

Integrated Flue Gas Purification and Latent Heat Recovery for Staged, Pressurized Oxy-Combustion

DE-FE0025193

PI: RICHARD AXELBAUM

ENERGY, ENVIRONMENTAL AND CHEMICAL ENGINEERING
WASHINGTON UNIVERSITY IN ST. LOUIS

2018 NETL CO₂ CAPTURE TECHNOLOGY

PROJECT REVIEW MEETING

AUG 13TH-18TH, 2018

Project Overview

Project Objectives

- Develop an enabling technology for simultaneous recovery of latent heat and removal of SO_x and NO_x from flue gas during pressurized oxy-coal combustion.

Funding

- Total award: \$1,291,964 { DOE share: \$996,652
Cost share: \$295,312

Project Performance Dates

- 09/01/2015 - 08/31/2018 (extended)

Project Participants

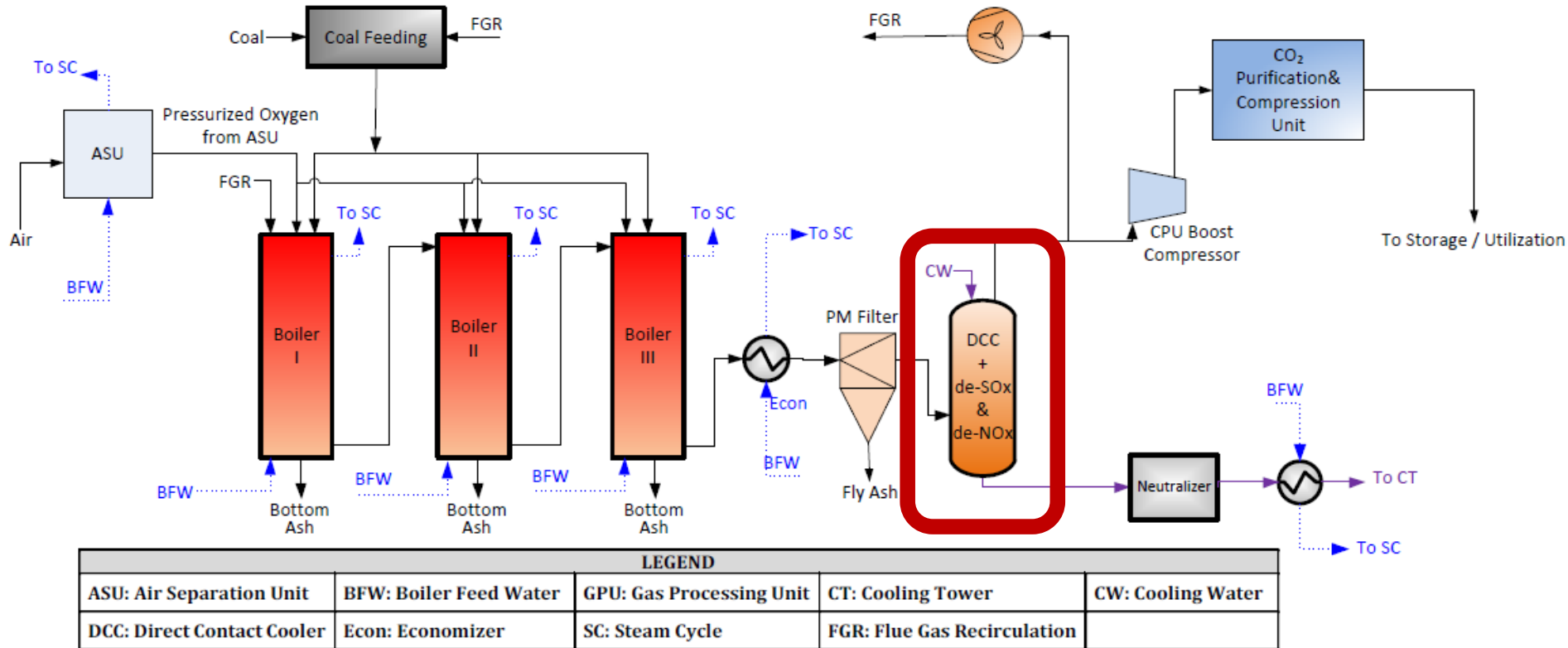
- Washington University in St. Louis

Technology

BACKGROUND

SPOC Process Flow Diagram

15 bar, 550 MW_e power plant with > 90% CO₂ capture

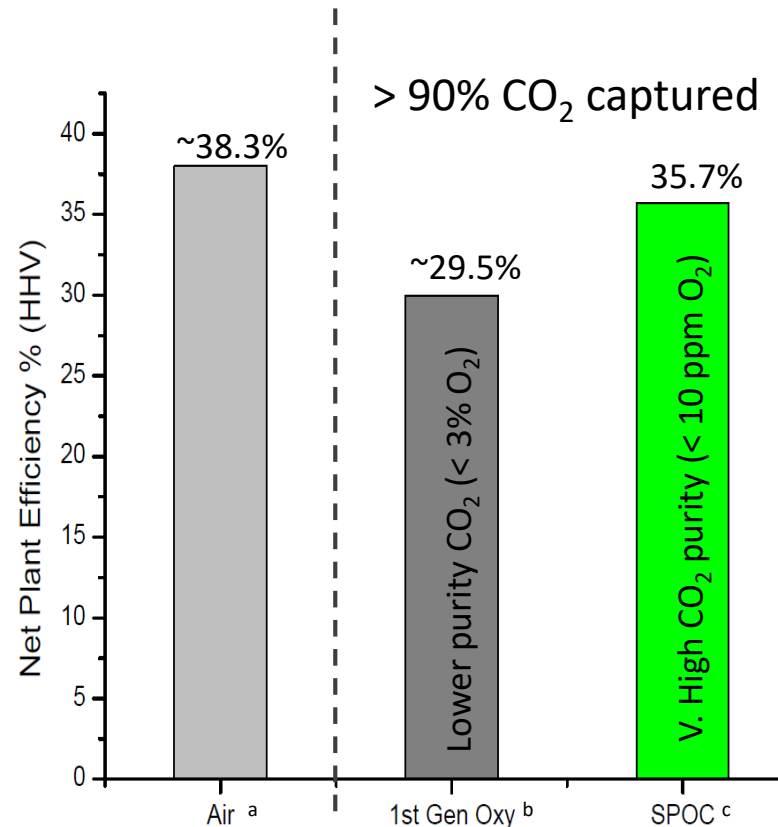


- Surface-moisture free feeding.
- Exhaust [O₂] ≈ 3 % (d.b.) = 0.26 bar (partial pressure), compared to 0.03 bar for atm. pressure

