective heat transfer between the regenerator walls and the environment. The convective heat transfer was calculated to be on the order of 100 Watts. Heat loss due to radiative heat transfer was calculated and found to be minimal (approx. 1 Watt)

$Q_{additional} \approx 100$ W

$Q_{req} = Q_{reaction} + Q_{gas} + Q_{sorbent} + Q_{additional}$
$= 152.6 + 17.9 + 77.3 + 50.0 = 347.7$ W

Heat transfer by internal coils

There are various correlations and approaches in the literature for determining the heat transfer coefficient h_c, none that can be found specifically for a coiled tube. A correlation by Vreedenberg for horizontal tubes in a bubbling bed will be used for the Nusselt number [4][2].

$$Nu = \frac{h_c D_t}{k_g} = 420\left(\frac{\rho_p}{\rho_g}\Pr_g \frac{\mu_g^2}{g\rho_p^2 d_p^3}\right)^{0.3} \mathrm{Re}_D^{0.3} \text{ for } \frac{\rho_p}{\rho_g}\mathrm{Re}_p \geq 2550 \qquad \text{(A)}$$

$$Nu = \frac{h_c D_t}{k_g} = 0.66\Pr_g^{0.3}\left(\frac{\rho_p(1-\varepsilon)}{\rho_g \varepsilon}\right)^{0.44} \mathrm{Re}_D^{0.44} \text{ for } \frac{\rho_p}{\rho_g}\mathrm{Re}_p \leq 2050 \qquad \text{(B)}$$

Where

$$\mathrm{Re}_D = \frac{D_t \rho_g U_g}{\mu_g}, \quad \mathrm{Re}_p = \frac{d_p \rho_g U_g}{\mu_g}$$

The extended regenerator is assumed to be fluidized with 10 slpm N_2 therefore the following conditions apply (N_2 @ 20°C):

ρ_{N2}= 1.16 kg/m^3
μ_{N2} = 1.76x10^{-5} kg/m-s
k_{N2} = 2.57x10^{-2} W/m-K
Pr = 0.714
Cp_{N2} = 1040 J/kg-K

Sorbent entrance temperature 80.0°C
U_g = 0.011 m/s (Fluidization at 10 slpm)
Void fraction = 0.516
Outer coil tube diameter (D_t) = 1.27x10^{-2} m
Coil height = 0.61 m
Outer coil tube length = 7.66 m
Outer coil tube surface area = 0.306 m^2

Particle Reynolds' #:

$$\mathrm{Re}_p = \frac{d_p \rho_g U_g}{\mu_g} = \frac{9x10^{-5} * 1.16 * (.011)}{1.76x10^{-5}} = 0.065$$

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[2] Handbook of Fluidization and Fluid Particle Systems (Yang) p. 263

$$\frac{\rho_p}{\rho_g}\mathrm{Re}_p = \frac{480}{1.16}*0.065 = 27 \quad \text{Laminar condition}$$

Since the term above is less than 2050 then the second (B) Vreedenberg correlation is used.

Convective heat transfer coefficient for outer coil:

Coil Reynolds number

$$\mathrm{Re}_D = \frac{D_t \rho_g U_g}{\mu_g} = \frac{1.27x10^{-2} *1.16*1.11x10^{-2}}{1.76x10^{-5}} = 9.2$$

Void fraction from Kings formula

$$\varepsilon = \frac{U_g + 1}{U_g + 2} = \frac{0.011+1}{0.011+2} \approx 0.50$$

Convective heat transfer coefficient from Vreedenburg correlation

$$Nu = \frac{h_c D_t}{k_g} = 0.66\,\mathrm{Pr}_g^{0.3}\left(\frac{\rho_p(1-\varepsilon)}{\rho_g \varepsilon}\right)^{0.44}\mathrm{Re}_D^{0.44} = 0.66*(0.714)^{0.3}*\left(\frac{480*(1-0.5)}{1.16*0.5}\right)^{0.44}*(9.2)^{0.44} = 22.34$$

$$h_c = Nu*\frac{k_g}{D_t} = 22.34*\frac{2.57x10^{-2}}{1.27x10^{-2}} = 45.2 \ \text{W/m}^2\text{-K}$$

The surface area of the 24” long ½” OD single coil is 0.3 m^2. Thus for each degree of temperature differential between the coil surface and particle bed, 13.8 W of energy can be transferred.

$$h_c * A_{coil} = 45.2*0.3 = 13.8 \quad \text{W/K}$$

Previously, in this example, the energy required to heat the sorbent and regenerate CO_2 was determined to be 348 W. Calculate the required ΔT to add energy assuming a constant temperature differential between tube and bed

$$\Delta T = \frac{\dot{Q}}{hA} = \frac{348}{13.8} = 25.2 \ \text{C}$$

This value can be used as the LMTD (log mean temperature difference) used in analysis of heat exchangers. The bed moving past the coils can be treated as a parallel flow heat exchanger

For a parallel flow heat exchanger

$$LMTD = \frac{\Delta T_{x=0} - \Delta T_{x=L}}{\ln\left(\Delta T_{x=0} / \Delta T_{x=L}\right)} = \frac{(T_{h,i} - T_{c,i}) - (T_{h,o} - T_{c,o})}{\ln\left[(T_{h,i} - T_{c,i})/(T_{h,o} - T_{c,o})\right]}$$

Where

$T_{h,i}$ - Temperature of fluid at the inlet.
$T_{c,i}$ - Temperature of sorbent at the inlet.
$T_{h,o}$ - Temperature of fluid at the outlet.
$T_{c,o}$ - Temperature of sorbent at the outlet.

Determine the required tube surface temperature:

Assume the tube surface is a constant temperature throughout the bed $T_s = T_{hi} = T_{ho}$. The temperature should be nearly constant during steady state operation since the coils are comprised of copper and the oil flowing through should not significantly vary in temperature if the flow rate is adequate. During operation the oil was seen to drop in temperature about 4°C. Assume that the tube surface temperature is an average of the inlet and outlet oil temperatures

Manipulate the LMTD equation to yield a tube wall temperature.

$$LMTD = \frac{(T_{h,i} - T_{c,i}) - (T_{h,o} - T_{c,o})}{\ln\left[(T_{h,i} - T_{c,i})/(T_{h,o} - T_{c,o})\right]} = \frac{(T_{c,o} - T_{c,i})}{\ln\left[(T_s - T_{c,i})/(T_s - T_{c,o})\right]}$$

$$\ln\left[(T_s - T_{c,i})/(T_s - T_{c,o})\right] = \frac{(T_{c,o} - T_{c,i})}{LMTD}$$

$$\frac{(T_s - T_{c,i})}{(T_s - T_{c,o})} = \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right]$$

$$(T_s - T_{c,i}) = (T_s - T_{c,o}) * \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right] = T_s * \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right] - T_{c,o} * \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right]$$

$$T_s * \left(1 - \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right]\right) = T_{c,i} - T_{c,o} * \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right]$$

$$T_s = \frac{T_{c,i} - T_{c,o} * \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right]}{1 - \exp\left[\frac{(T_{c,o} - T_{c,i})}{LMTD}\right]} = \frac{80.0 - 110 * \exp\left[\frac{(110 - 80.0)}{25.2}\right]}{1 - \exp\left[\frac{110 - 80.0}{25.2}\right]} = 123.1\,^{\circ}\mathrm{C}$$

Thus to increase the sorbent from 80°C incoming to 110°C outgoing and release the captured CO_2 the tube wall temperature must be greater than 123°C.

Heated oil circulation system

Mineral oil was circulated using a centrifugal pump and passed through a 2.5 kW oil heater with adjustable temperature control. The flow rate of the oil could not be adjusted but the heating rate was. The coil inlet oil temperature was the variable used to adjust heater power. The heated oil was then passed through the centrifugal pump and through the coils and was eventually returned to the heater (Figure 17). The oil was first heated then sent to the pump since it was required that the pump was located at the lowest point on the circulation system

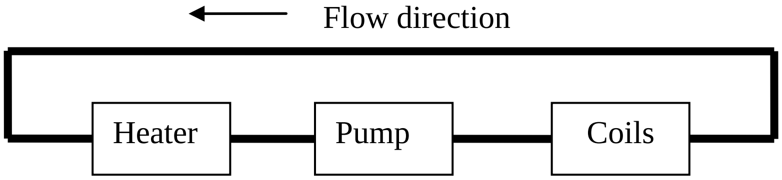


Figure 17. Heated oil circulation system

Oil flow rate requirement

The working fluid for the regenerator was mineral oil with a specific heat of approximately 1670 J/kg-K and a density of about 830 kg/m^3. According to the prior example the oil must deliver about 309 W of heat to the bed while dropping in temperature less than 4°C. The required oil circulation rate is determined by:

$$\dot{m} = \frac{\dot{Q}}{Cp * \Delta T} = \frac{348}{1670 * 4} = 0.052\ kg/s$$

Therefore the pump must circulate about 3.8 lpm which is reasonable.

The original concept called for the use of a liquid flow meter to be used to determine oil flow rate. However, this concept was abandoned because the meter required a substantial length of horizontally hung tubing that allowed air to be trapped which hampered liquid flow and led to over pressurization.

The oil flow rate can be determined from the response time between the oil inflow and outflow thermocouples. In Figure 18 the valve diverting oil flow to the cooling bath was initiated at 12 seconds, the response of the oil outflow thermocouple (TE3963) was seen 12 seconds later. The coil was comprised of 1.04 cm ID tubing, 7.7 m in length, with an internal volume of 0.65 liter. Thus, the oil circulation rate was about 3.3 lpm, slightly less than optimum.

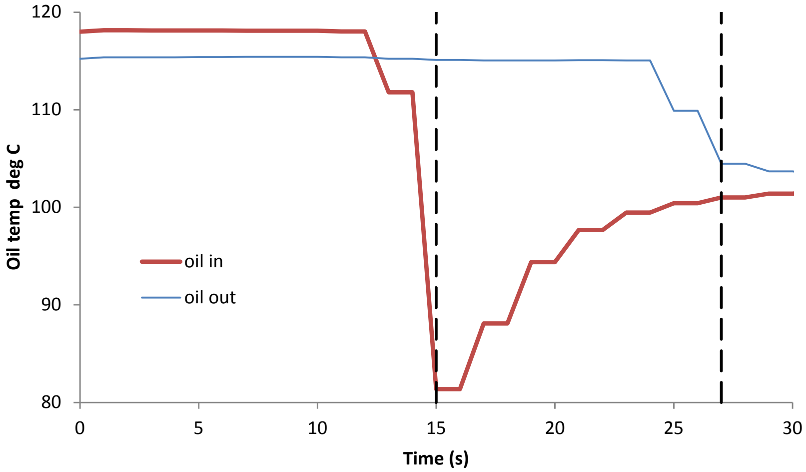


Figure 18. Time lag between response of oil flow inlet and outlet thermocouples

Batch test heating/cooling method

Batch tests were also performed in the regenerator. In this case both adsorption and regeneration were conducted in the regenerator. Therefore, both heat addition and heat subtraction was performed using the same coil system. For heat addition the oil was pumped through the coils in the bed and heated with the heater. In the heat subtraction case the oil was diverted through a small set of coils immersed in a water bath with the heater turned off which cooled the oil (Figure 20). This set of coils was intertwined with a set of coils where cooling water flowed maintaining the water bath at a cool temperature.

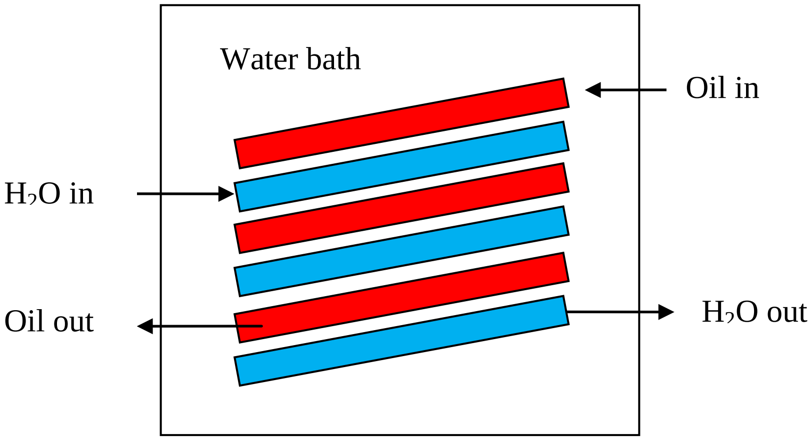


Figure 19. Cooling coil arrangement used for batch tests

Unit modifications

The C2U was originally comprised of polycarbonate which would have allowed a clear view of the solids as they circulate the system (Figure 20). However, a reaction with the amines within the sorbent degraded the polycarbonate. Figure 21 shows a sample of polycarbonate exposed to AX sorbent for a few hours. The actual reactors showed significantly more damage with cracks extending through the wall.

Throughout the course of investigation of sorbent performance, modifications were made to the physical dimensions of the C2U and some mass flow controllers were exchanged in position. Some of the physical changes include the lowering of the lower loopseal relative to the base of the unit about one foot. This was done to increase the length of the solids underflow on the regenerator side which would increase the pressure at the L-valve and aid in circulation. Also, the diameter of the riser on the adsorber side was decreased from 2” to 1” to increase circulation rate. The regenerator was extended by placing a one foot high spool piece at the bottom to increase the residence time of particles exposed to heating and thus increase desorption rate.

Figure 20. Initial version of C2U unit constructed with polycarbonate

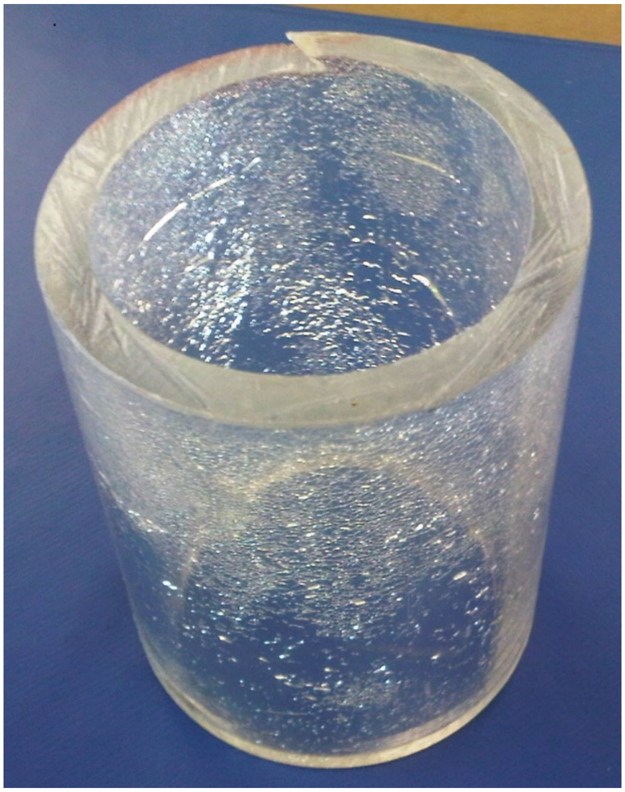


Figure 21. Sample of polycarbonate exposed to AX sorbent

Nomenclature

A – Area
A_{face} – Particle face area
Ar – Archimedes number
C_1 – Constant (27.2)
C_2 – Constant (0.0408)
C_D – Drag coefficient
C_p – Specific heat
D – Drag force
d_p – Particle diameter
g – Gravitational acceleration (9.8 m/s)
h_c – Convective heat transfer coefficient
k– Conductive heat transfer coefficient
MW – Molecular weight
Pr – Prandtl number
p – Gas pressure
Q – Heat energy
Re_D – Reynolds number for tube heat transfer
Re_{mf} – Reynolds number at minimum fluidization
R^* – Universal ideal gas constant (8314.3 J/kgmol-K)
T – Temperature
$T_{c,i}$ – Temperature of sorbent at the inlet(Heat exchanger LMTD).
$T_{c,o}$ – Temperature of sorbent at the outlet (Heat exchanger LMTD).
$T_{h,i}$ – Temperature of fluid at the inlet (Heat exchanger LMTD).
T_s – Temperature of tube surface (Heat exchanger LMTD).

U_{mf} – Superficial gas velocity at minimum fluidization
V_{Term} – Particle terminal velocity
W – Particle weight
z – $\log_{10}Re$

ΔH – Heat of reaction
ΔT – Temperature differential
κ - Permeability of porous media [m^2]
μ – Gas viscosity
ρ_g – Gas density
ρ_p – Particle density

Part 2

Experimental Results

Introduction – Batch tests

Batch tests were conducted in a single reactor where both adsorption and regeneration occurred but were generally performed in the regenerator reactor. Sorbent would normally be loaded into the reactor up to or below the level of the heat transfer coils, although some tests involved shallower beds.

Two types of batch tests were conducted: the determination of sorbent capacity regarding CO_2 capture and regeneration and heavy metal accumulation on sorbents. A single heavy metal accumulation test was performed at the National Carbon Capture Center (NCCC) while a variety CO_2 capture tests were conducted at NETL.

The heavy metal accumulation test involved a continuous flow of flue gas obtained from the slipstream of an operational power plant. Neither adsorption nor regeneration of CO_2 was relevant during this test; therefore, heat transfer was not a factor in this operation. A metered flow of flue gas was passed through the bed continuously. The planned period of operation was 1000 hours.

The performance of two types of sorbent, comprised of polyethylenimine on a synthetic amorphous silica substrate, was determined by varying a multitude of independent variables that could be controlled within the C2U during tests conducted at NETL using simulated flue gas. Batch tests at NETL were conducted in four phases: transition to adsorption, adsorption, transition to regeneration and regeneration. The bed was either heated or cooled using the method described in the "batch test heat transfer" section above. The usual time between the start of a transition to adsorption condition to the end of regeneration was nominally two hours; however, this was strongly dependent on bed mass and CO_2 flow rate. During transition to adsorption, the bed was brought to the desired temperature while being fluidized with N_2 flow only (Figure 22). If the bed was initially cool, the bed was heated to the desired adsorption temperature; in subsequent multi-cycle tests, the bed is cooled from the previous regeneration temperature. During the adsorption phase, CO_2 was added to the pre-adsorption phase N_2 flow. The oil flow was diverted through coils immersed in the water bath (Figure 19). The chiller was also operating allowing cooling water to flow through coils also immersed in the water bath. This extracted the heat of reaction from the CO_2 adsorption process and maintained the bed at a constant temperature. The exit gas composition was monitored; when it was observed that most inputted CO_2 was exiting the system (Figure 23) it was concluded that the bed was saturated and adsorption had ceased. At this time, the adsorption phase was discontinued and transition to regeneration phase was initiated. In some cases, the CO_2 flow was discontinued but in other cases the CO_2 flow was continued. At the initial switch between adsorption and transition to regeneration phases, if CO_2 flow is switched off, the exit was still detecting CO_2 that was previously inputted but the actual input is zero. This produced an erroneously large regeneration rate but stabilized within 30 to 60 seconds (Figure 24). The transition reflects the sweeping out of the internal dead volume of the system when a step change in feed gas composition is enacted. A correction can be made by extrapolating the response curve back to the initial time.

During the transition to adsorption phase, the bed was heated to the desired regeneration temperature. When the bed reached the regeneration temperature, the regeneration phase began, if CO_2 flow was being used during the transition phase it was switched off. The regeneration phase was conducted with the bed maintained at a constant temperature without CO_2 flow (Figure 25).

