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Carbon Capture Simulation for Industry Impact

Computational Approaches for Optimizing Decarbonization of Cement Plants using Solvent Based Carbon Capture

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FECM Cement and Lime Decarbonization Workshop
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NATIONAL ENERGY TECHNOLOGY LABORATORY | Berkeley Lab | Lawrence Livermore National Laboratory | Los Alamos National Laboratory | Pacific Northwest National Laboratory | Oak Ridge National Laboratory | West Virginia University | University of Notre Dame | The University of Texas at Austin | UT | University of Pittsburgh | Carnegie Mellon

CCSI² – Modeling, Optimization, and Technical Risk Reduction

Multi-lab modeling initiative to support carbon capture technology development

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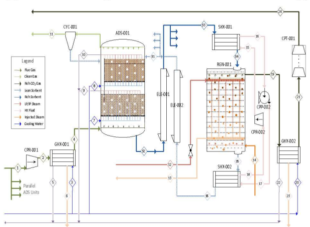
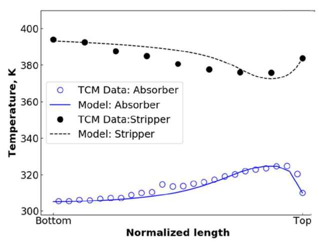
Modeling			Optimization	Risk Reduction	
High Fidelity Process Modeling	Model Validation	Uncertainty Quantification	Process Optimization	Robust Design	Maximizing Learning

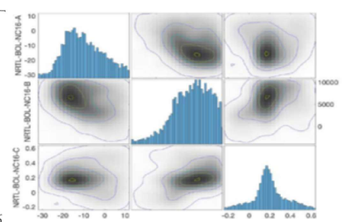
High Fidelity Process Modeling



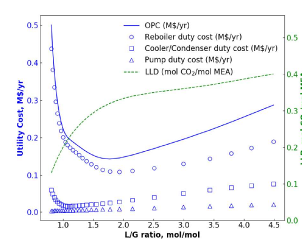
Model Validation



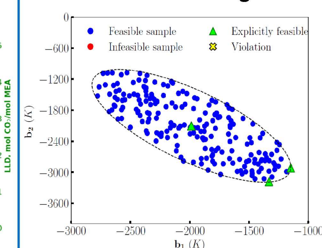
Uncertainty Quantification



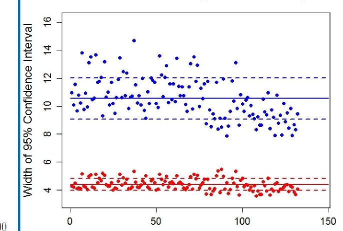
Process Optimization

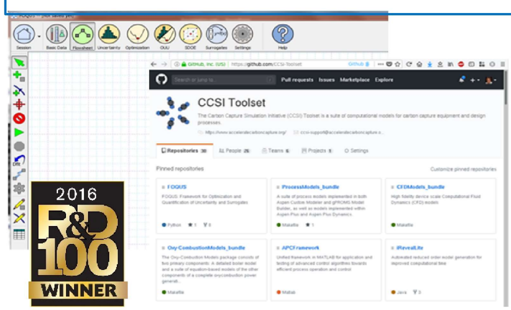


Robust Design



Maximizing Learning





Open Source: github.com/CCSI-Toolset

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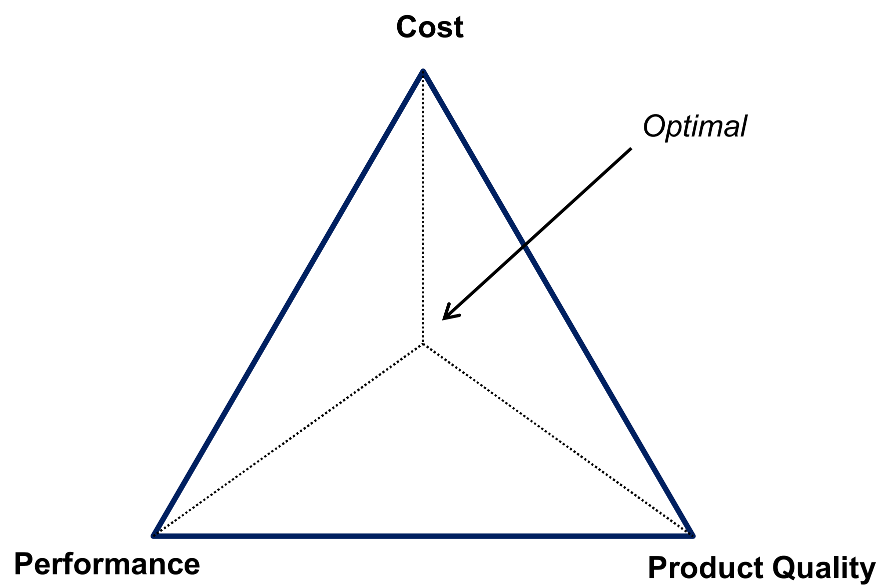
Motivation for Modeling Cement Plant Decarbonization

- Assess application of conventional and novel carbon capture processes for industrial applications
- Ensure modeling results respond to changes in process conditions
- Ensure base plant performance, especially changes in product quality, is captured in modeling
- Optimize CO_2 capture process design, optimization, and integration with base plant considering effects on product



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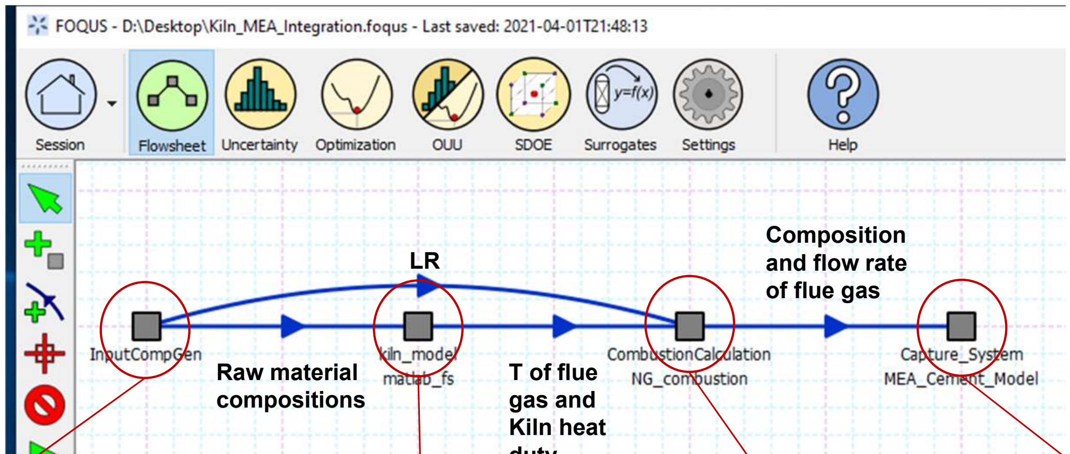
Integrated Cement Process Submodules



Feed compositions

Inputs:
- Lime saturation factor (LSF)
- Silica ratio (SR)
- Alumina ratio (AR)
- Limestone ratio (LR)

Output:
- Mass fraction of $CaCO_3$, CaO, SiO_2, Al_2O_3, and Fe_2O_3

Matlab Cement model

Inputs:
- Mass compositions of raw materials
- Peak gas temperature
- Location of peak gas temperature
- Solid flow rate
- Temperature of gas at inlet

Output:
- Compositions of clinker
- Emission of CO_2 from calcination reaction
- Heat required by kiln

Combustion Aspen

Inputs:
- Temperature of flue gas
- Heat duty (heat required by the kiln for clinker production)
- Limestone ratio

Output:
- Flue gas flow rate
- Mole composition of flue gas
- Flow rate of required fuel

MEA Aspen

Inputs:
- Flue gas flow rate
- Mole composition of flue gas
- Absorber packing height
- Stripper packing height
- Lean loading
- Heat exchange pinch point

Output:
- Stripper reboiler duty
- Other

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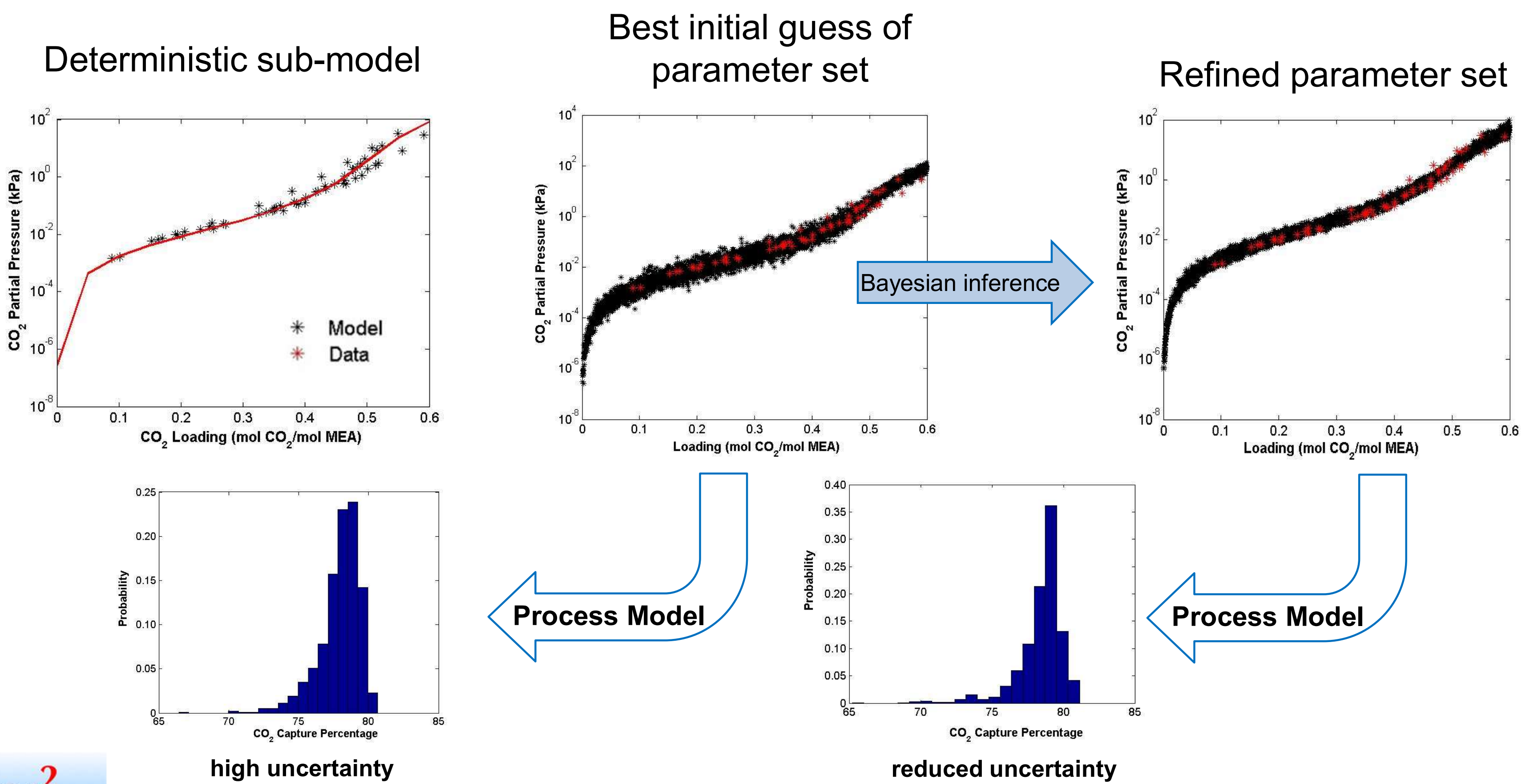
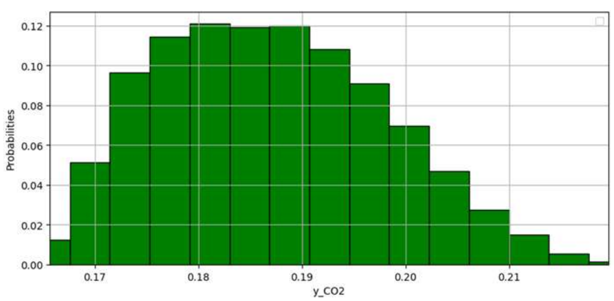
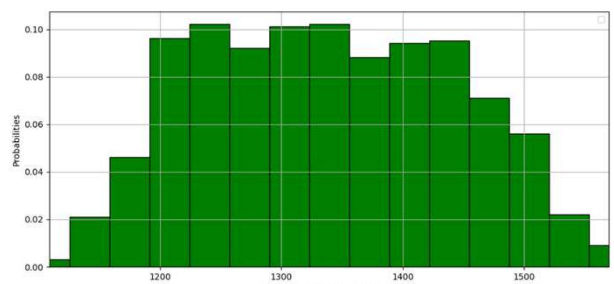
Uncertainty Quantification & Bayesian Inference EXAMPLE: VLE Models

