Accelerating Technology Development: Post Combustion Capture Sorbents

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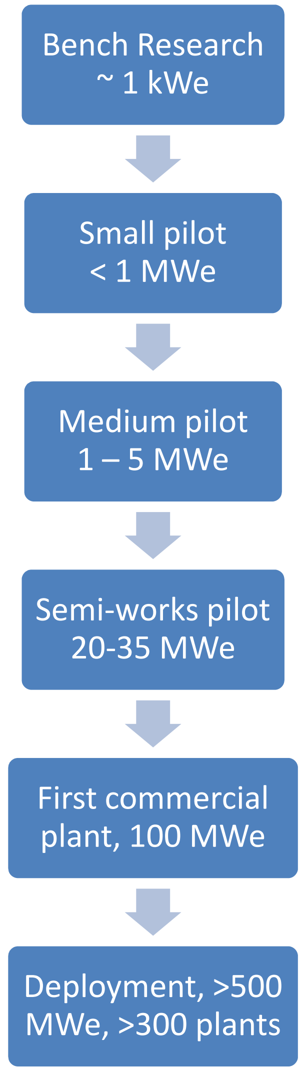
Outline

- Carbon Capture Challenge
- Computational Tools to Accelerate Technology Development
- Experimental Carbon Capture Research @ NETL
- Multiscale Model Development, Simulation & Optimization
- Experimental Validation
- Conclusions

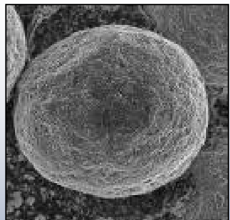
Carbon Capture Challenge

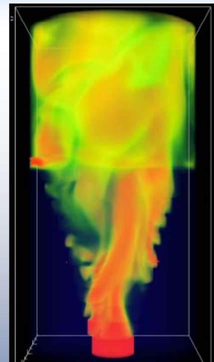
- The traditional pathway from discovery to commercialization of energy technologies can be quite long, i.e., 20-30 years
- New approaches are needed for taking carbon capture concepts from lab to power plant, quickly, and at low cost and risk
- Science-based simulations will accelerate the development of carbon capture technology, from discovery through deployment



CCSI For Accelerating Technology Development

Carbon Capture Simulation Initiative






Identify promising concepts → Reduce the time for design & troubleshooting → Quantify the technical risk, to enable reaching larger scales, earlier → Stabilize the cost during commercial deployment

National Labs

- Berkeley Lab
- Pacific Northwest National Laboratory
- NETL
- Los Alamos National Laboratory
- Lawrence Livermore National Laboratory

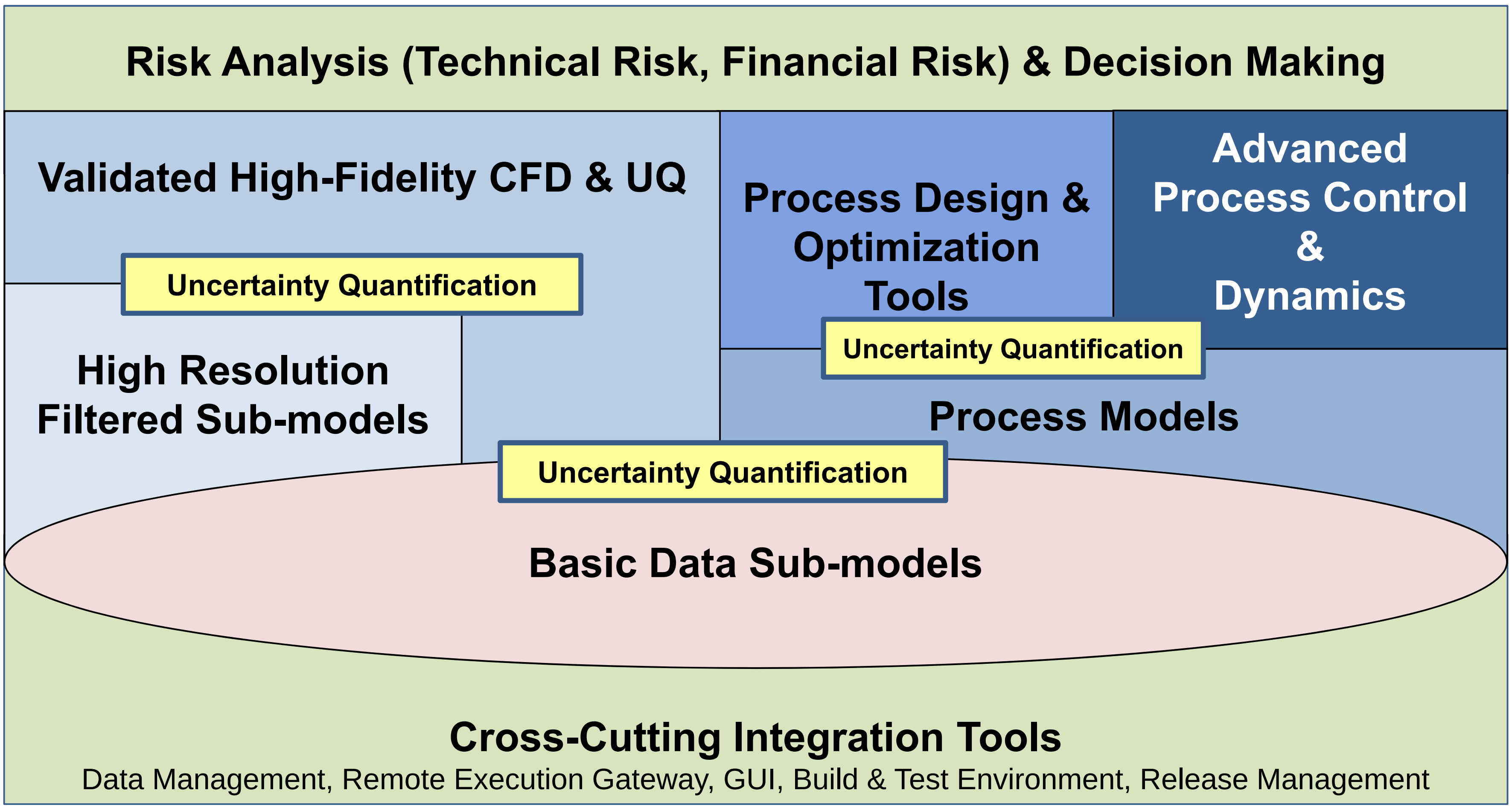
Academia

- Carnegie Mellon
- Princeton University
- West Virginia University
- Boston University
- The University of Texas at Austin
- Institute for Clean and Secure Energy, The University of Utah

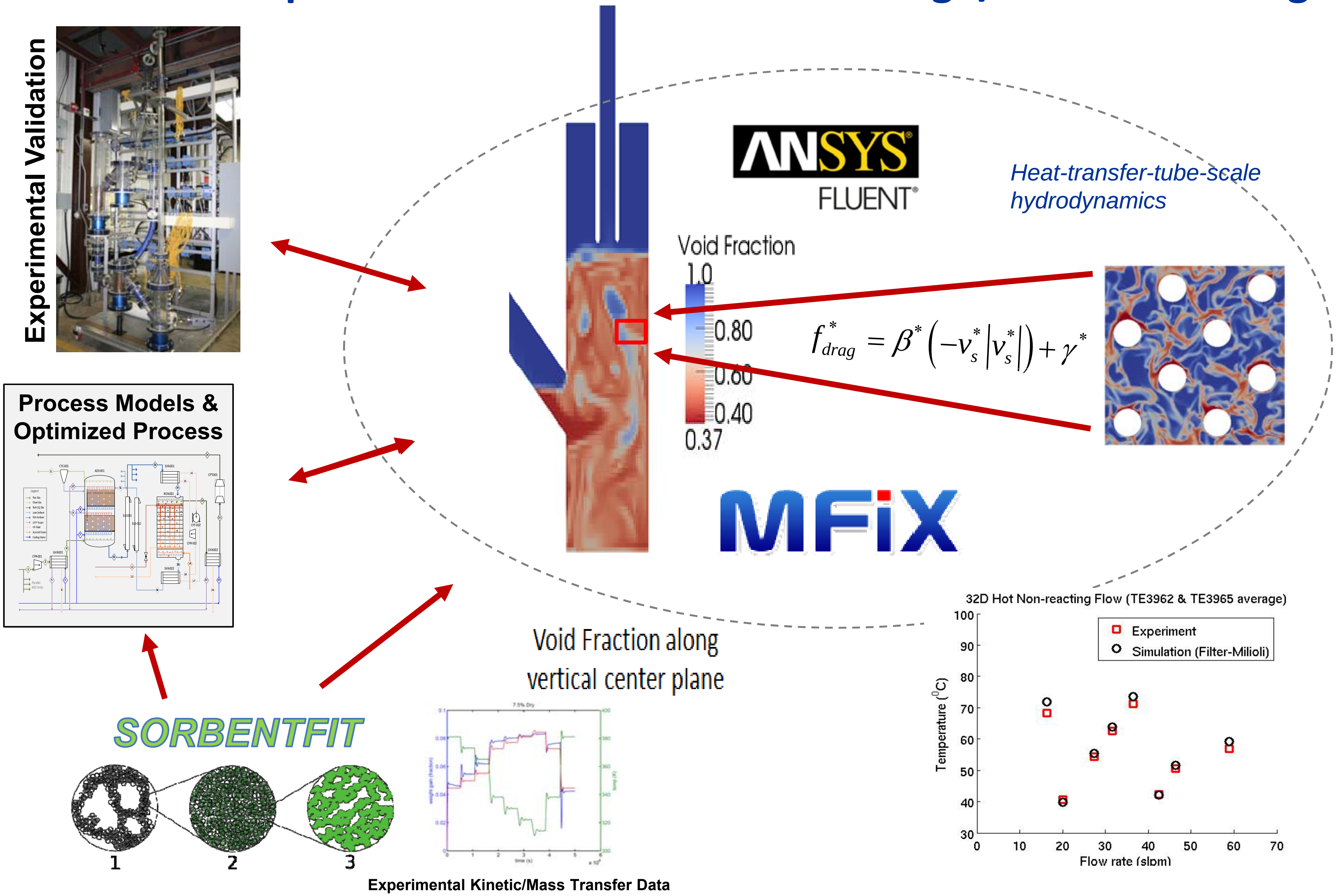
Industry

- ADA Environmental Solutions
- Alstom
- B&W
- GE
- EPRI Electric Power Research Institute
- Fluor
- Southern Company
- Phillips 66
- AEP American Electric Power
- Chevron
- Southern California Edison
- URS
- ExxonMobil
- Air Products
- Eastman
- ANSYS
- aspentech
- invensys
- PSE

Advanced Computational Tools to Accelerate Next Generation Technology Development



Simulation & Experiments to reduce time for design/troubleshooting



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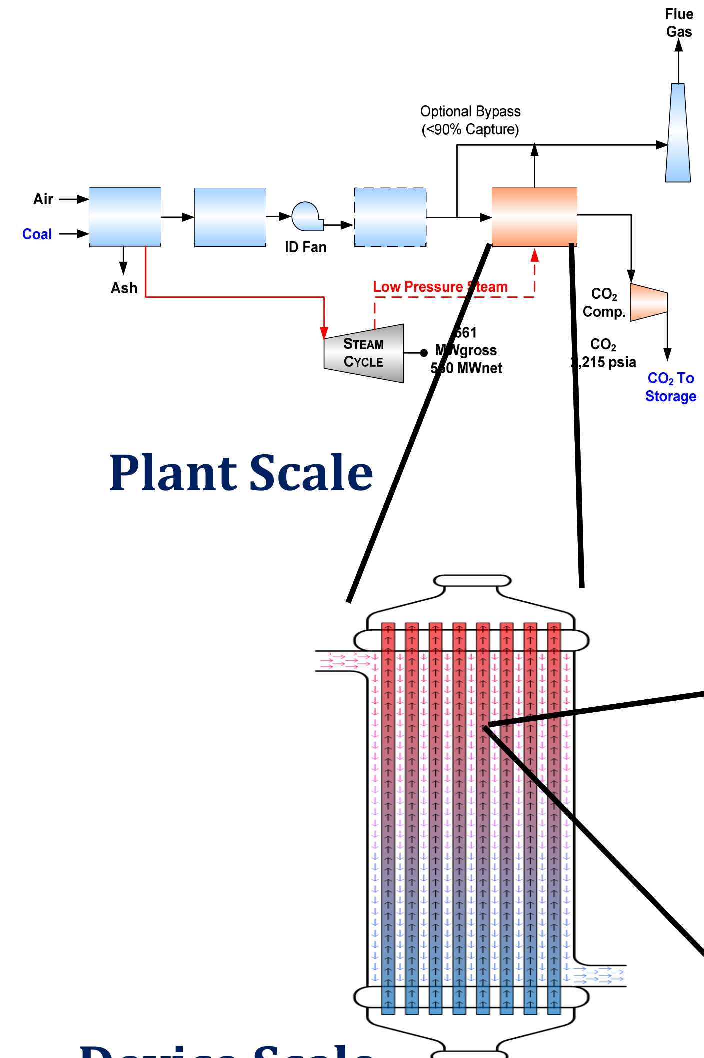
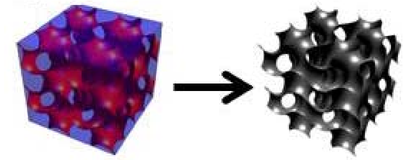
Carbon Capture

Development of efficient and economic carbon capture strategies applicable for post-, pre- and oxy-combustion schemes

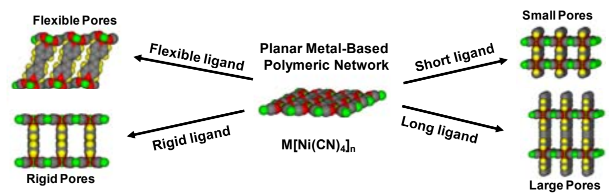


Plant Scale

Device Scale



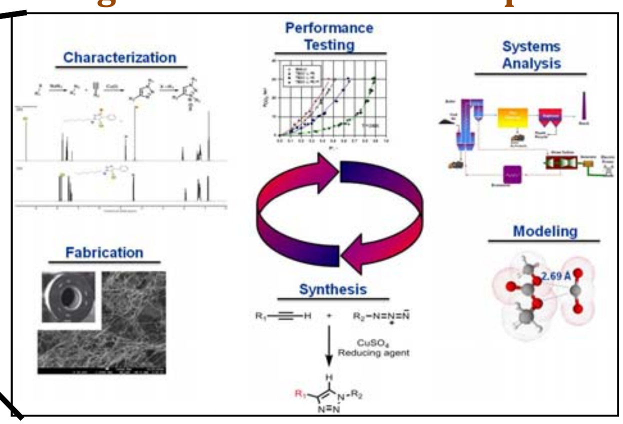
Polymers and Derivatives



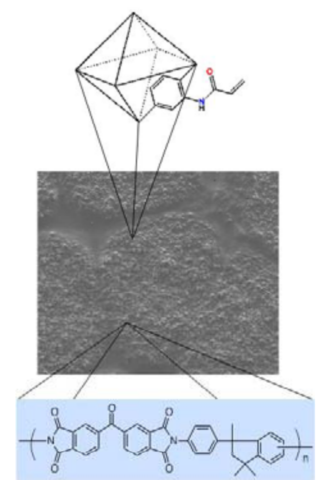
Metal-Organic Frameworks

Ionic Liquids

Integrated Materials Development



Materials Scale

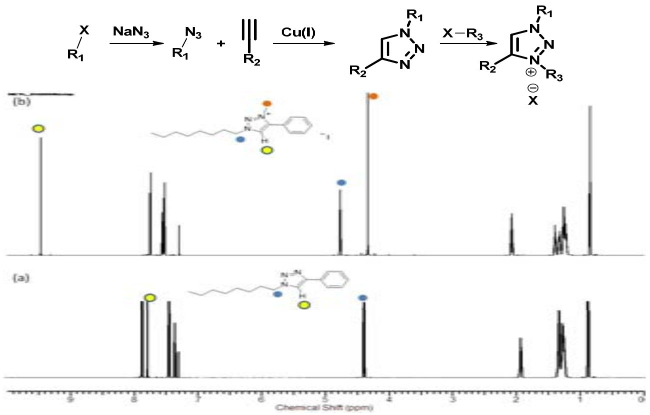


Composites

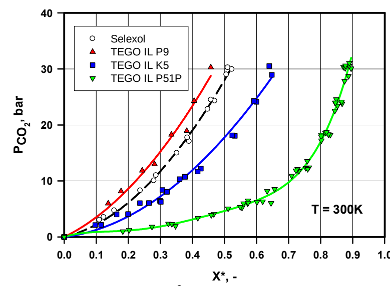
SOUTHERN COMPANY · PPG · CMS · Innovation Works · Berkeley Lab · GT · WV · Carnegie Mellon · University of Pittsburgh