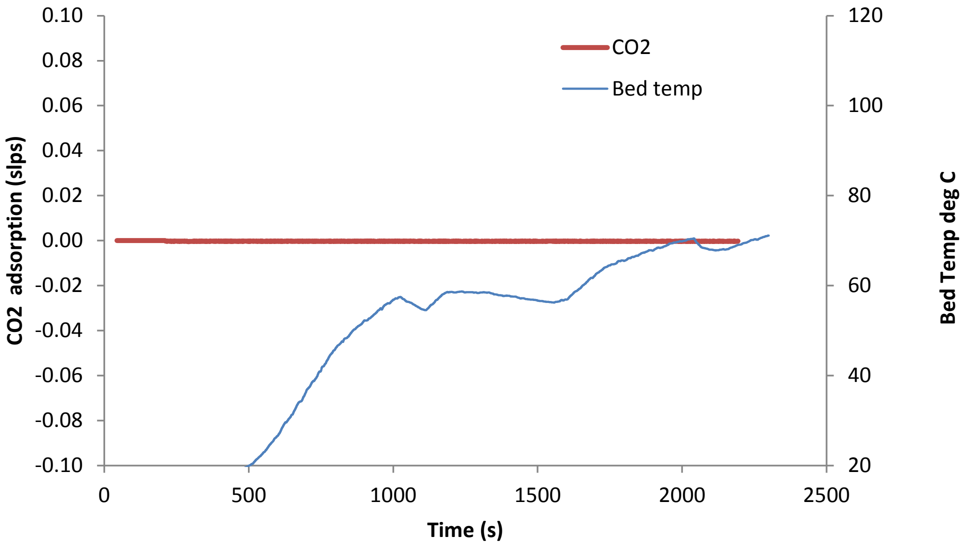


Figure 22. Typical transition to adsorption phase of batch test. No CO_2 flow, bed heating to adsorption temperature

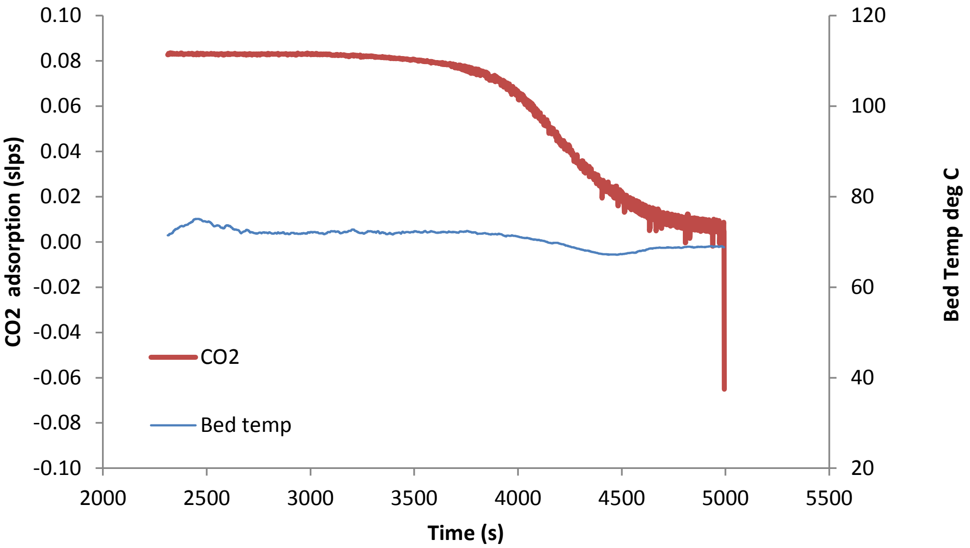


Figure 23. Typical adsorption phase of batch test. With CO_2 flow, bed maintained at adsorption temperature

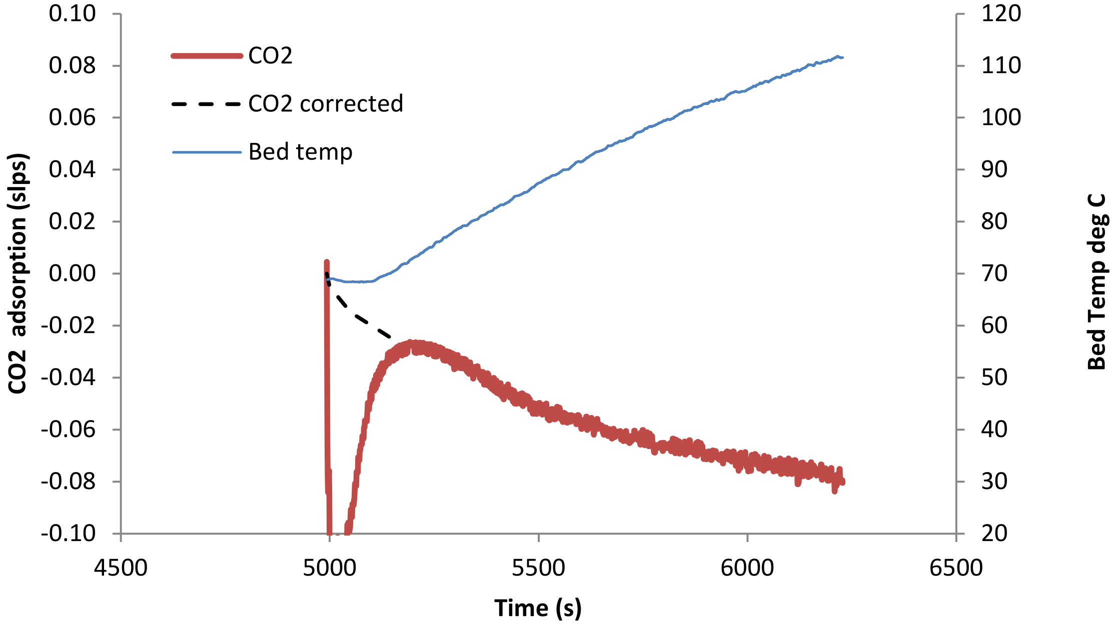


Figure 24. Typical transition to regeneration phase of batch test. No CO_2 flow, bed heating to regeneration temperature

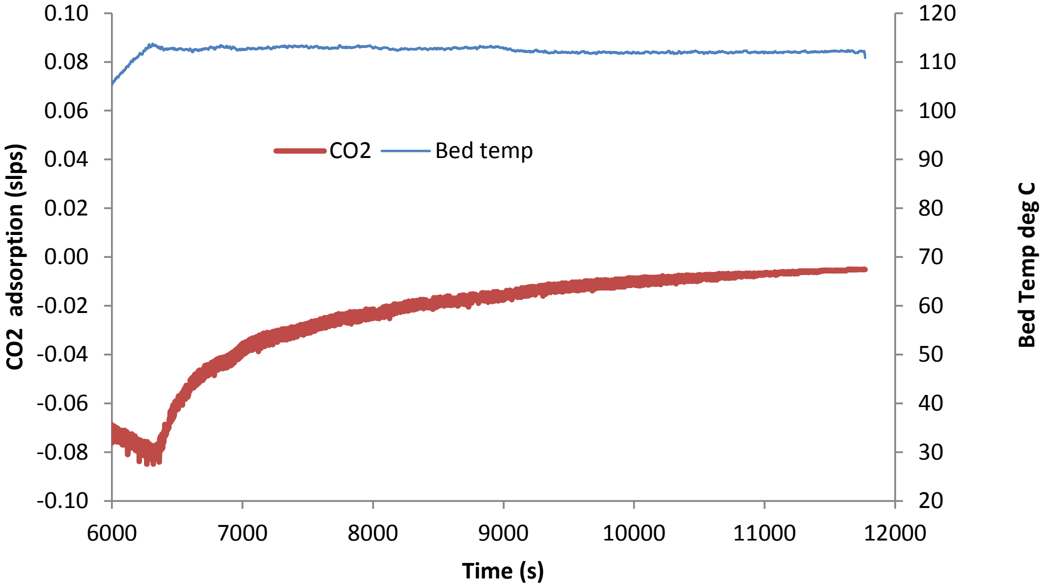


Figure 25. Typical regeneration phase of batch test. No CO_2 flow and no prior transitional phase CO_2 flow. Bed maintained at regeneration temperature

Figure 26 shows a typical temperature profile and CO_2 flow during the four phase sequence, plus a previous regeneration phase with no CO_2 flow during regeneration transition. Initially, the sorbent is being regenerated with no CO_2 being inputted and the bed temperature being maintained at 110°C. When the amount of CO_2 regenerated approached zero, the transition to adsorption phase began. Oil heating ceased and the oil flow was diverted to the cooling bath. When the bed was cooled to the desired adsorption temperature (90°C in this case) CO_2 flow was initiated (red line). The sorbent initially adsorbed all CO_2 inputted (negative value of green line) but as the inputted CO_2 continued, less CO_2 was adsorbed until adsorption ceased. CO_2 flow was discontinued and the bed was heated to the desired regeneration temperature (transition to regeneration). Once the bed reached the regeneration temperature, that temperature was maintained for the duration of the regeneration phase. Some CO_2 was regenerated during the transition phase while the remainder was released from the sorbent during the regeneration phase.

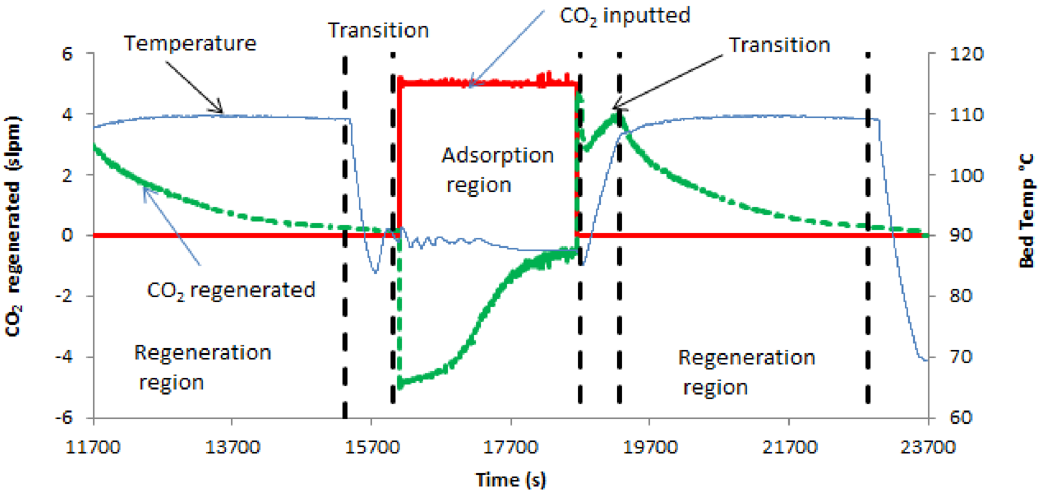


Figure 26. Typical temperature and CO_2 regenerated profile during batch test sequence without CO_2 flow during transition to regeneration phase

Figure 27 shows the response when CO_2 continues to flow during the transition to regeneration temperature. When the CO_2 flow was discontinued prior to heating for regeneration (Figure 24) there is an immediate desorption response to increasing bed temperature. The same appears to be true even with continued CO_2 flow as Figure 27 indicates. However, the rate of CO_2 desorption in Figure 27 is likely inhibited by the higher partial pressure of CO_2 due to continued CO_2 feed gas. Figure 28 indicates the response when CO_2 is employed during transition and then shut off when the bed reaches regeneration temperature. The transient response signal is again due to the sweeping out of the internal dead volume with a step change in feed gas composition.

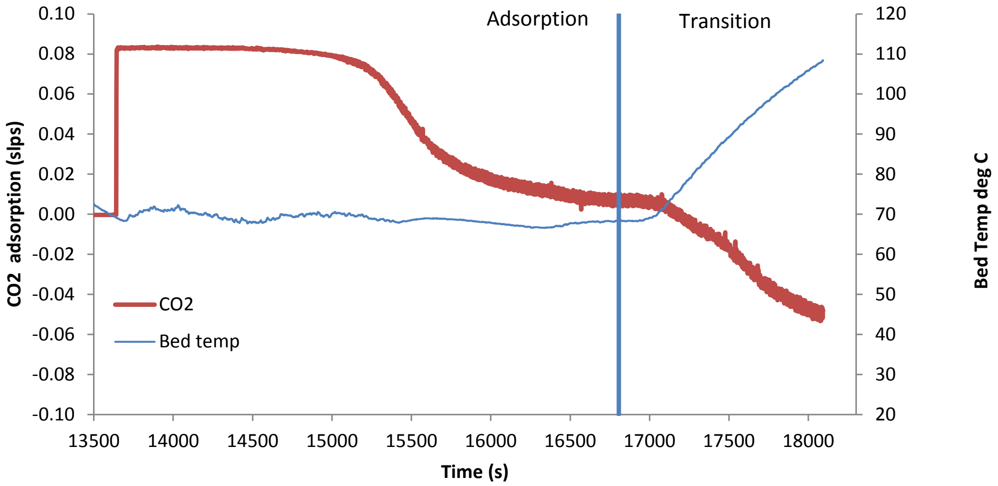


Figure 27. Typical adsorption and transition to regeneration phase of batch test with CO_2 flow during transition.

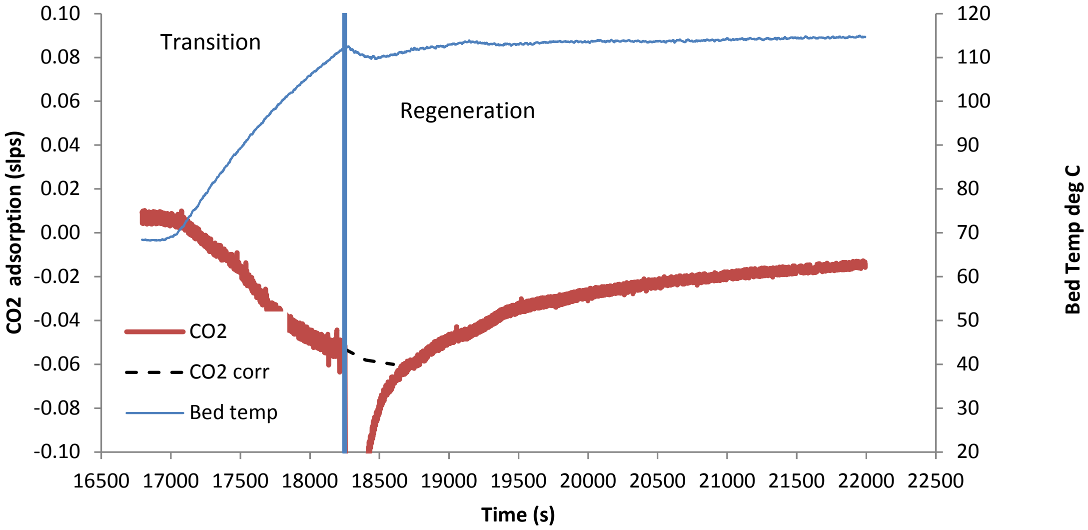


Figure 28. Typical regeneration phase of batch test (with prior transitional phase CO_2 flow)

National Carbon Capture Center (NCCC) batch tests

The accumulation of heavy metal compounds from flue gas by 32D sorbent was investigated from tests conducted at NCCC in Wilsonville Alabama. A slipstream facility (PC4) supplied flue gas for the heavy metal accumulation tests. The slipstream facility is installed at the Alabama Power Gaston power plant, unit 5, an 880 MW supercritical pulverized coal fired unit. The flue gas slip stream was originally comprised of 76% N_2, 12% CO_2, 6% O_2 and 6% H_2O. However, some of the H_2O was removed from the flue gas upstream of the C2U.

The slipstream did not have sufficient pressure to operate within the test unit, thus the pressure was boosted using vacuum pumps. Two vacuum pumps were used in parallel to deliver a flow rate of approximately 30 slpm of flue gas through the system. Using one pump would reduce flows to approximately 15 slpm. Initially, sorbent circulation tests were performed, after their conclusion; the C2U was reconfigured to perform a continuous batch test. During this batch test all heating and cooling was discontinued. New sorbent (2.4 kg) was added to the regenerator. The adsorber and both loopseals were removed from the system. The goal of this test was to supply flue gas to a single bed of sorbent for an extended period of time (1000 hours) and subsequently analyze the sorbent composition. Flue gas flow in this case was reduced to 15 slpm since it was desired to maximize the contact time between the flue gas and the sorbent; transport was not an issue. If the full 30 slpm were used, a turbulent flow would be produced allowing the flue gas to bypass the bed and increasing the chance of elutriation through the one inch gas exit port at the regenerator top. The only instrumentation in use was a vacuum pump, rotameter and magnehelic pressure gauge across the bed.

The flue gas initially supplied to the unit for the batch tests was diluted with air to simulate natural gas combustion products to accommodate other NCCC users. Although the sorbent was exposed to the diluted flue gas for 346 hours, the equivalent amount of flue gas exposure was 115 hours, due to dilution. After transitioning to regular coal-fired flue gas composition, an additional 282 hours were completed before a planned plant outage. The total equivalent flue gas exposure was 397 hours. The end result was that 2.4 kg of sorbent was exposed to the equivalent 357,000 standard liters (12,600 scf) of coal-fired flue gas.

Samples of the sorbent from these tests (after the diluted flue gas and after full strength flue gas), unused samples taken before and after all NCCC testing and samples taken after circulation tests (described below) were sent to Consol Energy for trace element analysis. Table 6 shows a comparison of the amount of arsenic, chromium, lead, mercury and selenium for these samples and compares the result with the amount required to be considered a hazardous waste by the EPA. In all cases, the trace element concentrations were significantly lower than the hazardous waste standards. To be considered a toxic hazardous waste, the EPA specifies a Toxicity Characteristic Leaching Procedure[5] (TCLP, Method 1311), whereby a solid sample is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. In lieu of the TCLP, a Total Consitituent Analysis (TCA) may be performed where the total constituent analysis may be divided by 20 to convert the total results into the maximum leachable concentration[6]. Conversely, the TCA limit may be considered to be 20 times the TCLP limit. This higher TCA limit is what is shown in Table 6.

To gauge whether this amount of flue gas exposure was sufficient for measurable deposition of selenium onto the sorbent bed, an estimate calculation was performed. The amount of coal burned to generate the volume of flue gas was calculated to be approximately 60.5 lbs, assuming 20% excess air using a PC-fired Illinois bituminous coal. Typical selenium content in bituminous coal was assumed to be 2 microgram Se/g coal (i.e., 2 ppm weight fraction). If all of the selenium (0.0549 g) was assumed to reach the skid and be deposited onto the sorbent bed (2.4 kg), the resulting weight fraction of selenium on the bed would be 23 ppm. This value is well in excess of the detection limit (<1 ppm) given in Table 6, and hence one would expect to be able to measure this quantity of selenium. However, to better gauge selenium accumulation on the sorbent, chemical analysis of the inlet flue gas slip stream to the skid should be conducted, due to the probable partitioning of selenium dropping out of the flue gas (i.e., fly ash collection device, FGD scrubber, etc.) and thus not reaching the skid.

Table 6. Trace element analysis of sorbent samples.

	Total Constituent Analysis Limit (ppm)	**Unused (ppm)**	**Post Circulation Tests (ppm)**	**Post Diluted Flue Gas (ppm)**	**Post Full Strength Flue Gas Tests (ppm)**	**Unused (ppm)**
Sample Date		2/15	6/15	8/15	8/25	10/3
Equivalent Hours of FG Exposure		0	44	115	397	0
As	100	0.20	0.22	0.25	0.22	0.20
Cr	100	<5	<5	<5	<5	<5
Pb	100	0.66	0.35	0.45	0.77	0.35
Hg	4	0.002	0.003	0.005	0.005	0.001
Se	20	<1	<1	<1	<1	<1

National Energy Technology Laboratory (NETL) batch tests

This section will review data acquired using the C2U unit during the years 2012 - 2013. At the beginning of 2014, the C2U unit was being prepared for transport to NCCC.

The data acquired can be separated into four distinct catagories: AX circulating, AX batch, 32D circulating and 32D batch.

AX sorbent was tested initially, 32D sorbent was not available until later. AX sorbent was shown to have a particle density of 0.90 g/cc and a Sauter diameter of 118 µm. The minimum fluidization velocity was calculated to be approximately 0.52 cm/s, the 32D sorbent minimum fluidization was 0.17 cm/s.

Batch tests of AX sorbent

A wide variety of parameters were varied and explored during batch tests of AX sorbent. These parameters include: bed mass, adsorption temperature, regeneration temperature, total bed flow, % CO_2 inputted, % H_2O inputted and heating rate during transition to regeneration. Two published articles resulted from data acquired during these tests Monazam et al 2013 [1] which explored kinetics during the adsorption process and Monazam et al. 2014 [3] focused on regeneration kinetics. Data relevant for kinetic analysis was acquired during a two year period (2012 – 2013) concerning these two aspects of carbon capture using solid amine sorbents. Tests conducted in 2012 focused primarily on the adsorption aspect and 2013 tests on regeneration although both processes were examined for all data. For adsorption tests, independent parameters related to adsorption were varied while maintaining constant regeneration parameters. The reverse was true for regeneration experiments

Adsorption tests

Although both adsorption and regeneration were performed during all batch experiments, sometimes the data analysis focused on a single aspect. Two articles were produced from data acquired during these experiments. Monazam [1], which accentuated adsorption kinetics of AX sorbent, utilized data acquired between 04/10/12 – 09/26/12. This data, designated as BMA 1 – BMA 257, consisted of thirty-nine transition to adsorption – regeneration sequences. For the most part, each sequence had four BMA points, however, in some instances; a cooldown at the end of a test day was designated as a BMA point. Likewise, special tests not part of a sequence had a BMA designation.

Table 7. Test matrix for data points BMA1 - BMA 247

Bed mass (kg)	1.75, 2.4, 3.1
Adsorption temp (°C)	40, 55,70, 90
Total adsorption flow (slpm)	15, 20, 30,
Vol % CO_2	17, 30, 33, 50
CO_2 flow during adsorber transition	Yes, No

The earliest data taken 4/10/2012 – 4/12/2012 (BMA1 – BMA25) employed the greatest bed mass in the BMA series (3.1 kg). However, these were shakedown tests and the data acquired may not be suitable for comprehensive analysis. Likewise, data taken 4/23/2014 – 5/10/2014 (BMA 26 – BMA 71) had the lightest bed (1.75 kg) and refinements to the system were continuing. One of the difficulties encountered during these tests was an over pressurization of the oil circulation system. Originally, a flow meter was used to determine oil circulation rate. However, the use of this meter required a substantial length of tubing suspended horizontally. This tubing allowed a substantial amount of air to be trapped within the system and thus when the oil was heated, gas expansion caused over pressurization. When this tubing and meter was removed the over pressurization problem was alleviated.

Data subsequently acquired (BMA72 – BMA 257) was acceptable. The total bed mass in this case was 2.4 kg with 2.1 kg in the active region and 0.3 kg residing in the solids underflow. This data can be divided into three groups. Fresh sorbent was added for BMA72 and used for subsequent cases up to BMA 160. This sorbent was replaced with fresh for tests BMA 161 – BMA199. Subsequently, after test BMA199, circulation tests were run. Later batch tests were resumed using the same sorbent as was uses for the circulation tests for BMA200 – BMA257.

Tests were performed where adsorption bed temperature was varied but with the same total gas flow of 30 slpm and 16.7 % CO_2 concentration. Figure 29 indicates that at higher initial temperatures, the rate of capture declines more rapidly than at lower initial temperatures. At the lowest bed temperature the sorbent adsorbs all of the CO_2 exposed to it but adsorption ceases earlier. At higher bed temperature the sorbent adsorbs longer but adsorbs less of the total inflow. These trends are consistent with TGA adsorption isotherm data that indicates maximum CO_2 equilibrium loading is achieved near 60°C.

Attempts were made to maintain the bed at a constant temperature during the adsorption process; however, the heat generated initially by the adsorption process was greater than the heat extracted. Thus, the bed temperature initially increased and then was brought to the desired value near the end of the process. The deviation in temperature was more acute at lower bed temperatures (Figure 30).