VLE Data/Model Comparison at 40°C



UQ of a Rotary Kiln Model for Cement Production: Uncertainty Analysis Results

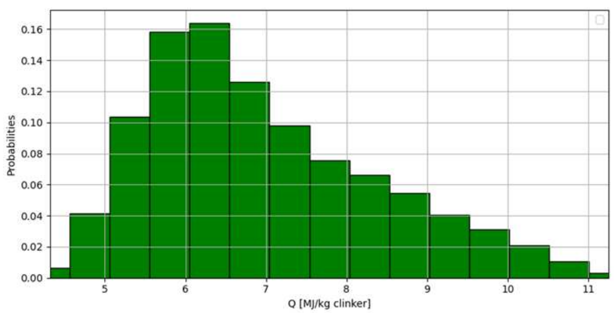


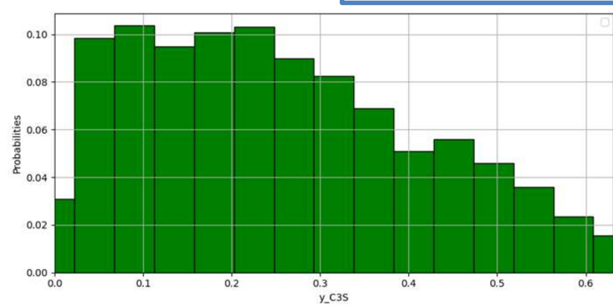


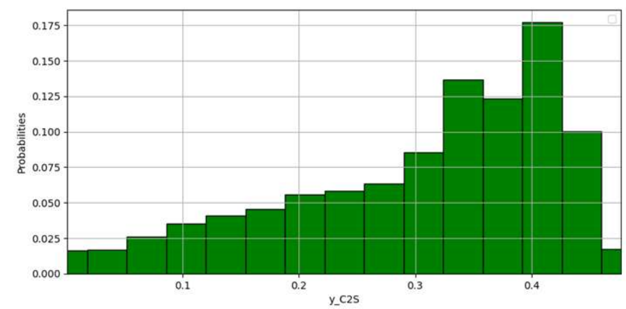
Uncertainty of outputs

Output	Lower Bound	Upper Bound	Mean	Standard Deviation
y_{CO_2}	0.165	0.22	0.189	0.0095
$\dot{m}_{FG}$ [tonne/hr]	1109	1570	1354	105
Q [MJ/kg clinker]	4.3	11.25	7.1	1.2
y_{C_3S}	0.014	0.63	0.28	0.14
y_{C_2S}	0.002	0.46	0.33	0.11

Wide range of cement quality







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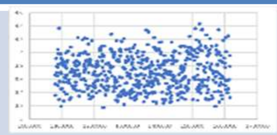
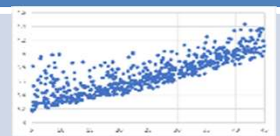
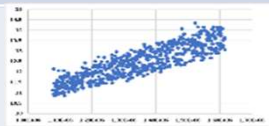
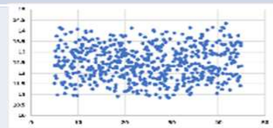
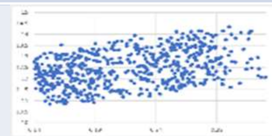
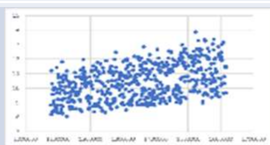
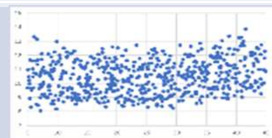
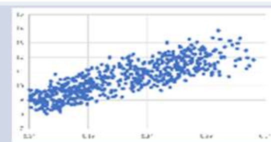
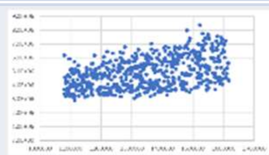
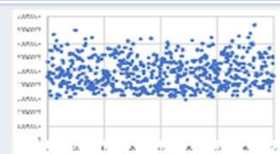
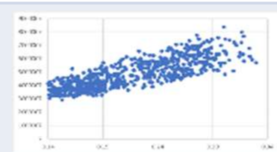
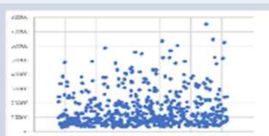
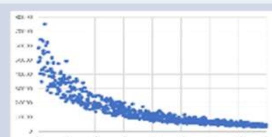
UQ analysis of MEA Solvent System for CO_2 Capture

Key performance Indicators (KPIs)	Flue gas (tonne/hr) [1078, 1617]	Heat exchange pinch point (K) [5, 45]	CO_2 mol% [14, 33]
SRD (MJ/kg) [3.17, 4.35]			
Absorber Diameter (m) [10.85, 14.11]			
Stripper Diameter (m) [8.06, 13.48]			
Lean Loading Flowrate (tonne/hr) [2926, 9006]			
Heat Exchange Area (sqm) [3029, 70385]			

Remarks:

1. Size of the MEA absorber and stripper columns increase as flue gas flow rate and CO_2 content increases
2. Absorber/stripper packing height, and lean loading has smaller impact compared to flue gas flow rate, heat exchange pinch point, and CO_2 composition. Details shown in CCS - UQ analysis of MEA in FOQUS

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Integrated Cement Kiln Model and MEA CCS Model: Optimization Problem

Optimization Problem

$$
\begin{aligned}
\min \quad & \text{SRD} \\
\text{s.t.} \quad & \text{Kiln MATLAB Model} \\
& \text{MEA Aspen Model} \\
& CO_2 \text{ capture } \geq 90\% \\
& \text{Absorber flooding } \leq 0.8 \\
& \text{Stripper flooding } \leq 0.8 \\
& 0.48 \geq y_{C_3S} \geq 0.55 \\
& 0.20 \geq y_{C_2S} \geq 0.25
\end{aligned}
$$

Fixed Cement Type

MATLAB Model

- Mass and Energy Balances
- Melting/Coating Formation
- Rx and Kinetic model

Decision Variables

	Process Parameter (Inputs)	Units	Initial Guess	Min	Max
Kiln Model	Lime saturation factor (LSF)	--	1.27	1.10	1.36
	Silica ratio (SR)	--	2.15	2.10	2.90
	Alumina ratio (AR)	--	1.00	0.62	1.13
	Limestone to lime ratio (LR)	--	0.46	0.42	0.56
	Peak gas temperature	K	1970	1970	2180
	Location of peak gas temperature	--	0.75	0.6	0.9
	Flow rate of raw material	kg/s	30.0	30	60
MEA Model	Absorber packing height	m	100	20	100
	Stripper packing height	m	31.06	12	48
	Lean loading	mol CO_2/mol MEA	0.156	0.10	0.18
	Heat exchange pinch point	K	5	5	45

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Integrated Cement Kiln Model and MEA CCS Model: Optimization Results

Optimal Operating Variables in the Kiln

Kiln Inputs	Optimum Value
Lime saturation factor (LSF)	1.12
Silica ratio (SR)	2.11
Alumina ratio (AR)	1.14
Limestone to lime ratio (LR)	0.43
Peak gas temperature (K)	1970
Location of peak gas temperature	0.75
Flow rate of raw material (kg/s)	30
Clinker composition	
C_3S (alite)	0.519
C_2S (belite)	0.249
C_4AF (ferrite)	0.132
C_3A (aluminate)	0.079
Total clinker composition (%)	98

Optimal Designs of MEA System

KPIs	Cement flue gas from Kiln	Baseline case
	CO_2: 17.7 mol%	CO2: 18.9 mol%
Flue gas flow rate (tonne/hr)	1125.9	1347.3
CO_2 captured (tonne/hr)	264.5	336.0
Absorber stage #	100	100
Stripper stage #	60	60
SRD (MJ/kg CO_2 captured)	**3.20**	**3.22**
Liquid/gas (kg solvent/kg flue gas)	3.11	3.19
Heat exchange area (sqm)	38311	46900
Absorber diameter (m)	11.27	12.23
Stripper diameter (m)	8.40	9.45

DFO Solver: Nlopt (88 iterations, ~2hr)
Objective Function (SRD) = 3.20 [MJ/kg CO_2 captured]