Integrated Materials Development

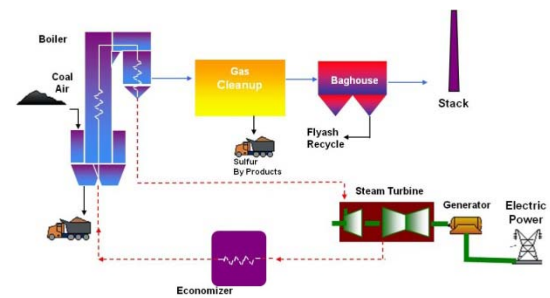
Characterization

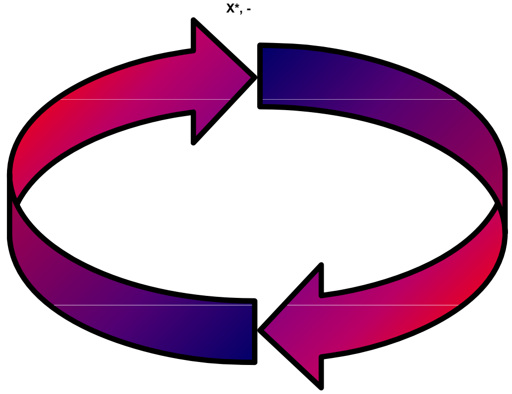


Performance Testing

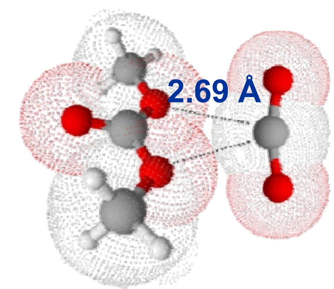


CCSI Simulation & Analysis

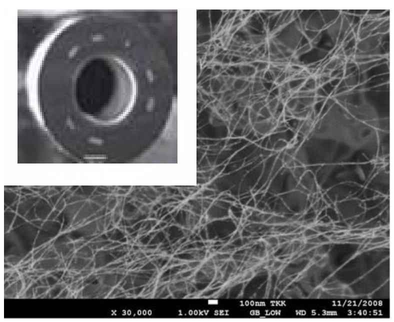




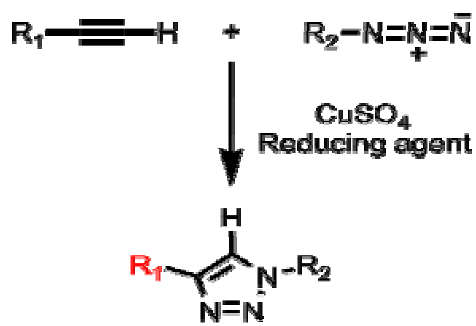
Molecular Modeling



Fabrication

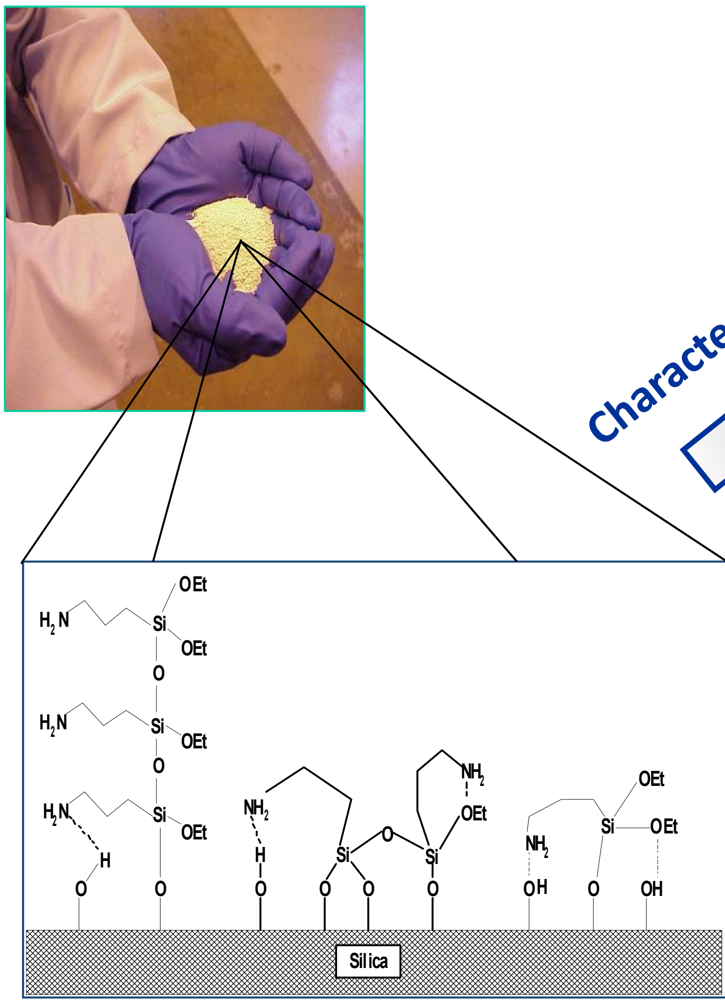


Synthesis

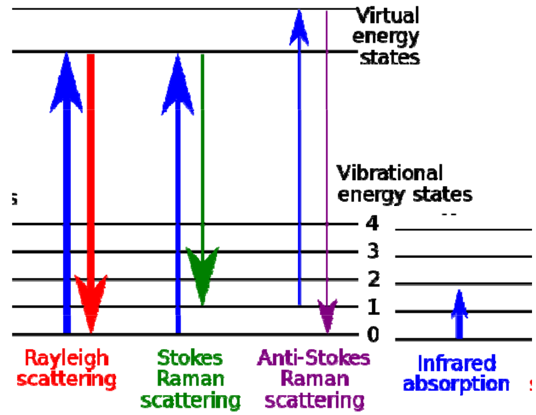


Carbon Capture

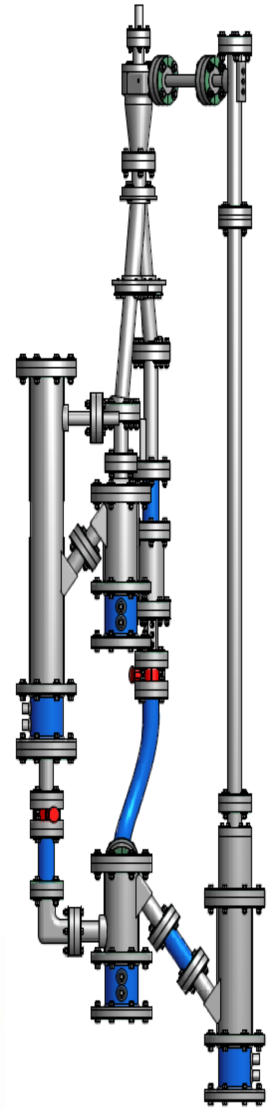
Supported Amine Sorbents



Characterization

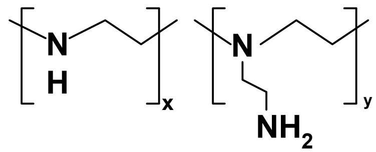


Scale-up

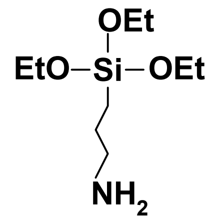


Components of Basic Immobilized Amine Sorbents (BIAS)

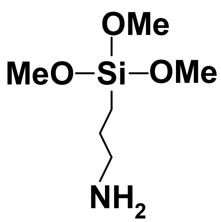
PQ 2129



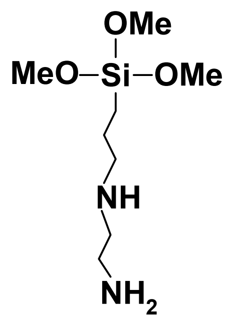
Polyethyleneimine
PEI
Mn 423-2000



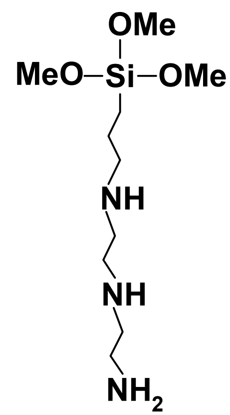
(3-Aminopropyl) triethoxysilane
APTES



(3-Aminopropyl)trimethoxysilane
APTMS



N1-(3-Trimethoxysilypropyl)
diethylenediaimine
DEDA



N1-(3-Trimethoxysilypropyl)
diethylenetraimine
DETA

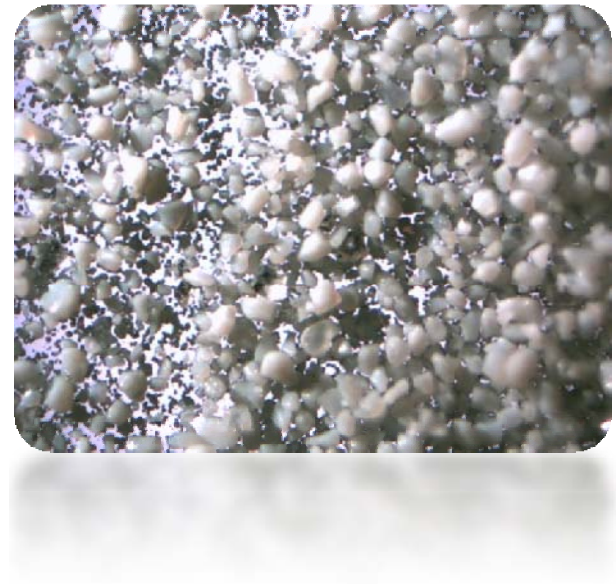
Modification of US 7,288,136 High Capacity Immobilized Amine Sorbents
US Patent Application 13212284 filed 8/11

Sorbent AX

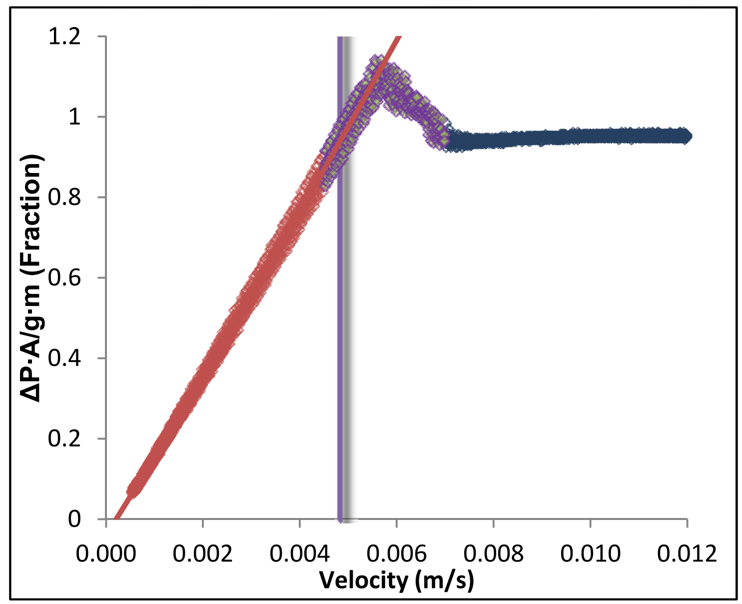
Two BIAS sorbents are being tested: AX and 32D

Sorbent AX

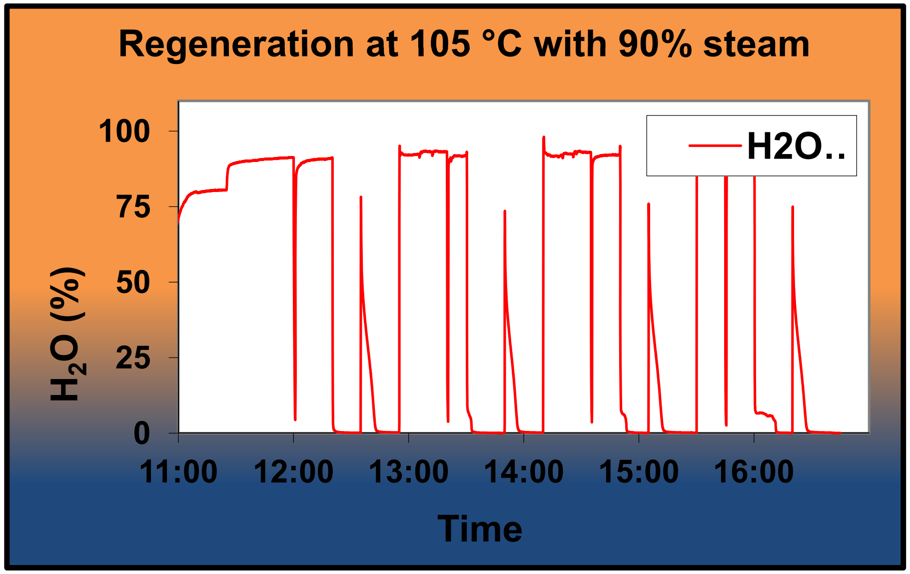
- **40% PEI - BASF M_n 2000**
- **Mesoporous Silica support- PQ Inc 2129**
- **8 - 15 gal. drums from ADA**
- **Capacity (avg.) = 2.82 mmole CO_2/g adsorbent ranging from 2.60-2.87 for n=7**
- **ADA packed bed, 13-14% CO_2, ~55°C Capacity (avg.) =1.25 avg. mmole CO_2/g adsorbent**
- **u_{mf}=0.48 cm/s**
- **Particles behavior is Geldart Group A**

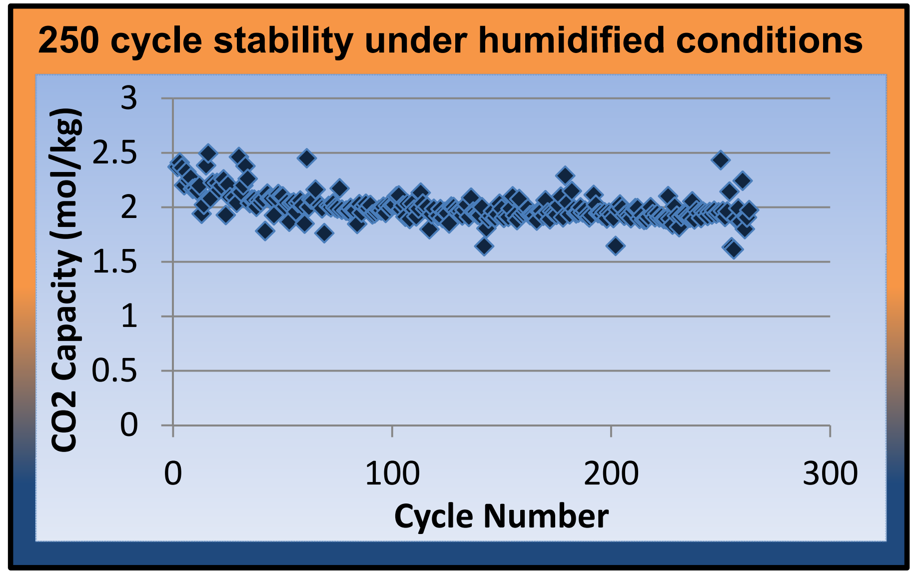


Sauter mean particle diameter	(µm)	114
Spericity	(UNITLESS)	0.86
Particle porosity	(UNITLESS)	0.39
Particle skeletal density	(g/cc)	1.50
Particle density	(g/cc)	0.91