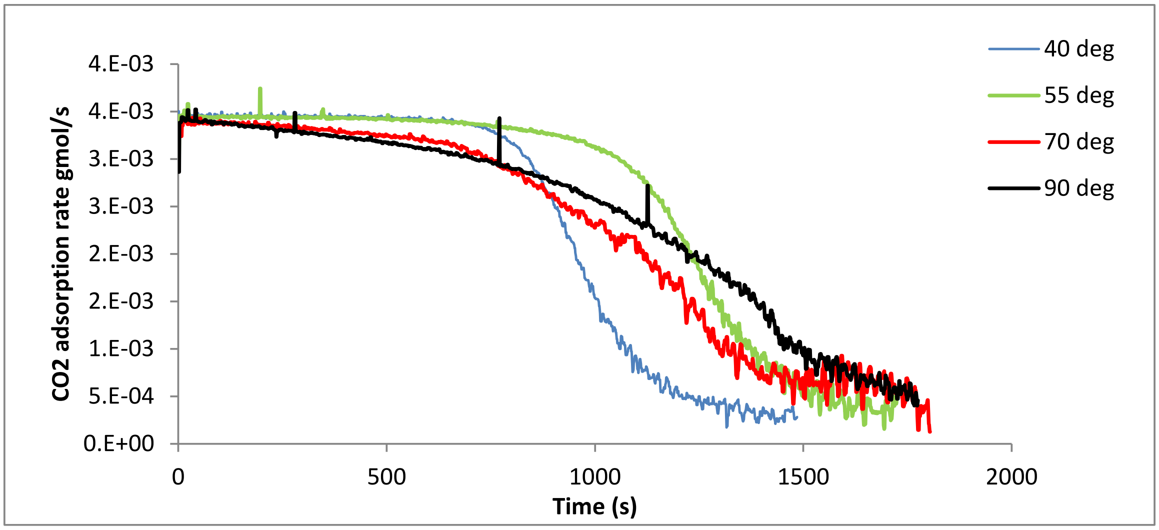


Figure 29. CO_2 adsorption rates with varied initial bed temperature (16.7% CO_2 concentration)

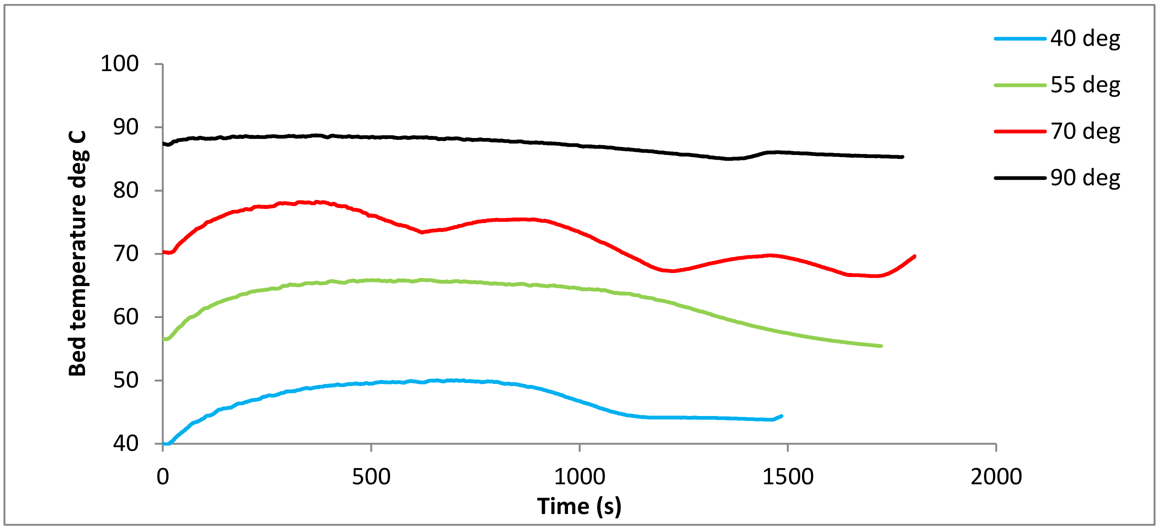


Figure 30. Bed temperature increase during adsorption with 30 slpm total flow and 16.7% CO_2 concentration

Additional tests were conducted with an increased CO_2 concentration (33%) with the same sorbent and total flow rate (Figure 31). At lower initial bed temperatures, the adsorption rate remains at nearly 100% removal for a period of time then rapidly drop to a minimum value. At higher initial bed temperatures, 100% adsorption is not achieved; however the rate of adsorption declines slower. At 33% CO_2 concentration, a constant bed temperature was more difficult to maintain (Figure 32) than at 16% CO_2. With an initial temperature of 40°C and a 16.7 % CO_2 concentration the bed temperature increased to approximately 50 °C, however, when the CO_2 concentration was 33% the bed temperature increased to 65°C at maximum. However, as the rate of adsorption declined, the bed could be cooled to the desired temperature in all cases. The adsorption capacity was approximately 2.0 gmol CO_2/kg sorbent in most cases for the AX sorbent.

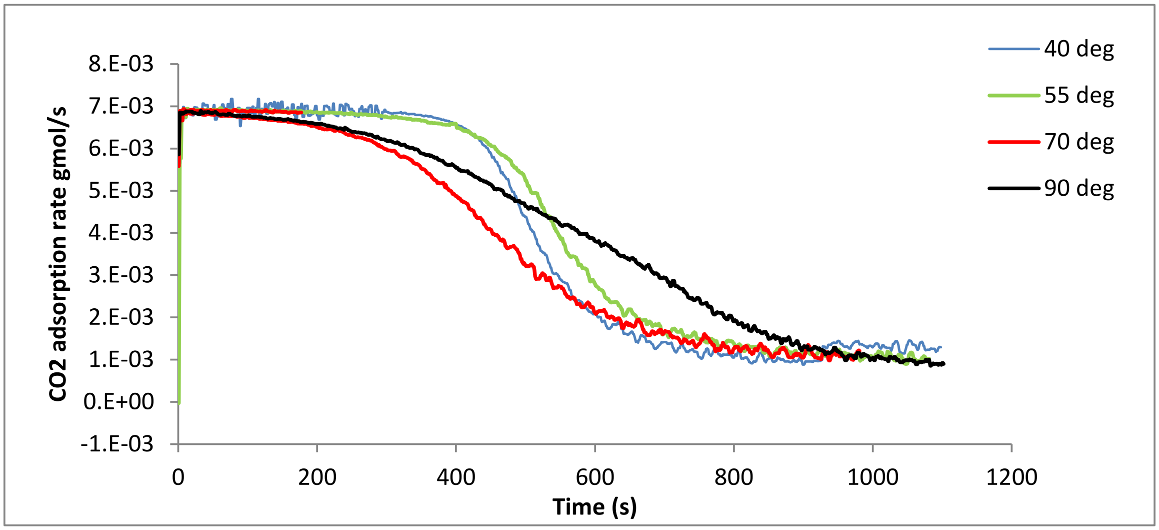


Figure 31. CO_2 adsorption rates with varied initial bed temperature (33% CO_2 concentration)

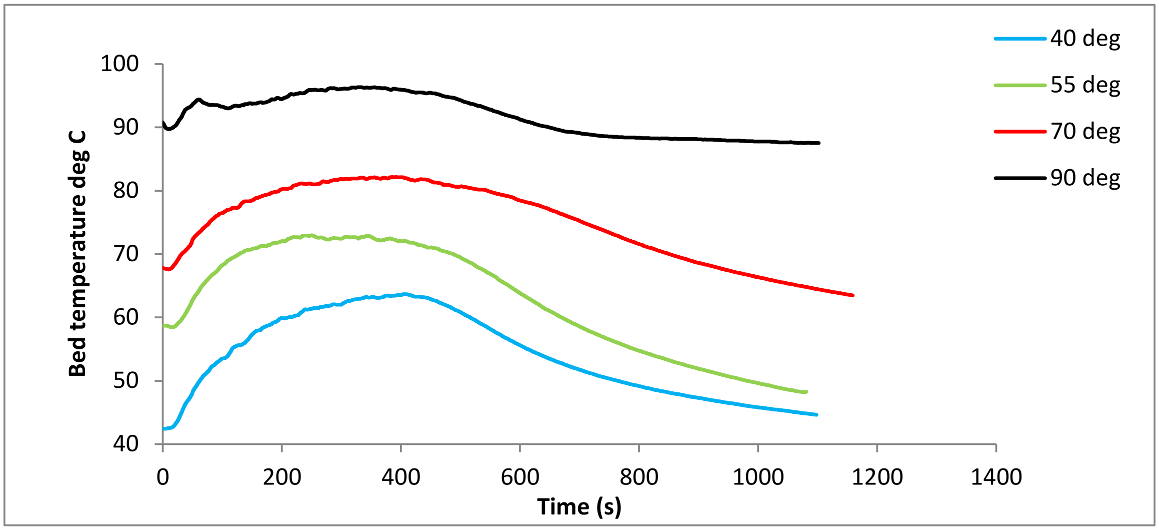


Figure 32. Bed temperature increase during adsorption with 30 slpm total flow and 33% CO_2 concentration

Regeneration tests

Two groups of regeneration tests were conducted one with varied heating rates (HR1 – HR15) and one with varied regeneration temperature (#2HR1 - #2HR19). A flow of 3.0 slpm was maintained to the upper loopseal (lpsl#2). This flow was maintained at 3.0 slpm since heating coils were present and connected to the regenerator coil system. This flow was assumed to exit the regenerator side and was included as dilution air for calculation of CO_2 exit mass flow.

Heating rate

Heating rate tests (Table 8) were conducted between 2/12 and 3/15 2013 with a bed mass of 3.1 kg AX sorbent. The adsorption temperature for all tests (HR1 – HR 15) was maintained at 70°C,. Total inlet plenum flow was 15 slpm and CO_2 concentration was either 16.7% or 33.3%, H_2O flow was 2% during all phases. The heater control output current was maintained at a fixed value (0.014, 0.016, 0.018, 0.02 mA) until the desired adsorption temperature (110°C) was achieved. The heating rate is directly related to the temperature increase of the bed per unit time and the control current corresponds to the fraction of the maximum output of the 3kW heater (0.7, 0.8, 0.9 and 1.0). Once the regeneration temperature of 110°C was reached, regeneration was complete. For tests HR1 – HR10, CO_2 flow was maintained at the adsorption flow rate during the transition to regeneration phase. However, for tests HR11 – HR15, CO_2 flow was discontinued during the transition to regeneration phase. A detailed kinetic analysis of this data can be found in Monazam [3].

Figure 33 indicates the regeneration rate during the transition phase and Figure 34 indicates bed temperature for each heating rate with 16.7% CO_2 concentration inputted during the transition phase. Figure 35 and Figure 36 report this information with 33% CO_2 concentration. The rate of regeneration increase with time is more rapid as the input from the heater is increased for both concentrations but is not dependent on concentration (Figure 37). If CO_2 flow is not present during the transition phase then a high heat input into the bed will precipitate a continued increase in the regeneration rate with time, however a moderate heat input will lead to a constant rate of regeneration (Figure 38) Figure 39 indicates that the rate of bed temperature increase is dependent on the heater output, as would be expected.

Even though CO_2 is being added to the bed during the transition phase, this CO_2 just passes through the bed and additional CO_2 collected during the adsorption phase is released. For Figure 33 through Figure 37 the CO_2 flow employed during adsorption was maintained during the transition phase. As the heating rate increased so did the CO_2 desorption and the bed temperature reached the desired value of 110°C faster. This was also true for the 33.3% CO_2 case (Figure 35 and Figure 36). In fact, the percentage of CO_2 inputted during the transition phase (either 17% or 33%) did not have a discernable effect on the regeneration rate (Figure 37) but the heating rate had a significant effect. Even with no CO_2 flow during the transition phase (Figure 38, Figure 39), the effect of heating rate on regeneration is comparable. The first 100 or so seconds of these figures should be disregarded because the CO_2 was shut off at the inlet but CO_2 concentration is measured at the outlet. Since the equation to determine CO_2 regeneration uses both inlet and outlet terms, there is a time period during transition when the equation is not suitable for the calculation of CO_2 mass balance. At the lowest heating rate the regeneration is nearly constant at about 2.0 slpm. As the heating rate increases the curves have a steeper sigmoidal shape and reach a higher maximum. For the heating rate of 0.02 mA the curve reaches a regeneration rate of 4.0 slpm. The effect of CO_2 flow through the bed while transitioning to the regeneration temperature had a greater impact on the rate of desorption than the rate at which the bed temperature increases (Figure 40). Therefore, CO_2 partial pressure has a stronger influence on regeneration than sorbent temperature ramp rate.

Table 8. Planned test conditions for AX batch- heating rate

Filename	Trans. Heat control	% CO2 transition	% CO2 adsorp.
	SSR3961		
	mA		
HR1	0.018	16.66	16.66
HR2	0.018	33.33	33.33
HR3	0.016	16.66	16.66
HR4	0.016	33.33	33.33
HR5	0.02	16.66	16.66
HR6	0.02	33.33	33.33
HR7	0.018	16.66	16.66
HR8	0.014	33.33	33.33
HR9	0.018	33.33	33.33
HR10	0.014	16.66	16.66
HR11	0.014	0	16.66
HR12	0.02	0	33.33
HR13	0.014	0	33.33
HR14	0.02	0	16.66
HR15	0.02	0	33.33
HR16	0.014	16.66	16.66
HR17	0.014	0	16.66

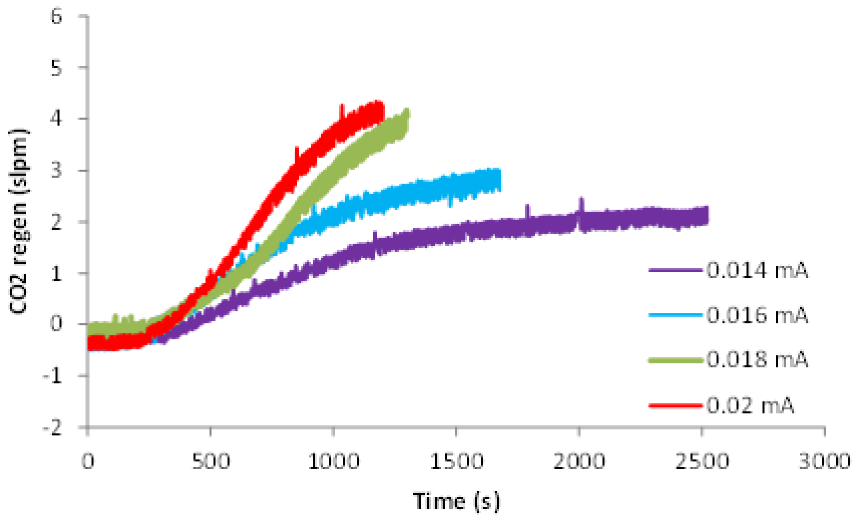


Figure 33. CO_2 regeneration during transition phase with 16.7% CO_2 flow for heating rates 0.014 - 0.020 mA

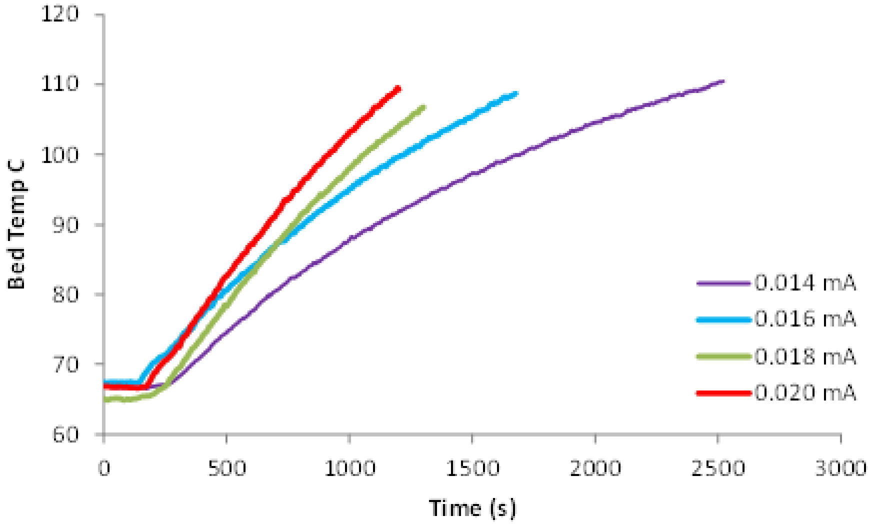


Figure 34. Bed temperature during transition phase with 16.7% CO_2 flow for heating rates 0.014 - 0.020 mA

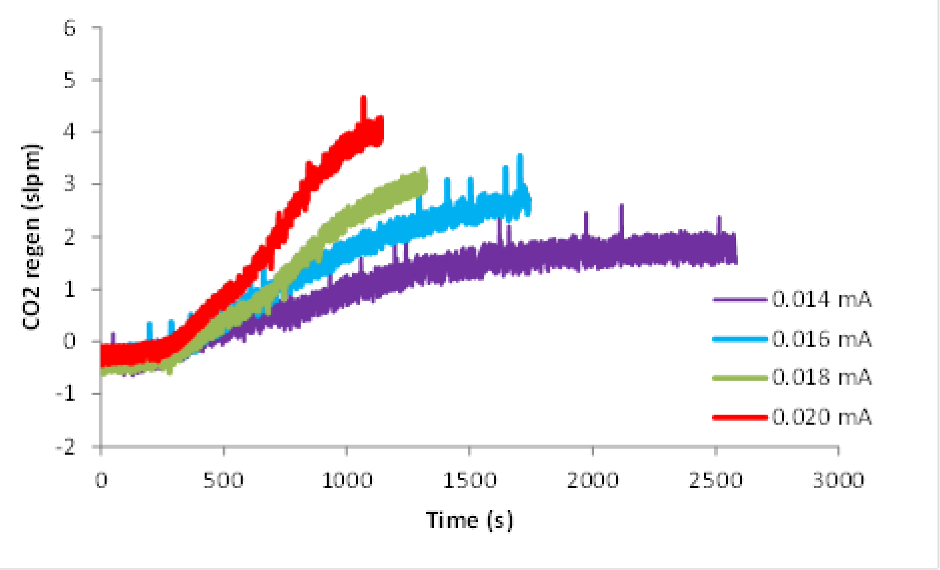


Figure 35. CO_2 regeneration during transition phase with 33.3% CO_2 flow for heating rates 0.014 - 0.020 mA

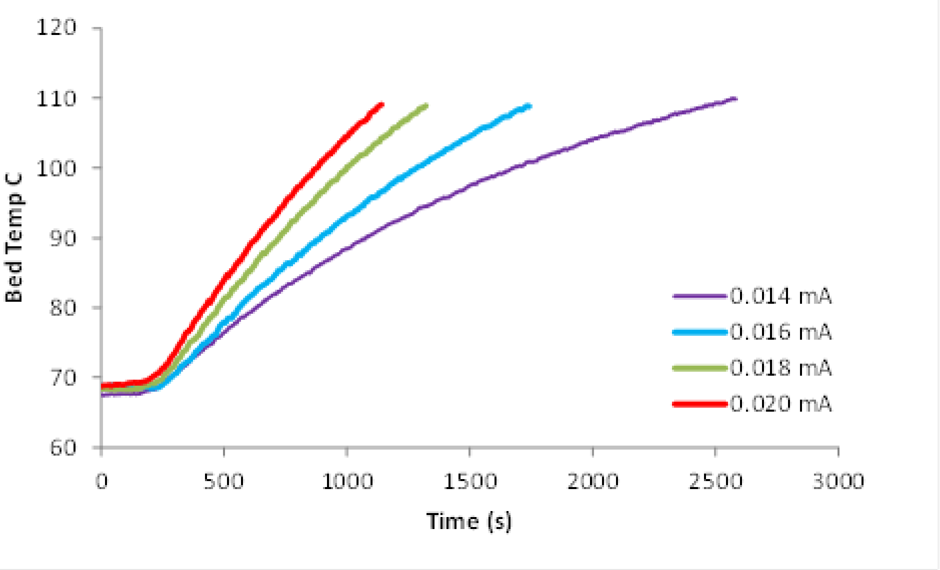


Figure 36. Bed temperature during transition phase with 33.3% CO_2 flow for heating rates 0.014 - 0.020 mA

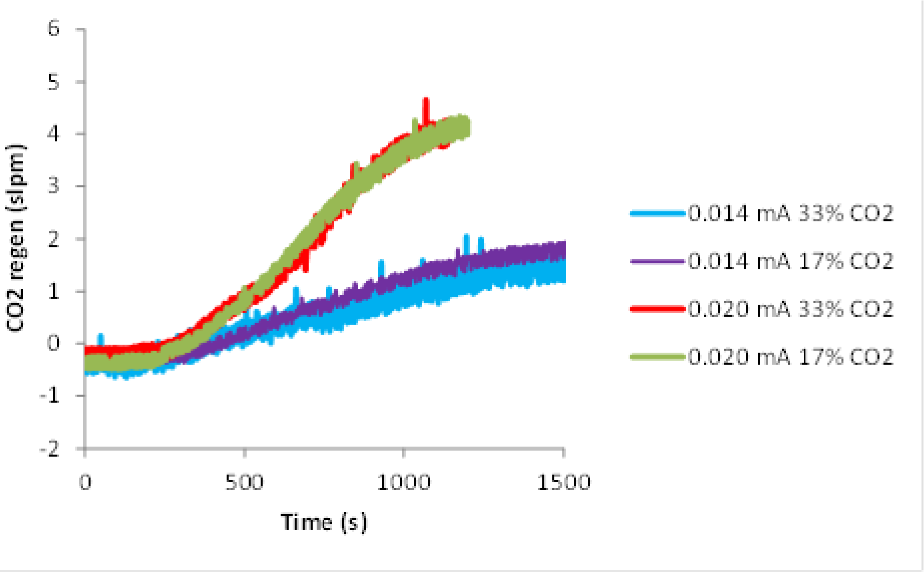


Figure 37. CO_2 regeneration during transition phase with 16.7 and 33.3% CO_2 flow for heating rates 0.014 and 0.020 mA