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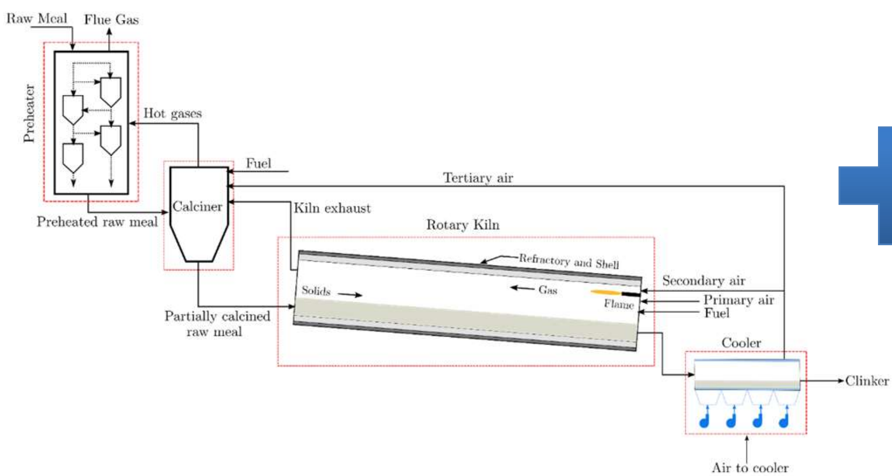
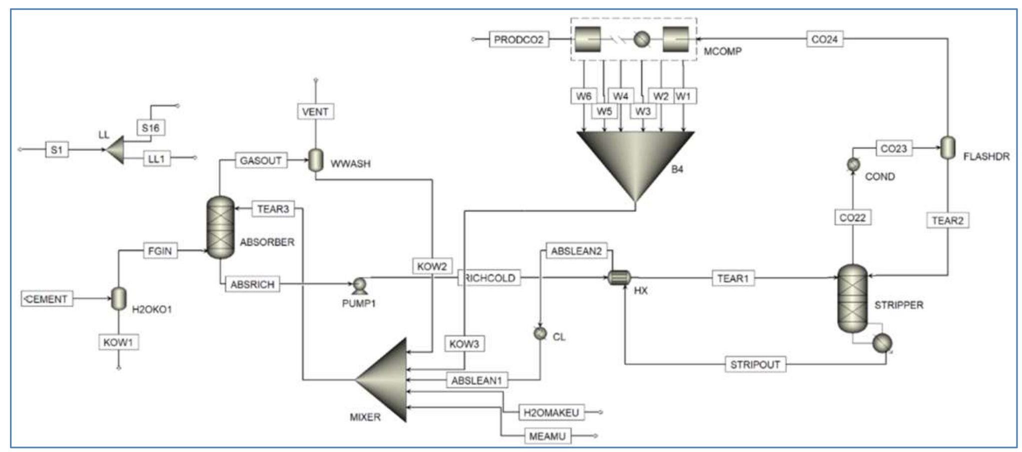
Optimization of an Integrated Cement Plant with MEA Carbon Capture Process

Accomplishments

- Improved CCS heat/energy consumption while maintaining high quality cement
- Developed a rotary kiln model in MATLAB
- Optimized the design of an MEA-based carbon capture system for cement industry
- Optimized the integrated cement kiln plant and MEA CCS system in FOQUS
- Uncertainty quantification of the integrated model





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Opportunities for Industrial Collaboration

- More detailed and responsive **cement plant models**
- Understand opportunities for **thermal integration**
- Validate **model of product quality** with operational data
- Detailed understanding of **uncertainty and its impacts** on key process indicators
- $CCSI^2$ can help **guide pilot test** designs to **maximize value of data** to refine understanding
- Refined models leveraged for **optimizing** decarbonized cement plant operation

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Acknowledgements

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Miguel Zamarripa (*)
Daison Yancy Caballero (*)

(*) NETL Support Contractor

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Summary

- Kiln model standalone:
  - The peak gas temperature and the mass flow rate of raw meal are the most sensitive variables that have a significant impact on the flue gas conditions and clinker production.
  - Alite/belite content have the largest standard deviation because the large variability of the composition of raw meal, while CO_2 emissions and energy have low standard deviation with mean values of 18.9% CO_2 in the flue gas and 7 MJ/kg of clinker, respectively.
- MEA model standalone:
  - Flue gas flow rate and CO_2 composition has biggest effect on the size of the plant
  - With fixed flue gas flow rate and CO_2 composition
    - The optimized **lean loading** is around **1.6**;
    - The optimized **heat exchange pinch point** gained at it **lower bound**;
    - The optimized **absorber packing height** gained at it **upper bound**
- Cement-MEA Integrated Model:
    - With given cement quality, the optimized CO_2 composition is **17.7 mol%**
    - The optimized integrated model has **SRD** similar as the MEA standalone model, which is around **3.2 MJ/kg CO_2** captured

Future Work – EY23 Superstructure Optimization

- Develop costing framework for cryogenic capture process:
  - Economic methods for cryogenic capital and operating expenditures, including tools for scale-up, sizing and year-index adjustments
  - Techno-economic analysis/optimization compared to kiln-MEA system

- Quantify feasibility of cryogenic capture for alternative emission point sources:
  - Assess capture feasibility from low CO_2 flue gases, such as from steel plants
  - Direct comparison with solvent/sorbent systems for power plant emissions
  - Development of a combined separation membrane-cryogenics model, with process and economic assessment

Future Work – EY24 Model Improvements & IDAES Collaboration

- Develop a rigorous vapor-liquid-solid, kinetics-based reaction model and equilibrium reactor model:
  - Properly account for impact of CO_2 concentration on equilibrium
  - Incorporate co-recovery desublimation of Hg, HCl, NO_x and SO_x
  - Account for solid CO_2 solubility in liquid isopentane
- Requirements for new models:
  - Temperature data in the cryogenic range, typically 125-200 K
  - Corresponding $K_{eq} = \frac{y_{CO_2}}{x_{CO_2}=1}$ data, where y_{CO_2} is the mole fraction of CO_2 for mole fractions in the range 14-33 % CO_2, and 1-14% CO_2 if available, for multicomponent flue gas mixtures containing O_2, Ar and balance N_2

Cryogenic Carbon Capture with External Cooling Loop Model Overview

EY22 - Direct Liquid Contact Column

- Incoming natural gas (pre-combustion) or flue gas (post-combustion) bubbles up through staged sieve plate trays
- Cold contact liquid (isopentane) is delivered to each tray which has ~5 cm of liquid height[1]
- Gas and liquid mix in counterflow
- Solid flows out with liquid as slurry, preventing fouling from ice formation
- Theoretically, impurities such as SO_x, NO_x, HCl, Hg desublimate here as well → will be a focus of future work.

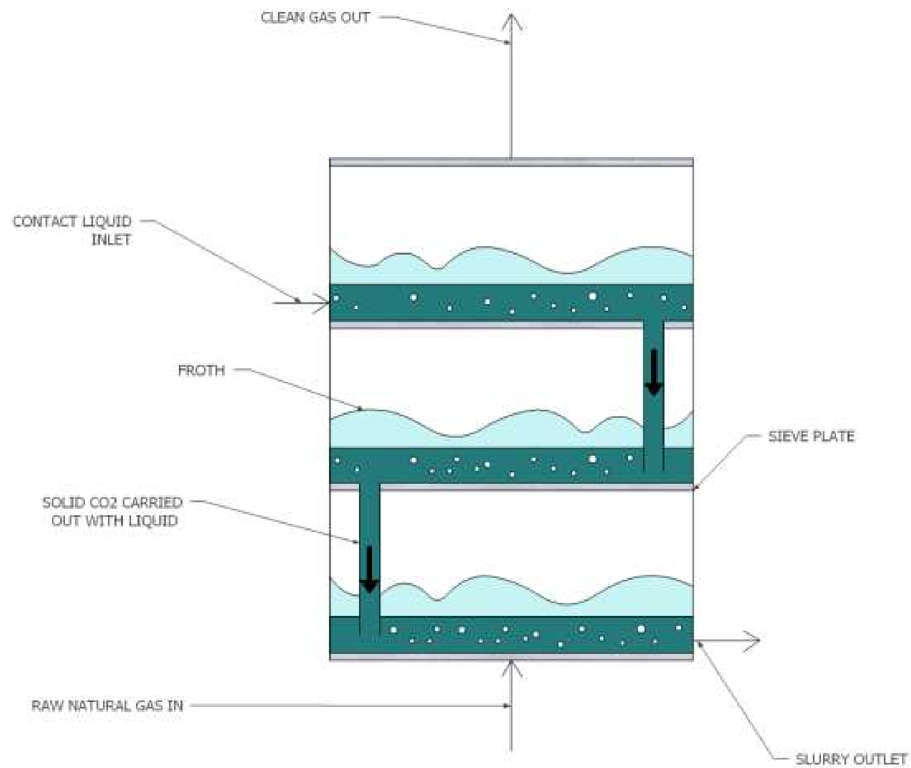

Figure Source: [1]Jensen et al., Int J Greenh Gas Con 42 (2015) 200-212

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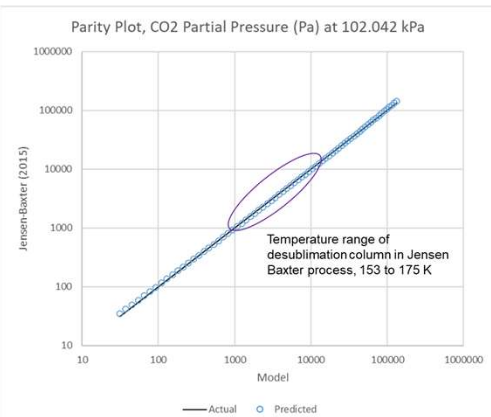
EY22: Refinement of VSE models for cryogenic carbon capture

Accomplishments

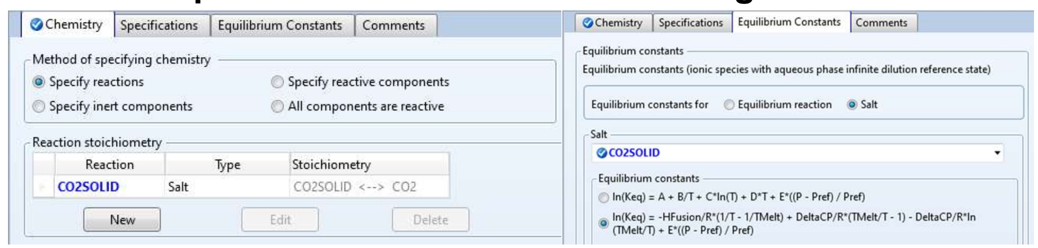
- Extensive literature review of cryogenic CO_2 thermodynamics and capture technologies
- Developed an initial vapor-solid equilibrium (VSE) desublimation model of binary CO_2-N_2
- Implemented VSE model via Aspen Plus Salt Chemistry module and RGibbs block
- Selected a base case flowsheet[1] and began process modeling

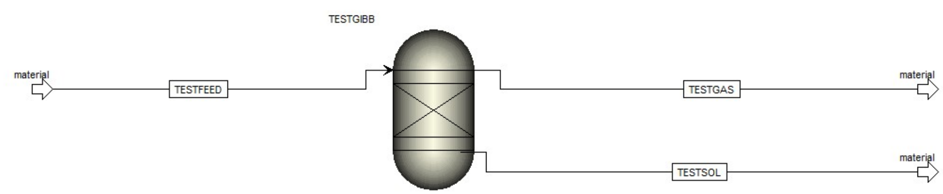
Salt Chemistry VSE Model



Quantity	CO_2-N_2	[2]Pure CO_2
Heat of Fusion (Δh_m), kJ/mol	26.16	26.20
Desub. Temp. (T_m), K	195.77	194.65
Desub. Heat Cap. Change (ΔC_p), J/mol-K	12.78	14.25

Aspen Plus Gibbs Reactor Modeling





[1]Jensen et al., Int J Greenh Gas Con 42 (2015) 200-212
[2]Nasrifar et al., Cryogenics 121 (2022) 103404