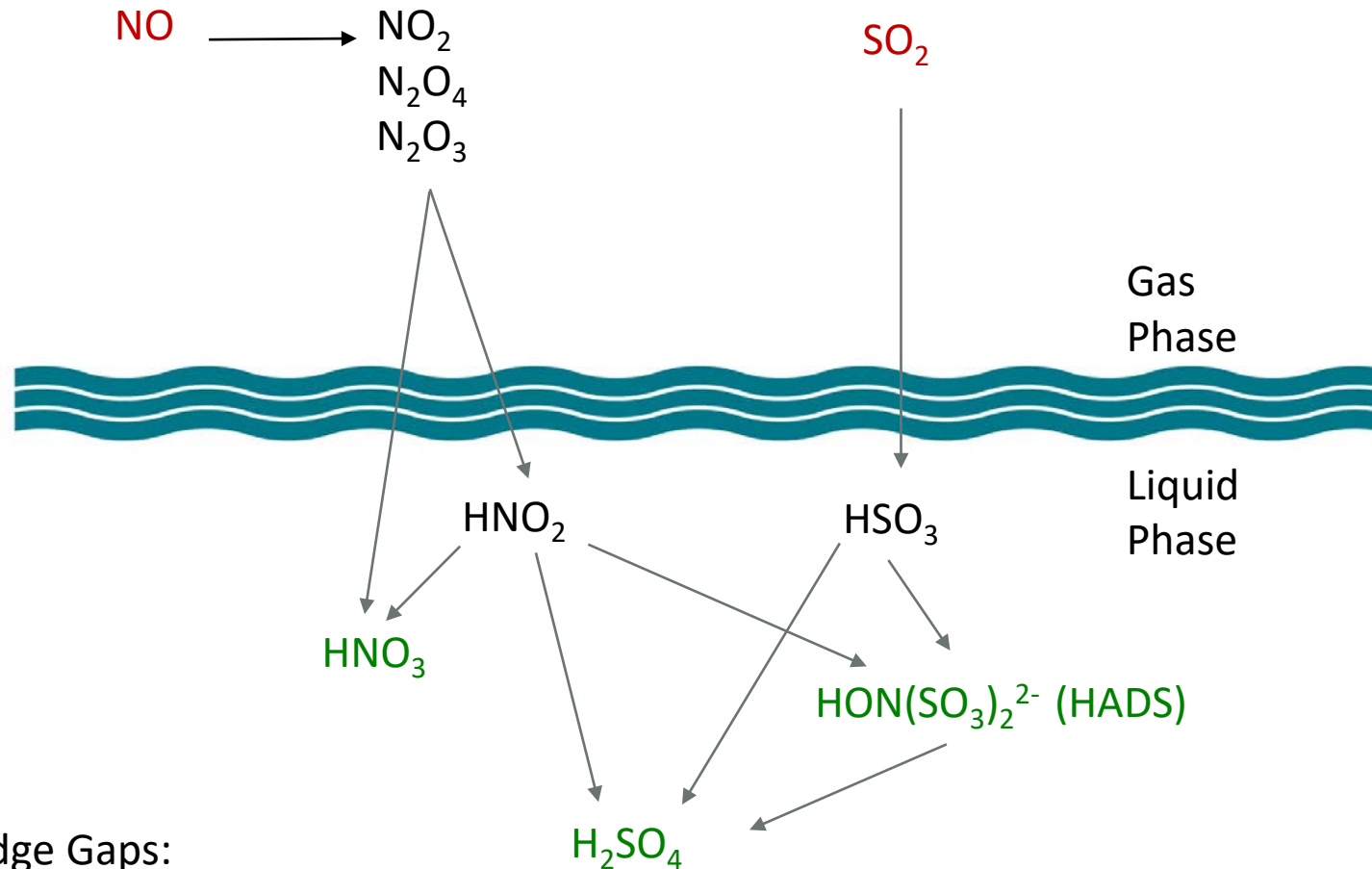
Efficiency Gains in SPOC

Main Contributors to efficiency gain:

- Heat from flue gas moisture condensation (~ 1.5 %-pts.)
- Lower exergy loss due to reduced recycle & surface-dry feeding (up to 3.5 %-pts.)
- Aux. load reduction due to staging & pressurization
- Effective integration of waste heat from oxygen production & compression



