National Carbon Capture Center: Post-Combustion

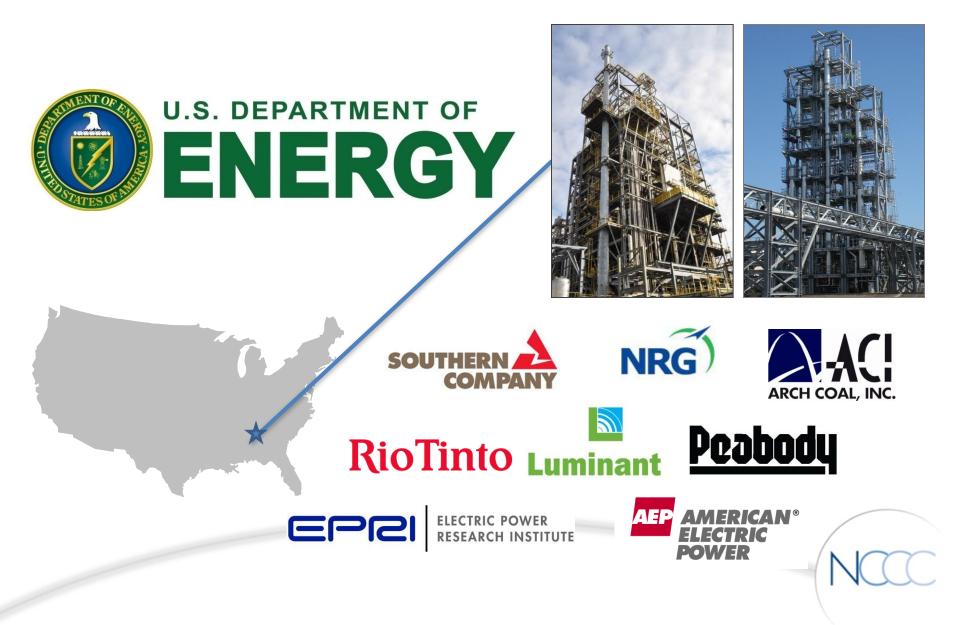
2012 NETL CO₂ Capture Technology Meeting

July 10, 2012



National Carbon Capture Center

Project Funding



DOE-Funded CO₂ Capture Test Facilities in Wilsonville, Alabama



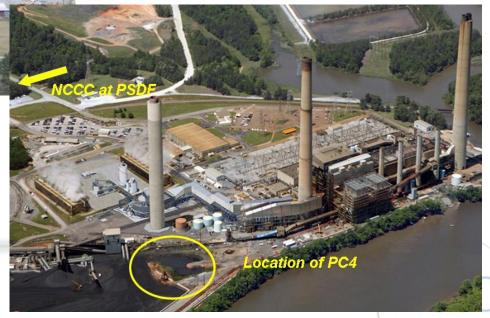
Power Systems Development Facility (PSDF) started combustion testing June 1996 and gasification Sept. 1999.

In May 2009 PSDF transitioned to the National Carbon Capture Center (NCCC).

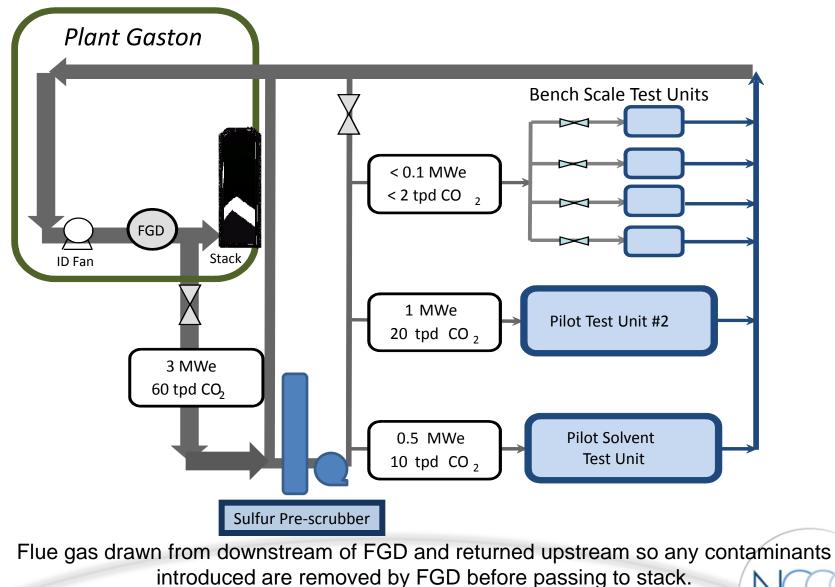
Existing facilities used to support development of pre-combustion CO₂ capture.