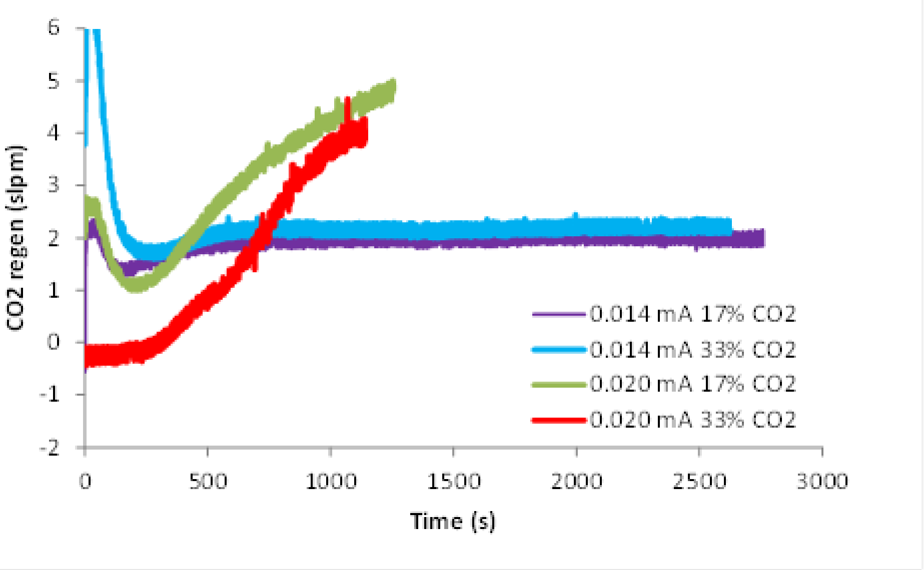


Figure 38. CO_2 regeneration during transition phase with 0% CO_2 flow during transition for heating rates 0.014 and 0.020. Adsorption concentrations were 16.7 and 33.3%

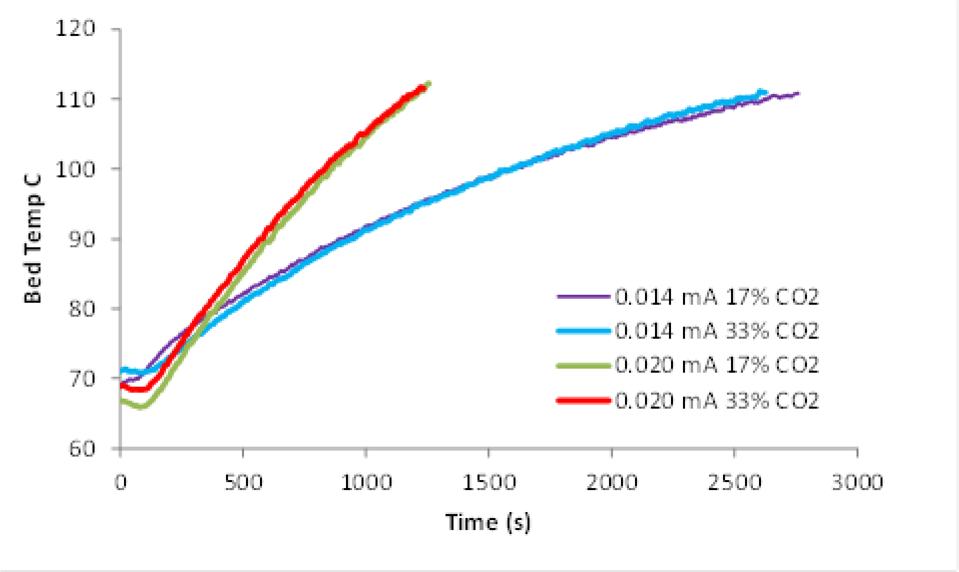


Figure 39. Bed temperatures during transition phase with 0% CO_2 flow during transition for heating rates 0.014 and 0.020. Adsorption concentrations were 16.7 and 33.3%

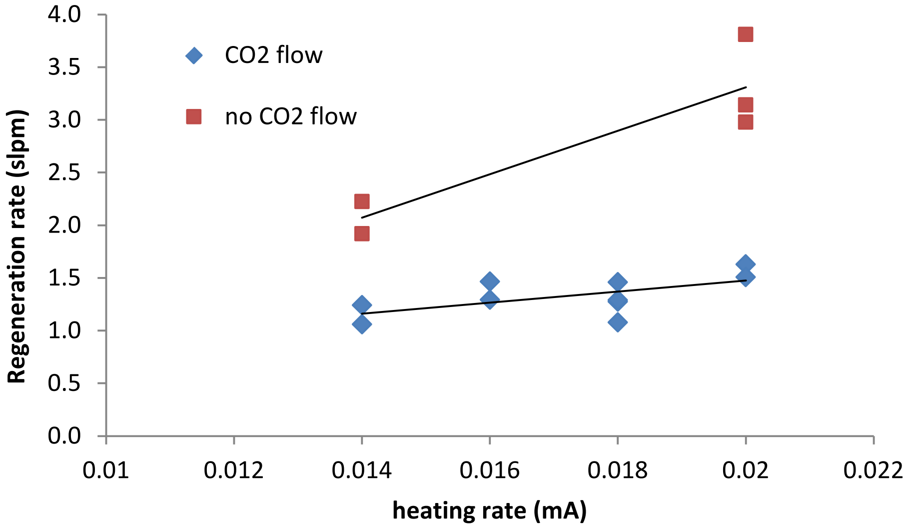


Figure 40. Averaged regeneration rate over transition period

Regeneration temperature

The regeneration temperature, in batch mode, was varied from 90 to 120°C in 10°C increments using AX sorbent in tests taken 7/30 – 8/14 (#2HR1 - #2HR19) with an inventory of 1.9 kg. Total plenum flow was maintained at 15 slpm, the CO_2 concentration, during adsorption and transition to regeneration phases was either 16.6 or 33.3%. Nineteen test conditions were acquired with two points at each condition (Table 9). Point #2HR18 was rejected.

The percentage of CO_2 in the gas during the adsorption phase and subsequent transition phase did not have a significant effect on the rate of regeneration once CO_2 flow was discontinued. Figure 41 shows that the regeneration rates with time are comparable independent of initial CO_2 concentration. The bed temperature does dramatically affect the regeneration rate. This is consistent with packed bed experiments that show temperature ramping is necessary to desorb the more strongly bonded CO_2. Swing in partial pressure of CO_2 at the same temperature (inert gas sweep) desorbs the more weakly-bonded $CO_,$ but temperature ramping is required for the remainder of the CO_2 to desorb. At the lowest bed temperature, the sorbent would not desorb all of the CO_2 it had previously adsorbed, no matter how long the experiment was conducted. Because of this fact, a carbon balance could not be established between the adsorption phase and subsequent regeneration phase. However, when possible, the amount of CO_2 left in the sorbent after a regeneration period was accounted for during the next adsorption phase.

It is assumed that the total amount of CO_2 adsorbed is constant after each adsorption phase and was approximately 100 liters (4.46 gmol) adsorbed by the 1.9 kg bed (capacity = 2.3 gmol/kg sorbent). Figure 42 indicates that as the bed heats CO_2 desorption rate increases linearly with bed temperature. At 120 °C the average rate was about 50 liter/hr per kg sorbent during the transition phase which is greater than the rate when the bed temperature was constant (regeneration phase) at 120 °C (Figure 43). This is most likely due to the fact that there was a finite amount of CO_2 available in the sorbent and a significant amount was released during the transition phase thus less was available during the regeneration phase.

Table 9. Planned test conditions for AX batch- regen temp

Filename	Treg	Adsorp. CO_2	total flow
	C	%	slpm
#2HR1	90	16.6	15
#2HR2	120	33.3	15
#2HR3	120	16.6	15
#2HR4	120	33.3	15
#2HR5	100	33.3	15
#2HR6	110	33.3	15
#2HR7	110	16.6	15
#2HR8	100	16.6	15
#2HR9	90	33.3	15
#2HR10	120	16.6	15
#2HR11	100	16.6	15
#2HR12	110	33.3	15
#2HR13	90	16.6	15
#2HR14	100	33.3	15
#2HR15	90	33.3	15
#2HR16	110	16.6	15
#2HR17	90	16.6	15
#2HR18	120	33.3	15
#2HR19	120	33.3	15

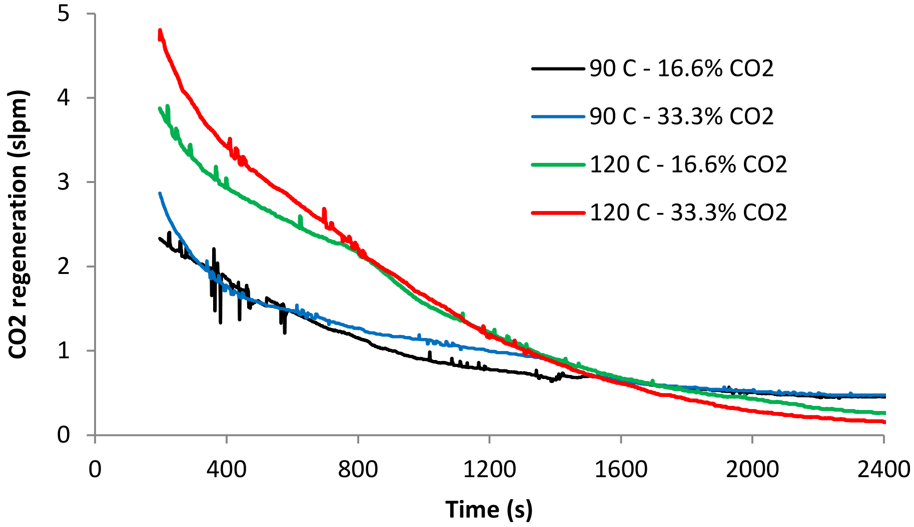


Figure 41. Regeneration rate during regeneration phase for 90 and 120°C beds with 17 and 33% CO_2 gas previously adsorbed

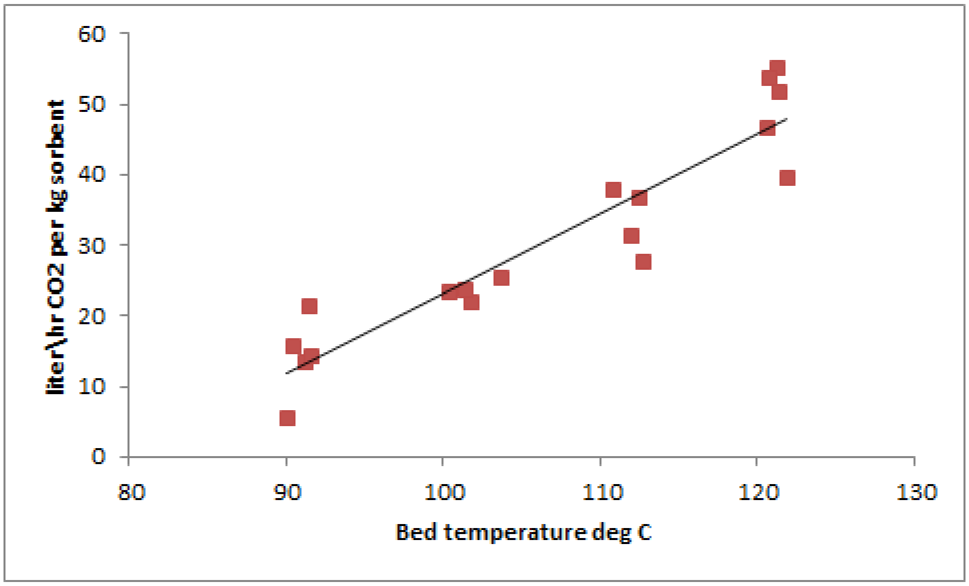


Figure 42. Averaged rate of CO_2 desorption during transition to regeneration phase

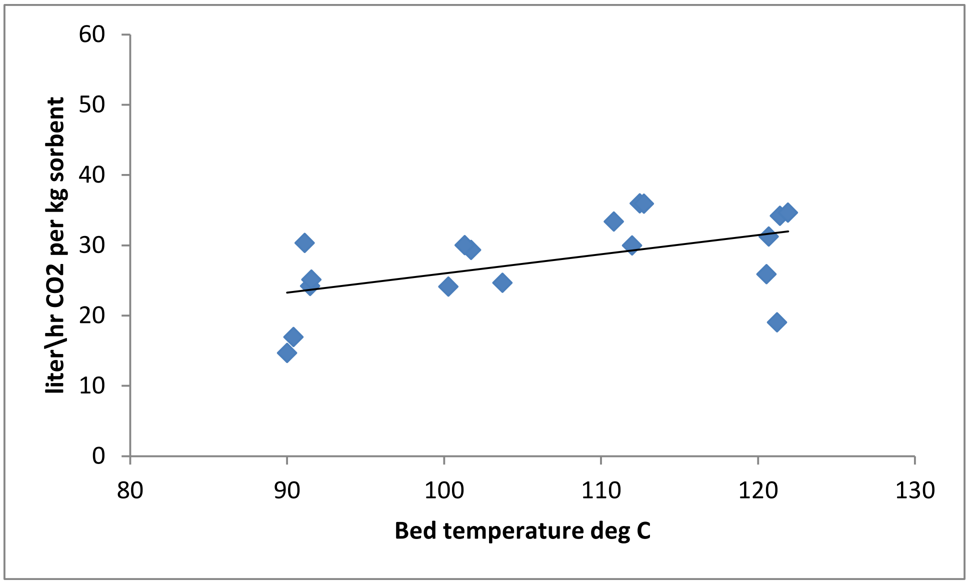


Figure 43. Averaged rate of CO_2 desorption during regeneration phase

Determining heat of reaction adsorption phase – AX sorbent

The energy balance equation determining heat of reaction during adsorption does not contain as many significantly relevant terms as that of the regeneration phase since cooled circulating oil is removing heat and the various components do not need to be heated to regeneration temperatures. Prior to the introduction of CO_2, the bed, reactor and sorbent is cooled to the desired temperature. The operating adsorption temperature was closer to ambient than during regeneration, thus environmental losses were less. The following analysis is of a case with 16% CO_2 and a desired adsorption temperature of 55°C.

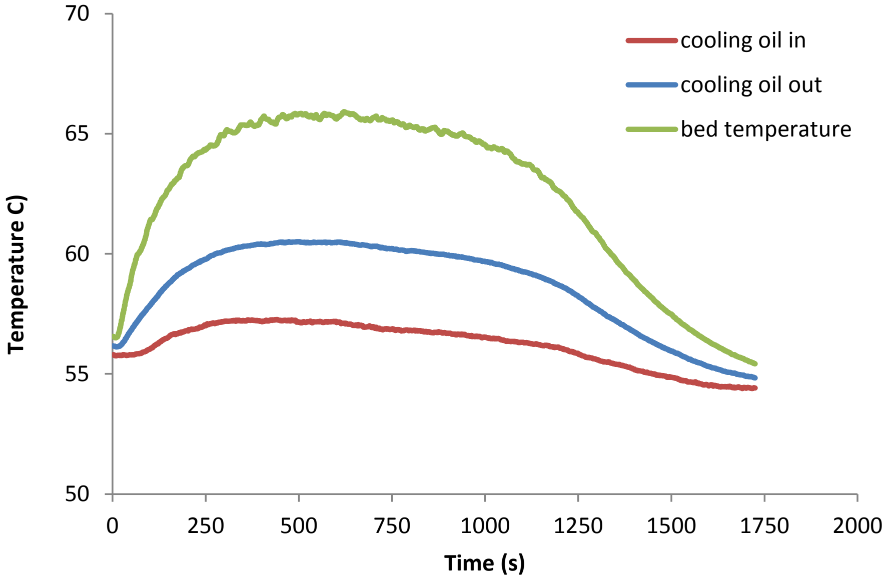


Figure 44 indicates that when CO_2 was initially introduced, the heat released by adsorption was greater than the ability of the cooling oil flow to extract, and thus the bed temperature increased. If there were no cooling flow, the bed temperature would have likely increased to the point where adsorption would cease and desorption would dominate.

Figure 45 shows the heat gains and losses of the various components. Comparing this figure with Figure 48 shows that the heat loss through the wall is less during adsorption but still present because the ambient temperature is still less than all other temperatures. The sorbent temperature increases, but not from oil flow but due to the exothermic reaction of adsorption. The oil flow is extracting energy in the adsorption case but adding energy in the regeneration case.

The CO_2 adsorption rate and oil heat transfer rates are shown on Figure 46. The adsorption rate is shown as a regeneration rate, thus the numbers are negative. As time progresses the adsorption rate approaches zero as well as the oil heat transfer rate.

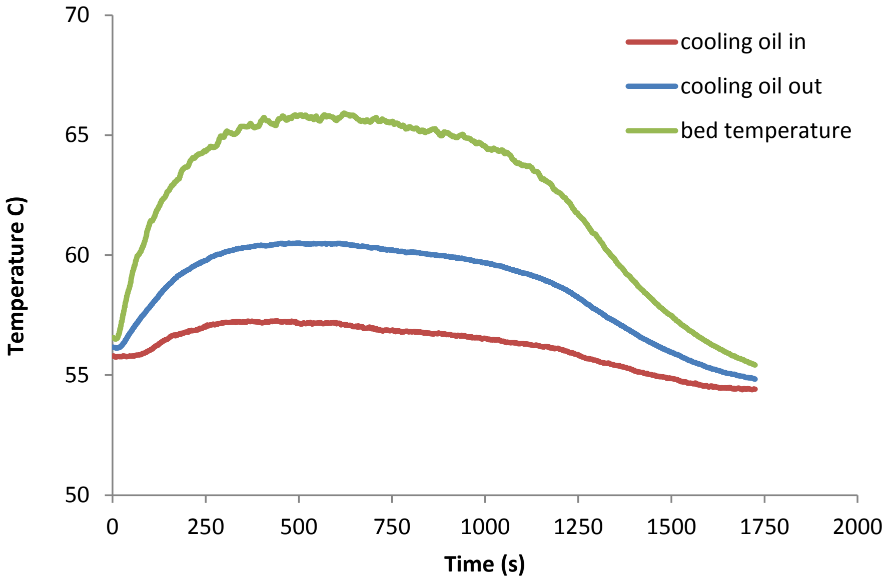


Figure 44. Bed, inlet and outlet temperatures during adsorption

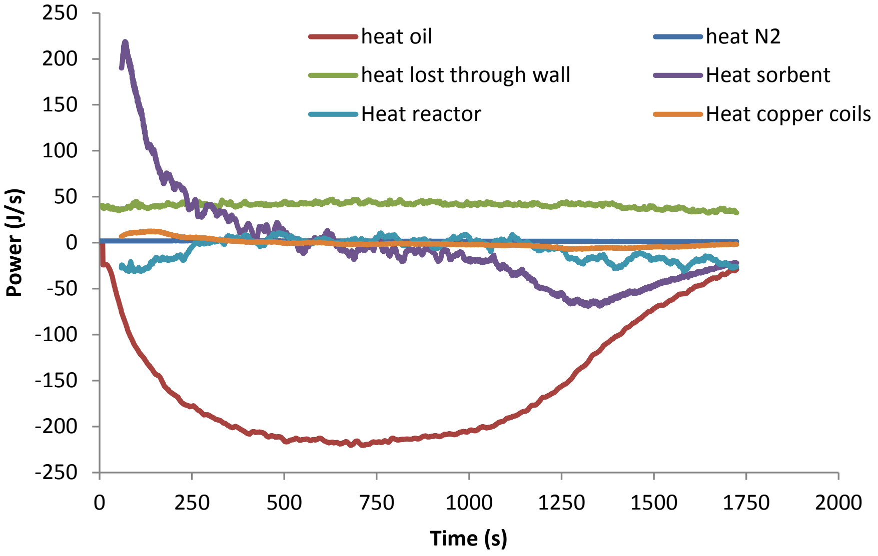


Figure 45. Heat exchange during adsorption

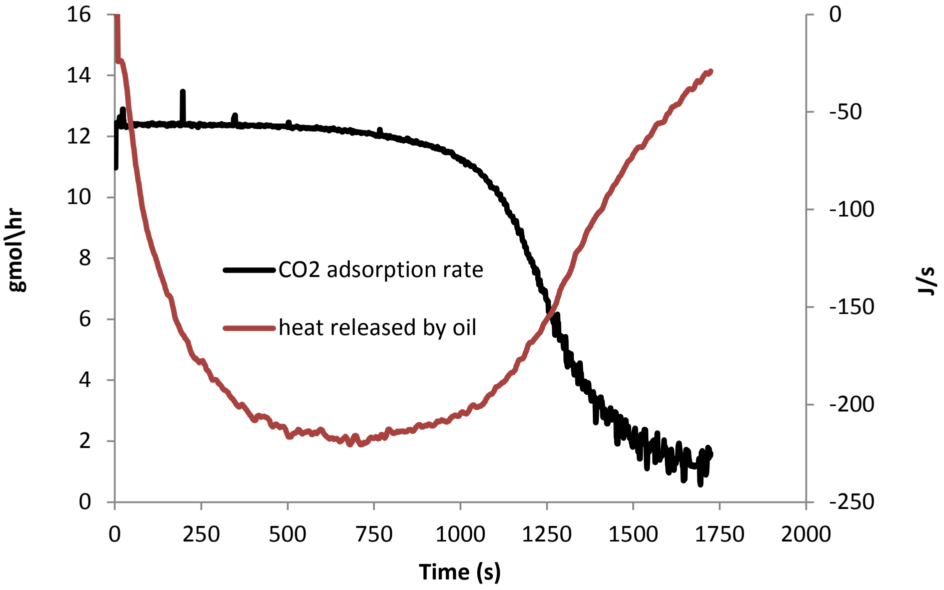


Figure 46. CO_2 adsorption rate and oil heat transfer rate.

Therefore, by summing the energy terms during the transition to regeneration and regeneration phase, a heat of reaction for AX sorbent was determined:

Total heat provided from circulating oil	-271.1 kJ
Heat loss to fluidizing gases	-2.0 kJ
Heat loss to environment	-70.0 kJ
Heating sorbent	- 8.0.kJ
Heating reactor	-11.6 kJ
Heating copper coils	-1.2 kJ
Heat left for reaction	-319.1 kJ

Since the amount of CO_2 captured was 4.41 gmol, the heat of reaction during this adsorption phase was -72.4 kJ/gmol CO_2.

This method was employed for the various experiments in both adsorption and regeneration. When data from all experiments was analyzed, the heat of reaction for AX sorbent was found to be 63 ± 16 kJ/gmol CO_2

Determining heat of reaction - regeneration phase – AX sorbent

The heat of reaction during regeneration was determined from the balance of energy entering and leaving during adsorption, desorption processes in the reactor.