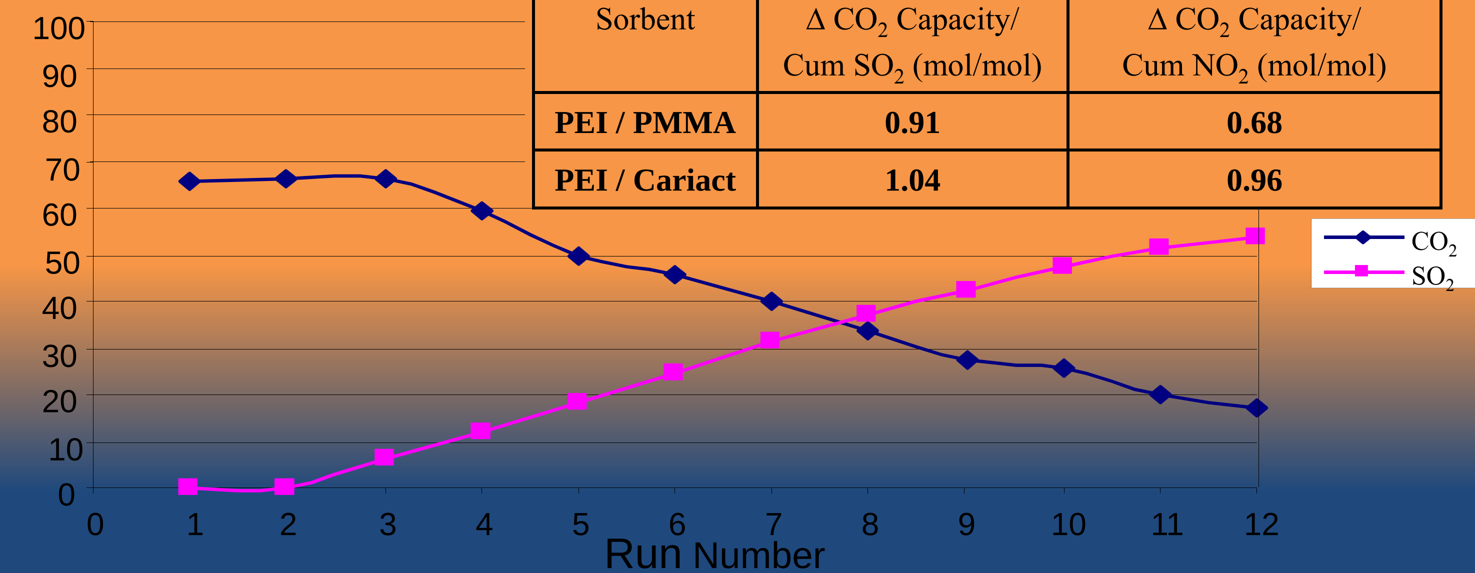
BIAS Sorbent Testing





Accelerated SO_X testing

Sorbent	Δ CO_2 Capacity/ Cum SO_2 (mol/mol)	Δ CO_2 Capacity/ Cum NO_2 (mol/mol)
PEI / PMMA	**0.91**	**0.68**
PEI / Cariact	**1.04**	**0.96**



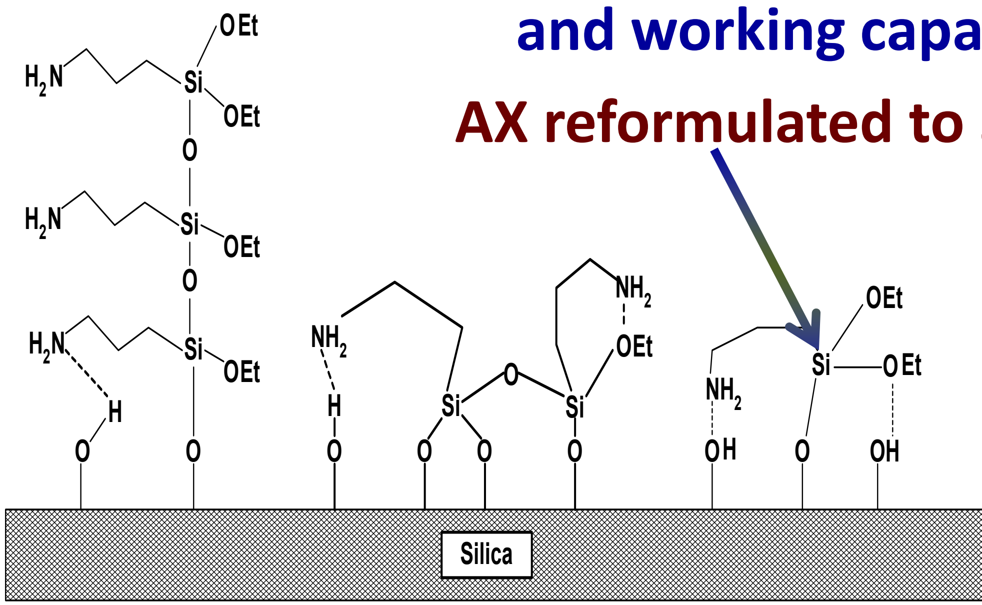
CCSI communication

Provided AX sorbent properties to CCSI

Feedback on working capacity and moisture requirements

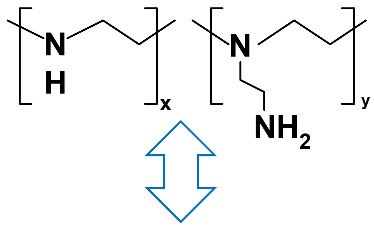
Reformulates sorbent based moisture and working capacity requirements

AX reformulated to 32D sorbent



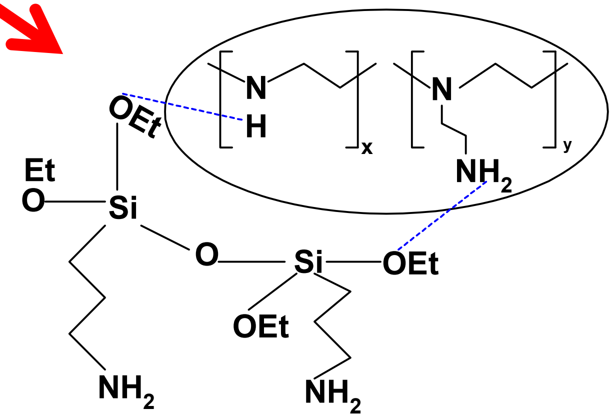
Polyethyleneimine Silane Coupling

Polyethyleneimine Mn 423-2000



Aminosilanes

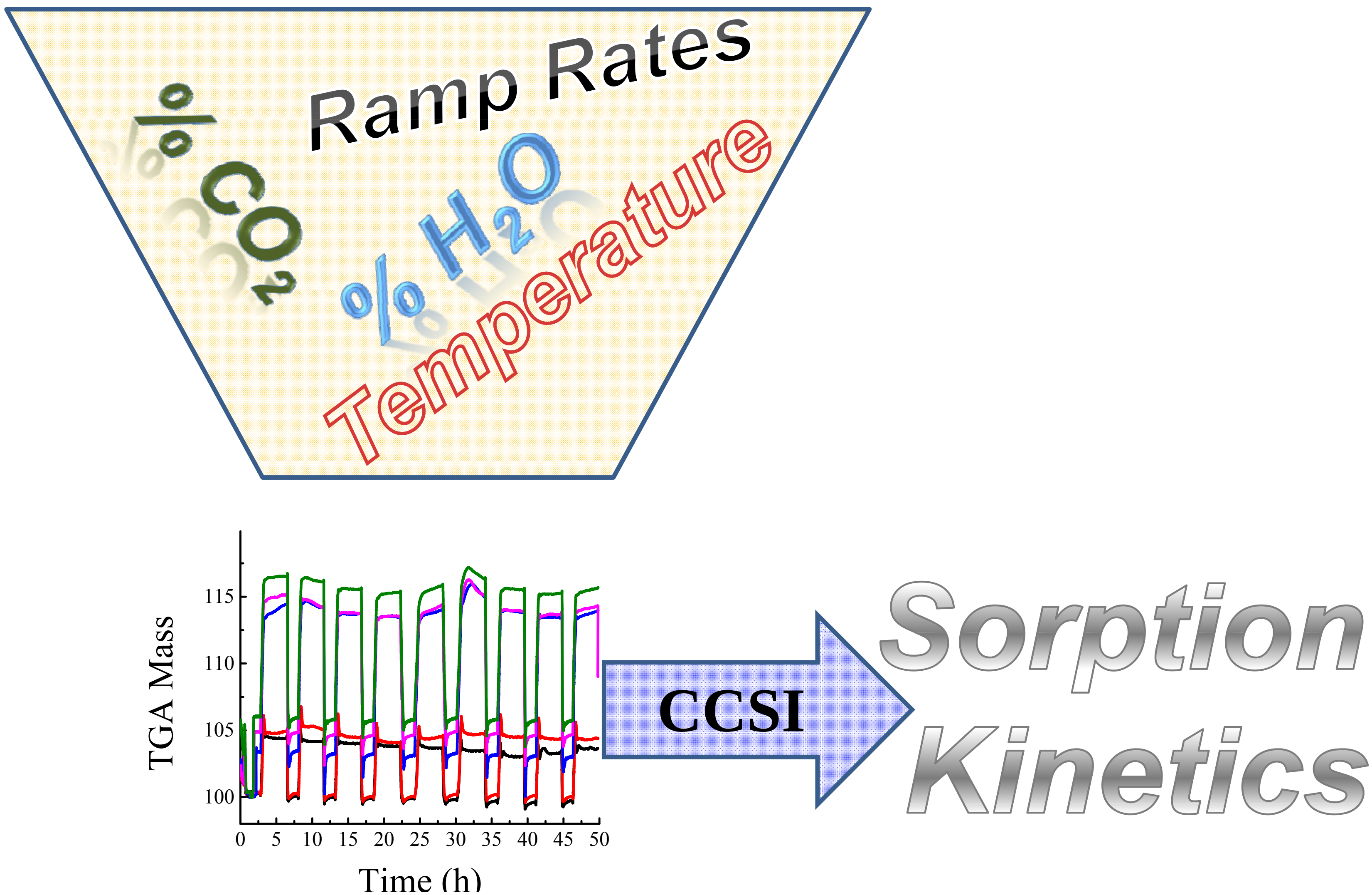
Simple
Scalable
Acceptable Capacity
Moisture Resistance
Stability
Saleable



Pressure Chemical – Pan Dyer

Synthesis was scaled to 1,000 lb range

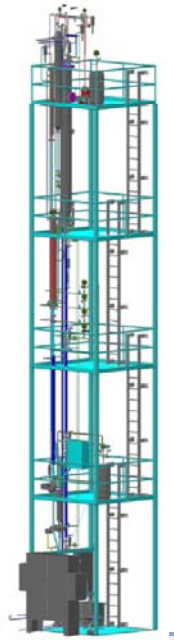
TGA Data Collection



Summary for Basic Immobilized Amine Sorbent

- High delta loadings in the 3-4mol/kg range
- CO_2 regeneration improbable
- Stable at elevated temperatures
- Silica substrate candidate of choice
- Loading results confirmed by TVA and ADA-ES
- Moisture adsorption may impact energetics
- Susceptible to poisoning with SO_2 and NO_2; upstream cleaning required in process
- Kinetic study conducted

PEI on CARiACT Q10
(100 to 350 µm dia.)



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Schematic and actual pilot unit

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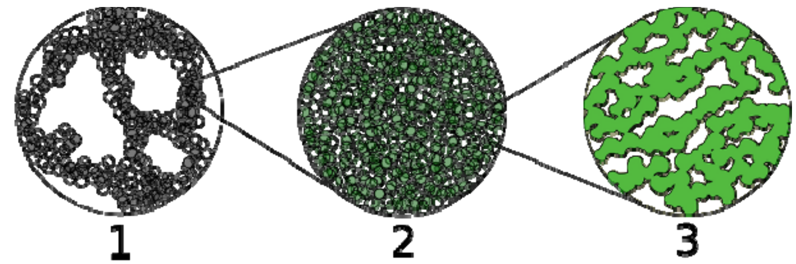
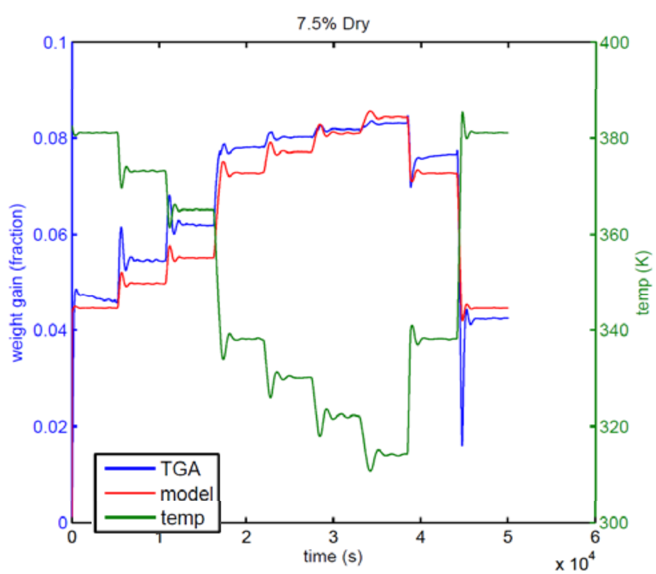
PEI-Impregnated Silica Sorbent Reaction Model

- **A general lumped kinetic model, quantitatively fit to TDA data, needed for initial CFD and process simulations**
- **High-fidelity model:**
  - Sorbent microstructure broken down into three length scales
  - Rate of reaction controlled by the diffusion of CO_2 through the amine polymer
  - Ab initio calculations indicate dependence of the diffusion process on water.