Additional facility, the Post-Combustion CO₂ Capture Center (PC4) built and started testing March 2011.

Located at adjacent power plant, Alabama Power's Plant Gaston.



Layout of PC4



Recap of MEA Baseline Run

- The 1140-hour MEA baseline test was completed May 2011
 - Achieved steady operation under controlled conditions
 - Competed 23 balance periods with good mass balance closures
 - Concluded that PSTU is ready to test developer's solvents and collect reliable data in support of commercialization
 - Some issues identified that required further investigation
 - MEA carryover greater than vapor equilibrium value
 - Exceeds VOC limits: excessive solvent make up rates
 - Labs used declined to measure degradation products in solvent
 - Degradation products in regenerated CO₂ stream not sampled
 - End-of-run analysis of solvent revealed selenium and chromium contents, each in excess of 1 ppm

Second MEA Test Campaign

- Follow-up program required to investigate issues raised in first MEA Test Campaign
 - Around 55% of solvent used was from previous run
- 400 hours of operation, March 6-23, 2012.
- 9 test periods with 30% MEA supported with mass and heat balances.
- Held at one set of flow rates but varied beds and intercoolers in service
 - 5000 lb/hr flue gas with 20,000 lb/hr solvent: L/G = 4.0
 - Steam 1400 lb/hr: S/L = 0.07
 - 3 beds, 0 and 2 intercoolers
 - 2 beds, 0 and 1 intercooler
 - CO₂ capture efficiency in line with previous results

Other Testing at PC4

- B&W OptiCap[™] solvent tested for ~2000 hours
- Currently testing Hitachi's H3-1 solvent
- Preparing to test Cansolv and Chiyoda solvents
- Aker's Mobile test Unit collected data for over 2,000 hours in latter half of 2011
- Amine solvent tested developed as part of SOLVit Program in Norway
- MTR's 0.05-MW CO₂ separation membrane approaching 500 hours of testing
- Modified version of unit tested at Arizona
 Public Service Cholla plant
- Tested Codexis enzyme in MDEA using their pilot module



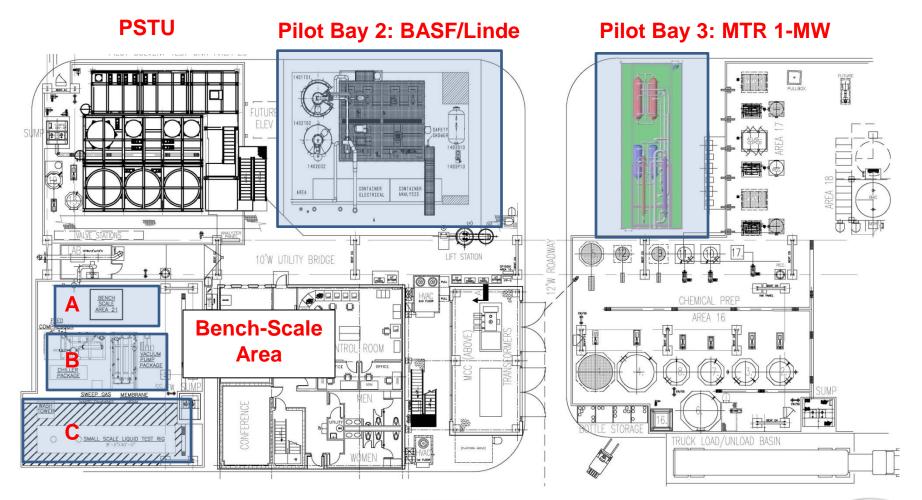
MTU being installed next to PSTU

Post-Combustion Test Plan for 2012

	1 st qtr		2 nd qtr		3 rd qtr	4 th qtr
	Post-Combustion					
PSTU		nd MEA Solvent Test		HITACHI Inspire the Next	<u>Cansolv</u>	CHIYODA
2 nd Pilot Bay	6	ker CleanCa	arbon"			
Bench Scale #1		CODEXIS				AKERMIN
Bench Scale #2	Membrane Technology & Research					

- Preparing to test MTR's 1-MW CO₂ separation membrane in 2013.
- Recently announced Linde had received \$15M award from DOE to build 1-MW integrated pilot plant to test CO₂ solvent (supplied by BASF) at NCCC. To be operational in 2014.