The following pathways of heat loss/gain were considered:

1. Heat supplied/ removed by circulating oil
2. Heat lost to gas flow through bed
3. Heat lost through reactor wall to environment
4. Heat addition/ removal required to raise temperature of sorbent
5. Heat addition/ removal required to raise temperature of reactor
6. Heat addition/ removal required to change temperature of copper coils
7. Heat required for reaction

The thermodynamic system for heat balance is shown in Figure 47. Oil was heated from an outside source and circulated through the system, other heat flows are internal. The values of pathways 2 through 6 are summed and subtracted from 1 which yields the heat supplied/removed for reaction. This was calculated on a second by second basis throughout the adsorption or regeneration process and yields a value in J/s (Watt), the power available. Figure 48 indicates the second by second values of the six parameters listed above during transition to regeneration and regeneration. The area under the heat oil curve represents the total energy supplied to the bed by the circulating oil. The areas under the other curves represents energy adsorbed from the circulating oil by each of the other parameters. Energy left over is assumed to have been used for the heat of reaction.

Figure 49 shows the oil heat loss and CO_2 liberation. In this example the CO_2 flow was maintained at the same level as during adsorption during the transition to regeneration. The bed was being heated but CO_2 flow remained constant during this particular transition phase. It can be seen that as the bed was being heated, CO_2 was being liberated. When the CO_2 supplied to the bed was discontinued, there was a large spike in CO_2 regeneration, again pointing to the inhibiting CO_2 partial pressure effect and the need to sweep with an inert gas (steam) during regeneration.

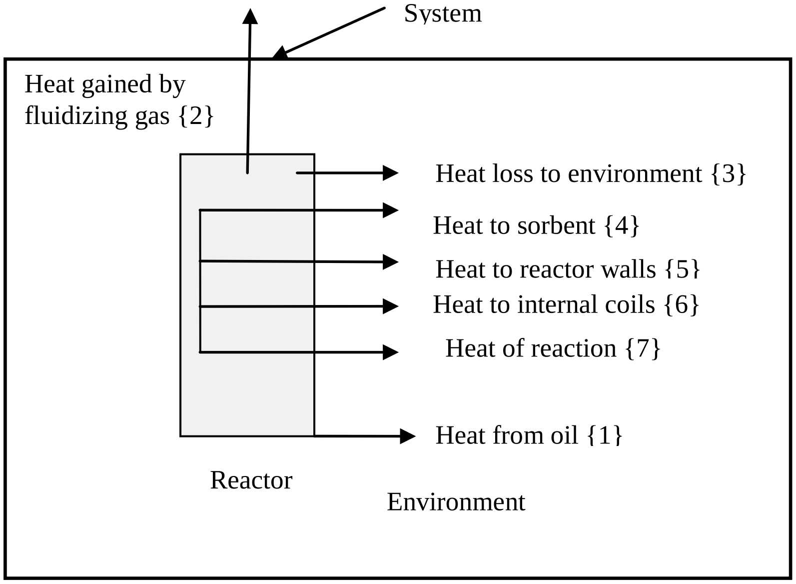


Figure 47. Thermodynamic system for heat of reaction balance

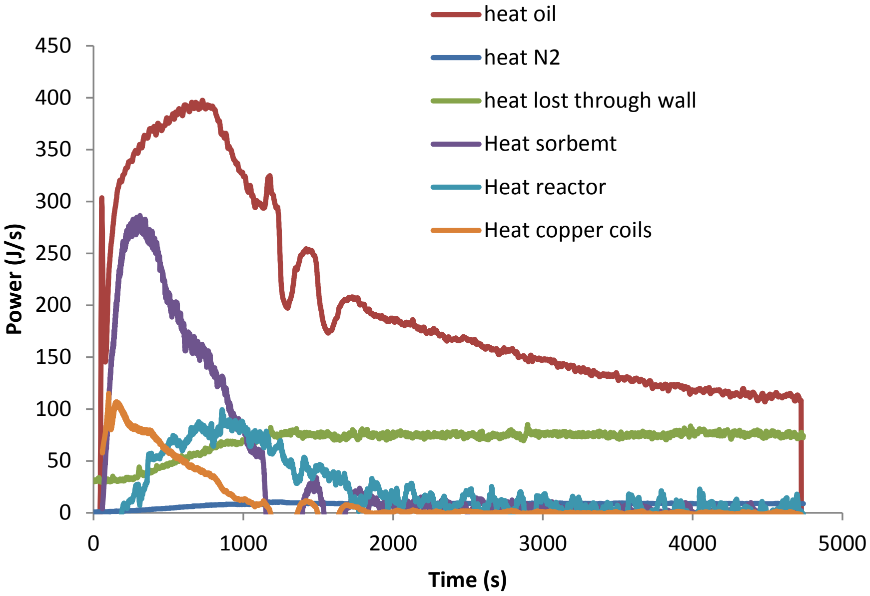


Figure 48. Heat exchange during transition to regeneration and regeneration (BMA 180 -181)

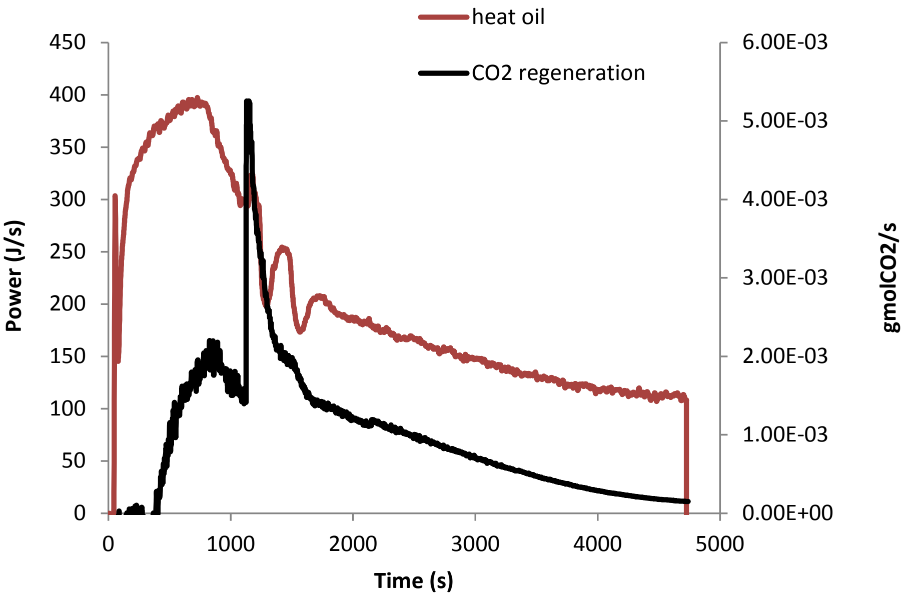


Figure 49. Oil heat loss and CO extraction during transition to regeneration and regeneration

These values of power summed over the reaction period and divided by the amount of CO_2 involved yields the heat of reaction in kJ/gmol CO_2.

The mineral oil used has a specific heat of approximately 1670 J/kg-K and a density of about 830 kg/m^3. The mineral oil was shown to have a circulation rate of about 4.5 lpm (61.8 g/s). In Figure 48 the maximum ΔT between oil inflow and outflow was 6°C and the total heat released by the oil was 934.3 kJ.

All terms were balanced on a second by second basis in the original analysis; however, in the example below each term is summed independently over the proper time period and then balanced. Both methods yield comparable results.

Energy lost to the fluidizing gas was minimal compared to the other factors due to the low mass flow. Even with a "high" fluidizing flow rate of 30 slpm the mass flow is only 5.8×10^{-4} kg/s. The gas normally enters the plenum at 20°C (TE3920) and normally reaches a temperature of about 60°C (TE3930) measured in the regenerator freeboard. The specific heat of N_2 is 1040 J/kg-K; therefore the power used to heat the N_2 would be 24 W. At a 20°C entrance temperature, however, throughout the day the plenum heats up thus the entrance temp increases and energy required to heat the gas reduces. In Figure 48 the maximum ΔT for N_2 was only 17°C and the total heat adsorbed by the 30 slpm gas flow was 38.1 kJ for the total time period.

Heat loss through the regenerator wall was reported from a heat flux gauge and was also determined from ΔT measured between the inner and outer wall and the conductive heat transfer coefficient of the wall material. These two values were averaged together. The average temperature differential between the vessel inner and outer wall was 13.6°C. The vessel was comprised of HDPE that had a conductive heat transfer coefficient of 0.48 W/m-k. The total mass of the bed was 2.4 kg, however, 0.3 kg was in the solids underflow and not involved in reactions. The 2.1 kg left filled the bed to a level of 0.18 m, the inner and outer reactor diameters were 0.140 and 0.152 m respectively. The heat flow by conduction through the cylindrical reactor was calculated by:

$$Q = \frac{2\pi k L}{\ln(r_o/r_i)}\Delta T = \frac{2\pi * 0.48 * 0.18}{\ln(0.152/0.140)} * 13.6 = 89.8\,W$$

The duration of the experiment was about 4660 seconds, so the calculated heat loss through the vessel wall using the above equation was 418 kJ. In the actual experiment the ΔT was evaluated at each interval (second) and yielded a slightly lower value or 391 kJ. The heat flux gauge indicated a slightly lower value (234 kJ), so an average of the interval ΔT value and the heat flux gauge value, 312 kJ, was used

Heating of the bed, reactor and copper primarily occurs during the transition phase. After the components are heated and the reactor is at the desired temperature the oil supplies heat to sustain heat loss through the wall and heat of regeneration.

The sorbent bed mass was 2.1 kg and the specific heat was assumed to be approximately 1600 J/kg-K. The sorbent was heated from the adsorption temperature of 55°C to the regeneration temperature of 110°C requiring 185 kJ

The HDPE pipe was heated from an initial average temperature of 50°C to a final average temperature of 75°C (average of the inner and outer wall temperatures). The total length of the reactor including freeboard, was not considered. Only the height to which the coils extended was considered since HDPE has a low thermal conductivity 0.48 W/m-K and thus heat would not be readily transmitted axially. The mass of HDPE material under consideration was 0.97 kg for a 14 inch length of 5.5 inch diameter pipe. Specific heat of HDPE is 1800 J/kg-K. Therefore, the heat required to increase the reactor wall temperature during transition to regeneration was 43.8 kJ.

The total mass of the copper coils was 2.3 kg with a specific heat of 384 J/kg-K. The coil temperature is assumed to be an average of the inlet and outlet oil temperatures at that particular instant. To raise the temperature of the copper from the initial temperature of 55°C to the final temperature of 115°C required 53 kJ.

Therefore, the summed heat balance during the transition to regeneration and regeneration phase indicates a heat of reaction for AX sorbent to be

Total heat provided from circulating oil	934.3 kJ
Heat loss to fluidizing gases	-38.1 kJ
Heat loss to environment	-391.0 kJ
Heating sorbent substrate	-184.8 kJ
Heating reactor	-43.8 kJ
Heating copper coils	-53.1 kJ
Heat of reaction	223.9 kJ

The area under the CO_2 regeneration curve on Figure 49 gives the total amount of CO_2 liberated (4.46 gmol). Thus, for this example case, the heat of reaction was determined to be 50.2 kJ/gmol CO_2. The heat of regeneration, derived from a multitude of experiments similar to the one described above, was found to be comparable to the heat of adsorption, 63 ± 16 kJ/gmol CO_2.

Batch tests of 32D sorbent

The 32D sorbent is somewhat lighter than the AX sorbent, AX sorbent had a particle density of 0.9 g/cc where the 32D particle density was about half that at 0.48 g/cc.

An extensive amount of testing was conducted in 2013 regarding the adsorption aspect for the Carbon Capture Simulation Initiative (CCSI) and that will be the focus of this section. CCSI required experimental data from the C2U to develop and validate various sub-models for a sorbent based CO_2 removal process. Some batch testing was conducted independent of CCSI; however, that data will not be examined at this time. CCSI required three modes of testing: cold, warm and reacting. Cold testing was to establish the U_{mf} and investigate elutration. Warm testing was equivalent to cold testing but with a heated bed. The reacting flow tests consisted of 67 individual test points in a Latin hypercube experimental design, of which 51 were unique points. A center point condition was repeated eight times. Three parameters were varied: Total flow, adsorption temperature and CO_2 concentration. The flow rates varied between 15 – 30 slpm, temperatures between 40.5 – 79.5°C and CO_2 concentration 10.1 – 19.8 % (Table 10). This data was acquired between 6/13/2013 to 7/10/2013 and required about 2 hours of operation for each point. The overall bed mass was 1.9 kg with 1.6 kg within the coil region of the shorter regenerator and filled a volume of 4200 cc. The bed height was 30 cm (12 in).

The overriding variable observed during these tests, pertinent to adsorption capacity, was the time that data was acquired. The capacity would degrade linearly with the number of hours the sorbent was in use. Figure 50 (using all points) indicates that 32D sorbent lost about 0.0022 gmol/kg of CO_2 capacity per hour of operation. This value is confirmed by Figure 51 where only the eight center points of the experimental matrix were examined.

Since the independent variable was influenced by time, a compensation factor was employed when examining the influence of the independent variables (flow rate, bed temperature, and CO_2 concentration) on the dependent variable (capacity). According to Figure 52, total flow rate does not influence sorbent capacity. Capacity is weakly effected by bed temperature, the capacity is diminished by 0.003 gmol/kg per °C increase in bed temperature for the range of temperatures investigated (Figure 53). However, capacity increases as concentration increases at a rate of 0.015 gmol/kg per 1.0 percent increase in CO_2 concentration (Figure 54).

Heat of adsorption of 32D was found to be comparable to that of AX with a value approximately 65 kJ/mol CO_2.

Table 10. Latin hypercube test matrix for reacting 32D CCSI batch tests

SN #	Flow.Rate slpm	Temp °C	CO2 %	Test #
1	15.0	40.5	10.1	1, 12
2	15.5	53.5	18.9	5, 53
3	15.8	69.3	11.0	57
4	16.2	41.0	19.7	38
5	16.4	51.8	12.4	31
6	16.7	63.2	17.9	67
7	16.9	60.8	12.6	16
8	17.3	50.1	14.6	61
9	17.6	68.2	15.0	25
10	17.8	77.9	15.4	47
11	18.2	58.4	15.1	17
12	18.4	54.1	10.5	39
13	18.9	69.7	13.4	26
14	19.0	43.5	19.1	22
15	19.5	66.6	18.5	28
16	19.7	58.9	18.3	59
17	19.9	44.7	14.1	10, 45
18	20.2	65.0	10.9	4, 24
19	20.5	79.2	16.7	41
20	20.9	56.0	14.5	50
21	21.1	74.7	11.6	64
22	21.4	42.6	16.8	33
23	21.7	50.7	18.7	18
24	22.0	71.4	14.3	23
25	22.3	72.1	16.3	58
26	22.5	60.0	15.0	7,11,19,27,35, 43,52,60
27	22.7	63.4	17.6	13
28	22.9	76.9	18.1	8
29	22.9	76.9	18.1	34
30	23.1	55.6	16.5	37
31	23.6	57.6	11.2	62
32	23.7	62.2	12.8	48
33	24.3	49.1	15.7	44
34	24.4	47.5	12.6	32
35	24.9	46.5	17.0	3,15
36	24.9	73.4	13.1	20
37	25.4	48.5	10.7	49
38	25.5	67.3	15.4	65
39	26.0	64.6	17.6	40
40	26.4	79.5	11.9	9, 29
41	26.6	59.4	12.1	66
42	26.8	73.9	15.9	42
43	27.1	42.3	13.4	36
44	27.4	52.2	19.2	56
45	27.7	46.3	16.0	63
46	28.0	70.8	13.8	55
47	28.4	54.6	13.7	2, 14
48	28.7	76.6	10.4	54
49	28.9	75.8	19.8	30
50	29.3	65.6	17.3	6, 51
51	29.4	60.6	19.5	21
52	30.0	45.0	11.6	46

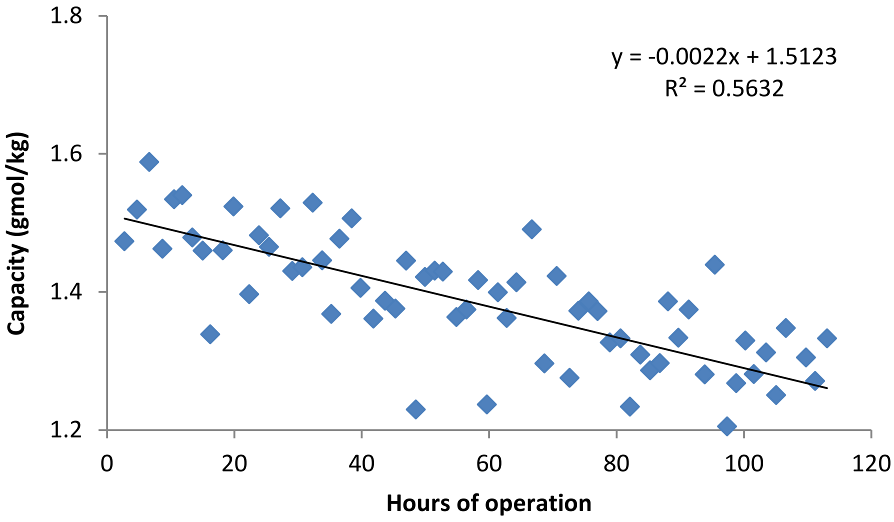


Figure 50. Degradation of 32D sorbent as function of time in use (all 67 points)

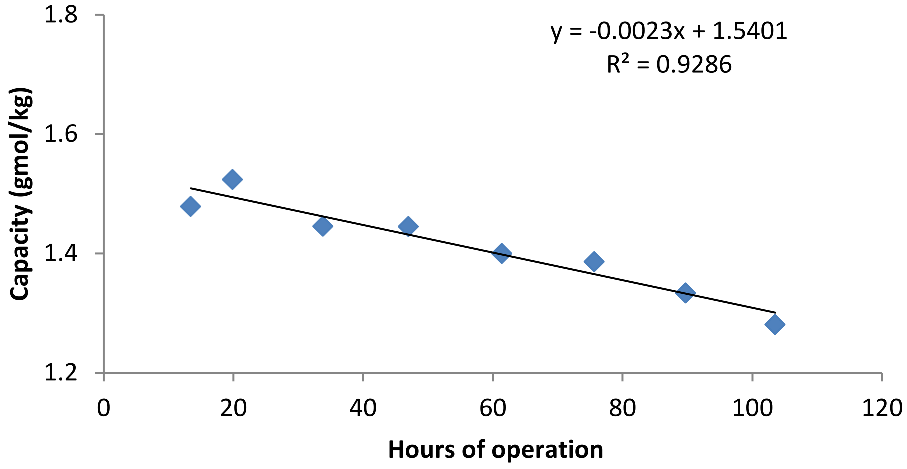


Figure 51. Degradation of 32D sorbent as function of time in use (center points only)

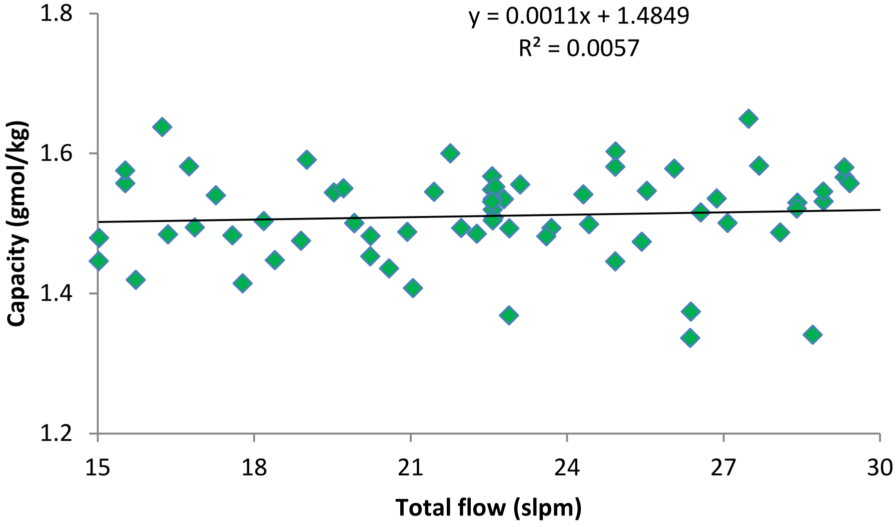


Figure 52. Variation of 32D sorbent capacity as a function of total flow rate

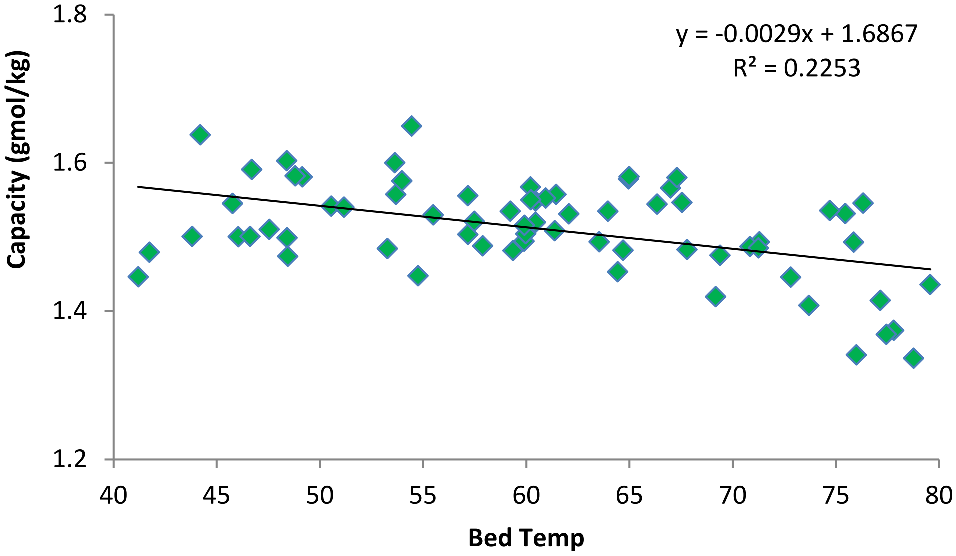


Figure 53. Variation of 32D sorbent capacity as a function of bed temperature

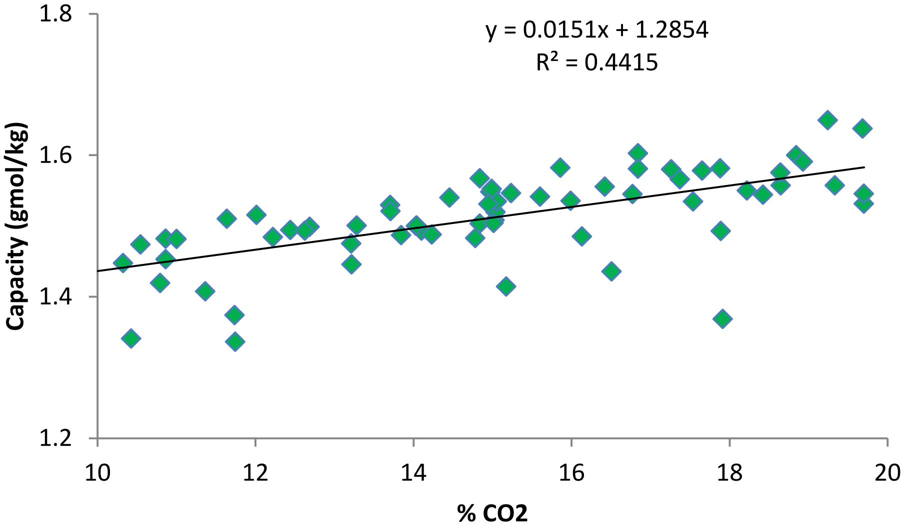


Figure 54. Variation of 32D sorbent capacity as a function of CO_2 concentration

Introduction - Circulation tests

Circulation tests were conducted at NETL using both sorbents under a variety of conditions (circulation rates, CO_2 concentration, flow rates etc.) The tests conducted at NCCC involved 32D sorbent only with a limited number of parameters. Various C2U configurations were employed at NETL as a method to maintain reliable circulation rates: the regenerator was increased in length, relative positions of the loopseals were changed and the riser diameter was decreased. The final version was used at NCCC for those circulation tests.

