National Carbon Capture Center: Post-Combustion CO₂ Capture Program

John Wheeldon, Science and Technology Team Leader, NCCC

NETL CO₂ Capture Technology Meeting Pittsburgh, July 8 to 11, 2013



National Carbon Capture Center

NCCC Team



- DOE major funder with several co-funders providing essential cost share.
- NCCC gratefully acknowledges their support and encouragement with special thanks to our NETL Project Manager, Mike Mosser.

DOE-Funded CO₂ Capture Test Facilities in Wilsonville, Alabama



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

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

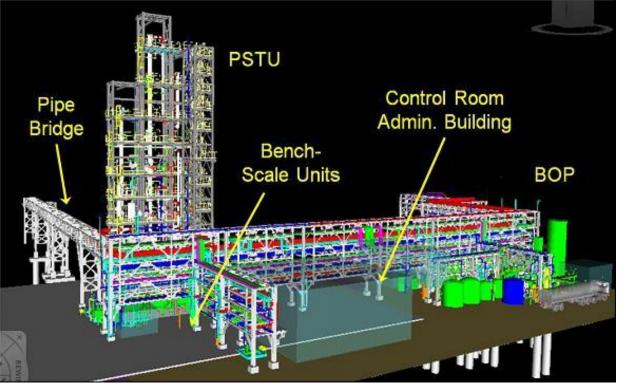
Existing facilities used to support development of pre-combustion CO_2 capture technologies.

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, which provides commercially representative flue gas for testing (hot ESP, SCR, and wet FGD).



Views of PC4 and Pilot Solvent Test Unit (PSTU)





Computer-generated view of PC4

View of 0.5-MW PSTU

Flexible facility supporting investigation of different technologies over a range of sizes thereby accelerating their commercialization.

Testing Support to Advance Developer's Technologies is NCCC's Top Priority



- NCCC provides first-class facilities to test developer's technologies for extended periods under commercially representative conditions with coalderived flue gas and syngas.
- Supports transition from laboratory to commercial environment.
- Civil, electrical, mechanical, and controls design support, and maintenance and construction services.
- All necessary infrastructure to support testing of developer's technology.
- Experienced operators and maintenance staff.
- Comprehensive data collection and analysis capability.
- Access to advanced analytical techniques at SRI/UAB Birmingham.
- Flexible facilities allow for scale-up from bench- to engineering-scale.

Developer's Technologies Tested

- PSTU solvents tested
 - Monoethanolamine (MEA) base line tests
 - Data supporting CO₂ Capture Simulation Initiative modeling activity (*)
 - · Comparison of analytical procedures used by other researchers
 - Investigation of performance aspects of value to end users (*)
 - Babcock and Wilcox's OptiCapTM
 - Hitachi's H3-1
 - Cansolv's DC-201
 - Chiyoda's T3
 - Preparing to test in 2013
 - Cansolv's DC-201 solvent with diluted flue gas simulating NGCC operation
 - Carbon Capture Solutions' solvent.



Developer's Technologies Tested (cont'd)

- Bench-scale tests
 - Codexis's enzyme-MDEA technology (mixed with solvent)
 - Akermin's enzyme-K₂CO₃ technology (immobilized on absorber packing) (*)
 - MTR's 500-lb/hr polymeric CO₂ separation membrane (*)
 - Preparing to test in 2013
 - SRI International's sorbent test skid (*)
 - NETL's sorbent test skid
 - Carbon Capture Scientific's pressurized stripping test skid (*)
 - Green Technologies solvent in Slipstream Solvent Test Unit.
- Pilot-scale tests
 - Aker Clean Carbon's Mobile Test Unit (MTU) in 2011/12
 - Preparing to test 2 x 10,000 lb/hr pilot plants in 2014
 - Linde's optimized solvent pilot unit (*)
 - MTR's polymeric CO₂ separation membrane. (*)

Other developer's in discussion with NCCC for testing at various scales. Several developer's will test technologies at NCCC if successful in recent FOA.