PC4 Test Locations



A. Codexis then Akermin B. MTR 0.05-MW

C. SSTU

PC4 Pilot Bay Units

1401701 NCCC provides industrial experience to support developers on site integration, construction, and safety/environmental compliance. 🗆 = BASF The Chemical Company 1402102 inde CROSSING TO PIPE RACK 1401K01 1402E04 1401A01 1401E12 SOUTHERN COMPAN 1403810 1403P10 MTR 1-MW Membrane Module 1402P01A 1402E02 BASF/Linde 1401P12 14016 CONTAINER 1-MW Pilot Plant ELECTRICA

PC4 Bench-Scale Units

Slipstream Solvent Test Unit

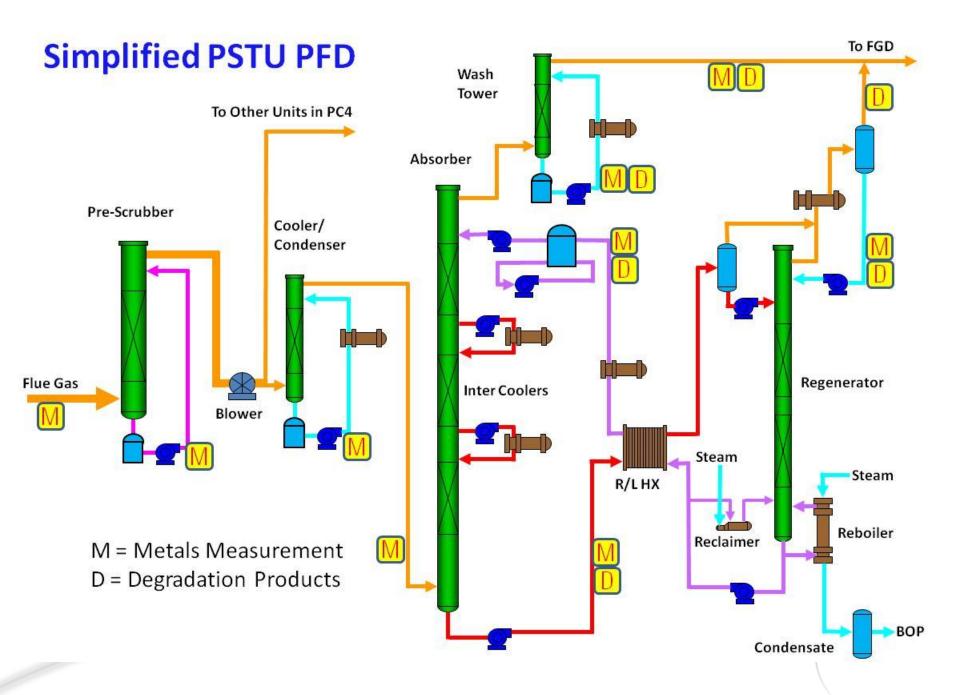


MTR 0.05-MW Membrane Module

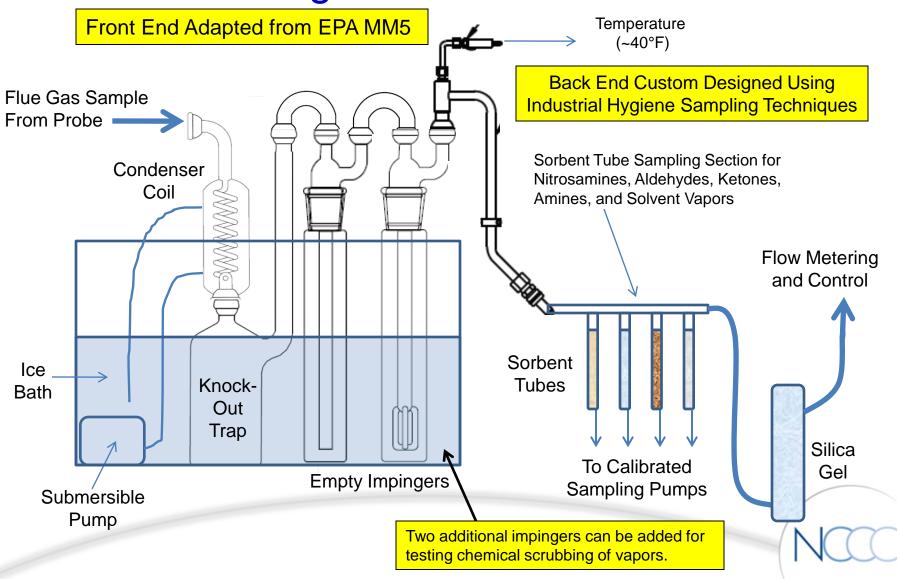
 NCCC provides similar support to that for pilot-bay units and makes modifications to allow testing to proceed.