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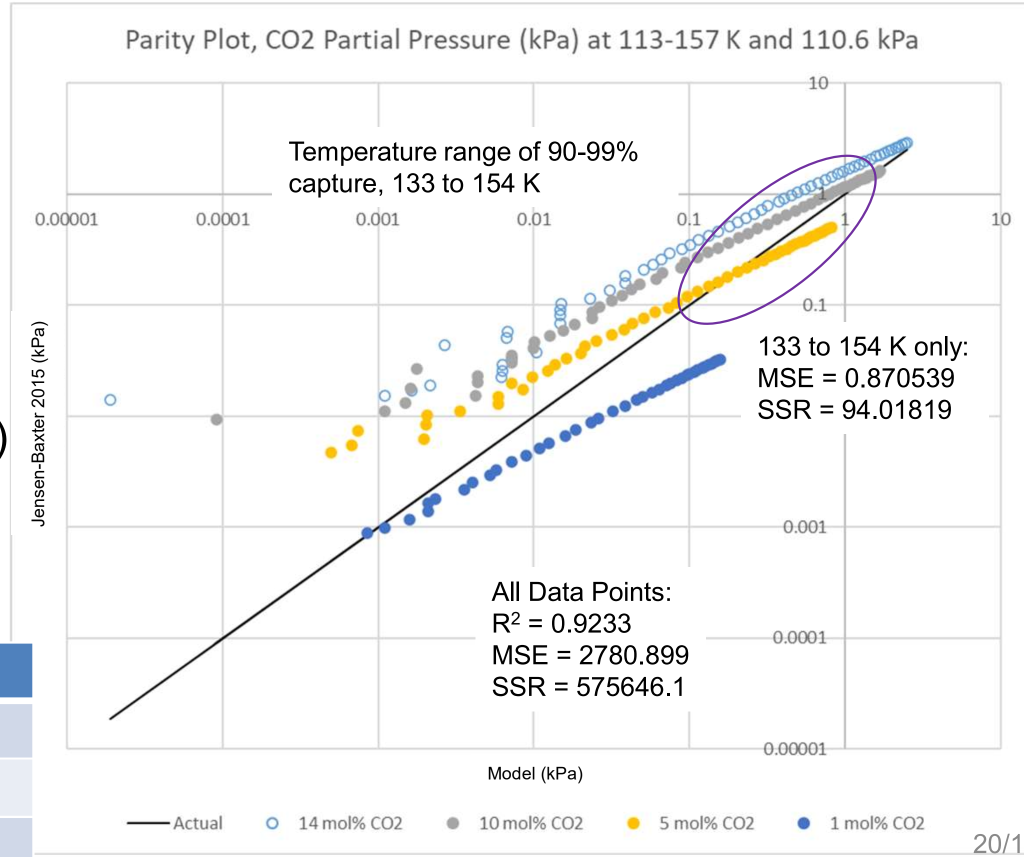
Salt Chemistry VSE Model - Improvement & Validation

- The Jensen CO_2/N_2 model is well correlated, but for the form required by Aspen does not represent multicomponent flue gas (O_2, Ar, pollutants) well at cryogenic conditions where solid forms (expect 90% capture from 13.53 mol% CO_2 feed at 155.85 K[4])

- New data[4] was obtained to fit a surrogate model for the equilibrium constant for typical compositions (1-14 mol% CO_2, 3 mol% O_2, <100 ppm each of SO_x, NO_x, HCl, balance N_2) and temperatures (113-157K)

- We validated the results below for Flue Gas with a correction of $E = 0.03439$ for $P_{ref} = 101.325\ kPa$:



Quantity	Flue Gas	Jensen	[3]Pure CO_2
Heat of Fus. (Δh_m), kJ/mol	19.35	26.16	26.20
Desub. Temp. (T_m), K	175.66	195.77	194.65
Δ Heat Cap. (ΔC_p), J/mol-K	14.26	12.78	14.25

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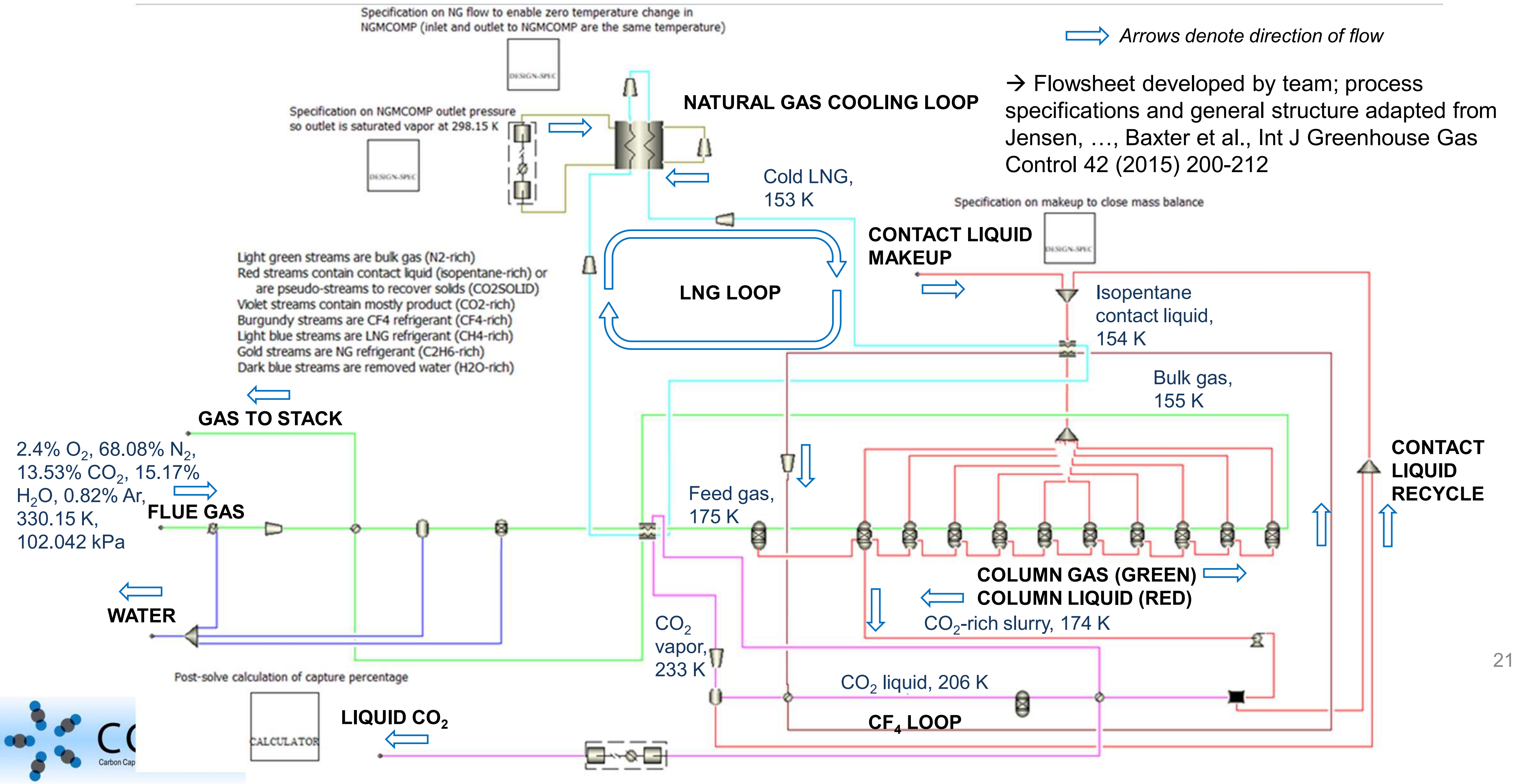
[3]Nasrifar et al., Cryogenics 121 (2022) 103404
[4]Baxter, L.; Baxter, A.; Burt, S. PCC 2009, Volume 1.

Process Model - Full CCC ECL Flowsheet, Annotated



Process Model – Column Optimization

- Optimize column to solve for stage temperatures and liquid delivery:

$$\min_{\hat{x}} f(\hat{x}) \quad s.t.\ \hat{x}^L \le \hat{x} \le \hat{x}^U, \quad h(\hat{x}) = 0, \quad g(\hat{x}) \le 0$$

Where f represents the objective function, $\hat{x}$ is the vector of decision variables bounded by the minimum values $\hat{x}^L$ and maximum values $\hat{x}^U$, $h(\hat{x})$ represents the fixed CO_2 capture percentage and material/energy balances calculated internally to Aspen, and $g(\hat{x})$ represents inequality constraints.

→ Maximizing slurry temperature keeps product close to 175 K, reducing duty to melt pure solid CO_2 downstream and introducing a natural upper bound of 175 K to prevent a diverging objective:

$$\max T_{SLUR}(T_i \text{ for } i \in [1,10], D_i \text{ for } i \in [1,9])$$
$$s.t.$$
$$100 \le T_i \le 200 \text{ for } i \in [1,10]$$
$$0.05 \le D_i \le 0.15 \text{ for } i \in [1,9]$$
$$\left(1 - \sum_{i=1}^{9} D_i\right) - 0.05 \ge 0$$

* the constraint above effectively enforces $D_{10} \ge 0.05$

$$100 * \frac{PROD_{CO_2}}{FEED_{CO_2}} - CAPP_{SPEC} = 0$$
$$T_1 - T_0 \le 0$$
$$T_{i+1} - T_i \le 0 \text{ for } i \in [1,9]$$
$$T_{10} - T_{CL} - 0.1 \ge 0$$

Where:

i is a column stage on $i \in [1,\ 10]$

T_i is the temperature of a column stage i,

T_0 is the feed flue gas temperature to the bottom of the column,

D_i is the fraction of total contact liquid delivered to stage i,

$PROD_{CO_2}$ is the flow of CO_2 product from the system,

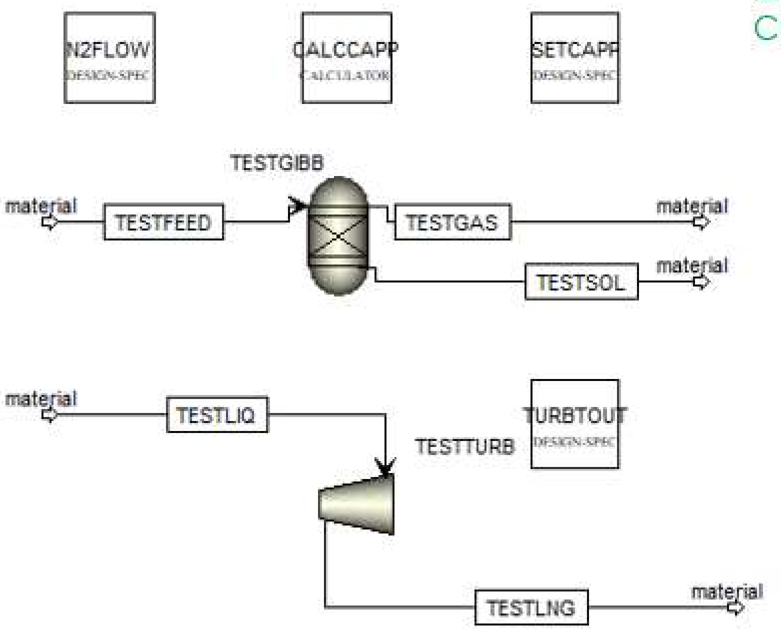
$FEED_{CO_2}$ is the flow of CO_2 in the inlet flue gas, and