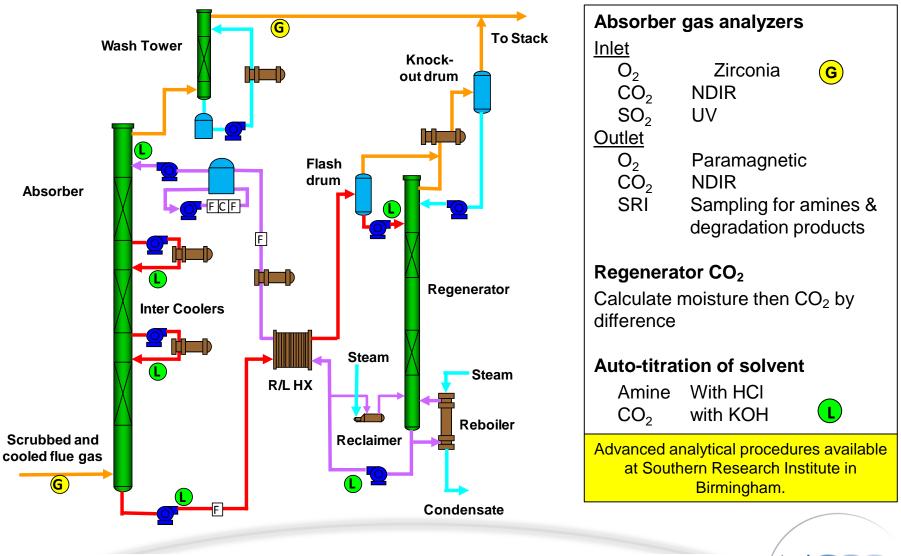
ERMIN







PSTU 0.5-MW Equivalent



Up to 6,500 lb/hr flue gas, 26,000 lb/hr solvent, 3 absorber beds

Solvent Carryover from PSTU Wash Tower

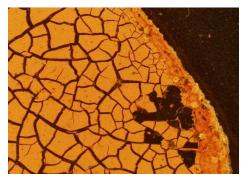


- During MEA tests, solvent emissions from the PSTU in excess of 100 ppmv: vapor predicted to be <3 ppmv
- SO₃ aerosol (~0.1 micron) is present in flue gas: 10⁶ particles per cm³
 - In warm absorber aerosol grows (>1 micron) and a fog appears
 - These small droplets are not collected efficiently in wash tower and many escape with CO₂-depleted flue gas
 - Solvent losses increase operating cost and infringe VOC limits.
- Soluble issue: two approaches, there are likely others
 - Remove SO₃ in power plant: wet ESP, spray dryer absorption, cool to slightly below acid dew point to condense SO₃ on ash
 - During MTU tests at NCCC Aker demonstrated ability to eliminate solvent carryover using proprietary approach
 - What is most cost-effective approach?

How might SO₃ or other minor flue gas constituents affect development of your technology?

How SO₃ Aerosol has Affected Other Tests

- Increased carryover from absorber increases solvent concentration in wash water
 - For one developer's solvent this produced foaming and further deterioration in wash tower performance
 - A defoaming agent was injected and this eliminated foam immediately.
- Deposits formed at exit of flue gas compressor on MTR membrane skid
 - Composed mainly of sulfates, ~20% soluble ammonium sulfate (and/or bisulfate), ~25% soluble ferrous, and ~25% insoluble ferric (both corrosion products from reaction with ammonia)
 - Similar to deposits in air heaters
 - SO₃ ammonia aerosol complex originating in SCR
 - Hot compressor exit first location where gas below saturation level: hot aerosol sticks to dry surface.



Yellow-brown particulate filtered from solution

Change to direct cooled ring compressor dissolves any deposits formed.

Insights such as these from NCCC analysis and tests help improve developer's technologies and show value of using commercially representative flue gas.

RCRA Metals in MEA from PSTU Testing

	Inlet Gas, ppbw	Liquid Concentrations, ppbw			RCRA	Probable
Metals		Fresh MEA	Makeup Water	Rich MEA Solution (1)	Limit, ppbw (2)	Source of Buildup
Arsenic	1.13	< 12	0.462	219	5,000	Flue Gas
Barium	3.40	< 12	54.3	265	100,000	Flue Gas
Cadmium	< 0.14	< 12	< 0.225	< 10	1,000	
Chromium	0.315	< 12	0.927	45,090	5,000	Corrosion
Lead	0.271	< 12	2.34	< 10	5,000	
Mercury	0.009	< 0.50	< 0.50	< 0.50	200	
Selenium	9.74	44.1	< 0.225	1,950	1,000	Flue Gas
Silver	< 7.00	< 12	< 0.225	< 500	5,000	

(1) MEA at end of run (2) Limit actual defined in mg/L: 1,000 ppbw ~ 1 mg/L

- Chromium can be limited by materials of construction and low solvent corrosivity. <u>Note</u>, no corrosion inhibitor used in tests.
- Decided to concentrate initial studies on removal of selenium while monitoring effect on other metals of interest.

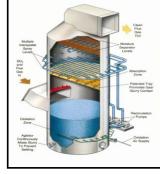
In What Form are RCRA Metals Present in Flue Gas Entering Absorber?

- Used EPA Method 29 to determine metals present in flue gas
 - Without pre-filtration
 - Using filter paper specified to remove 99% of particles above 0.3 microns.