Codexis Test Module



NCCC Sampling System for Amine and Degradation Products



Solvent Carryover

- During the baseline test, the MEA emissions from the PSTU were in excess of 100 ppmv
- Vapor emissions level was predicted to be less than 3 ppmv
- SO₃ aerosol (~0.1 micron) present in flue gas leaving Gaston scrubber
 - Too small to scatter much light so flue gas appears clear
- In warm absorber aerosol grows to sizes that scatter light efficiently (>1 micron) and a fog appears
 - These small droplets are not collected efficiently in wash tower and many escape with CO₂-depleted flue gas
 - Theorized controlling absorber temperature (higher or lower) may increase droplet size, making them more easily removed, and lower MEA carryover

Results of MEA Carryover Tests

Test	Beds	Inter- Coolers	Max Temp °F	MEA in Wash Water, %	MEA Emission Rate Total, lb/hr		
Alabama Bituminous Coal (flue gas SO ₃ 1.8 ppmv)							
1	3	0	174	1.05 (1)	2.1		
2	3	2	160	0.98 (2)	7.3		
3	2	1	162	1.06 (2)	4.9		
4	2	1	163	0.22 (3)	3.8		
5	2	0	174	0.92 (1)	1.1		
6	2	1	164	5.58 (1)	5.9		
Higher Sulfur Illinois Coal (flue gas SO ₃ 3.2 ppmv)							
7	2	0	176	1.16 (1)	1.8		
8	2	0	175	1.02 (1)	2.1		
9	2	0	175	1.08 (1)	1.7		

(1) Intrinsic values

ues (2) Adjusted to ~ 1%

to ~ 1% (3) Redu

(3) Reduced using fresh water

MEA carryover:

Increased with and SO₃ level and upper absorber bed inactive Decreased with wash water MEA content and solvent temperature

SO₃ and MEA Carryover

- Single-stage wash tower designed from data collected with bottled gases.
 - Shows value of using coal-derived flue gas.
- Investigating adding wash stages incorporating condensate from regenerator that has low MEA concentration.
- Contacting suppliers to identify more efficient demisters.
- Acid wash column or wet ESP after wash tower may help.
 - Ideas such as these could be investigated on slipstream solvent test unit (SSTU).
- Hitachi and MHI have processes that cool flue gas to between acid and water dew points so SO₃ condenses on fly ash to be neutralized by alkali present.
- Alstom has Integrated Emissions Control System combining SDA with FGD, SDA removing chlorine and SO₃.

Amine and Degradation Product Carryover

Analyta	Wash Tower Outlet, ppm		Regenerator Outlet, ppm	
Analyte	Vapor (1)	Liquid (2)	Vapor (1)	Liquid (2)
MEA	4.40	131	0.061	ND
Formaldehyde	0.035	0.28	0.505	1.58
Acetaldehyde	0.63	0.063	1.78	0.36
Ammonia	53.7	86.4	0.152	3.3
Ethyl amine	0.036	ND	ND	ND
Acetone	NM	0.18	NM	0.033
Acetonitrile	NM	0.039	NM	0.023
Acetic acid	NM	0.021	NM	0.020
Propionic acid	NM	0.23	NM	0.26
N-Nitrosodimethylamine	0.000225	ND	0.0000058	ND
N-Nitrosodiethanolamine (NDELA)	0.00106	ND	ND	ND

(1) As vapor sample by sample tubes

(2) Removed in sample train condensed liquid but expressed as ppmv in vapor stream