SO_x and NO_x Removal



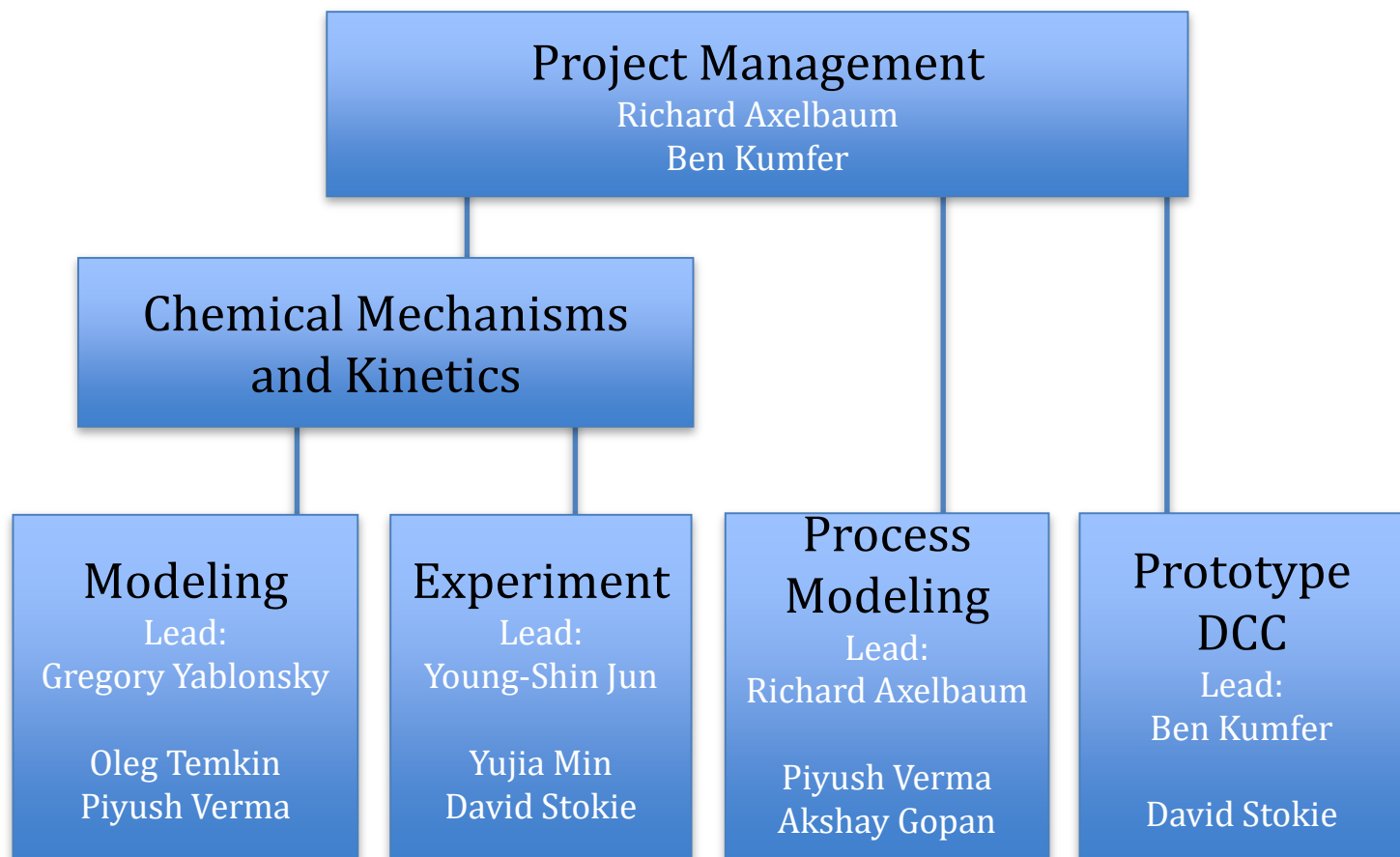
Knowledge Gaps:

There are discrepancies about the role of N₂O₃ and N₂O₄ in NO_x dissolution
Aqueous phase kinetics and mechanism remain unclear

Project Objectives

- Develop a predictive model for reactor design & operation.
- Experimentally determine critical reactions and rates.
- Conduct parametric study (T and pH) to optimize process.
- Design, build, test prototype for 100 kW pressurized DCC.
- Determine size of the DCC for a full-scale SPOC plant in order to estimate capital and operating costs.