As observed during batch tests the sorbent was seen to lose the ability to adsorb CO_2 after a period of operation. The amine would appear to disengage from the silica substrate in some portions of the C2U (most notably the regenerator freeboard), forming a sticky substance which would hinder circulation.

The sorbents would adsorb all of the CO_2 exposed to it for a period of time, however, this occurred at low CO_2 concentrations (<6%), higher concentrations the 90% CO_2 removal criteria could not be achieved.

National Carbon Capture Center circulation tests

Sorbent circulation tests at NCCC were performed to investigate for any potential accumulation of heavy metal contaminants on 32D sorbent and, as a secondary consideration, CO_2 capture efficiency. It was desired to circulate the sorbent for 100 hours; however only 43.5 hours of circulation were obtained. A slipstream facility (PC4) supplied flue gas for the heavy metal accumulation tests. The slipstream facility is installed at the Alabama Power Gaston power plant, unit 5, an 880 MW supercritical pulverized coal unit. The flue gas was originally comprised of 76% N_2, 12% CO_2, 6% O_2 and 6% H_2O. Some of the H_2O was removed from the flue gas upstream of the test unit. Other flows, supplied for fluidization, are listed in Table 11. The slipstream did not have sufficient pressure to operate within the test unit; thus the pressure was boosted using vacuum pumps. Two vacuum pumps were used in parallel to deliver a flow rate of approximately 35 slpm of flue gas through the system using both pumps, (18 slpm with a single pump). The tag #s in Table 11 vary slightly from those listed in Table 2, some of the flow controllers were replaced with controllers with different ranges. Also, controllers which had previously supplied simulated flue gas were unnecessary. Flue gas flow rate was monitored using a rotameter.

Table 11. Fluidization flows for heavy metal accumulation tests at NCCC

Tag #	Description	Flow rate	Units
2100	Dipleg	1.0	SLPM
2150	Upper loopseal plenum	5.0	SLPM
3100	Sparger	0.5	SLPM
4150	Regen plenum	5.0	SLPM
3170	Move	0.5	SLPM
4100	Lower loopseal plenum	5.0	SLPM
3150	Underflow	0.5	SLPM

A modification was performed on the C2U unit which differed from experiments conducted previously at NETL. The exit gas flows from the adsorber and regenerator were combined and directed to a site wide flue gas exit line.

Fresh 32D sorbent (7.5 kg) was added to the system. Approximately, forty-four hours of circulation were obtained under steady-state conditions of adsorption/desorption of CO_2. Because the test unit required continuous monitoring by an operator, and only one operator was available, data could not be acquired continuously. Approximately, six-hours of data could be acquired per day. The unit was first brought to the proper thermal conditions (heating of the regenerator) using nitrogen as a substitute for flue gas. This stage would require about one hour. When the regenerator reached the proper temperature, flue gas flow was initiated and the N_2 flow to the adsorber removed. After circulating the sorbent for about six hours, the flue gas flow would be discontinued and substituted with N_2. The oil heater would be switched off and the oil would be allowed to cool while circulating through the regenerator bed. This would reduce the sorbent and regenerator temperatures to an acceptable level (70°C). Cooling would normally require about one-half hour. On the next day of operation, the unit would be brought up to operating temperature and the procedure would be repeated. The sorbent was analyzed for heavy-metal contamination, see Table 6.

A typical circulation condition with 17.5 slpm of flue gas flow introduced approximately 2.0 slpm (5.5 gmol/hr) CO_2. The circulation rate of 32D sorbent during this condition was nominally 8.2 kg/hr. The capacity of 32D sorbent, determined during batch tests, was 1.8 gmol CO_2/kg 32D. Therefore, at this circulation rate, the sorbent had the capacity to adsorb 5.5 slpm of CO_2 assuming equilibrium loadings could be attained.

Initially, the sorbent adsorbed most of the CO_2 exposed to it; however, as hours of operation progressed the adsorption rate declined dramatically. Each point on Figure 55 represents an average of the CO_2 adsorbed during the period of continuous operation for that day of operation. Although detailed analysis of the degradation in performance of the system was not performed, incomplete regeneration of the sorbent is thought to be the cause of the reduced performance, resulting in an elevated lean CO_2 loading and a concomitant lower working capacity. Post-test thermo-gravimetric analysis (TGA) of sorbent samples from the NCCC batch and circulation tests shows no permanent loss of CO_2 capture capacity (see Table 12). Complete regeneration of the sorbent would allow the system to attain the performance initially observed during the first few hours of testing with a fresh inventory of sorbent.

Table 12. TGA Results – Unused, Post-Circulation Test and Post-Batch Test

	Unused	Post Circulation Test	Post Batch Test
Sample Date	10/3	6/15	8/25
Equivalent Hours of FG Exposure	0	44	396
Delta Loading (mol CO2/kg sorbent)	1.39	1.33	1.40

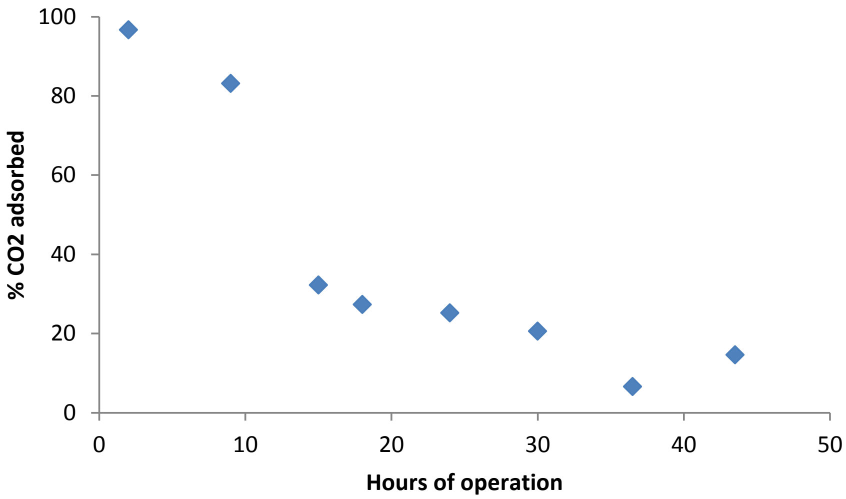


Figure 55. Decline in adsorption efficiency during operation

An example of a typical operational day will be shown using the day depicted by 30 operational hours in Figure 55. The total flow entering the adsorber side consists of the flue gas lower loopseal fluidization (5 slpm N_2), move (0.5 slpm N_2) and sparger (0.5 slpm N_2) flows. Flue gas flow was 17.5 slpm. Including additional flows, the total inlet flow was approximately 23.5 slpm at a temperature of 27°C. The gas analyzer at the exit of the adsorber reported a CO_2 concentration of 7.0 % CO_2; therefore, the amount of CO_2 adsorbed was calculated as 0.42 slpm or 21% of the inputted CO_2, with 1.6 slpm CO_2 escaping.

Total flow entering the regenerator side consisted of regenerator fluidization (10 slpm N_2), upper loopseal (5 slpm N_2) and underflow (0.5 slpm N_2), plus regenerated CO_2. The exit CO_2 concentration was 2.5%, translating into 0.4 slpm CO_2 regenerated. Bed temperature during regeneration was 116°C.

National Energy Technology Laboratory circulation tests

General circulation test procedure

At the beginning of a daily operation of the C2U in the circulating mode, power was initiated to the unit and operating computers. Fluidizing gases were supplied to all reactors. The adsorber was initially suppled with N_2 only at a flow rate that would fluidize but not transport (5 - 10 slpm). Move and sparger supplies remain off until circulation was desired. Heated oil was supplied to the regenerator bringing the sorbent temperature up to the desired level. Once the regenerator bed had reached the desired temperature, move and sparger flows were initiated. N_2 flow to the adsorber was then increased allowing transport of solids through the riser. When the circulation rate was established CO_2 was mixed with the N_2 flow in the adsorber reactor.

Circulation rate

Circulation rates were initially quantified using a diversion valve. A diversion valve existed below the cyclone which allowed solids to be diverted into a sampling chamber and away from the normal flow into the upper loopseal for a short period (30 – 60 seconds). Solids collected in the sampling chamber were weighed and with the collection time known, circulation rate was determined. A correlation between the circulation rate and the pressure drop across the crossover (PDT1841) was created (see Figure 56); thus the diversion valve was infrequently used. If the diversion valve was used frequently then too many solids would be removed from the system, hampering performance.

Using the method described in the terminal velocity section of this report, the terminal velocity of 32D sorbent was found to be 0.11 m/s and AX was about 0.15 m/s. To be able to transport significant amount of solids, the velocity through the riser should be a significant multiple of the terminal velocity. In the preceding “Experimental Apparatus” section, a flow rate of 31 slpm through the riser was examined, produced a velocity of about 1.0 m/s. This is about 9x the terminal velocity of 32D sorbent. Assuming there is a linear relationship between the multiple of terminal velocity and circulation rate then the AX sorbent requires a flow of 42 slpm to achieve the same circulation rate as the 32D with 31 slpm flow.

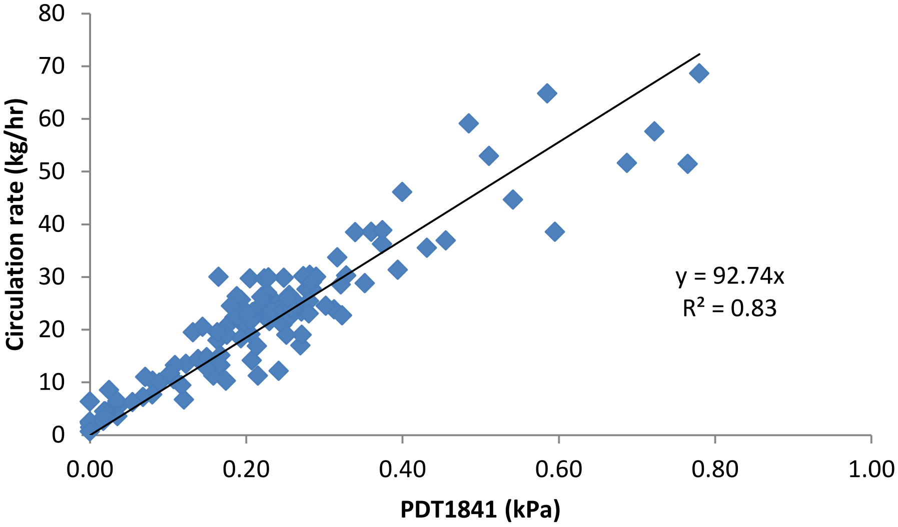


Figure 56. Correlation between circulation rate and crossover pressure drop

The goal of carbon capture using sorbents in a regenerable process employing a circulating bed is to capture CO_2 within a flue gas stream in one reactor, move the solids to a separate reactor where CO_2 is removed, then transport the solids back to the first reactor to adsorb more CO_2. Therefore, the rate at which CO_2 is introduced must be comparable to the sorbent circulation rate coupled with the capacity of the sorbent to adsorb CO_2 and the rate at which CO_2 is desorbed in the regeneration reactor.

From batch tests previously performed, the maximum capacity of the AX sorbent was found to be approximately 2.0 gmol CO_2/kg sorbent and the capacity of 32D sorbent was approximately 1.5 gmol CO_2/kg sorbent. Batch tests yield the maximum capacity and not necessarily the true working capacity. It was shown that the regeneration process initially desorbs the CO_2 rapidly; however, the regeneration rate declined with time (Figure 41). The residence time of the sorbent in the regenerator could be insufficient to fully regenerate the sorbent and therefore the working capacity of the sorbent is a fraction of the total capacity. The size of the fraction depends on the circulation rate, regenerator residence time and total inventory. Adsorber residence time is also critical and determines whether the equilibrium rich loading is attained

Assume AX sorbent is being used and the flue gas flow rate is 41 slpm with 10% CO_2 concentration. Therefore, 4.1 slpm (11.0 gmol/hr) of CO_2 must be adsorbed. Also assume the working capacity is 75% of the maximum capacity, thus the sorbent can adsorb 1.5 gmol CO_2/kg sorbent. To accomplish this, the circulation rate must be at least 7.4 kg/hr. The magnitude of the circulation rate is achievable, as seen on Figure 56, in fact in most cases the circulation rate was well above this value. Therefore, the continuous adsorption of CO_2 should be achievable.

Regenerator extension

The regenerator was lengthened to increase the residence time of sorbent in the regenerator which would increase exposure time at elevated temperatures. Also, the increased head above the L-valve was thought to aid in increasing circulation rate.

The total AX inventory in the C2U during short regenerator tests was about 11 kg, 1.7 kg of which resided in the regenerator. With a circulation rate of 7.4 kg/hr a particle entering the top of the regenerator would exit within 13.7 minutes (822 seconds) assuming the particle transports steadily through the bed as other particles are transported through the L-valve. From Figure 42 and Figure 43, the rate of CO_2 desorption in a 110 °C bed is about 30 liter/hr CO_2 per kg sorbent (1.4 gmol/hr per kg sorbent). This value is comparable to the assumed capacity of 1.5 gmol/kg sorbent. However, in the batch test the sorbent was heated until the CO_2 had been completely removed. Reexamining Figure 41, and looking only at the 120 °C bed and for the interval that a circulating particle would be in the bed, shows that the particle does not completely regenerate. The area under the entire curve on Figure 57 indicates the total amount of CO_2 (55.2 liter) that was regenerated from the 1.7 kg bed. This corresponds to a capacity of 1.3 gmol/kg. (This chart was produced from a batch test where the transition to regeneration phase desorbed some of the CO_2 within the sorbent so the capacity appears lower). The point, however, is that during the residence time of the circulation particle the area under the curve between the lines is only 39 liters or 70% of the total CO_2. This is true for each individual particle, the allowed residence time in the short regenerator permits only 70% desorption of CO_2 within the particle. The extended regenerator length is approximately twice that of the short regenerator, thus the residence time would be double and regeneration should be nearly complete.

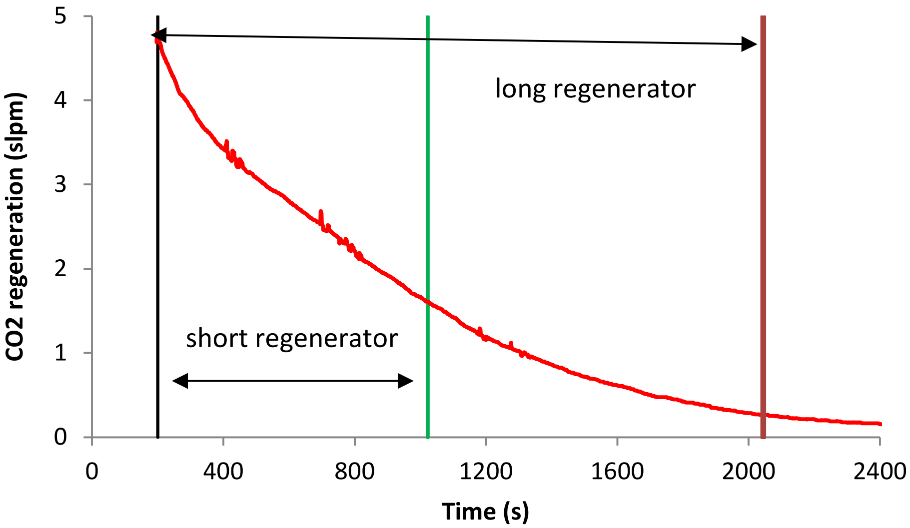


Figure 57. Amount of CO_2 regenerated during particle residence time within regenerator

Circulation tests of AX sorbent at NETL

Tests were performed using both AX and 32D sorbent. AX sorbent was tested in both the short and long regenerator configurations, 32D in the long configuration only. Data examined here for AX sorbent includes short regenerator data acquired from 1/19/13 to 4/20/13 (see Table 13) and long regenerator data acquired 9/10/13 – 11/12/13 (see Table 14).

A circulation rate of approximately 7.4 kg/hr was considered in the analysis above. In practicality, it was difficult to maintain circulation rates this low and confidently measure the circulation rate. One of the major difficulties with the C2U was to maintain a consistent circulation rate; therefore most of the circulation rates employed were higher than optimum.

Circulation tests were performed using the short regenerator where the synthesized flue gas CO_2 concentration was varied between 6 – 20%, regenerator fluidization varied between 5 – 30 slpm and target adsorption temperatures of 60 and 70°C (Table 13). The total adsorber flow was approximately 52 slpm in all cases.

It is desired to remove 90% of the CO_2 from a flue gas stream which is the capture efficiency. During these tests, the capture efficiency reached this criteria when the CO_2 concentration was low but not when the CO_2 concentration was comparable to what would be found in an actual flue gas stream. Figure 58 indicates a good capture efficiency with superior efficiency at low CO_2 concentrations. The capture efficiency increases with sorbent capacity (Figure 59) which is to be expected. From batch tests, the total capacity of AX sorbent was approximately 2.0 gmol/kg, but the working capacity in circulating experiments did not exceed 1.0 gmol/kg. Increasing the sweep gas in the regenerator appears to improve the capture efficiency seen in the adsorber (Figure 60) but there is significant variation at low regenerator fluidization flow conditions.

The regenerator was extended by adding a spool piece as a lower section which extending the bed depth 12 inches. However, the heating coils were simultaneously changed from dual coils to a single set. This may be the reason that a significant difference in results was not seen between configurations. Figure 61 shows a more pronounced effect of CO_2 concentration in the flue gas on capture efficiency using the extended regenerator than seen with the short regenerator. While both configurations had high capture efficiencies with low CO_2 concentrations, the extended regenerator had a greater rate of decline with increased concentration. The extended regenerator showed multiple instances of nearly complete carbon capture but this only occurred at relatively low CO_2 concentrations. Figure 62 indicates a trend of declining capture efficiency with increased sorbent capacity which given the result of Figure 61 would be expected. Figure 63 indicates no correlation between regenerator fluidization and capture efficiency.