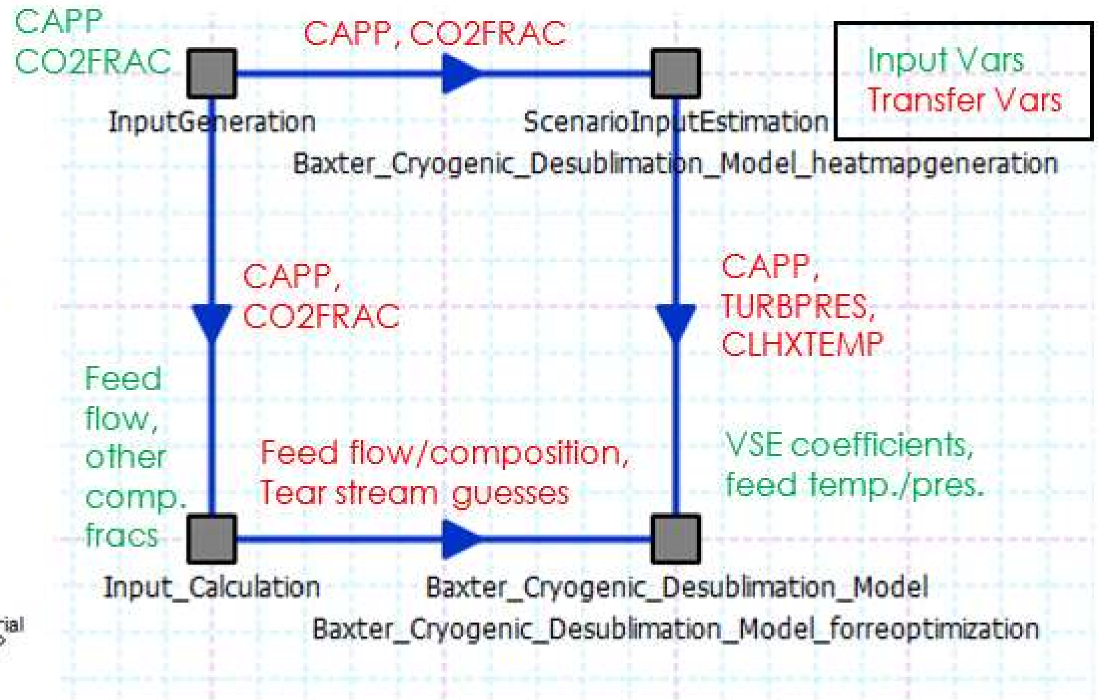
$CAPP_{SPEC}$ is the desired CO_2 capture percentage set by the user.

→ Column gas exit temperature is pre-determined by VSE chemistry, specified capture level and feed gas composition

Process Model – FOQUS Implementation

"ScenarioInputEstimation" model





⇐

VSE Model Form Derivation From First Principles

- Equations from Jensen, Mark, "Energy Process Enabled by Cryogenic Carbon Capture" (2015). Theses and Dissertations. 5711

- Raoult's Law, $x_{CO_2} P^{sub}_{CO_2} = y_{CO_2} P$, relates vapor (y_{CO_2}) CO2 to solid (x_{CO_2}) dry ice. The solid is pure and the sublimation pressure is temperature dependent, yielding $P^{sub}_{CO_2}(T) = P y_{CO_2}$. This is true for all EOS, and any gas-phase reaction.

- Using fugacities and adding a Poynting correction, we express this as $\phi^{sub}_{CO_2} f P^{sub}_{CO_2}(T) = \bar{\phi}^{vap}_{CO_2} P y_{CO_2}$ for the CO2 fugacity coefficients in each phase.

- De Guido & Pellegrini (2014) derived a more specific form for Peng-Robinson, a common EOS for flue gas mixtures: $\phi^{sub}_{CO_2} \exp\left(\frac{\Delta h_m}{RT_m}\left(1-\frac{T_m}{T}\right)+\frac{\Delta C_p}{R}\left(\frac{T_m}{T}-1-\ln\left(\frac{T_m}{T}\right)\right)\right) = y_{CO_2}\bar{\phi}^{vap}_{CO_2}$ where the heat of fusion (Δh_m), melting/desublimation temperature (T_m) and heat capacity change due to melting/sublimation (ΔC_p) depend on the non-CO2 component ratios.

- At equilibrium, the solid and vapor fugacities are equal. Therefore, quantifying these three unknowns for $\ln\left(\frac{y_{CO_2}}{x_{CO_2}=1}\right) = ln\, K_{eq} = \frac{\Delta h_m}{RT_m}\left(1-\frac{T_m}{T}\right)+\frac{\Delta C_p}{R}\left(\frac{T_m}{T}-1-\ln\left(\frac{T_m}{T}\right)\right)$ models solid-vapor equilibrium for a cryogenic CO2 system using the PR EOS.

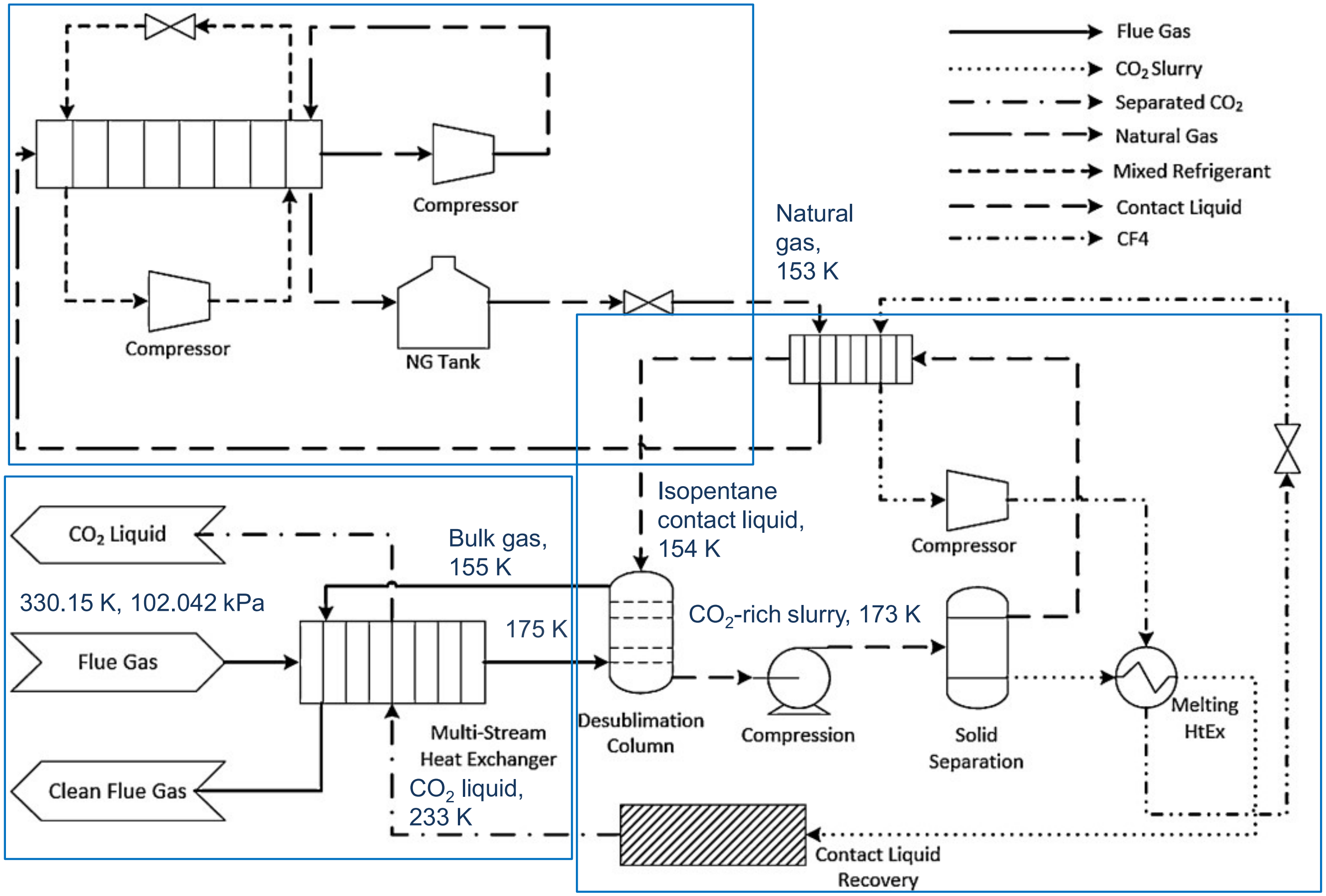
CCSI2 Carbon Capture Simulation for Industry Impact

Process Model - Baxter Cryogenic Carbon Capture Process (4/4)

Natural gas refrigerant loop for external cooling

Cool initial feed to 290 K to remove bulk of water, then blower pressurize to 127.6 kPa and cool to 273 to remove residual water prior to multi-stream heat exchanger