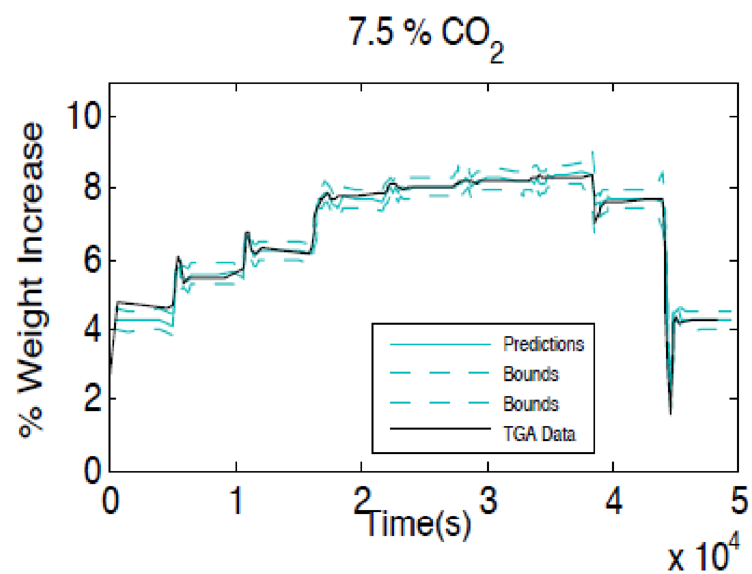
$$2R_2NH + CO_2(gas) \rightleftharpoons R_2NCO_2^- + R_2NH_2^+$$
$$R_2NH + H_2O(phys) + CO_2(gas) \rightleftharpoons HCO_3^- + R_2NH_2^+$$
$$H_2O(gas) \rightleftharpoons H_2O(phys)$$





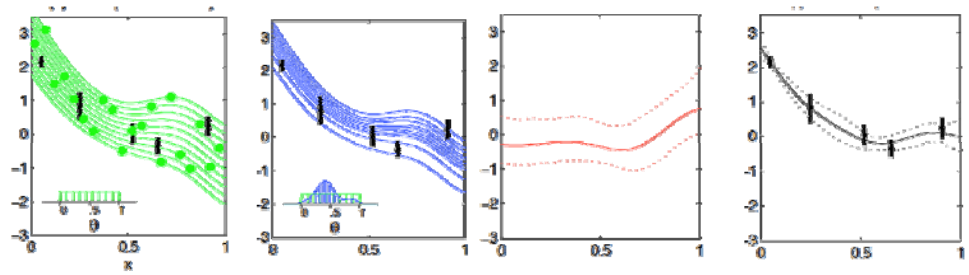
(left) lumped kinetic fit to experimental TGA for NETL-32D sorbent

(right) calibrated model with discrepancy and error bounds



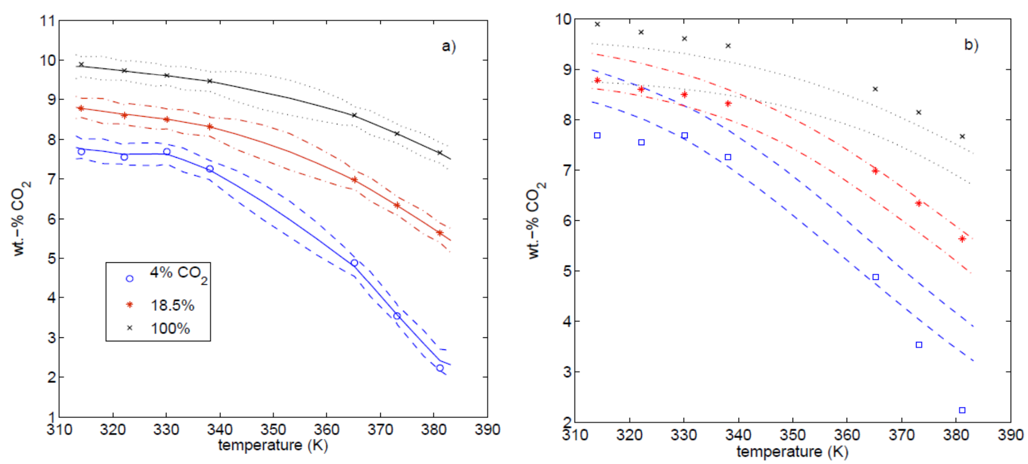
Bayesian Methods in Parameter Estimation

- *Experimental data tends to constrict the prior distribution, resulting in a experiment-based estimate influenced by theoretical calculations.*
- *A stochastic function representing the model error can also be estimated in this way.*



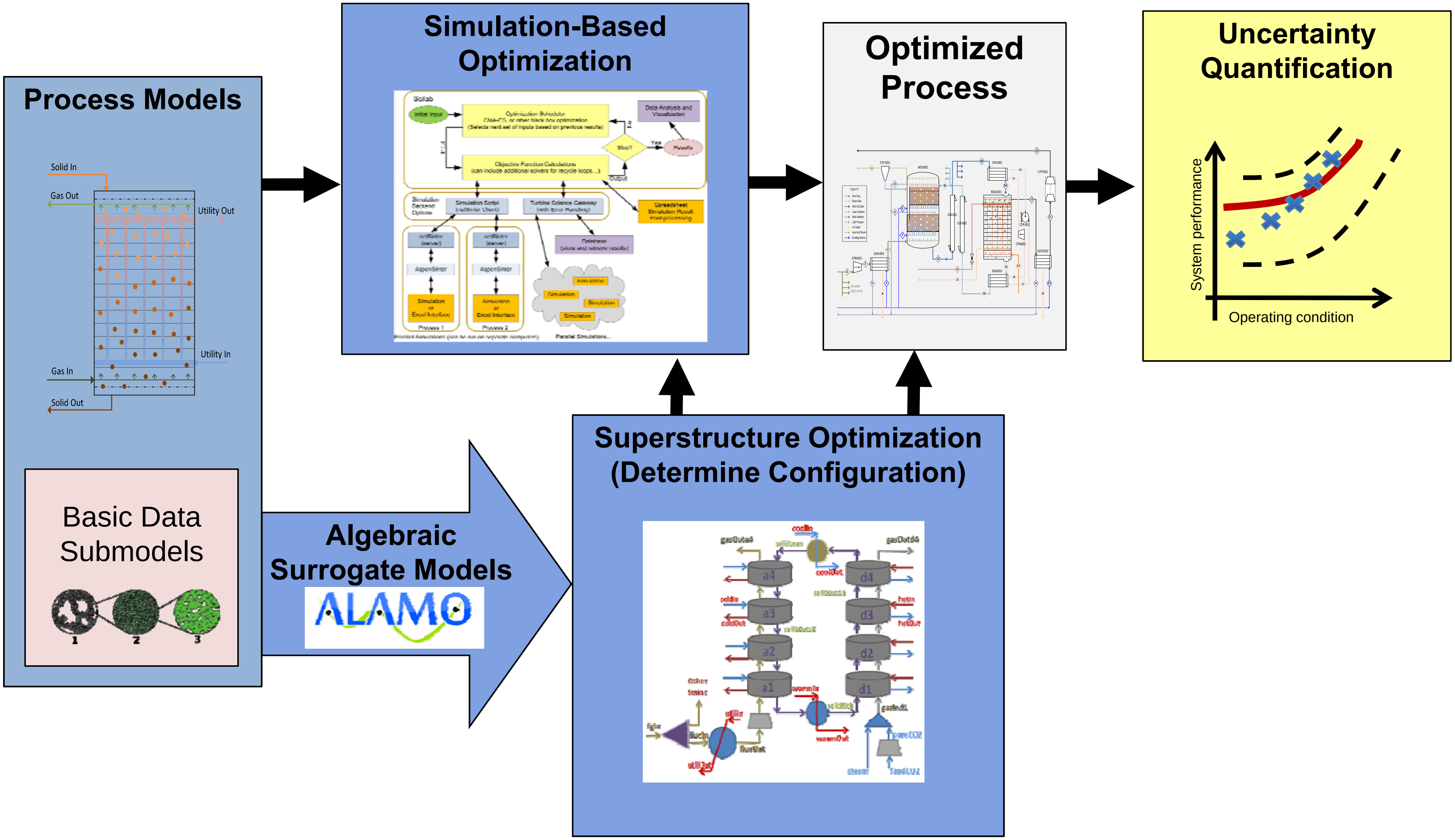
Above: schematic of the calibration process. Left to right: draws from the prior, draws from the posterior, discrepancy, and predictions.

Right: model-plus-discrepancy (a) and model-only predictions (b), with confidence bounds.



Mebane DS, Bhat KS, Kress JD, Fauth DJ, Gray ML, Lee A, Miller DC., Bayesian calibration of thermodynamic models for the uptake of CO2 in supported amine sorbents using ab initio priors. Phys Chem Chem Phys. 15 (2013) 4355-66. doi: 10.1039/c3cp42963f.

CCSI Tools to develop an optimized process using rigorous models



Miller, D.C.; Sahinidis, N.V.; Cozad, A.; Lee, A.; Kim, H.; Morinelly, J.; Eslick, J.; Yuan, Z. "Computational Tools for Accelerating Carbon Capture Process Development". In Proceedings of The 38th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, FL, USA. June 2 to 6, 2013.

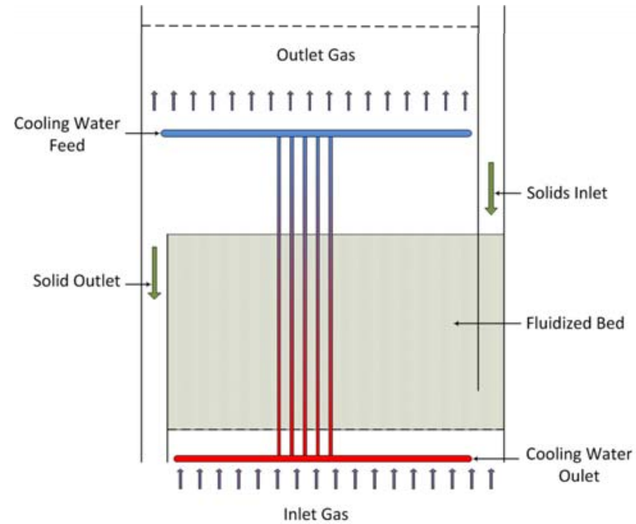
Solid Sorbent System Models

Bubbling Fluidized Bed (BFB) Models

- Flexible BFB models with immersed heat exchangers have been developed to be used as adsorber or regenerator, as needed, with varying locations for solids inlet and outlet streams

- Any number of BFB adsorbers and/or regenerators can be connected in series and/or in parallel depending on the user requirements

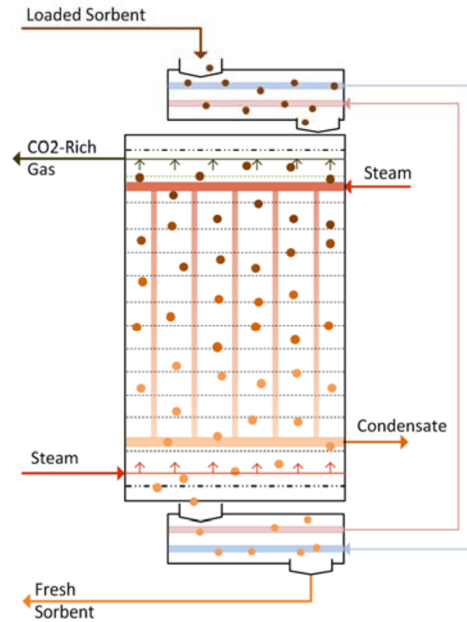
- A 2-stage adsorption model with customized variables suitable for incorporating UQ has been developed



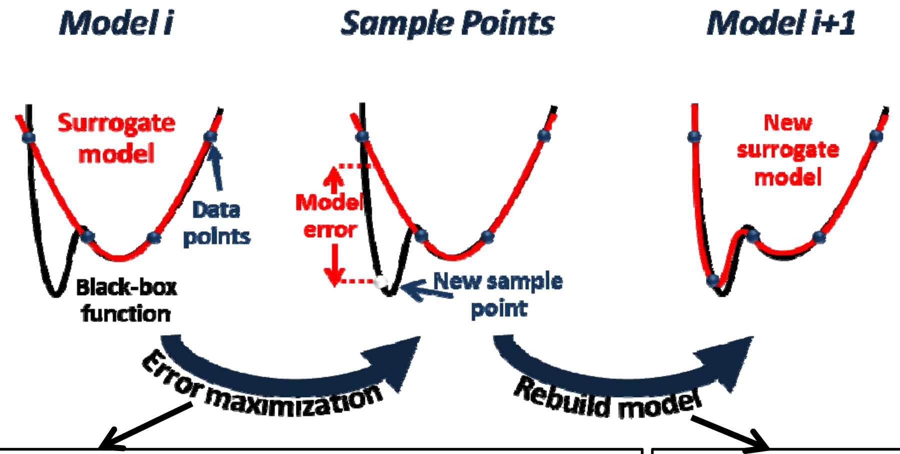
Moving Bed (MB) Models

- External resistance to mass transfer has been modeled. This is particularly important in the regenerator model due to the high operating temperature.

- Heat exchanger model, mass and heat transfer coefficients, boundary conditions, temperature specifications, and properties models are revisited for better model accuracy.



Automated Learning of Algebraic Models for Optimization



For building accurate, simple algebraic surrogate models of simulated processes

$$\max_x \left(\frac{z(x) - \hat{z}(x)}{z(x)} \right)^2$$

Surrogate model

Simulation/black-box

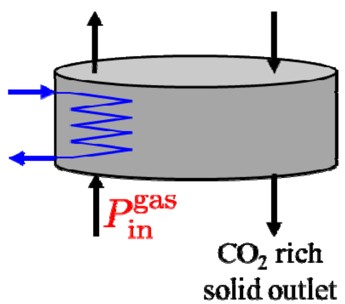
Step 1: Define a large set of potential basis functions

$$\hat{z}(x) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_1 x_2 + \beta_4 \frac{x_1}{x_2} + \beta_5 \frac{x_2}{x_1} + \beta_6 e^{x_1} + \beta_7 e^{x_2} + \ldots$$

Step 2: Model reduction

$$\hat{z}(x) = \beta_0 + \beta_2 x_2 + \beta_5 \frac{x_2}{x_1} + \beta_7 e^{x_2}$$