Table 13. Test conditions for AX circulation - Short regenerator

					cyc			regen	Total	CO2 in	
	adsorber			Ipsl#2	aeration	underflo	Ipsl#1	dilute	adsorber	ads	T ads
	FTC-1100	FTC-1011	FTC-1200	FTC2100	FTC2150	FTC3170	FTC4100	FTC-3300			TE1961
Run no.	slpm	gph	slpm	slpm	slpm	slpm	slpm	slpm	slpm	%	C
REG0	50.0	10.4	0.0	3.0	0.5	0.5	3.0	0.0	54.9	0.0	
REG0	50.0	10.4	0.0	3.0	0.5	0.5	3.0	0.0	55.0	0.0	
REG1	36.0	27.0	9.0	5.0	1.0	0.5	5.0	25.0	50.7	17.7	75.5
REG1	36.0	27.0	9.0	5.0	1.0	0.5	5.0	40.0	50.5	17.8	70.1
REG2	42.0	27.0	3.0	5.0	1.0	0.5	5.0	40.0	50.5	5.9	61.5
REG2	42.0	27.0	3.0	5.0	1.0	0.5	5.0	40.0	50.5	5.9	65.6
REG0	49.9	27.0	0.0	9.1	0.5	1.0	5.0	12.4	55.5	0.0	68.3
REG0	50.0	27.0	0.0	9.0	1.0	1.0	5.0	15.0	55.6	0.0	78.1
REG3	41.4	27.0	3.0	9.0	1.0	1.0	5.0	15.0	50.0	6.0	70.5
REG3	41.4	27.0	3.0	9.0	1.0	1.0	5.0	15.0	50.0	6.0	78.1
REG2	41.4	27.0	3.0	5.0	1.0	1.0	5.0	5.0	50.0	6.0	67.4
REG2	41.4	0.0	3.0	5.0	1.0	1.0	5.0	10.0	50.0	6.0	69.4
REG4	38.4	27.1	6.0	9.1	1.0	1.0	5.0	0.0	50.0	12.0	77.2
REG4	38.4	27.1	6.0	9.0	1.0	1.0	5.0	15.0	50.0	12.0	71.4
REG5	35.4	27.1	9.0	9.0	1.0	1.0	8.0	0.0	53.2	16.9	60.9
REG5	35.4	27.1	9.0	9.0	1.0	1.0	8.0	30.0	53.8	16.7	71.2
REG6	37.7	48.0	6.0	9.0	1.0	1.0	5.0	0.0	50.1	12.0	71.4
REG6	37.7	48.1	6.0	9.0	1.0	1.0	5.0	15.0	50.0	12.0	72.6
REG6	37.7	48.1	6.0	9.0	1.0	1.0	5.0	30.0	49.9	12.0	72.6
REG7	37.8	48.1	6.0	9.0	1.0	1.0	5.0	30.0	50.0	12.0	72.8
REG7	37.7	48.1	6.0	9.0	1.0	1.0	5.0	30.0	49.9	12.0	74.1
REG8	37.7	48.0	6.0	9.0	1.0	1.0	5.0	30.0	49.9	12.0	61.6
REG8	37.7	48.0	6.0	9.0	1.0	1.0	5.0	30.0	49.9	12.0	70.5
REG9	41.9	48.1	1.7	9.0	1.0	1.0	5.0	30.0	49.8	3.4	51.1
REG9	37.7	48.1	6.0	9.0	1.0	1.0	5.0	30.0	49.9	12.0	67.0
REG10	36.3	48.0	7.5	9.0	1.0	1.0	5.0	30.0	50.2	15.0	57.1
REG10	36.3	48.0	7.5	9.0	1.0	1.0	5.0	30.0	49.7	15.1	65.0
REG11	35.1	48.3	7.5	9.0	1.0	1.0	6.0	30.0	50.2	14.9	47.3
REG11	32.1	44.1	7.5	9.0	1.0	1.0	8.0	30.0	49.4	15.2	74.0
REG12	33.8	48.1	9.0	9.1	1.0	1.0	6.0	30.0	50.4	17.8	72.1
REG12	33.8	48.1	9.0	9.0	1.0	1.0	6.0	30.0	50.5	17.8	59.6
REG13	32.3	48.3	7.5	9.0	1.0	1.0	9.0	30.0	50.3	14.9	78.4
REG13	32.3	48.4	7.5	9.0	1.0	1.0	9.0	30.0	50.2	14.9	69.4
REG14	32.3	48.3	7.5	9.0	1.0	1.0	6.0	30.0	46.7	16.0	69.6
REG14	32.3	48.2	7.5	9.1	1.0	1.0	6.0	30.0	46.6	16.1	75.7
REG15	32.3	48.1	7.5	9.0	1.0	1.0	6.0	30.0	46.6	16.1	75.9
REG15	32.3	48.3	7.5	9.0	1.0	1.0	6.0	30.0	46.6	16.1	69.3
REG16	32.3	48.2	7.5	9.0	1.0	1.0	6.0	30.0	46.6	16.1	69.4
REG16	32.3	48.0	7.5	9.0	1.0	1.0	6.0	30.0	46.6	16.1	74.2
REG17	32.4	48.2	7.5	9.1	1.0	1.0	6.0	30.0	47.1	15.9	69.5
REG17	32.3	48.2	7.5	9.0	1.0	1.0	6.0	30.0	46.6	16.1	78.0
REG13	32.3	48.2	7.5	9.0	1.0	1.0	6.0	30.0	47.0	16.0	77.3
REG13	32.3	48.1	7.5	9.0	1.0	1.0	6.0	30.0	47.0	16.0	76.3
REG18	34.8	48.1	5.0	9.0	1.0	1.0	6.0	30.0	47.1	10.6	29.7
REG18	34.8	48.2	5.0	9.1	1.0	1.0	6.0	30.0	46.7	10.7	71.7
REG18	34.8	48.3	5.0	9.0	1.0	1.0	6.0	30.0	46.6	10.7	70.1
REG19	29.8	48.1	10.0	9.0	1.0	1.0	6.0	30.0	46.6	21.5	83.4
REG19	29.8	48.3	10.0	9.0	1.0	1.0	6.0	30.0	46.6	21.5	83.4
REG19	29.8	48.2	10.0	9.0	1.0	1.0	6.0	30.0	46.6	21.5	81.8
REG20	32.3	48.2	7.5	9.0	1.0	1.0	5.0	14.9	45.7	16.4	27.6
REG20	32.3	48.3	7.5	9.0	1.0	1.0	6.0	30.0	46.9	16.0	63.0
REG20	32.3	48.1	7.5	9.0	1.0	1.0	6.0	30.0	46.5	16.1	55.7

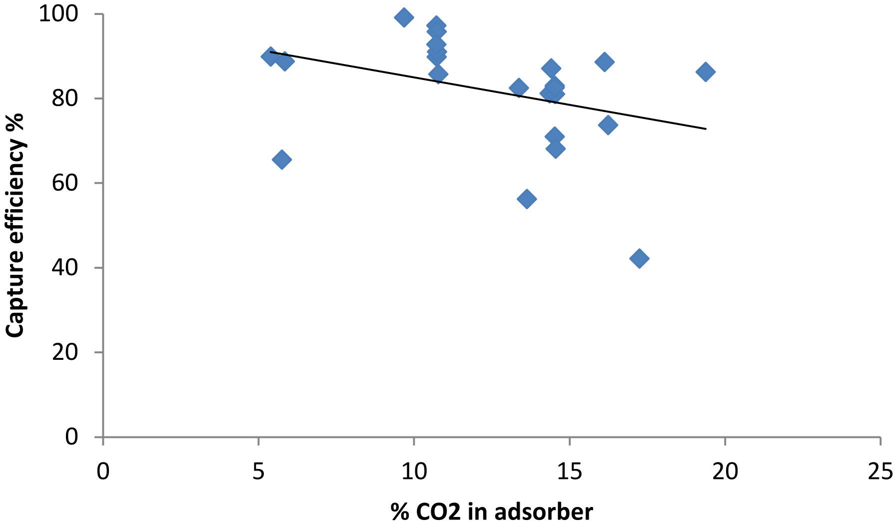


Figure 58. Capture efficiency as function of CO_2 concentration during circulation test with short regenerator

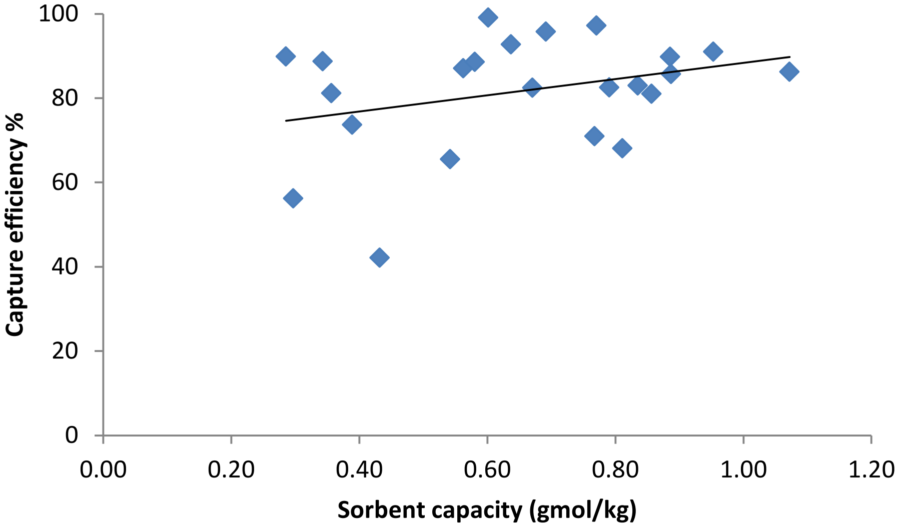


Figure 59. Capture efficiency as function of sorbent capacity during circulation test with short regenerator

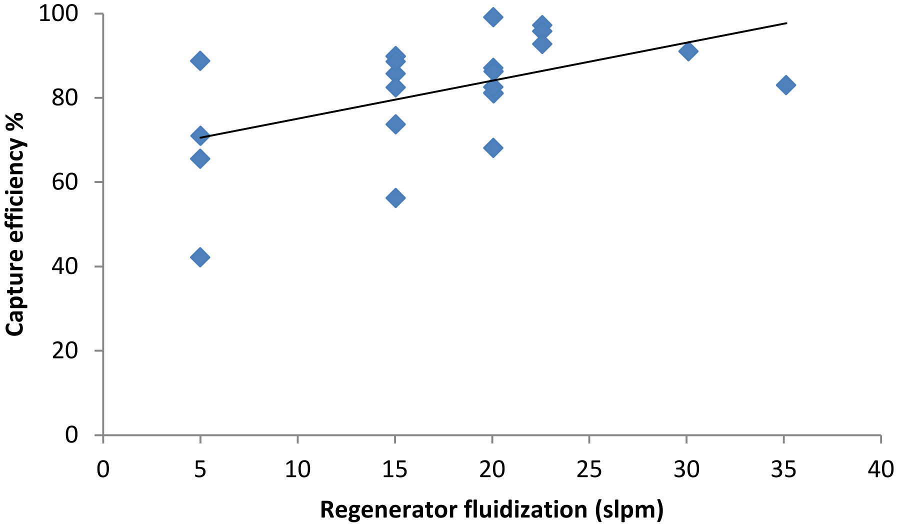
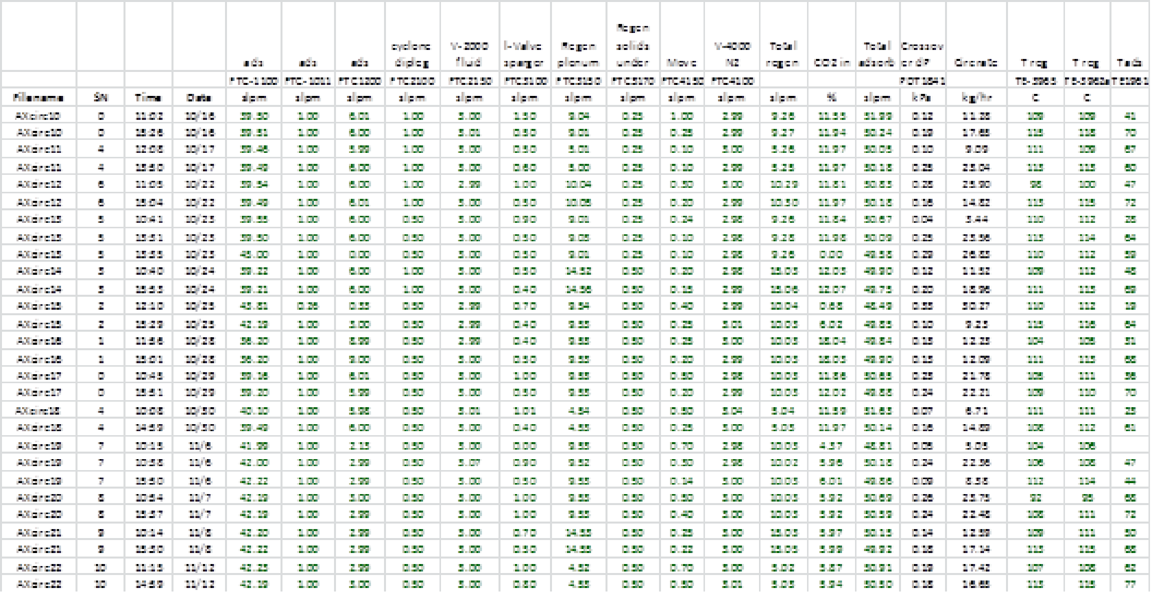


Figure 60. Capture efficiency as function of regenerator fluidization during circulation test with short regenerator

Table 14. Test conditions for circulating AX sorbent extended regenerator 1

				ads	ads	ads	cyclone dipleg	V-2000 fluid	I-Valve sparger	Regen plenum	Regen solids under	Move	V-4000 N2	Total regen	CO2 in	Total adsorb	Crossover dP	Circ rate	T reg	T reg	T ads
				FTC-1100	FTC-1011	FTC1200	FTC2100	FTC2150	FTC3100	FTC3150	FTC3170	FTC4150	FTC4100				PDT1841		TE-3965	TE-3962a	TE1961
Filename	**SN**	**Time**	**Date**	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	%	slpm	kPa	kg/hr	C	C	
AXcirc 1	0	9:24	17-Sep	37.5	0.0	7.5	0.5	3.0	0.5	14.1	1.0	0.5	3.0	15.1	49.8	44.9	0.1	8.2	103	106	19
AXcirc 1	0	10:56	17-Sep	37.5	0.0	7.5	0.5	3.0	0.5	14.0	1.0	0.4	3.0	15.0	49.9	45.0	0.5	48.7	99	94	44
AXcirc2	0	14:01	23-Sep	39.0	0.0	6.0	0.5	3.0	0.5	9.0	1.0	0.5	3.0	10.0	12.3	49.0	0.3	29.4	100	106	33
AXcirc2	0	16:25	23-Sep	39.0	0.0	6.0	0.5	3.0	0.5	9.0	1.0	0.3	3.0	10.1	12.3	48.8	0.1	10.5	114	113	77
AXcirc3	4	12:31	24-Sep	39.0	0.0	6.0	0.5	3.0	0.8	4.0	1.0	0.7	3.0	5.1	12.1	49.5	0.3	28.1	92	87	21
AXcirc3	4	15:58	24-Sep	39.0	0.0	6.0	0.5	3.0	0.5	4.0	1.0	0.5	3.0	5.0	12.2	49.0	0.3	24.0	113	115	60
AXcirc4	6	12:03	25-Sep	39.0	0.0	6.0	0.5	3.0	0.4	9.0	0.5	0.3	3.0	9.6	12.3	48.7	0.3	28.6	107	104	69
AXcirc4	6	15:25	25-Sep	39.0	0.0	6.0	0.7	3.0	0.6	9.0	0.5	0.2	3.0	9.6	12.3	48.8	0.2	19.9	113	110	67
AXcirc5	5	9:49	26-Sep	39.0	0.0	6.0	0.5	3.0	0.8	9.0	1.0	0.0	3.0	10.0	12.3	48.8	0.1	12.2	116	109	47
AXcirc5	5	12:38	26-Sep	38.9	0.0	6.0	0.5	3.0	0.8	9.0	1.0	0.0	3.0	10.1	12.3	48.8	0.1	7.4	113	115	65
AXcirc6	3	12:05	27-Sep	39.0	1.0	6.0	1.0	3.0	0.9	14.0	1.0	0.0	3.0	15.1	12.0	49.9	0.1	12.6	117	118	81
AXcirc6	3	15:28	27-Sep	39.0	0.6	6.0	1.0	3.0	0.8	14.1	1.0	0.0	3.0	15.0	12.2	49.3	0.1	8.8	118	119	76
AXcirc7	2	10:07	30-Sep	42.2	1.0	3.0	1.0	3.0	1.0	9.0	1.0	0.0	3.0	10.0	6.0	50.2	0.2	18.1	107	105	43
AXcirc7	2	13:03	30-Sep	42.2	1.0	3.0	1.0	3.0	0.9	9.0	1.0	0.0	3.0	10.1	6.0	50.1	0.2	16.7	113	113	78
AXcirc8	1	11:06	1-Oct	36.2	0.7	9.0	1.0	3.0	1.0	9.0	1.0	0.0	3.0	10.0	18.0	49.9	0.2	18.8	115	115	77
AXcirc8	1	13:24	1-Oct	36.2	1.0	9.0	1.0	3.0	0.8	9.0	1.0	0.0	3.0	10.0	18.0	50.0	0.2	19.8	117	119	76
AXcirc9	0	10:25	2-Oct	39.2	1.0	6.0	1.0	3.0	1.2	9.0	1.0	0.2	3.0	10.0	11.9	50.6	0.1	8.6	114	118	65
AXcirc9	0	16:45	2-Oct	39.3	1.0	6.0	1.0	3.0	0.7	9.0	0.5	0.1	3.0	9.6	12.0	50.1	0.2	15.6	118	116	67
AXcirc9b	0	11:54	3-Oct	39.2	1.0	6.0	1.0	3.0	0.7	9.0	1.0	0.1	3.0	10.0	12.0	50.1	0.2	17.3	115	115	68
AXcirc9b	0	17:08	3-Oct	39.2	1.0	5.3	1.0	3.0	0.7	9.0	0.5	0.1	3.0	9.5	10.8	49.3	0.2	15.8	119	118	70

Table 15. Test conditions for circulating AX sorbent Extended regenerator 2



				ads	ads	ads	cyclone dipleg	V-2000 fluid	l-Valve sparger	Regen plenum	Regen solids under	Move	V-4000 N2	Total regen	CO2 in	Total adsorb	Crossover dP	Circrate	T reg	T reg	Tads
				FTC-1100	FTC-1011	FTC1200	FTC2100	FTC2150	FTC3100	FTC3150	FTC3170	FTC4150	FTC4100				PDT1841		TS-3963	TS-3962a	TE1961
Filename	SN	Time	Date	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	slpm	%	slpm	kPa	kg/hr	C	C	
AXcirc10	0	11:02	10/16	39.50	1.00	6.01	1.00	3.00	1.50	9.04	0.25	1.00	2.99	9.26	11.53	51.99	0.12	11.28	109	109	41
AXcirc10	0	13:26	10/16	39.51	1.00	6.00	1.00	3.01	0.50	9.01	0.25	0.25	2.99	9.27	11.94	50.24	0.19	17.68	115	115	70
AXcirc11	4	12:06	10/17	39.46	1.00	5.99	1.00	3.00	0.50	5.01	0.25	0.10	3.00	5.26	11.97	50.05	0.10	9.09	111	109	67
AXcirc11	4	13:50	10/17	39.49	1.00	6.00	1.00	3.00	0.60	5.00	0.25	0.10	2.99	5.25	11.97	50.18	0.25	25.04	113	113	60
AXcirc12	6	11:05	10/22	39.54	1.00	6.00	1.00	2.99	1.00	10.04	0.25	0.30	3.00	10.29	11.81	50.83	0.26	25.90	98	100	47
AXcirc12	6	13:04	10/22	39.49	1.00	6.01	1.00	3.00	0.50	10.05	0.25	0.20	2.99	10.30	11.97	50.18	0.16	14.82	113	115	72
AXcirc13	5	10:41	10/23	39.55	1.00	6.00	0.50	3.00	0.90	9.01	0.25	0.24	2.98	9.26	11.84	50.67	0.04	3.44	110	112	25
AXcirc13	5	13:51	10/23	39.50	1.00	6.00	0.50	3.00	0.50	9.05	0.25	0.10	2.98	9.28	11.96	50.09	0.25	23.56	113	114	64
AXcirc13	5	13:53	10/23	48.00	1.00	0.00	0.50	3.00	0.50	9.01	0.25	0.10	2.98	9.26	0.00	49.56	0.29	26.83	110	112	59
AXcirc14	3	10:40	10/24	39.22	1.00	6.00	1.00	3.00	0.50	14.52	0.50	0.20	2.98	15.03	12.03	49.90	0.12	11.52	109	112	45
AXcirc14	3	13:53	10/24	39.21	1.00	6.00	1.00	3.00	0.40	14.56	0.50	0.15	2.99	15.06	12.07	49.73	0.20	16.96	111	113	69
AXcirc15	2	12:10	10/25	43.81	0.26	0.33	0.50	2.99	0.70	9.54	0.50	0.40	2.99	10.04	0.68	46.49	0.33	30.27	110	112	19
AXcirc15	2	13:29	10/25	42.19	1.00	3.00	0.50	2.99	0.40	9.53	0.50	0.25	3.01	10.03	6.02	49.83	0.10	9.23	113	116	64
AXcirc16	1	11:56	10/28	36.20	1.00	8.99	0.50	2.99	0.40	9.53	0.50	0.25	3.00	10.03	18.04	49.84	0.15	12.23	104	108	31
AXcirc16	1	13:01	10/28	36.20	1.00	9.00	0.50	3.00	0.50	9.53	0.50	0.20	2.99	10.03	18.03	49.90	0.13	12.09	111	113	68
AXcirc17	0	10:45	10/29	39.16	1.00	6.01	0.50	3.00	1.00	9.53	0.50	0.30	2.98	10.03	11.86	50.68	0.25	21.76	108	111	56
AXcirc17	0	13:51	10/29	39.20	1.00	5.99	0.50	3.00	0.50	9.53	0.50	0.20	2.99	10.03	12.02	49.88	0.24	22.21	109	110	70
AXcirc18	4	10:08	10/30	40.10	1.00	5.98	0.50	3.01	1.01	4.54	0.50	0.30	3.04	5.04	11.59	51.63	0.07	6.71	111	111	23
AXcirc18	4	14:59	10/30	39.49	1.00	6.00	0.50	3.00	0.40	4.55	0.50	0.25	3.00	5.05	11.97	50.14	0.16	14.69	106	112	61
AXcirc19	7	10:15	11/6	41.99	1.00	2.15	0.50	3.00	0.00	9.53	0.50	0.70	2.98	10.03	4.37	48.61	0.05	3.05	104	106	
AXcirc19	7	10:58	11/6	42.00	1.00	2.99	0.50	3.07	0.90	9.52	0.50	0.30	2.98	10.02	5.96	50.16	0.24	22.56	106	106	47
AXcirc19	7	13:50	11/6	42.22	1.00	2.99	0.50	3.00	0.50	9.53	0.50	0.14	3.00	10.03	6.01	49.56	0.09	8.58	112	114	44
AXcirc20	8	10:54	11/7	42.19	1.00	3.00	0.50	3.00	1.00	9.53	0.50	0.30	3.00	10.03	5.92	50.69	0.26	23.73	92	98	66
AXcirc20	8	13:57	11/7	42.19	1.00	2.99	0.50	3.00	1.00	9.53	0.50	0.40	3.00	10.03	5.92	50.59	0.24	22.48	108	111	72
AXcirc21	9	10:14	11/8	42.20	1.00	2.99	0.50	3.00	0.70	14.53	0.50	0.25	3.00	15.03	5.97	50.13	0.14	12.59	109	111	50
AXcirc21	9	13:50	11/8	42.22	1.00	2.99	0.50	3.00	0.50	14.53	0.50	0.22	3.00	15.03	5.99	49.92	0.18	17.14	113	113	66
AXcirc22	10	11:13	11/12	42.23	1.00	2.99	0.50	3.00	1.00	4.52	0.50	0.70	3.00	5.02	5.87	50.91	0.19	17.42	107	108	62
AXcirc22	10	14:59	11/12	42.19	1.00	3.00	0.50	3.00	0.80	4.53	0.50	0.30	3.01	5.03	5.94	50.50	0.16	16.65	113	113	77