$2.4\%\ O_2$, $68.08\%\ N_2$, $13.53\%\ CO_2$, $15.17\%\ H_2O$, 0.82% Ar

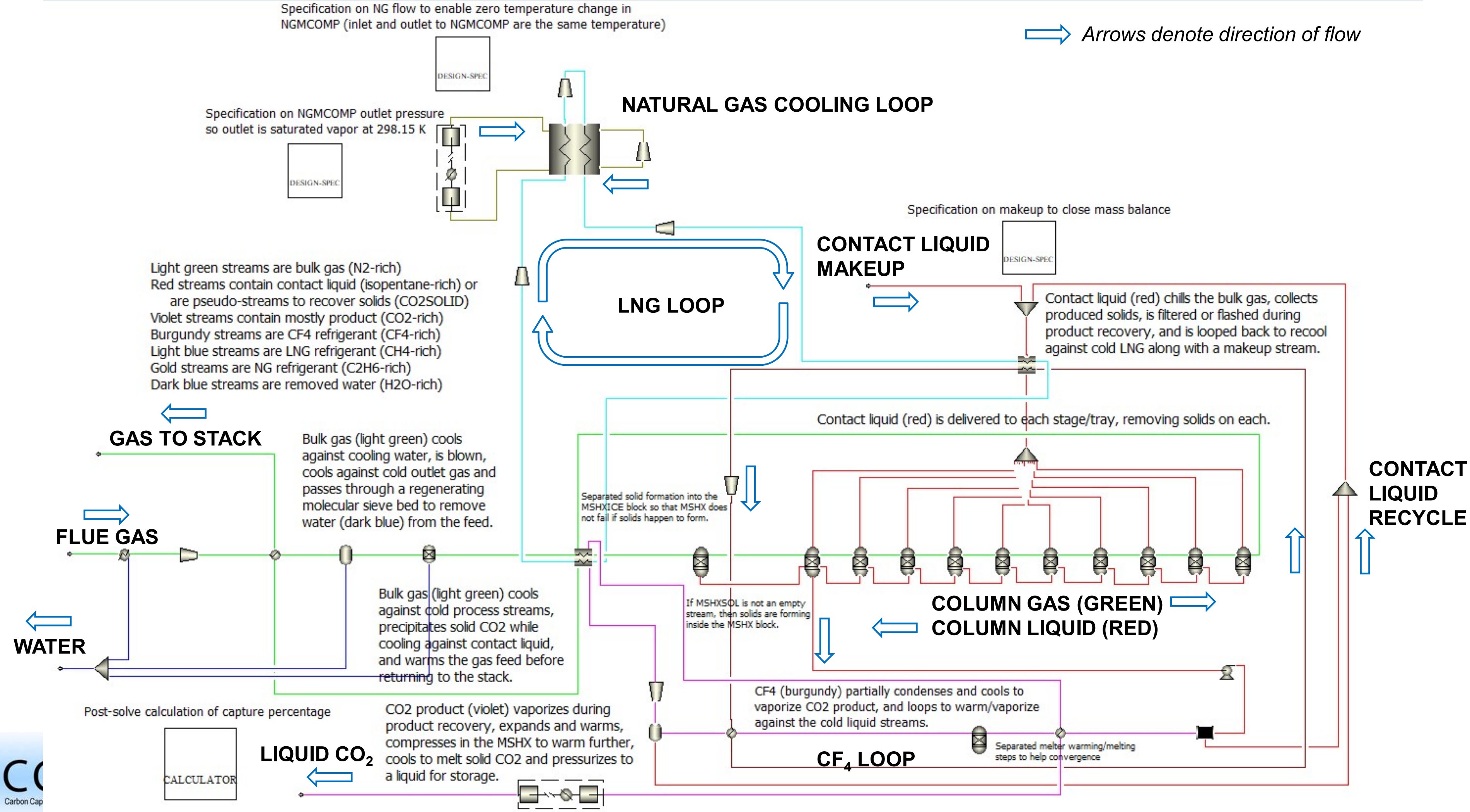


Dual loops to recover contact liquid and CF_4 refrigerant from the process

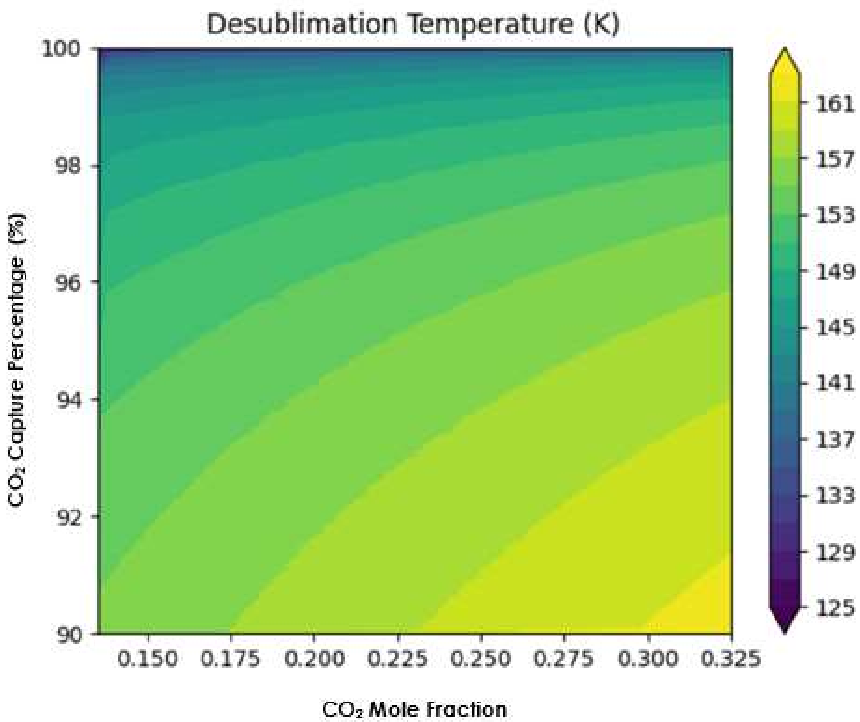
CCSI² Carbon Capture Simulation for Industry Impact

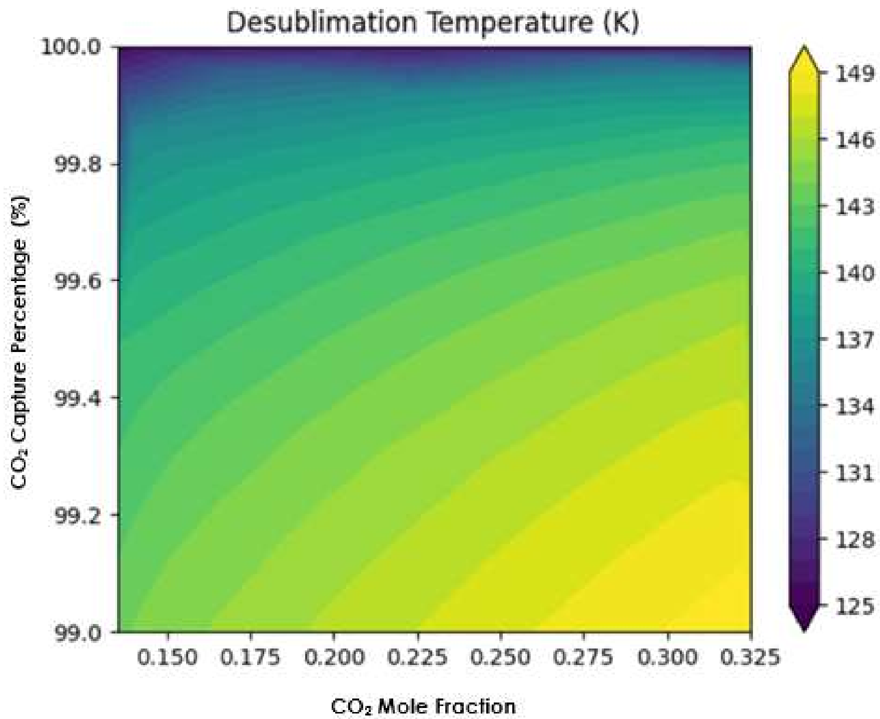
Jensen, …, Baxter et al., Int J Greenhouse Gas Control 42 (2015) 200-212