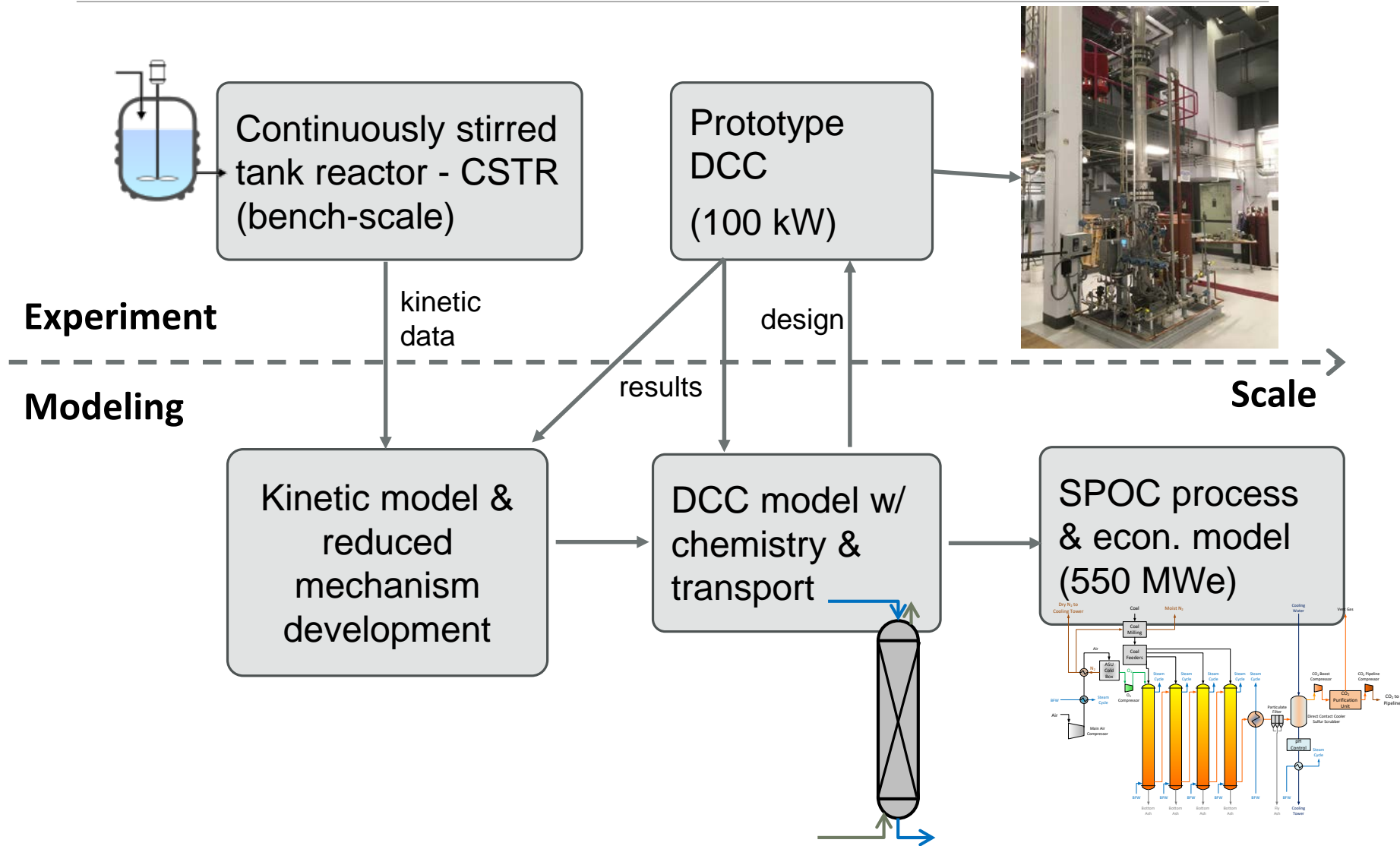
Project Organization



Technical Approach

PROJECT SCOPE

Technical Approach



Progress and Current Status

MECHANISM AND KINETICS
BENCH-SCALE EXPERIMENTS

Objectives of Bench Scale Experiments

- Experimentally validate the gas to liquid chemical mechanism
- Identify and determine the key reactions, reaction pathways and rates of the liquid chemistry
- Develop a robust kinetic model capable of accurately predicting the removal efficiency of a direct contact column

Proposed mechanism

NO_x Reactions

Gas Phase

1. $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
2. $2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$
3. $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_3(\text{g})$

Gas + Liquid Phase

4. $2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}, \text{aq}) \rightarrow \text{HNO}_2(\text{aq}) + \text{HNO}_3(\text{aq})$
5. $\text{N}_2\text{O}_4(\text{g}) + \text{H}_2\text{O}(\text{g}, \text{aq}) \rightarrow \text{HNO}_2(\text{aq}) + \text{HNO}_3(\text{aq})$
6. $\text{N}_2\text{O}_3(\text{g}) + 2\text{H}_2\text{O}(\text{g}, \text{aq}) \rightarrow 2\text{HNO}_2(\text{aq})$
7. $3\text{HNO}_2(\text{aq}) \rightarrow \text{HNO}_3(\text{aq}) + 2\text{NO}(\text{g}, \text{aq}) + \text{H}_2\text{O}(\text{g}, \text{aq})$