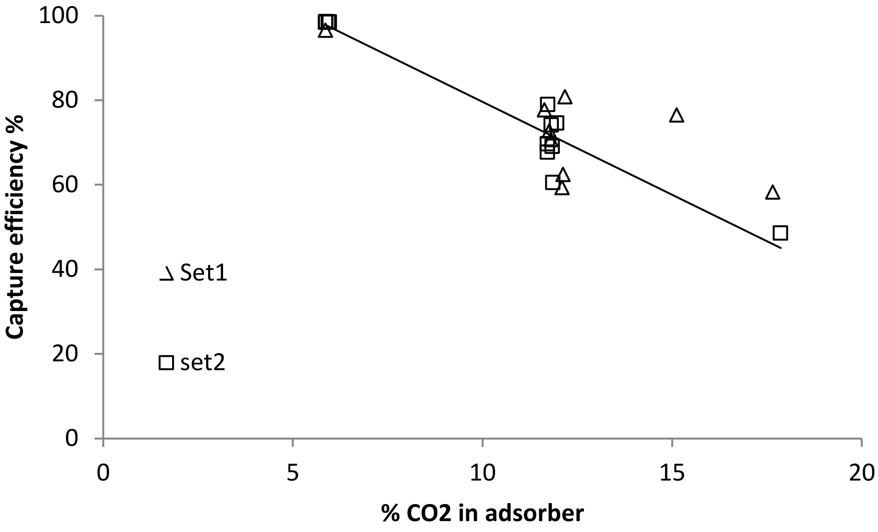


Figure 61. Capture efficiency as function of CO_2 concentration during circulation test with long regenerator

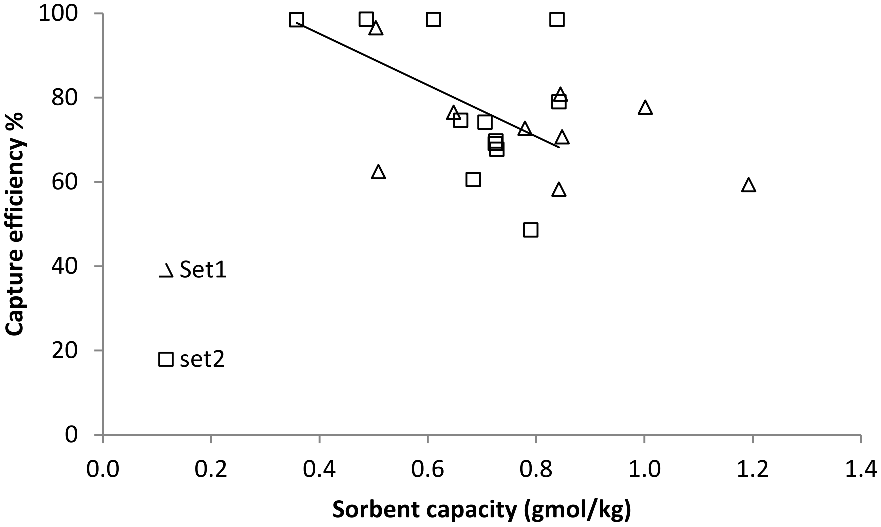


Figure 62. Capture efficiency as function of sorbent capacity during circulation test with long regenerator

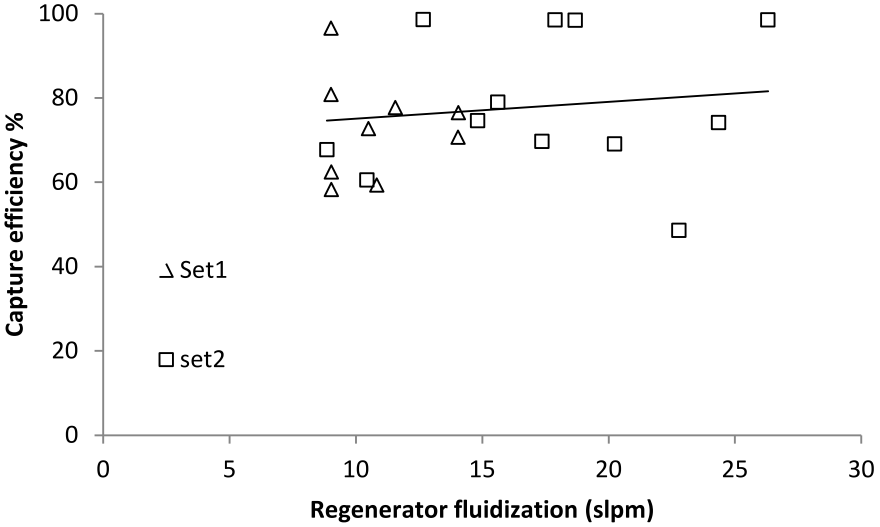


Figure 63. Capture efficiency as function of regenerator fluidization during circulation test with long regenerator

When sorbent was initially loaded, good results would be observed regarding capture efficiency but this would change with time. The morphology of the AX sorbent would change and the ability to fluidize would diminish. Material would begin to adhere to the walls of the vessels; this was most prevalent in the regenerator. Figure 64 shows an example of AX sorbent deposition seen during the second set of AX circulation experiments.

Figure 64. AX sorbent inside regenerator vessel (Photo taken 10/25/13)

Circulation tests of 32D sorbent at NETL

A limited amount of data was acquired for 32D sorbent in the circulating mode with one set acquired 5/17/13 – 5/24/13 in the short regenerator and another set acquired 11/21/13 – 11/26/13 in the long regenerator (Table 16).

During the latter tests samples were extracted from each reactor to determine CO_2 loading on the sorbent (Table 17). Samples were extracted using a tube inserted through each reactor wall. Approximately 5 g of sorbent was extracted and retained in a reservoir. The reservoir was weighed and then placed in an oven that was heated to 110°C. Nitrogen flowed through the reservoir during heating and the CO_2 composition of the outflowing gas was measured using an IR based analyzer. When the outflowing CO_2 fraction reached near zero the reservoir was extracted from the oven and then reweighed. This allowed two methods for determining the amount of CO_2 captured by the sorbent: before and after heating weight difference and the integrated value of CO_2 composition over time. With the weight loss method the adsorption of H_2O was unaccounted for which may account for the significant amount of variation is seen in the data.

Regenerator samples were extracted near the bottom of the reactor and should be relatively free of CO_2. The amount of CO_2 still remaining in the sorbent after regeneration was still about 1.0 gmol/kg (average of the two methods). The lower loopseal capacity should be the lowest since this is the “fully regenerated” sorbent prior to CO_2 exposure but it is consistently higher than expected (1.63 gmol/kg). The upper loopseal should have the most CO_2 but this was lower than expected (1.68 gmol/kg). However, there was preheating in the upper loopseal, thus some CO_2 may have been liberated prior to extraction. The adsorber sample had the largest capacity, 2.23 gmol/kg. The apparent averaged working capacity from these tests was 1.2 gmol/kg by subtracting the capacity seen in the regenerator from that seen in the adsorber.

Nearly the same capacity is seen during circulation when the circulation rate and CO_2 adsorption rates are considered (Figure 65) with capacity slightly declining with circulation rate. The single point with a high capacity and very low circulation rate is questionable. An increase in capture efficiency is also observed with increasing circulation rate (Figure 66).

Table 16. Setpoints for 32D circulation tests

		32D-circ2	32D-circ1	32D-circ3	32D-circ4	Circ2-32D-1	Circ2-32D-2	Circ2-32D-3	Circ2-32D-4
Date taken		5/21/13	5/22/13	5/23/13	5/24/13	11/21/13	11/22/13	11/25/13	11/26/13
Adsorber N2 flow	slpm	35.8	35.8	35.8	27.5	27.4	27.4	27.4	27.4
Adsorber CO2 flow	slpm	7.5	7.5	7.5	6.0	4.2	4.2	4.2	4.2
H2O adsorber	gm/hr	33.8	33.8	33.8	33.8	33.8	33.8	33.8	33.8
Total adsorber flow	slpm	50.0	50.0	50.0	40.0	35.0	35.0	35.0	35.0
H2O	%	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
CO2	%	15.0	15.0	15.0	15.0	12.0	12.0	12.0	12.0
T_{ads}	°C	70	70	70	60	70	70	70	70
Total regen flow	slpm	15	10	20	15	5	3	5	5
T_{reg}	°C	120	120	120	120	110	110	110	110

Table 17. Amount of CO_2 found in 32D sorbent from each reactor

			Circ2-32D-1	Circ2-32D-2	Circ2-32D-3	Circ2-32D-4	Average	Average of both methods
Adsorber	Sorbent mass extracted (g)	g	4.74	4.79	4.71	4.66	4.72	
	CO_2 msss (g)	g	0.42	0.33	0.35	0.34	0.36	
	Capacity from mass loss	gmolCO_2 per kg sorbent	-	1.68	1.82	1.79	1.76	2.23
	Capacity from integrated CO_2	gmolCO_2 per kg sorbent	-	2.78	3.18	2.10	2.69	
Upper loopseal	Sorbent mass extracted (g)	g	5.87	7.19	7.01	6.98	6.76	
	CO_2 msss (g)	g	0.42	0.51	0.62	0.6	0.54	
	Capacity from mass loss	gmolCO_2 per kg sorbent	1.72	1.78	2.21	2.47	2.05	1.68
	Capacity from integrated CO_2	gmolCO_2 per kg sorbent	1.34	1.3	1.27	1.35	1.32	
Regenerator	Sorbent mass extracted (g)	g	4.6	4.76	4.58	4.59	4.63	
	CO_2 msss (g)	g	0.27	0.26	0.23	0.17	0.23	
	Capacity from mass loss	gmolCO_2 per kg sorbent	1.41	1.31	1.20	0.87	1.20	1.03
	Capacity from integrated CO_2	gmolCO_2 per kg sorbent	0.96	0.89	0.76	0.83	0.86	
Lower loopseal	Sorbent mass extracted (g)	g	5.06	5.27	3.56	5.24	4.78	
	CO_2 msss (g)	g	0.35	0.3	0.13	0.22	0.25	
	Capacity from mass loss	gmolCO_2 per kg sorbent	1.69	1.37	0.86	1.00	1.23	1.63
	Capacity from integrated CO_2	gmolCO_2 per kg sorbent	2.32	2.03	1.82	1.95	2.03	

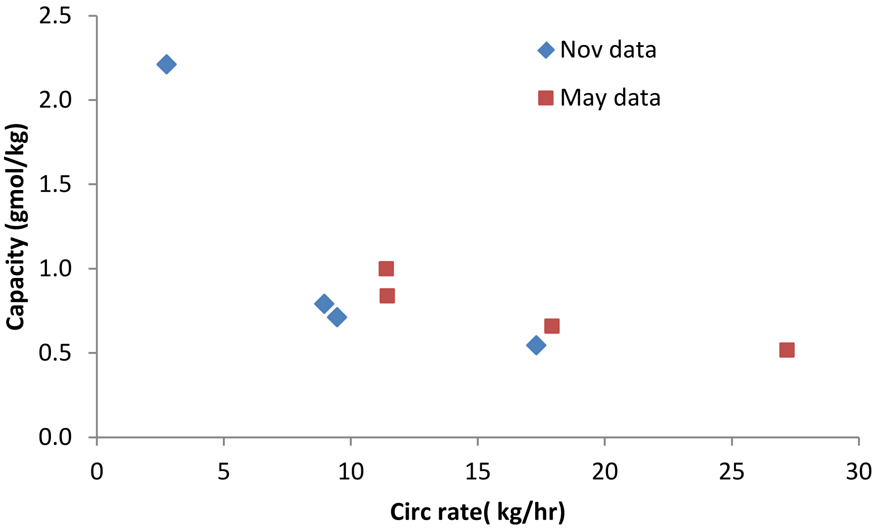


Figure 65. Working capacity of circulating 32D sorbent

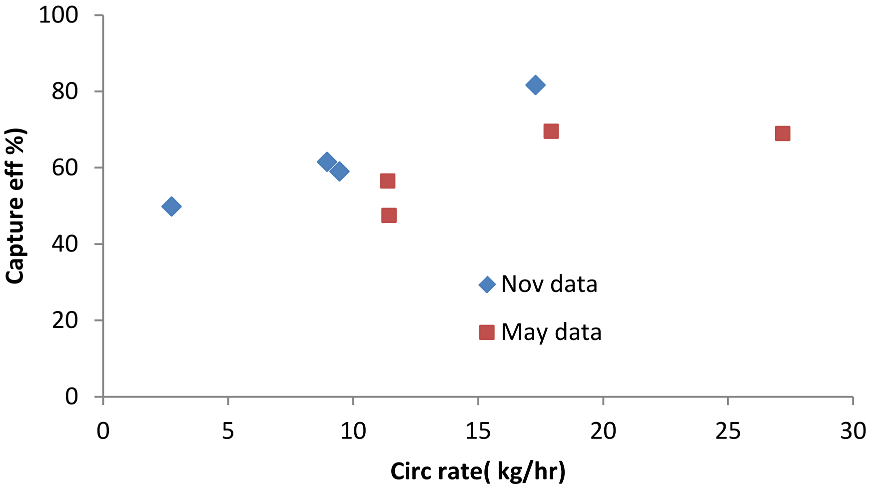


Figure 66. Capture efficiency of circulating 32D sorbent

Conclusions

- A Carbon Capture Unit (C2U) that utilizes aminated sorbent to capture carbon dioxide from flue gas was designed and constructed at the National Energy Technology Laboratory in Morgantown West Virginia. After approximately three years of operation at NETL, the unit was moved to the National Center for Carbon Capture in Wilsonville, Alabama in January 2014 to take advantage of the PC4 flue gas slipstream. Testing of the C2U was conducted at the NCCC to determine if exposure to flue gas in continuous and batch mode would result in the accumulation of trace elements on the 32D sorbent or degradation of the sorbent.

- In the circulating mode, a total of 43.5 hours of testing was observed. A reduction in the system's capacity to capture CO_2 was seen as testing progressed. Incomplete regeneration of the sorbent is thought to be the cause of the reduced performance, resulting in an elevated lean CO_2 loading and a concomitant lower working capacity. Post-test thermo-gravimetric analysis (TGA) of sorbent samples from the NCCC circulation tests shows no permanent loss of CO_2 capture capacity.

- In the batch mode, tests were conducted with diluted and neat flue gas for an equivalent exposure of 397 hours. No regeneration of the sorbent was conducted. Samples taken before testing, after the circulating tests, after the diluted batch tests and after the neat batch tests showed that, in all cases, the trace element concentrations were significantly lower than the hazardous waste standards. Due to the possibility of trace elements being removed from the flue gas prior to exposure to the sorbent, chemical analysis of the inlet flue gas stream is recommended to better gauge trace element accumulation. Similar to the results in the circulating tests, post-test thermo-gravimetric analysis (TGA) of sorbent samples from the NCCC batch tests showed no permanent loss of CO_2 capture capacity.

References

1. Fisher, D., Keller, G. Process Analysis and R&D Plans Forward for Dry-Sorbent Based Processes for Removal of CO_2 from Power Plant Flue Gas, Mid Atlantic Technology, Research and Innovation Center, 2006.

2. Monazam, E. R., Spenik, J. L., Shadle, L. J., Fluid bed adsorption of carbon dioxide on immobilized polyethylene (PEI):Kinetic analysis and breakthrough behavior, Chem. Eng. J., 223 (2013) 795-805.

3. Monazam, E. R., Spenik, J. L., Shadle, L. J., CO_2 desorption kinetics for immobilized polyethylenimine (PEI) Energy and Fuels, 28 (2014) 650-656.

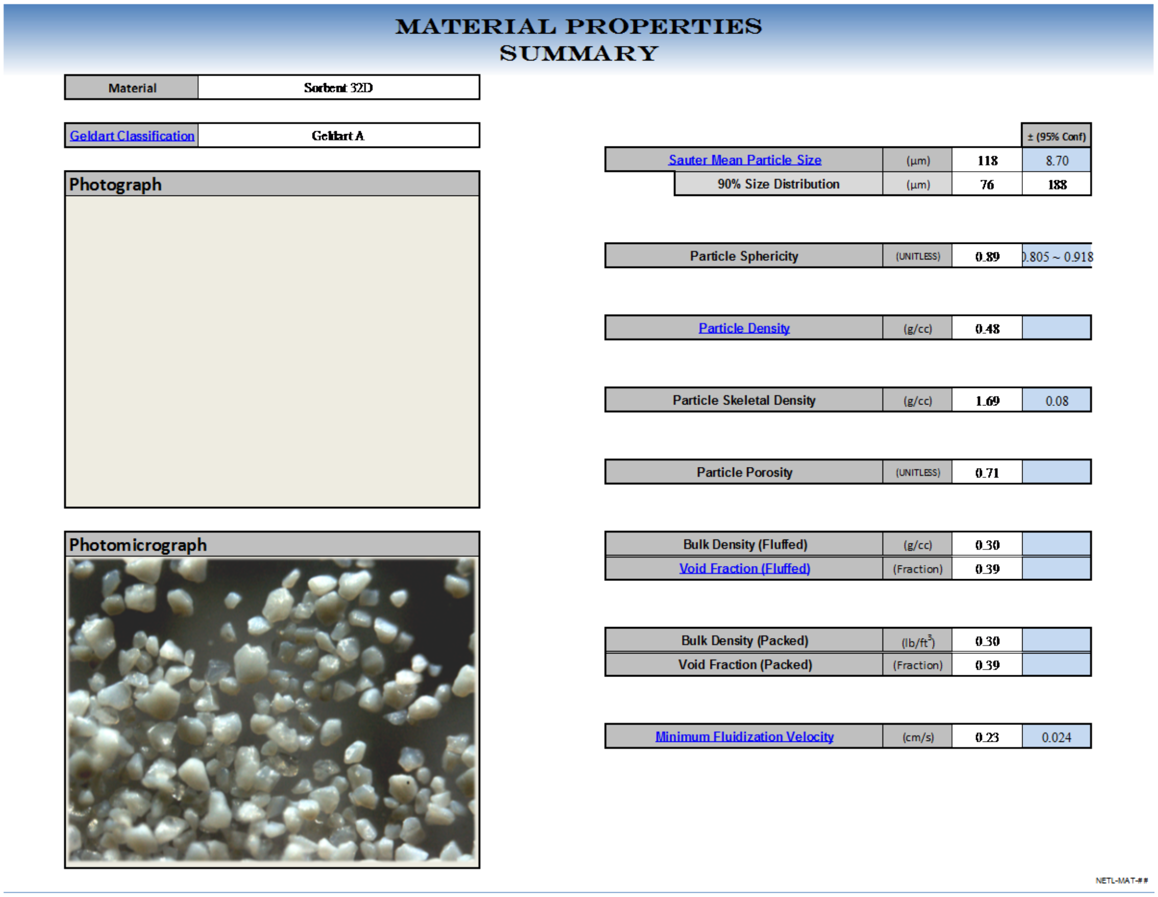
4. Yang, WC, Handbook of Fluidization and fluid-particle systems, Marcel Dekker Inc., (2003)

5. CFR 261.24 Identification and Listing of Hazardous Waste – Toxicity Characteristic

6. http://www.epa.gov/wastes/hazard/testmethods/faq/faq_tclp.htm

Appendix Sorbent properties

Sorbent 32D



MATERIAL PROPERTIES SUMMARY

Material	Sorbent 32D
Geldart Classification	Geldart A

Photograph

Photomicrograph

			± (95% Conf)
Sauter Mean Particle Size	(µm)	118	8.70
90% Size Distribution	(µm)	76	188
Particle Sphericity	(UNITLESS)	0.89	.805 ~ 0.918
Particle Density	(g/cc)	0.48	
Particle Skeletal Density	(g/cc)	1.69	0.08
Particle Porosity	(UNITLESS)	0.71	
Bulk Density (Fluffed)	(g/cc)	0.30	
Void Fraction (Fluffed)	(Fraction)	0.39	
Bulk Density (Packed)	(lb/ft^3)	0.30	
Void Fraction (Packed)	(Fraction)	0.39	
Minimum Fluidization Velocity	(cm/s)	0.23	0.024

NETL-MAT-##

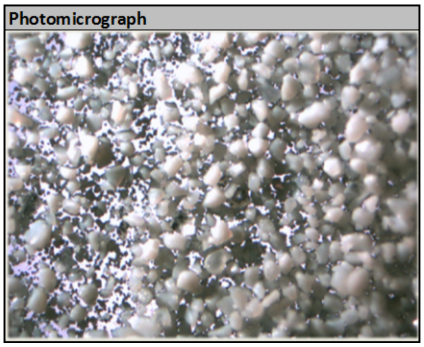
Sorbent AX

MATERIAL PROPERTIES SUMMARY

Material	Sorbent Ax
Geldart Classification	Geldart A

Photograph

Photomicrograph



			± (90% Dist)
Sauter Mean Particle Size	(µm)	115	44 ~ 163
Sphericity	(UNITLESS)	0.86	
Particle Porosity	(UNITLESS)	#DIV/0!	
			± (95% Conf)
Particle Skeletal Density	(lb/ft^3)	#DIV/0!	#DIV/0!
	(g/cc)	#DIV/0!	#DIV/0!
			± (95% Conf)
Particle Density	(lb/ft^3)	56.16	
	(g/cc)	0.90	
			± (95% Conf)
Bulk Density (Fluffed)	(lb/ft^3)	33.80	
	(g/cc)	0.54	
Void Fraction (Fluffed)	(Fraction)	0.40	
			± (95% Conf)
Bulk Density (Packed)	(lb/ft^3)	33.80	
	(g/cc)	0.54	
Void Fraction (Packed)	(Fraction)	0.40	
			± (95% Conf)
Minimum Fluidization Velocity	(ft/s)	0.02	0.002
	(cm/s)	0.48	0.054
			± (95% Conf)
Deaeration Rate	(1/s)		