Example Model: BFB Adsorber Inlet Gas Pressure



- ACM Simulation
- >900 terms possible
- 14 input variables
- 0.13% error

$$\hat{P}_{in}^{gas} = P_{out}^{gas} + 0.019\, L_b + 0.0055 \sqrt{D_T}$$

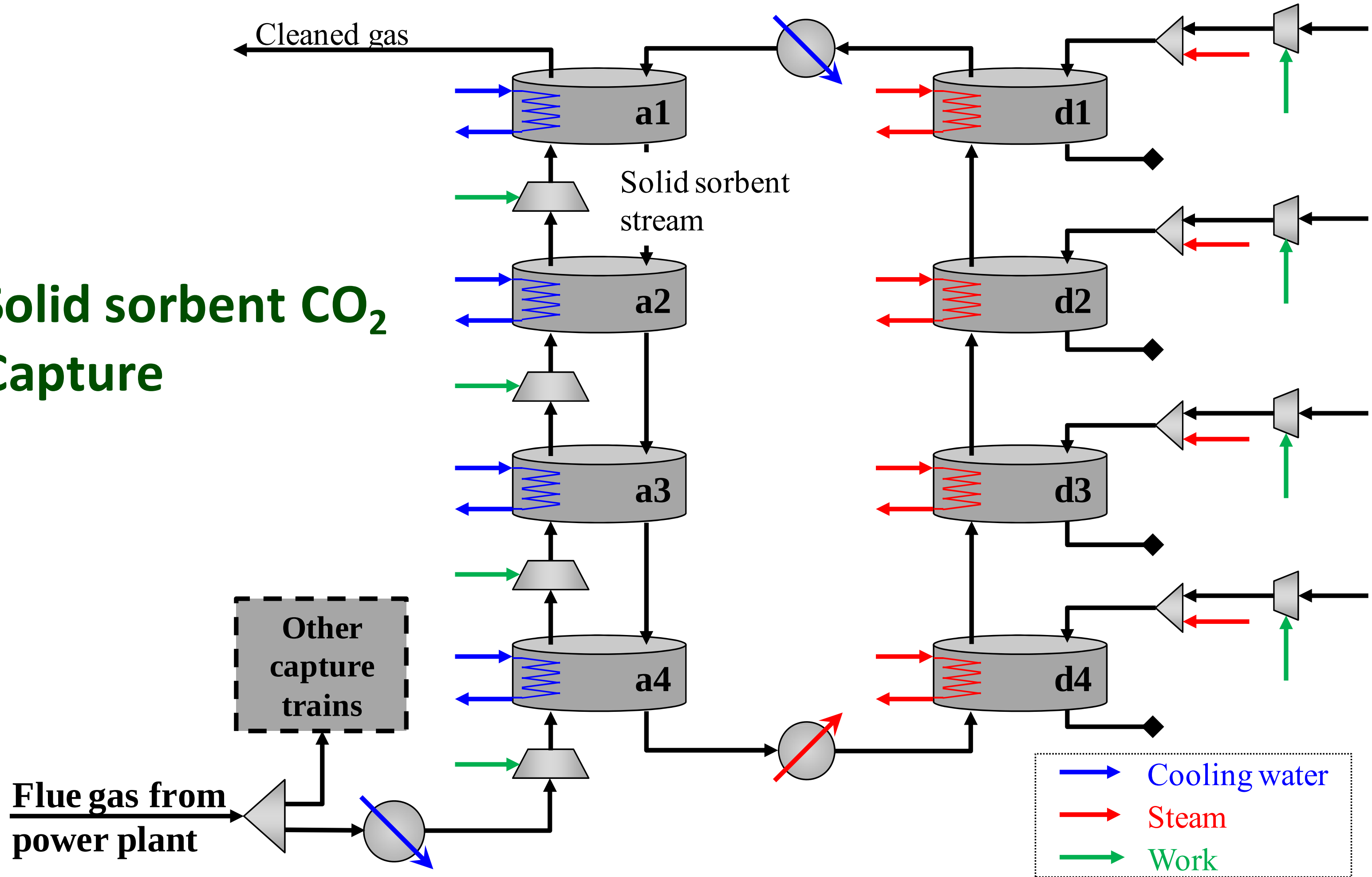
Pressure drop across length of bed

Proportional to outlet pressure

Pressure drop due to bed diameter

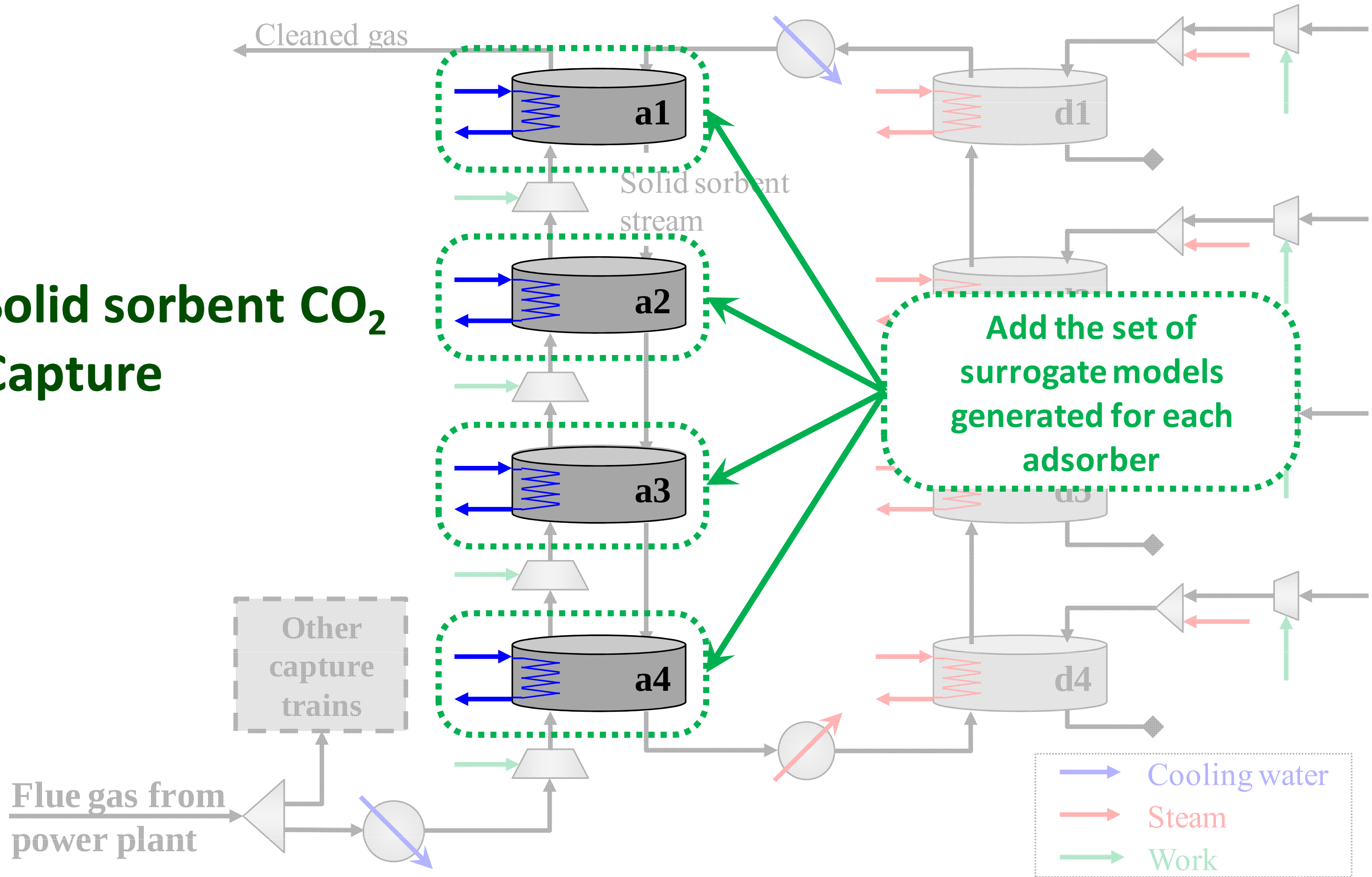
Superstructure Formulation & Optimization