SO_x Reactions

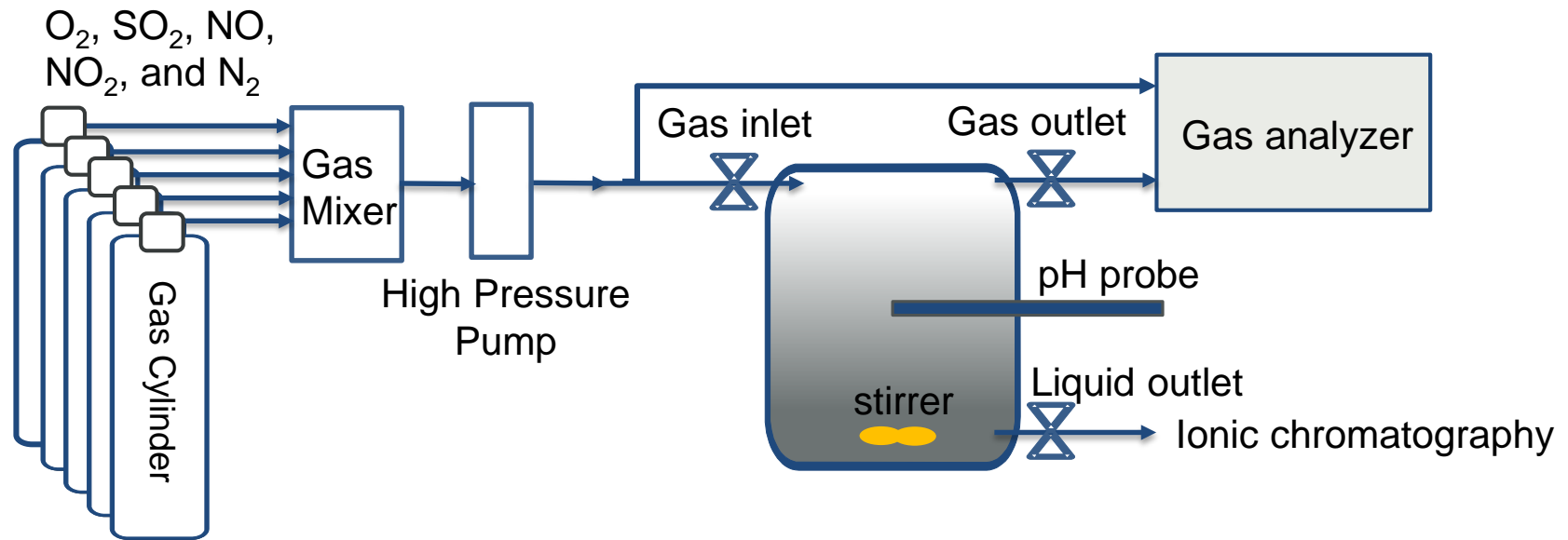
8. $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}, \text{aq}) \leftrightarrow \text{HSO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$

SO_x + NO_x Reactions

9. $\text{HNO}_2(\text{aq}) + \text{HSO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{SO}_4(\text{aq}) + \frac{1}{2}\text{N}_2\text{O}(\text{g}) + \frac{1}{2}\text{H}_2\text{O}(\text{aq})$
10. $2\text{HNO}_2(\text{aq}) + \text{HSO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow 2\text{NO}(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{aq})$
11. $\text{HNO}_2(\text{aq}) + 2\text{HSO}_3^-(\text{aq}) \rightarrow \text{HON}(\text{SO}_3)_2^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Experiment to Obtain Kinetic Data

The reactor design is optimized for conducting experiments under high pressure and temperature and highly acidic conditions



In situ pH measurements under high pressure/temperature conditions

- Pressure of 15 bar, 900 ppm NO_x , NO_x/SO_x ratio of 2

Reduced mechanism

NO_x Reactions

Gas Phase

1. $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
2. $2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$ **Equilibrium**
- ~~3. $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_3(\text{g})$~~

Gas + Liquid Phase

4. $2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{g, aq}) \rightarrow \text{HNO}_2(\text{aq}) + \text{HNO}_3(\text{aq})$
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- ~~7. $3\text{HNO}_2(\text{aq}) \rightarrow \text{HNO}_3(\text{aq}) + 2\text{NO}(\text{g, aq}) + \text{H}_2\text{O}(\text{g, aq})$~~