Process Model - Full CCC ECL Flowsheet, Annotated

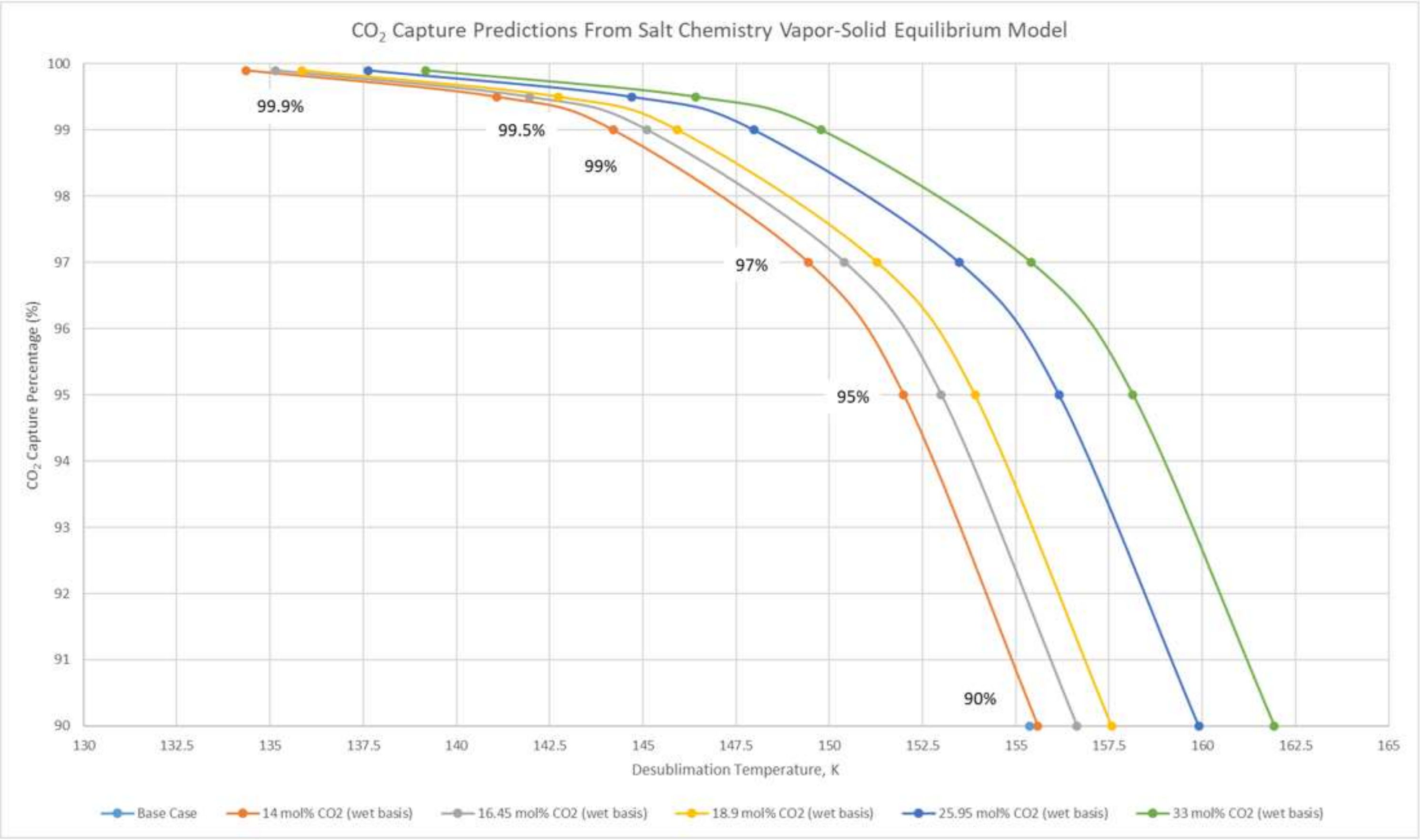


Salt Chemistry Model - Results



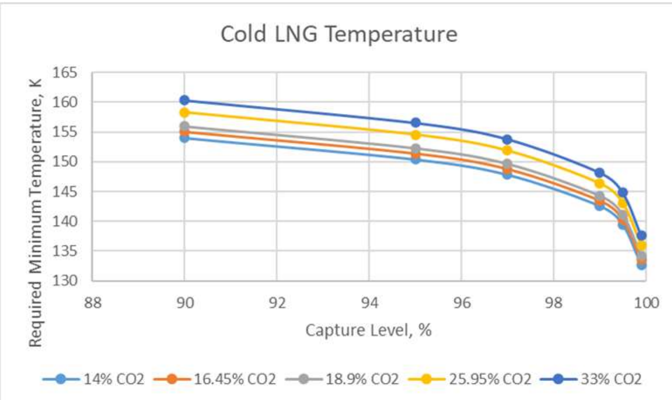


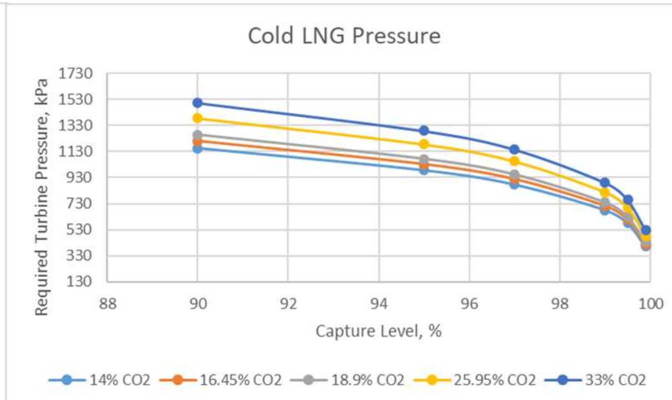
Salt Chemistry Model - Results

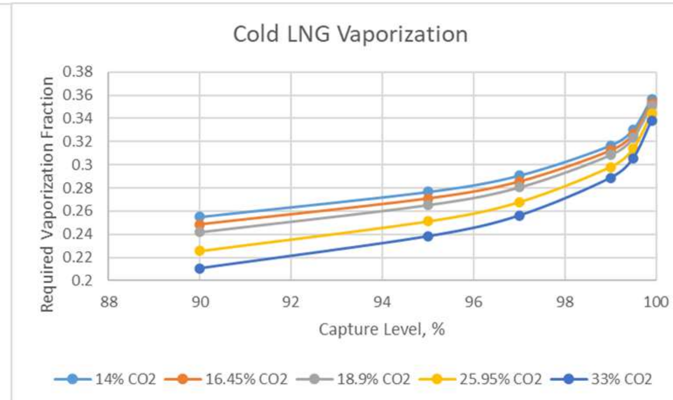


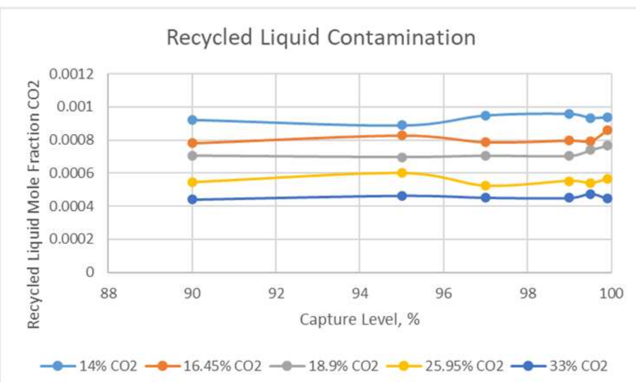
CCSI²
Carbon Capture Simulation for Industry Impact

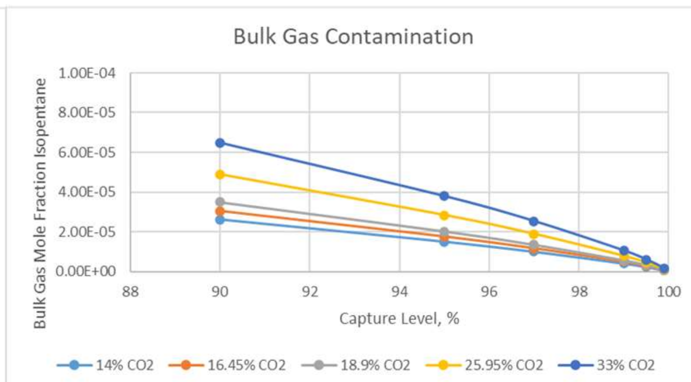
Process Model – Results

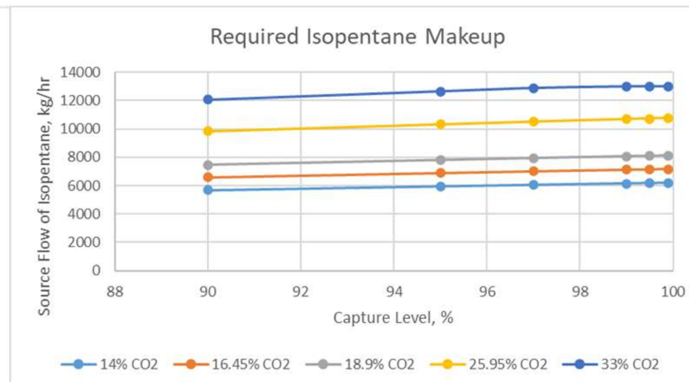




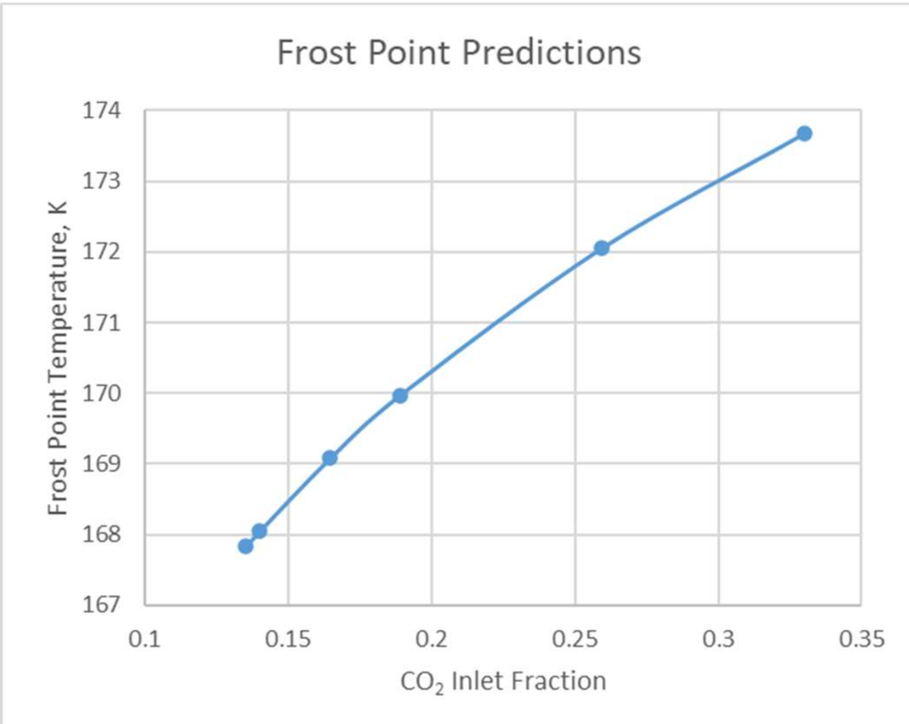


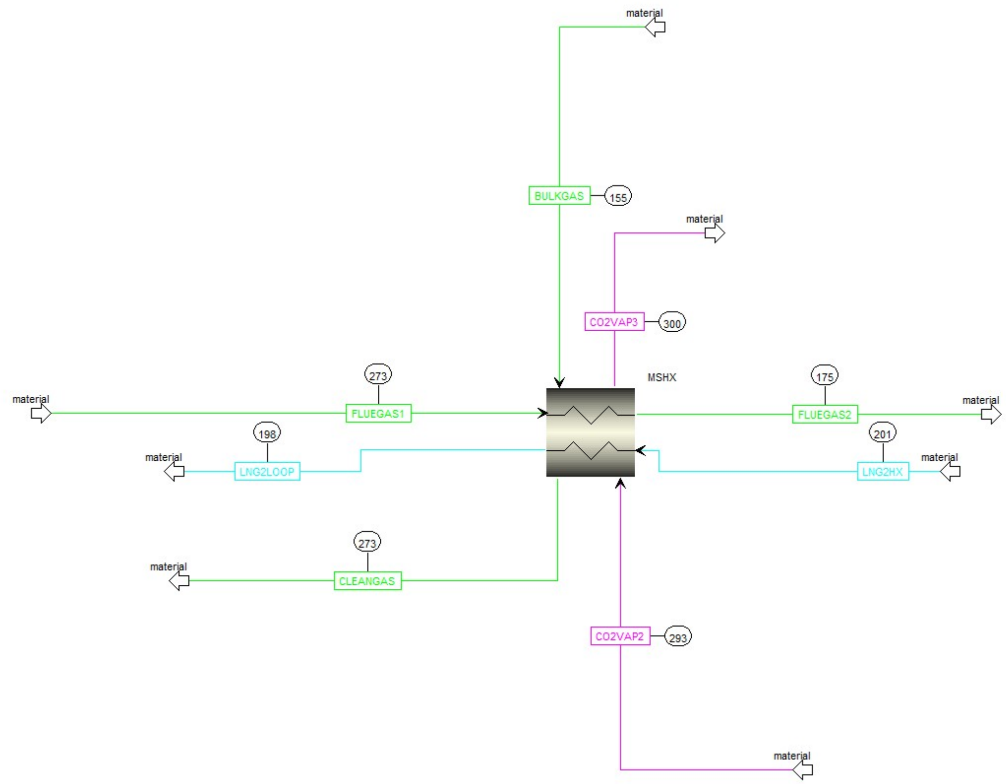




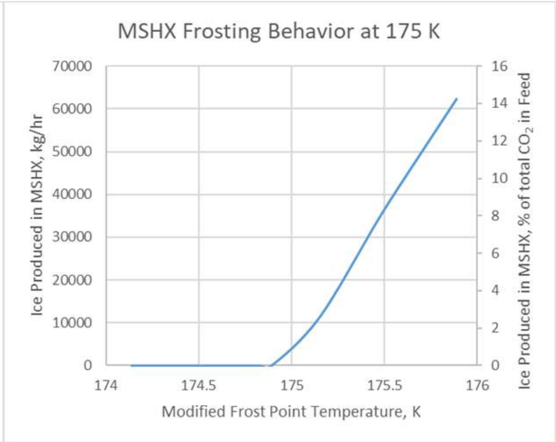


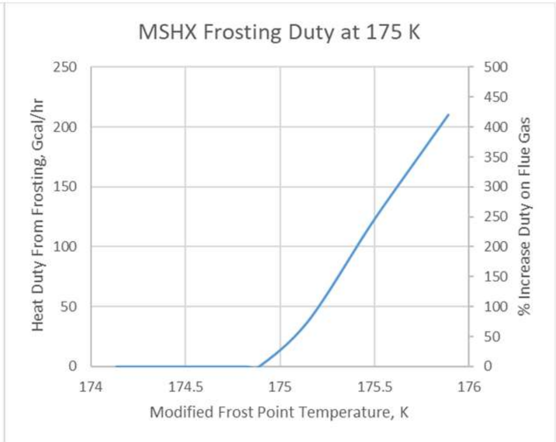
Multi-Stream Heat Exchanger – Fouling Uncertainty Analysis