Solid sorbent CO_2 Capture

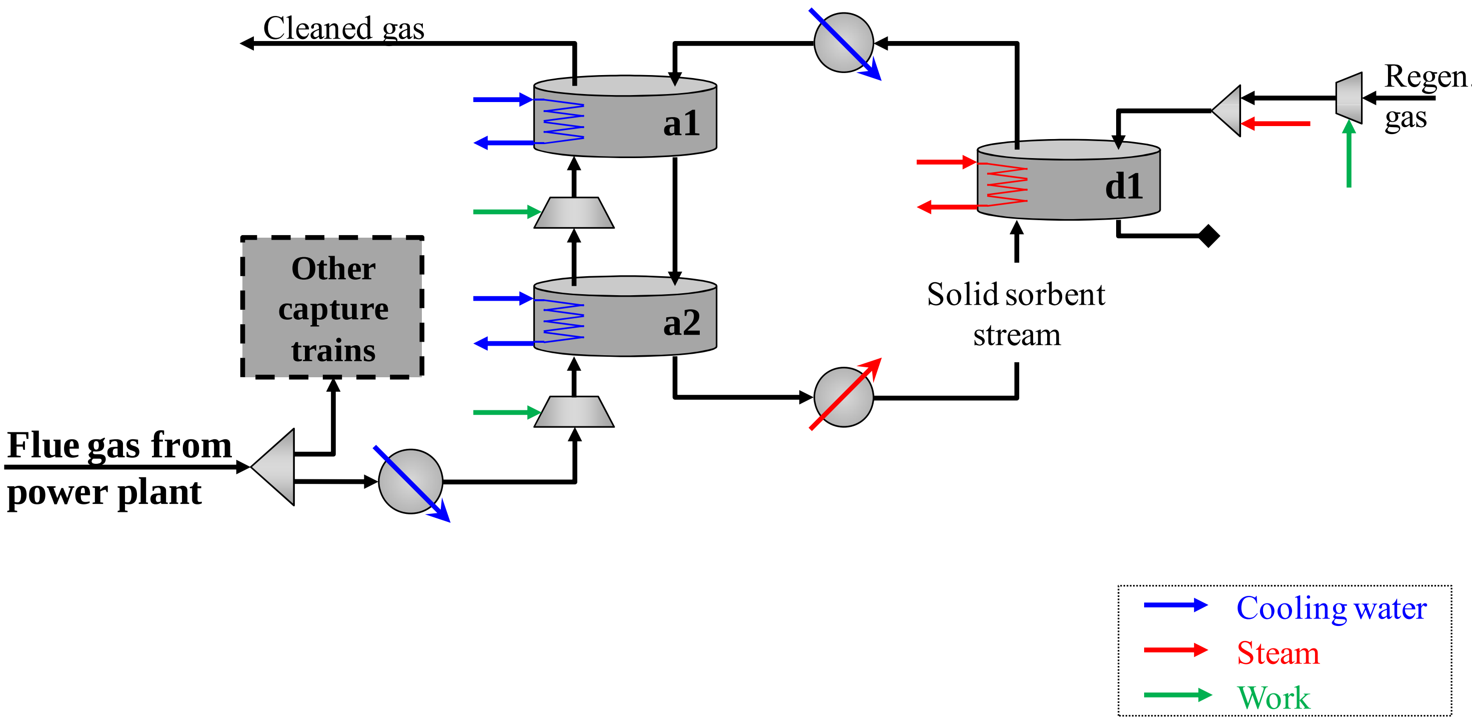


Insert Algebraic Surrogates into Superstructure

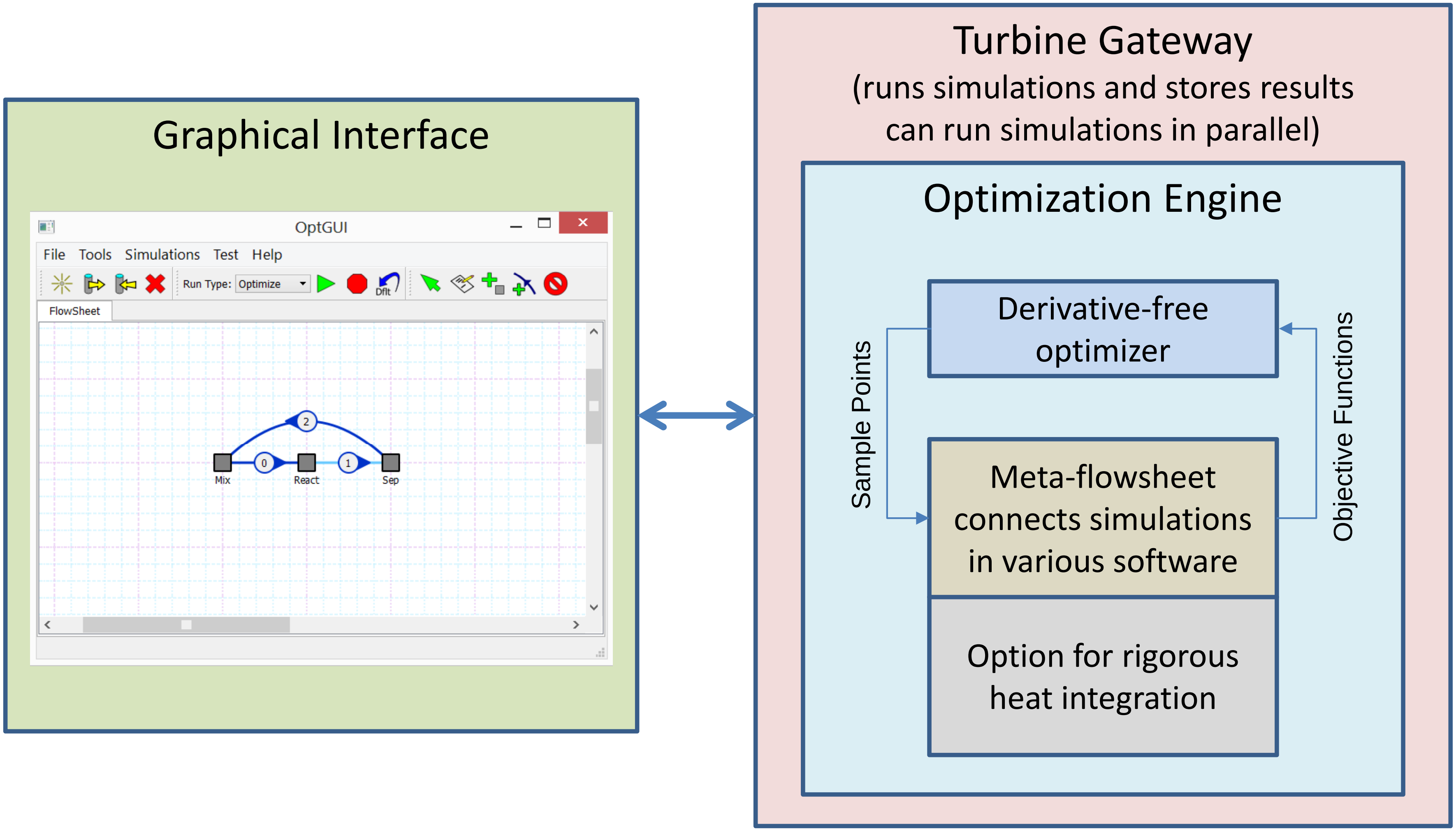
Solid sorbent CO_2 Capture



Initial Superstructure Solution



Simulation-Based Optimization Framework



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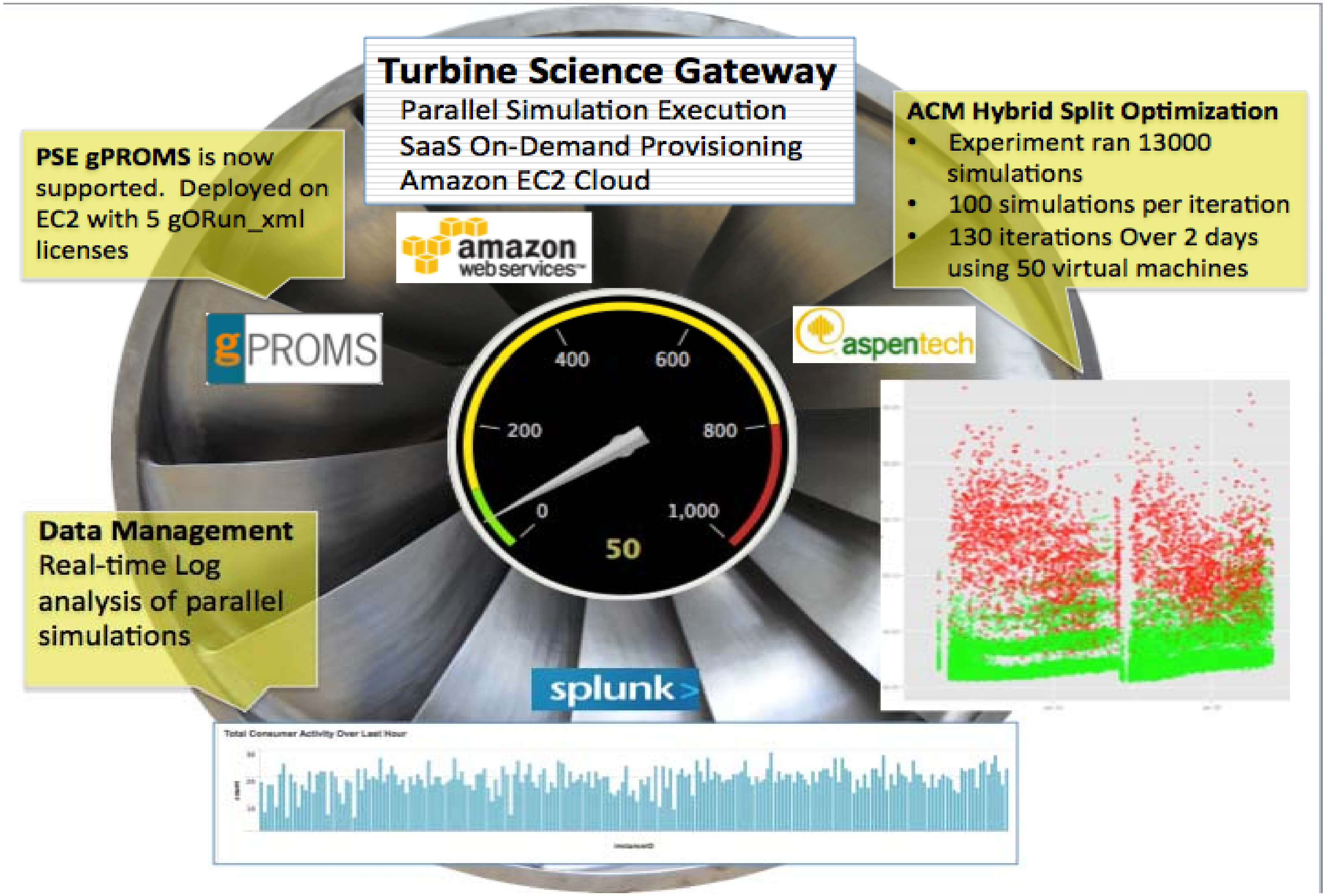
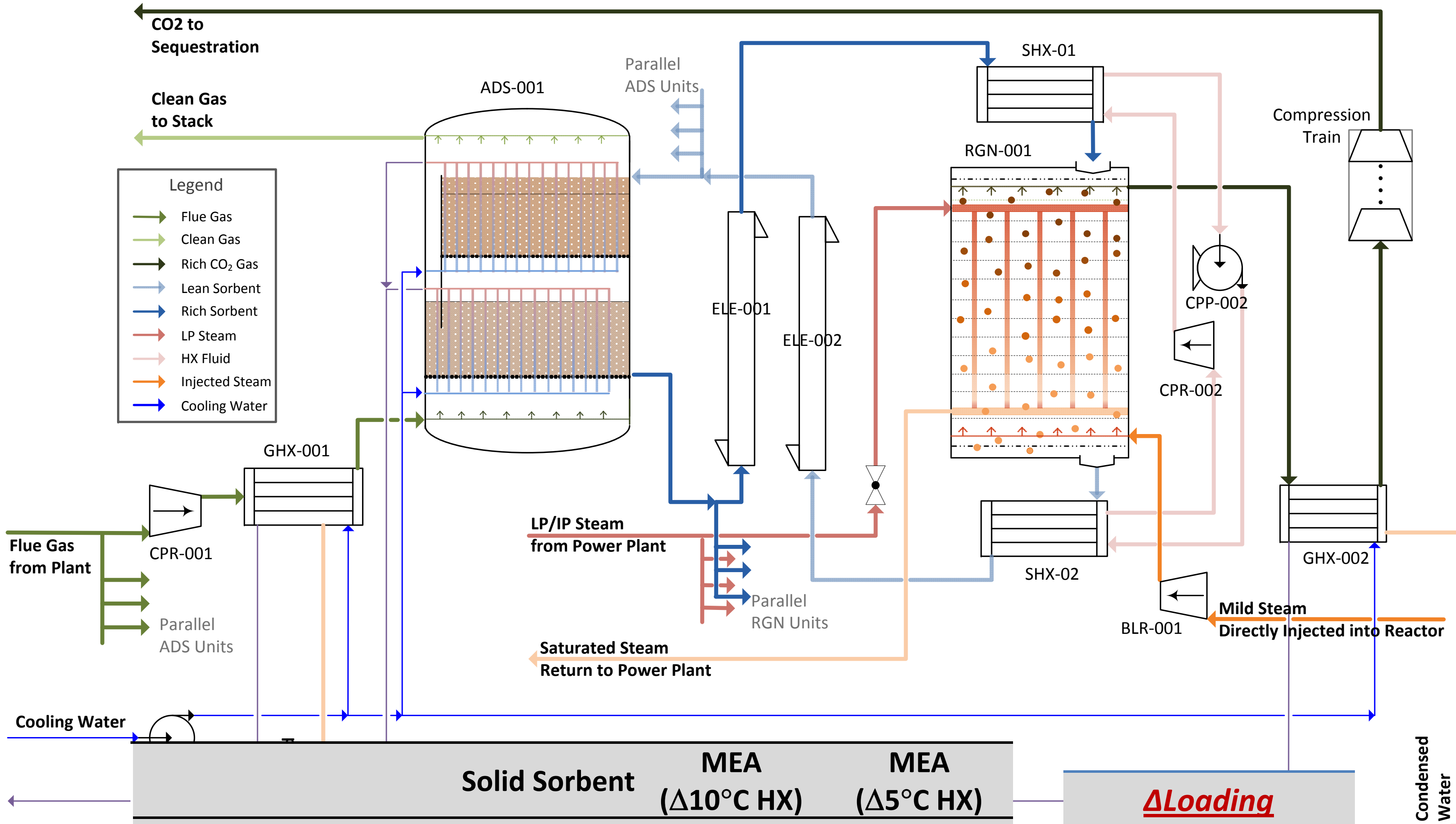
Turbine Science Gateway



Decision Variables

Input Variable	Lower Bound	Upper Bound
Adsorber Diameter (m)	7	10
Top & Bottom Adsorber Bed Depth (m)	4	10
Top & Bottom Adsorber Heat Exchanger Tube Diameter (m)	0.01	0.05
Top & Bottom Adsorber Heat Exchanger Tube Pitch (m)	0.1	0.2
Top & Bottom Adsorber Cooling Water Flowrate (kmol/hr)	30,000	60,000
Sorbent Flowrate per Adsorber (kg/hr)	350,000	600,000
Gas Pre-Cooler Temperature (^{o}C)	40	60
Regenerator Height (m)	3	7
Regenerator Diameter (m)	6	10
Regenerator Heat Exchanger Tube Diameter (m)	0.01	0.05
Regenerator Direct Steam Injection Rate (kmol/hr)	900	1400
Regenerator Heat Exchanger Steam Flowrate (kmol/hr)	2,500	5,000

Optimized Capture Process Developed using CCSI Toolset



	Solid Sorbent	MEA (Δ10°C HX)	MEA (Δ5°C HX)
Q_Rxn (GJ/tonne CO2)	1.82	1.48	1.48
Q_Vap (GJ/tonne CO2)	0	0.61	0.74
Q_Sen (GJ/tonne CO2)	0.97	1.35	0.68
Total Q	2.79	3.44	2.90

ΔLoading
1.8 mol CO2/kg
0.66 mol H2O/kg

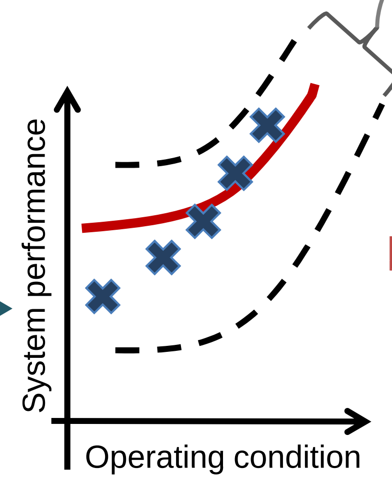
Miller, D.C.; Sahinidis, N.V.; Cozad, A.; Lee, A.; Kim, H.; Morinelly, J.; Eslick, J.; Yuan, Z. "Computational Tools for Accelerating Carbon Capture Process Development". In Proceedings of The 38th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, FL, USA. June 2 to 6, 2013.

Uncertainty Quantification: How certain are we that our model can predict the system performance accurately?

- How to quantify these error bounds *a priori*?
- How to reduce these bounds?

Scaled-up design

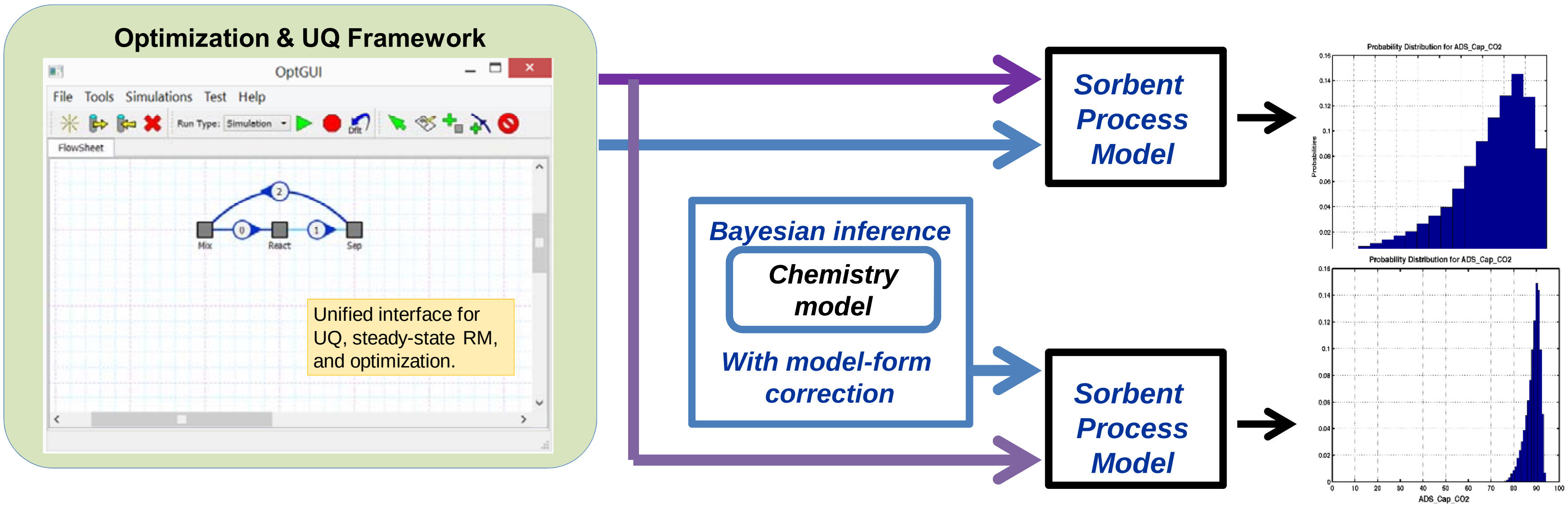
CCSI simulation



Risk analysis

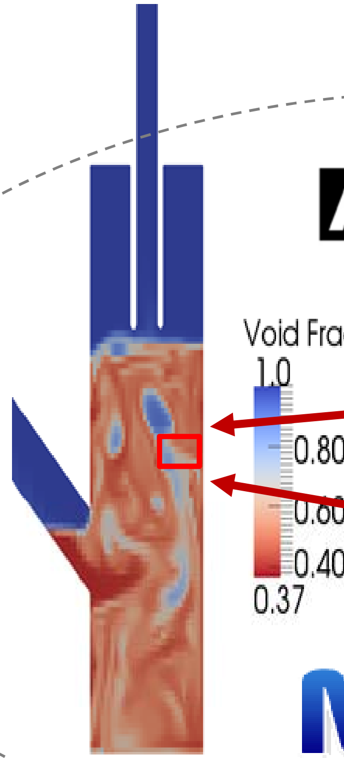
How does the uncertainty in the prediction affect the risk assessment outcome?

Multi-Scale Uncertainty Quantification Framework



- **UQ for basic data models**
  - Bayesian UQ methodology
  - Integration of model form discrepancy into process & CFD models
- **UQ for CFD models**
  - Adaptive sampling capability for RM/UQ
  - Bayesian calibration capability
  - UQ of discrepancy between CFD/process models
- **UQ for process models**
  - Integration with optimization platform
  - Optimization under uncertainty

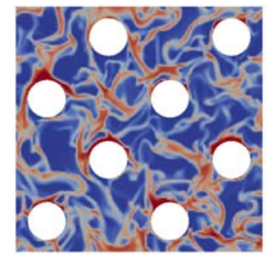
Detailed CFD Simulations of Specific Equipment



ANSYS FLUENT

Heat-transfer-tube-scale hydrodynamics

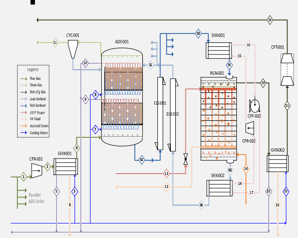
$$f^*_{drag} = \beta^* \left(-v^*_s \left| v^*_s \right| \right) + \gamma^*$$



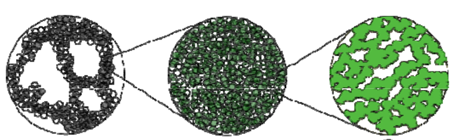
MFIX

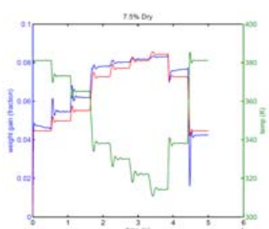
Void Fraction along vertical center plane

Process Models & Optimized Process



SORBENTFIT

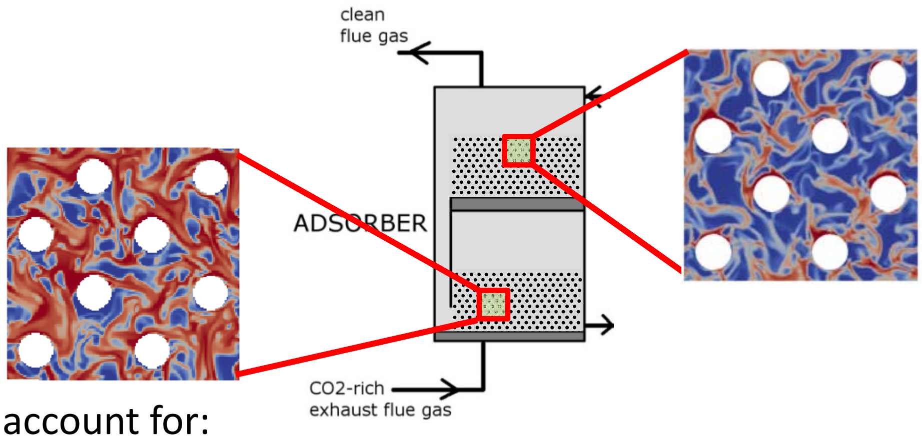




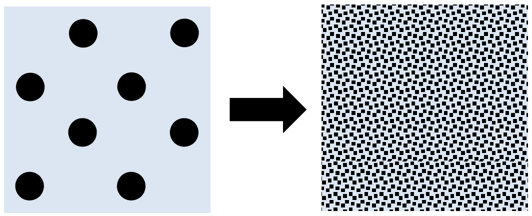
Experimental Kinetic/Mass Transfer Data

High Resolution Particle Models

- Problem: Explicit resolution of small-scale particle clusters and cooling tubes in large devices computationally infeasible!



- Solution – Develop sub-grid 'filtered' that account for:
  - Unresolved particle clusters,
  - Drag exerted by cylinders on suspension. Work well along the way for horizontal tubes

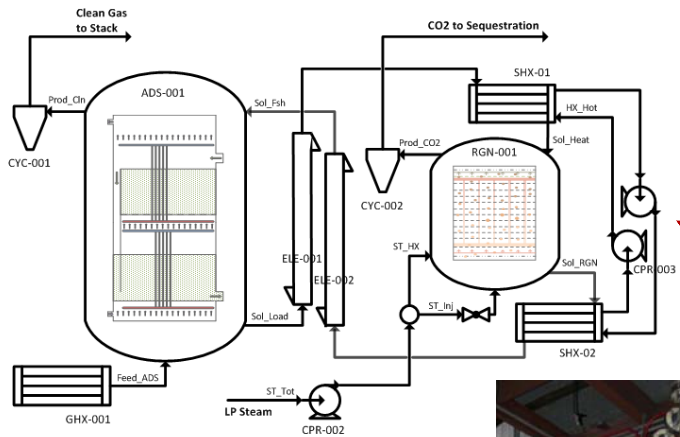


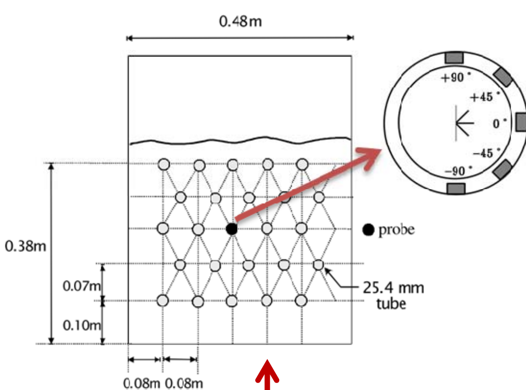
*Cylinders replaced by an **equivalent** stationary, porous medium.*

- Benefit: The sub-grid 'filtered' models can be implemented in faster, coarse-grid simulations.