ND - not detected

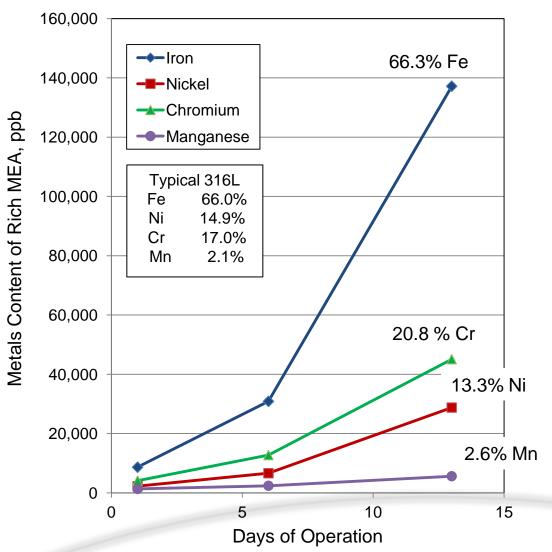
NM - not measured

Heavy Metals in MEA

NA-1-L-	Inlet Gas,	Liqu	Suspected Source			
Metals	ppb	Fresh MEA	Makeup Water	Rich MEA End(*)	of Metal Buildup	
Arsenic	3.62	<12	0.46	219	Flue Gas	
Barium	10.90	<12	54.3	265	Flue Gas	
Cobalt	<0.23	<12	0.43	1,020	Corrosion (?)	
Chromium	1.01	<12	0.93	45,090	Corrosion	
Manganese	239	<60	83.2	5,620	Flue Gas & Corrosion	
Nickel	0.66	24.8	2.42	28,770	Corrosion	
Selenium	31.3	44.1	<0.23	1,950	Flue Gas	
Zinc	9.5	<120	27.4	940	Flue Gas	
Iron	56.6	191	18,410	137,200	Corrosion	

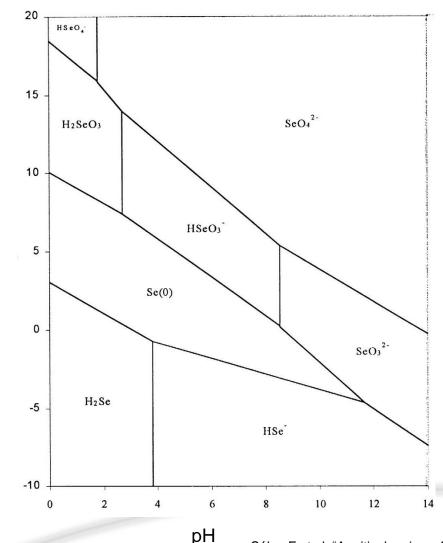
Elements below detection limits : Silver, Beryllium, Cadmium, Copper, Lead, Antimony, Thallium (*) 50:50 fresh MEA and MEA from 2011 tests

Major Constituents of 316L



- Proportions of Fe:Cr:Ni:Mn in solvent are close to those in 316L
- Stainless selected to resist corrosion but inhibitor appears still to be required

Selenium Chemistry



Oxidation-reduction potential



- At end of run 50% selenide, 25% selenite, 25% elemental, selenate below LDL.
- pH of solvent in range 9 to 10.
- Adding hydrogen peroxide (for example) changes valence state from selenide (-2) to selenate (+6).
- At VS 4 the non-toxic selenite can precipitate out using iron or polymers
- Speciating other metals to identify how they also might be removed.

Séby, F et al, "A critical review of thermodynamic data for selenium species at 258°C", Chemical Geology 171, pp173 to 194, 2001.

Selenium Findings

- Levels of total selenium in the MEA exceed allowable RCRA limits of 1 ppm for hazardous waste classification.
- Established water treatment processes but may need to be adapted to this new requirement.
- Contacting water treatment experts to identify removal approaches.
- Laboratory program to evaluate approaches with potential for commercial application.
- Test selected approaches on SSTU.
- Working closely with other carbon capture research projects to find a path forward.
- Gaston has an ESP for particulate clean up. Selenium transmissions may be lower with a baghouse.

Results are preliminary. Work is being done with partners and technology developers to confirm and determine the details of the issue.

Summary

- PC4 is a flexible facility that allows multiple technologies to be tested simultaneously at different scales.
 - Almost 6,500 data collecting hours since March 2011 supporting five developers plus MEA baseline testing on PSTU.
- Provide real industrial expertise to support developers looking to test their technology on real coal derived flue gas.
 - Engineering support to facilitate site integration as well as compliance with safety and environmental regulations.
 - On site E&I, I&C, and mechanical maintenance support for on-the-go upkeep on equipment for continuous operation.
- Continuously upgrading infrastructure to support other developers.
- Contract negotiations in progress to bring future developers to site.
- MEA results from PSTU show significant value to be gained from testing with coal-derived flue gas.
 - Some unexpected results were found but research infrastructure is well established to resolve issues as they arise.