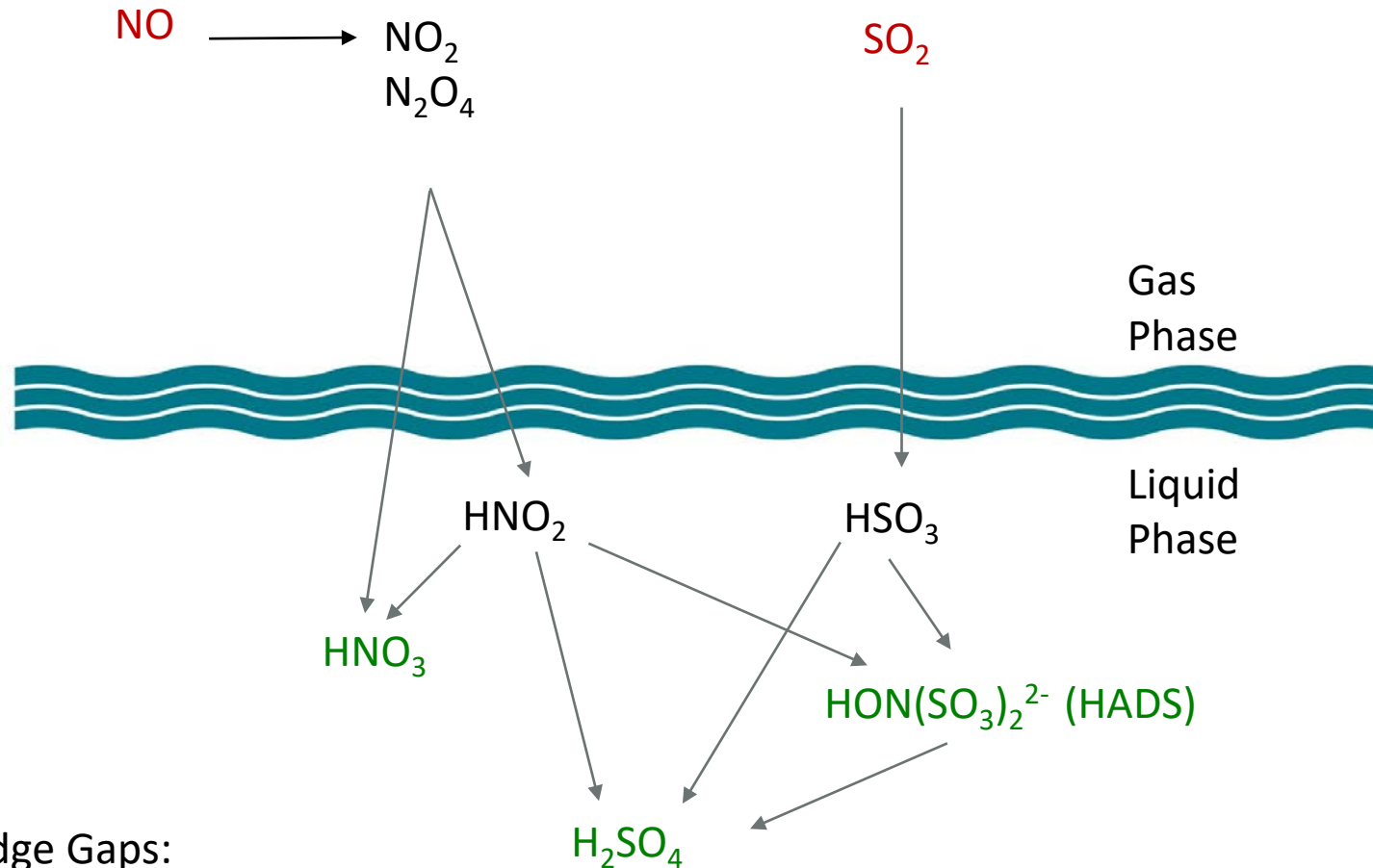
SO_x Reactions

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SO_x + NO_x Reactions

9. $\text{HNO}_2(\text{aq}) + \text{HSO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{SO}_4(\text{aq}) + \frac{1}{2}\text