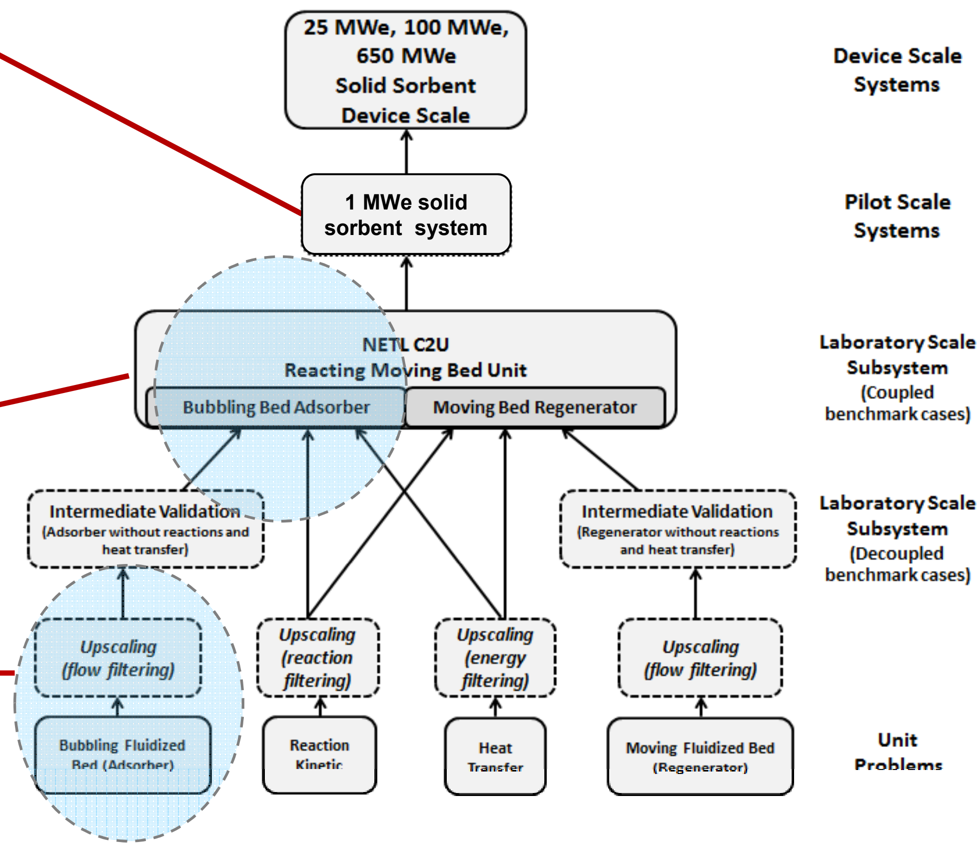
Validated CFD Models at the Device Scale

Objective: To provide quantitative confidence on device-scale (CFD) model predictions for devices that are yet to be built.





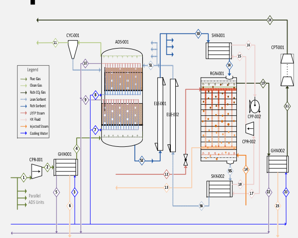
CCSI CFD Validation Hierarchy

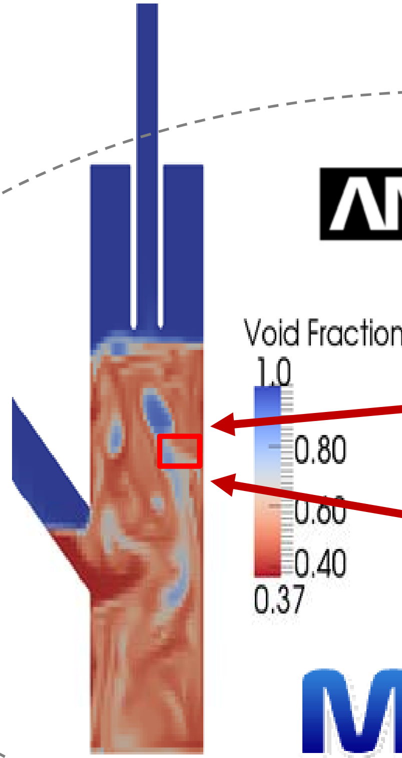


Rigorous Validation of Models

Experimental Validation

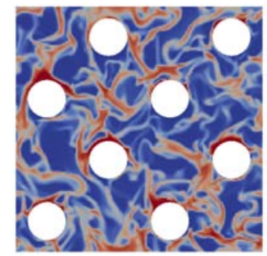
Process Models & Optimized Process





ANSYS FLUENT

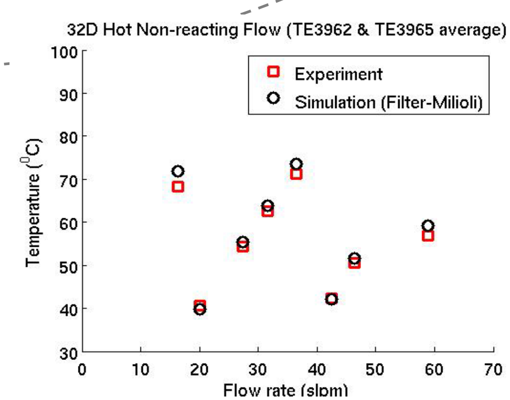
Heat-transfer-tube-scale hydrodynamics



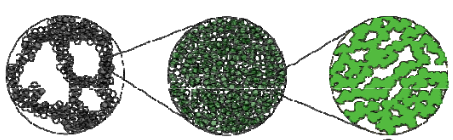
$$f_{drag}^{*} = \beta^{*}\left(-v_s^{*}\left|v_s^{*}\right|\right) + \gamma^{*}$$

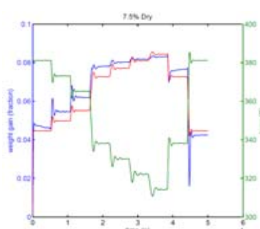
MFIX

Void Fraction along vertical center plane



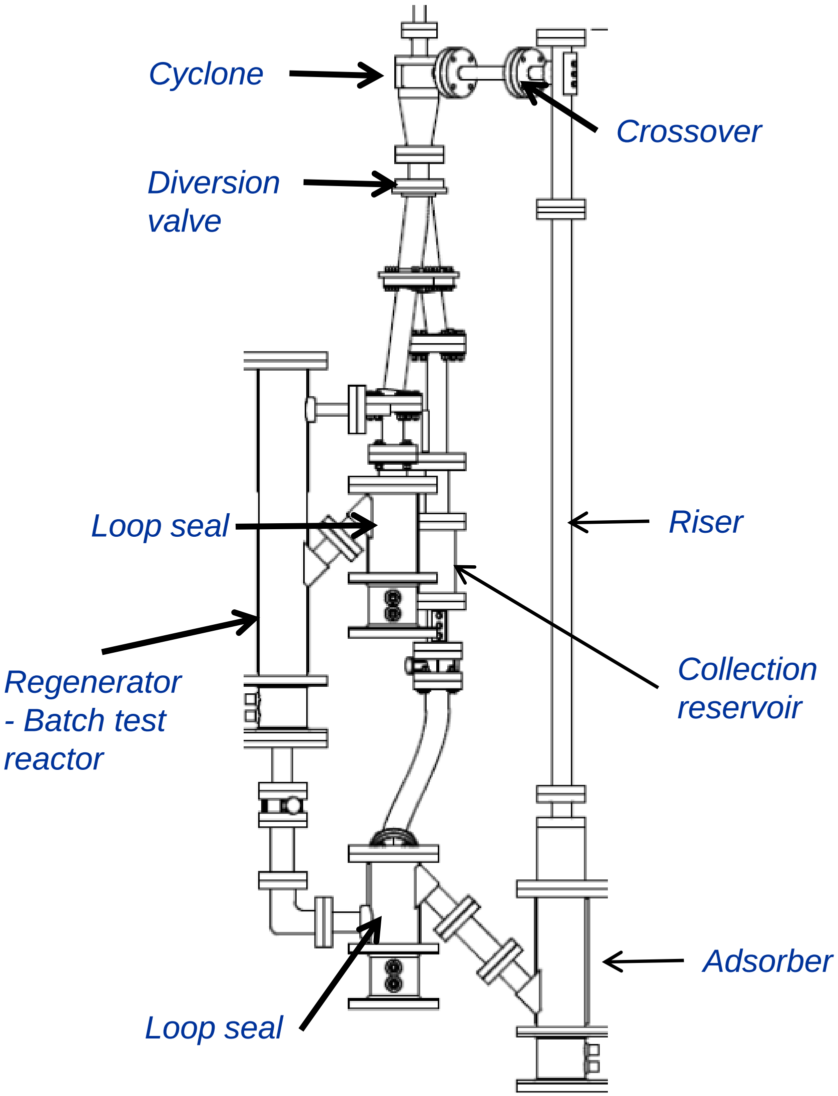
SORBENTFIT



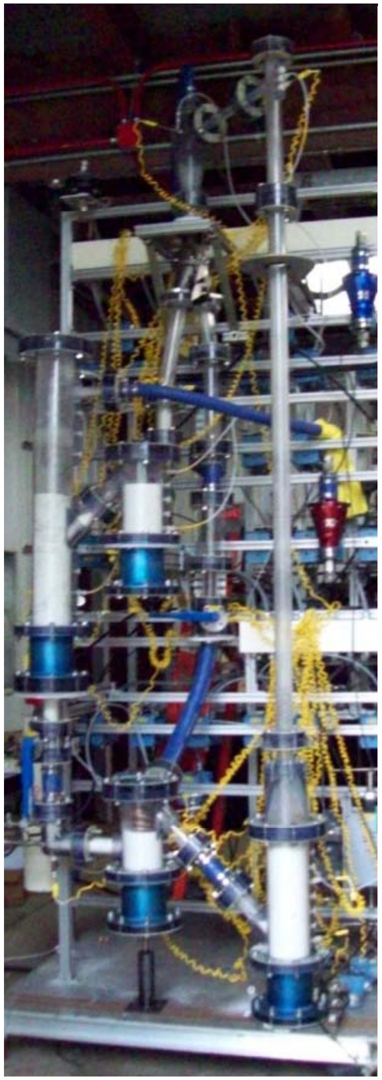


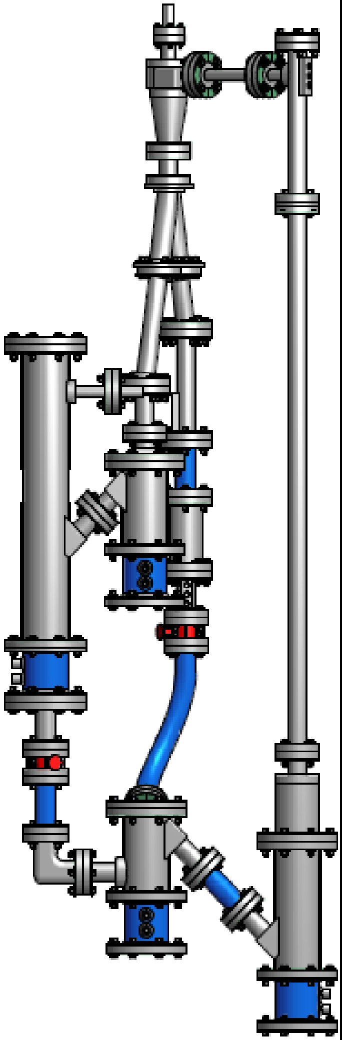
Experimental Kinetic/Mass Transfer Data

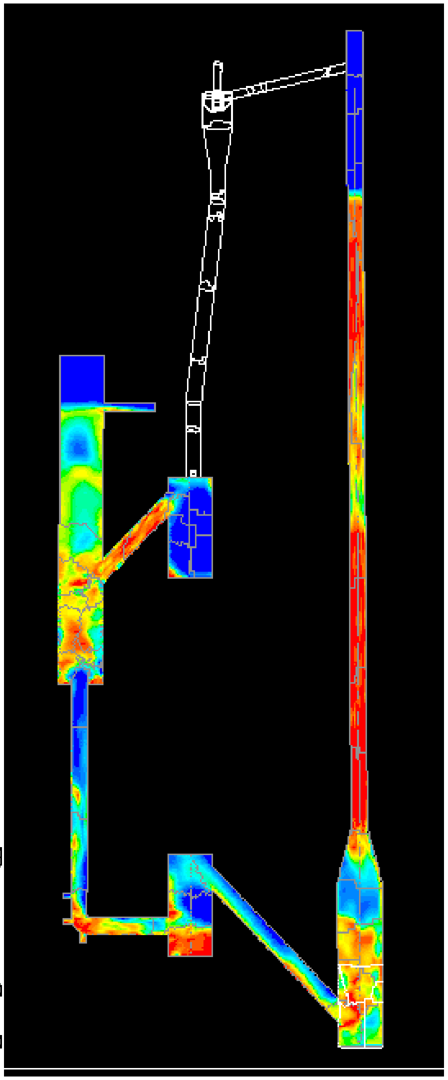
C2U and validation data



C2U and validation data







<u>C2U Progression</u>

1. Design and construction
2. Shakedown and modification as needed
3. Revise design drawing
4. Create system models from revised drawings.

C2U and validation data

To validate individual models, three sets of tests where statistically devised and randomized

1. Cold Flow testing – hydrodynamics
2. Hot Flow testing – heat transfer, hydrodynamics
3. Reaction testing – reaction kinetics, heat transfer, hydrodynamics