	Flue gas concn., ppmw		
	Without filter	With filter	
RCRA			
Arsenic	0.65	ND	
Barium	0.97	0.49	
Selenium	14.4	15.2	
Others			
Aluminum	9.9	ND	
Calcium	32.4	4.54	
Iron	14.7	4.38	
Magnesium	10.7	3.08	
Sodium	40.0	ND	

 Only metal not affected by filter was selenium, suggesting it may be in gaseous form (SeO₂?), rather than bound up with particulate. If present as fine flume not easily removed by solvent in absorber.

Mercury and Air Toxics Standards



- Selenium MATS limit in FGD waste water 6 lb/TBtu.
- EPRI has major program investigating how best to achieve this standard.
- Preliminary conclusions (investigation and analysis still in progress)
 - Bituminous coal poses a greater challenge than sub-bituminous coal
 - Selenium levels lower for units with baghouses compared to those with ESPs
 - Spray dryer absorption (includes baghouse) is more effective than wet FGD
 - Capture by ash an important means of reducing selenium in FGD waste water.
 - Bromine added to boiler to enhance SO₂ capture <u>reduces</u> selenium absorbed by ash
 - Cooling to promote SO₃ removal may co-capture selenium
 - Use of Trona to control SO₃ and activated carbon injection to control mercury removes selenium from flue gas.
- Hence, the issue of selenium in CO₂ solvent likely to be alleviated by measures taken in power plant to meet MATS criteria
 - Solvent quality still needs to be managed to prevent solvent performance deterioration, fouling of equipment, foaming, corrosion etc.

Some Other Cations and Anions Present in MEA

Metals	Rich MEA ppbw	Probable Source of Buildup
Aluminum	4,060	Flue Gas
Calcium	23,100	Flue Gas/FGD
Magnesium	15,340	Flue Gas/FGD
Potassium	6,480	Flue Gas
Sodium	399,100	Flue Gas/Prescrubber

Anion	Rich MEA Concentration ppmw	Probable Source of Buildup	
Sulfate	1010	Flue Gas (with cations)	
Chloride	21.2	Flue Gas	
Nitrate	19.3	Flue Gas	
Nitrite	2.3	Flue Gas	
Oxalate	393	Solvent Degradation	
Formate	1820	Solvent Degradation	

 Accumulations over less than 1000 hours operation from a variety of sources, each possibly having to be managed in a unique way.

Solvent Cleanup Processes Required



- Conventional measures (copper and ferric chloride, and sorbents) proved ineffective, the amine interfering with removal mechanism.
- Zero-valent iron process being developed by Texas A&M shows promise removing 80% of selenium and other metals of interest but does not remove aluminum, sodium, calcium, or anions.
- Petrochemical industry uses MEA extensively and has developed suitable clean-up processes, primarily to remove degradation products
 - Ion exchange and electrodialysis
 - Samples of used MEA sent to suppliers for laboratory testing to determine if these two techniques remove metals and anions as well as degradation products.

Closing Comments



- Testing developer's technologies is NCCC's top priority
 - Support provided at design stage and during operation (with operators and mechanical, electrical, and I&C services) to ensure reliable accurate data are collected, efficiently and safely, and allow the next stage of development to be planned successfully.
- Post-combustion CO₂ capture technologies have been tested over the flue gas range 80 to 5,000 lb/hr and plans are in place for testing up to 10,000 lb/hr of flue gas
 - Test programs completed for 11 developers with firm plans for seven more: discussions with other developers in progress.
- Testing has identified several issues prompted by trace contaminants present in coal-derived flue gas and solutions being pursued.
- Similarly successful pre-combustion CO₂ capture program in progress.
- If you believe we can help you be successful, please contact: John Wheeldon (205) 670 5857 <u>x2wheeld@southernco.com</u> Frank Morton (205) 670 5874 <u>fcmorton@southernco.com</u>

Abbreviations Used

- DOE US Department of Energy
- EPA US Environmental Protection Agency
- EPRI Electric Power Research Institute
- ESP electrostatic precipitator
- FGD flue gas desulfurization
- FOA Funding Opportunity Announcement
- MATS Mercury and Air Toxics Standards
- MDEA methyldiethanolamine
- MEA monethanolamine
- MTR Membrane Technology and Research
- MTU Mobile Test Unit
- NCCC National Carbon Capture Center
- NDIR non-dispersive infra red

- ND not detected
- NETL National Energy Technology Laboratory
- PC4 Post-Combustion CO₂ Capture Center
- PSDF Power Systems Development Facility
- PSTU Pilot Solvent Test Unit
- RCRA Resource Conservation and Recovery Act, regulation for solid waste disposal
- SCR selective catalytic reduction of NO_X
- SRI Southern Research Institute
- SRII Stanford Research Institute International
- A&M Agricultural and Mechanical University
- UAB University of Alabama, Birmingham
- UV ultra violet
- VOC volatile organic compounds