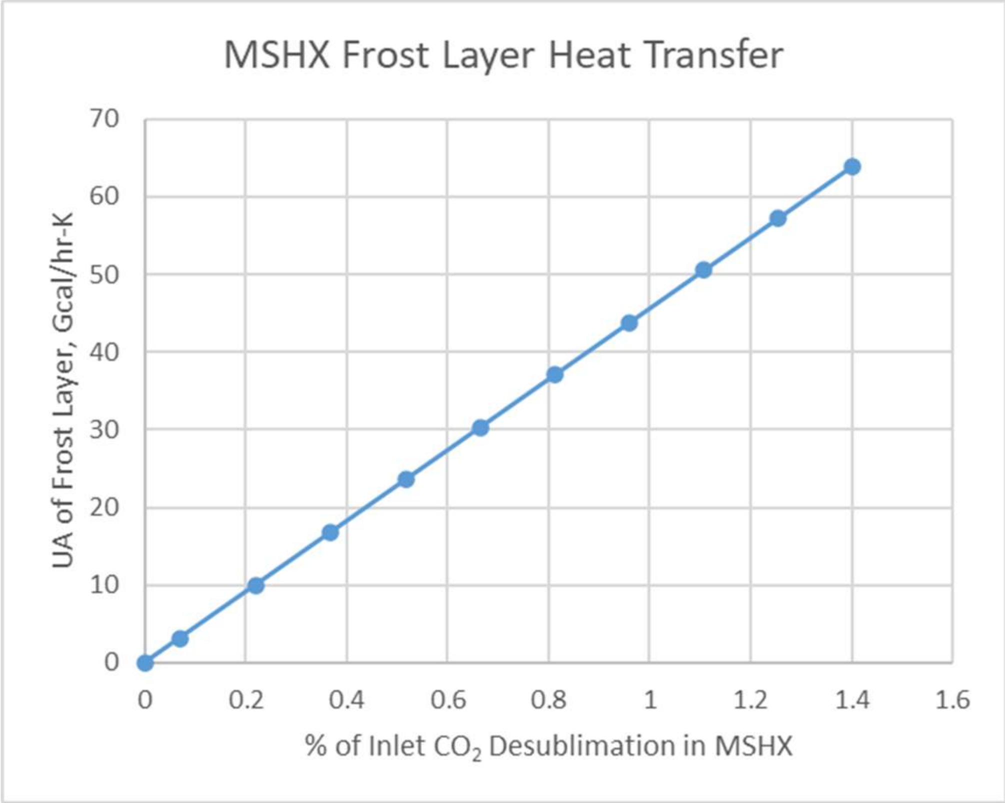




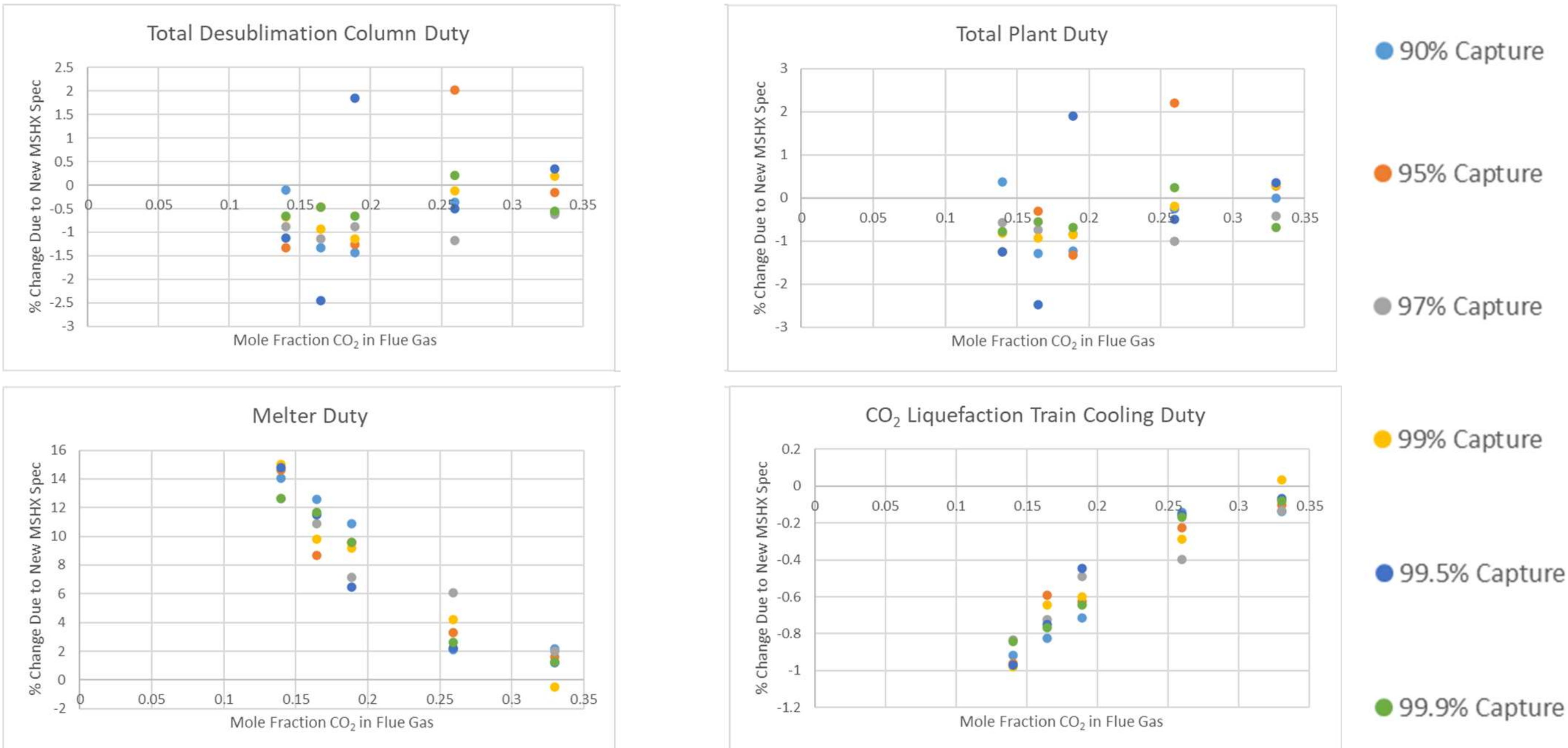
Multi-Stream Heat Exchanger – Fouling Uncertainty Analysis





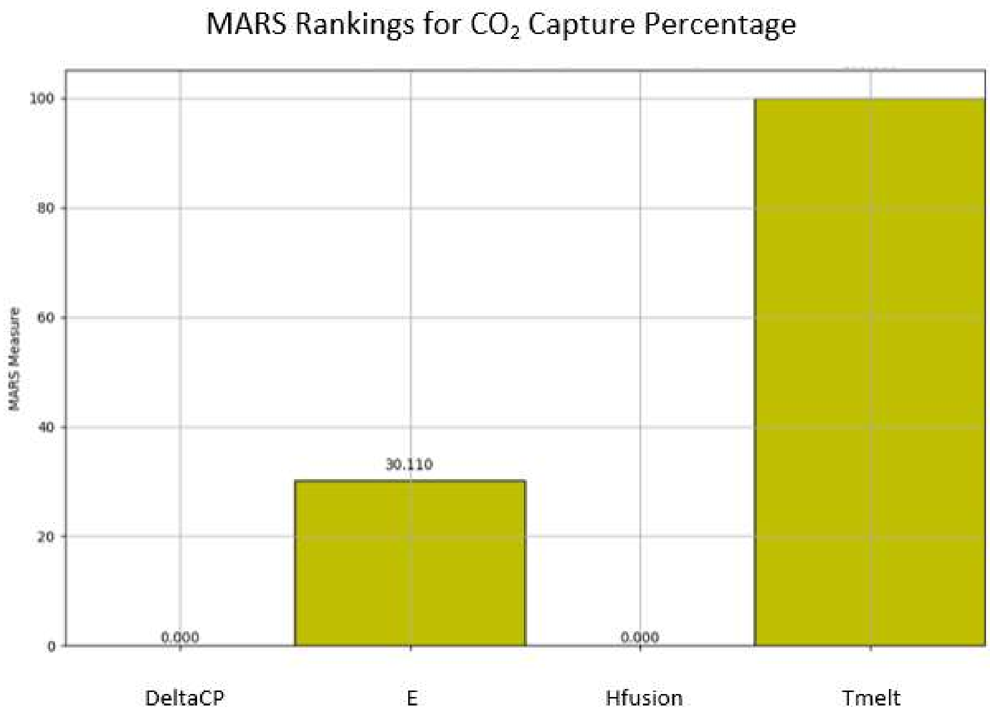


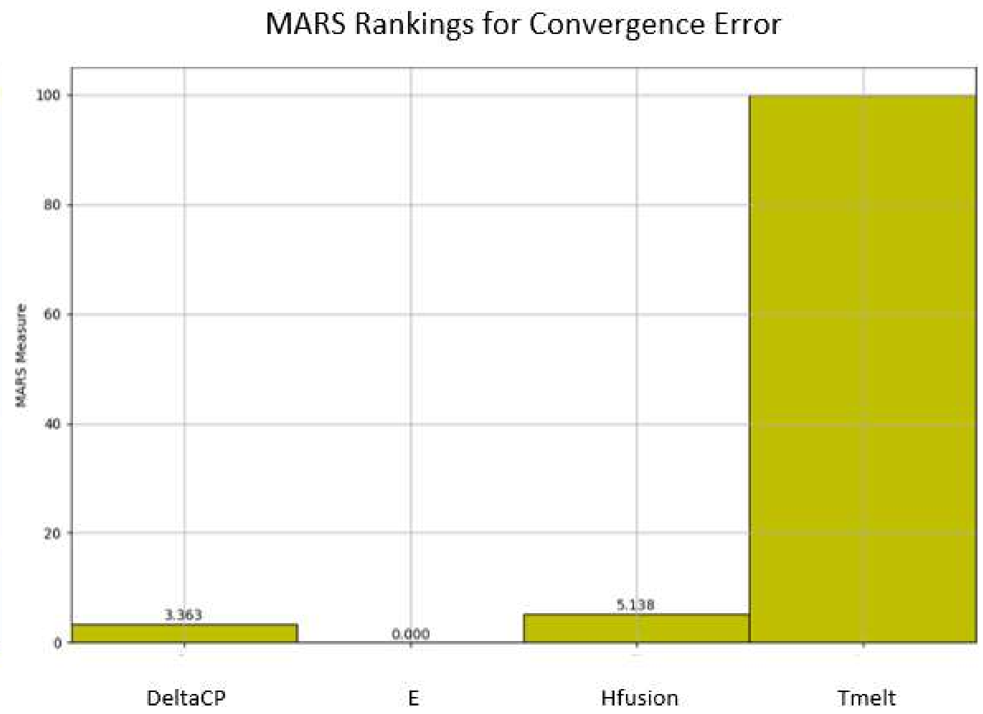
Multi-Stream Heat Exchanger – Outlet Temperature Improvement



CCSI[2]
Carbon Capture Simulation for Industry Impact

Salt Chemistry Model MARS Analysis





CCSI[2]
Carbon Capture Simulation for Industry Impact

Process Model Feed Gas MARS Analysis