Sorbent AX			Sorbent 32D					
Cold Flow	Hot Flow		Cold Flow	Hot Flow		Reacting Flow		
Flow (SLPM)	Flow (SLPM)	Temp(°C)	Flow (SLPM)	Flow (SLPM)	Temp(°C)	Flow (SLPM)	Temp(°C)	CO_2 Conc.
49.8	16.9	70.3	19.2	21.9	60.4	51.3	62.9	18.9
15	48.8	60.2	23.6	39.5	66.7	40	62.3	10.8
58.9	35.4	56.3	50.3	43.8	45.3	37	68.2	14.6
43.7	38.6	67.4	51.7	46.3	40.3	27.3	72.8	15.7
35.7	57.1	43.5	37	36.7	65	[illegible]	57.5	14.2
29.8	20.8	58.4	31.9	31.9	52.1	59	40.7	17.4
25.1	27.1	52.4	[illegible]	16.4	71.1	33.7	[illegible]	16.3
20.4	30	42.7	[illegible]	26.7	47.7	35.6	[illegible]	10.4
54.6	48.6	49	[illegible]	22.7	53.4	23.1	64.3	[illegible]
40.3	26	77.2	25.4	52.7	78.1	32.8	59	[illegible]
38.4	54.7	65.6	59.6	58.1	57.7	41.3	70.4	20
23.2	41.9	74.2	33.3	51	73.4	20.5	44.8	14.3
31.6	40.6	61.8	16.1	[illegible]	79.1	56.4	63.6	13.7
28	52	73	27.4	[illegible]	68.8	17.9	48	10.5
47.8	23	47.4	21.6	[illegible]	55.2	43	71.7	18.2
18	15.8	45.3	43.3	19.3	65.7	56.9	57.9	10.2
33.4	29.5	69.7	54.9	39.3	43.5	32	79.1	15.3
52.6	44.4	40.5	41.4	49.4	63	49.1	61.6	17.1
46	36	50	29.6	29.7	[illegible]	44.8	65.4	19.7
56.9	19.2	76.3	47.7	56.1	[illegible]	50.2	46.2	16.5
15	32.2	63.8	16.1	35.2	58.5	59.7	44.3	13
31.6	46.1	54.4	45.9	17.1	48.5	57.5	59.3	15.9
49.8	53.3	56.8	57.5	42.3	51.6	38.2	76.9	14.9
35.7	58.7	79.4	41.4	25.8	71.9	[illegible]	67.8	12
20.4	15.8	45.3	25.4	17.1	48.5	[illegible]	52.7	19.5
46	38.6	67.4	33.3	30.6	79.1	[illegible]	50.2	11.4
25.1	36	50	21.6	58.1	57.7	45.9	60.1	12.6
43.7	58.7	79.4	29.6	51	73.4	15.9	67	12.2
56.9	53.3	56.8	51.7	19.3	65.7	35.8	53.1	13.9
54.6	19.2	76.3	50.3	43.8	45.3	55	[illegible]	14.6
29.8			37			48.2	[illegible]	13.1
38.4			43.3			54.4	75.7	11.9
47.8			19.2			15.1	56.4	15.1
23.2			27.4			34.6	47	12.7
58.9			54.9			30.2	77.6	[illegible]
33.4			39.7			26.7	48.3	[illegible]
18			31.9			19.9	44	17.9
40.3			47.7			28.6	50.7	13.3
28			59.6			25.1	74.5	11.6
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						46.8	40.9	19.2
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Sorbent 32D					
Cold Flow	Hot Flow		Reacting Flow		
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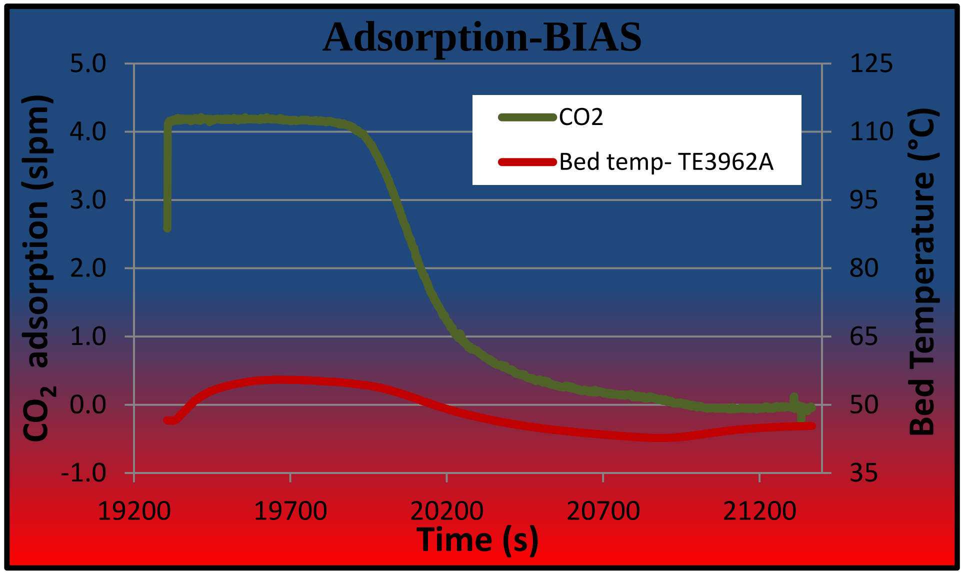
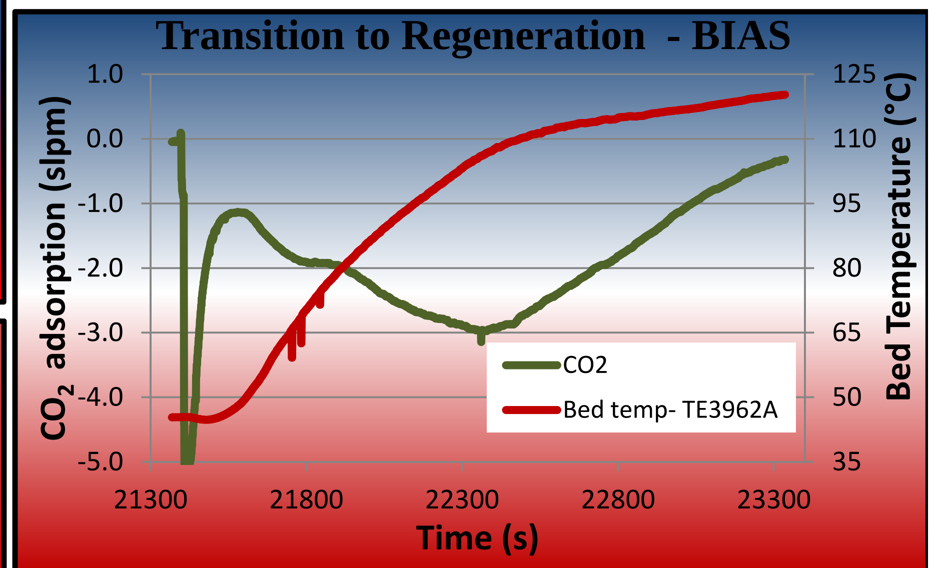
19.2	21.9	60.4	51.3	62.9	18.9
23.6	39.5	66.7	40	62.3	10.8
50.3	43.8	45.3	37	68.2	14.6
51.7	46.3	40.3	27.3	72.8	15.7

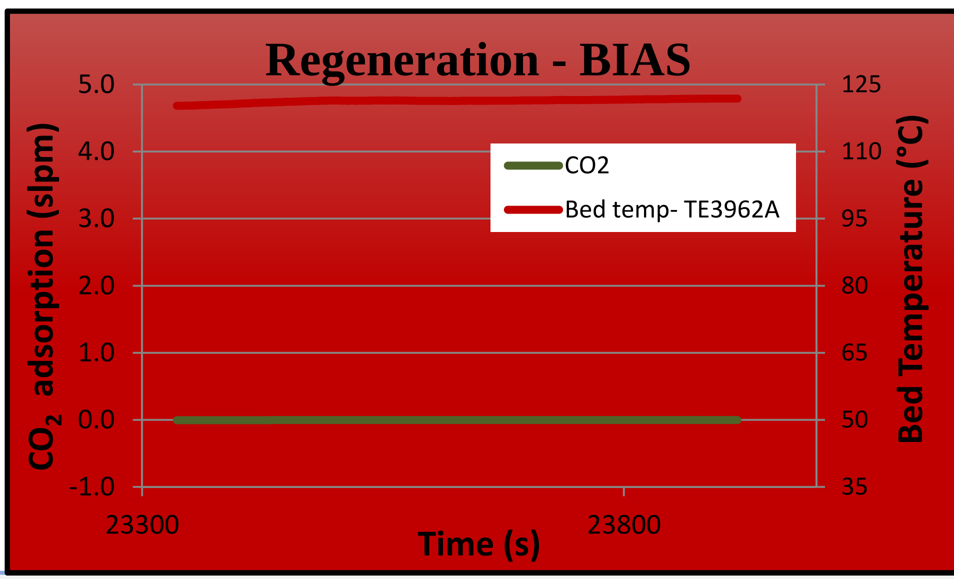
C2U Initial testing data



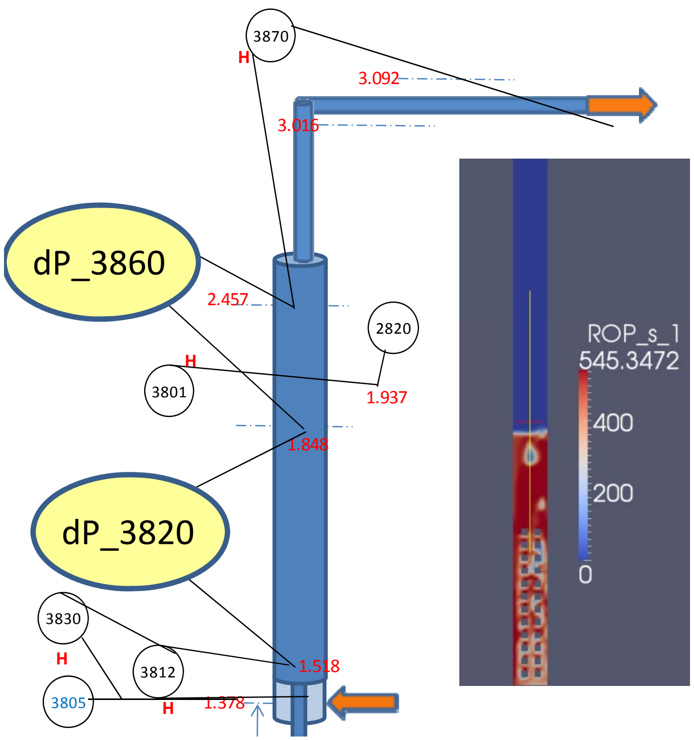
Batch test conducted in the regenerator with the BIAS sorbent



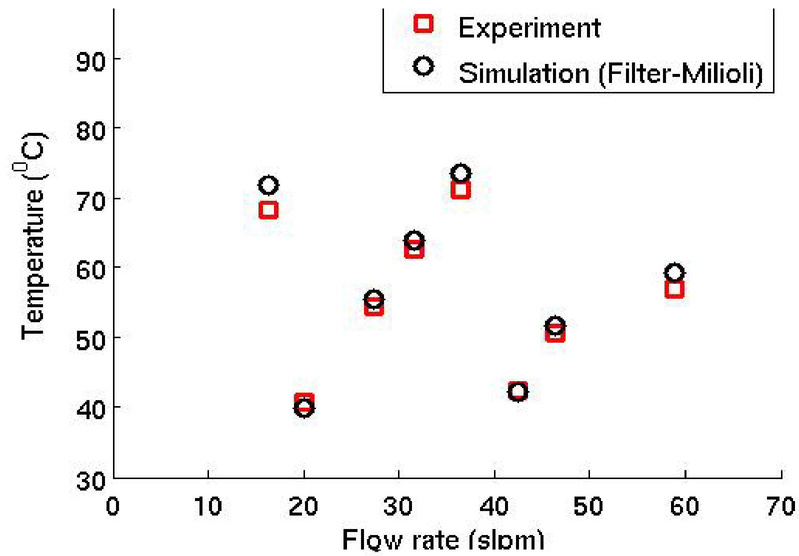
Most CO_2 is released before achieving the regeneration temperature

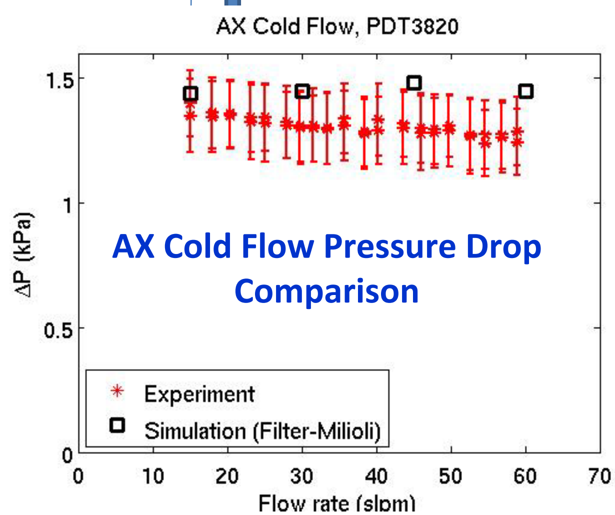


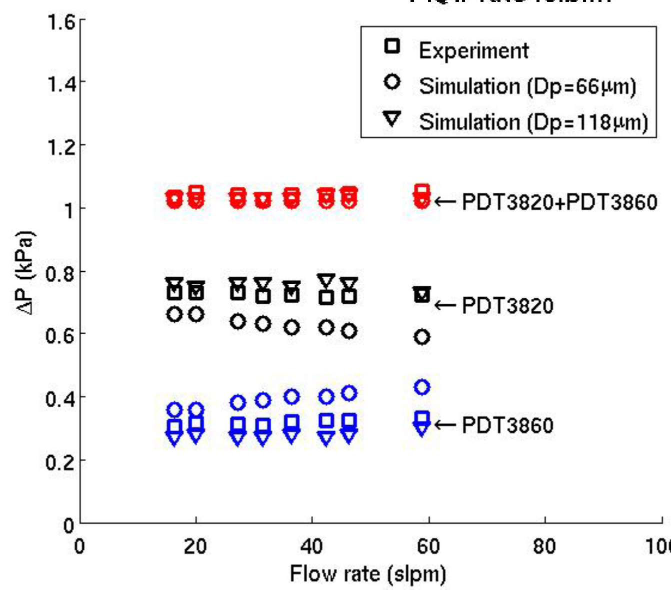
CFD Validation with C2U non-circulating Experiments

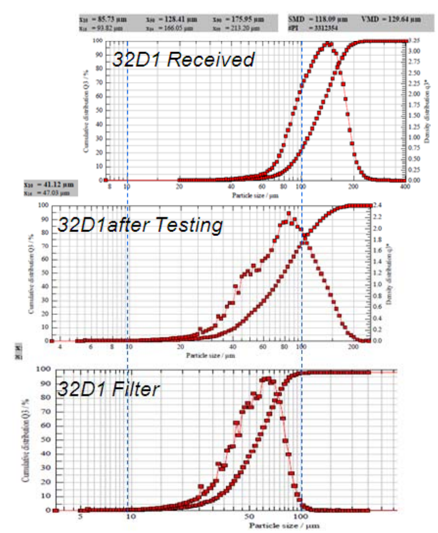


32D Hot Non-reactive Flow









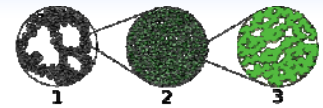
Conclusion

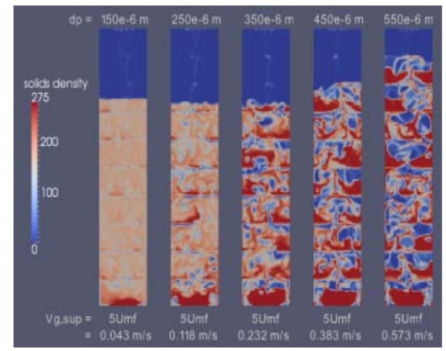
- **Coupling experimental development with simulation enables**
  - New approaches to be screened more quickly
  - Focuses development on most promising material & process conditions
- **Simulation with uncertainty quantification**
  - Focuses experimental efforts on elements with the most impact to the process/technology
- **Focused experiments for model validation enable**
  - Lower risk for scale up through quantitative confidence of model predictions

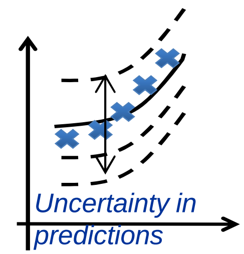
CCSI Computational Toolset Demonstration

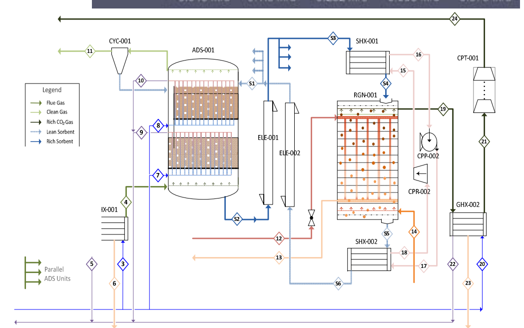
Carbon Capture Simulation Initiative

- **5-7 PM today in Woodlawn I**
  - Demonstration & detailed discussion of capabilities
- ***Sorbents, Solvents, Membranes, Oxycombustion***
- Initial toolset released Oct. 2012
  - 4 companies already have already licensed
  - Additional releases planned for Fall 2013, 2014, 2015.
  - Final release planned for Jan. 2016









Risk Analysis (Technical Risk, Financial Risk) & Decision Making

Validated High-Fidelity CFD & UQ

Process Design & Optimization Tools

Advanced Process Control & Dynamics

Uncertainty Quantification

High Resolution Filtered Sub-models

Uncertainty Quantification

Process Models

Uncertainty Quantification

Basic Data Sub-models

Cross-Cutting Integration Tools

Data Management, Remote Execution Gateway, GUI, Build & Test Environment, Release Management