{N}_2\text{O}(\text{g}) + \frac{1}{2}\text{H}_2\text{O}(\text{aq})$
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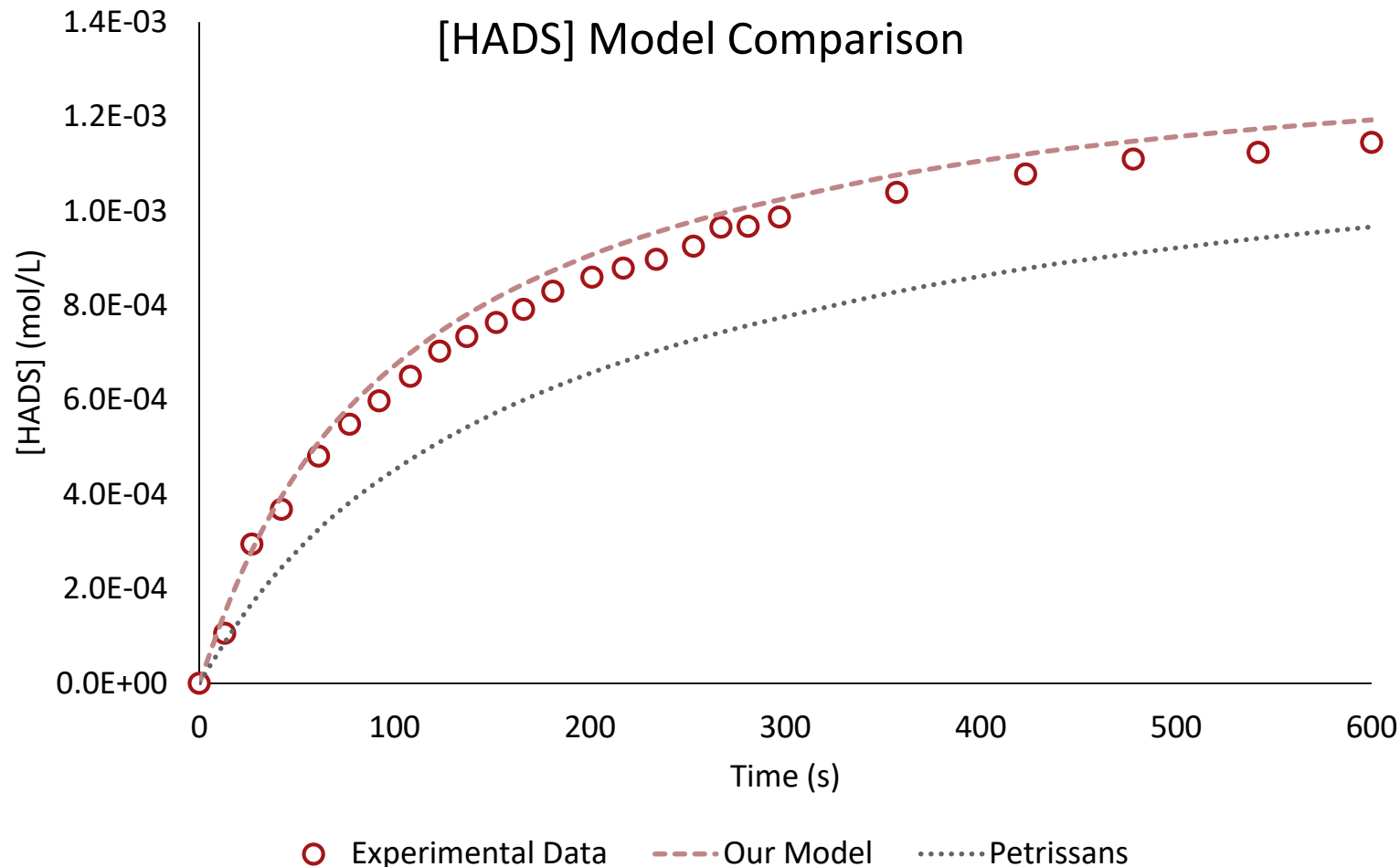
SO_x and NO_x Removal



Knowledge Gaps:

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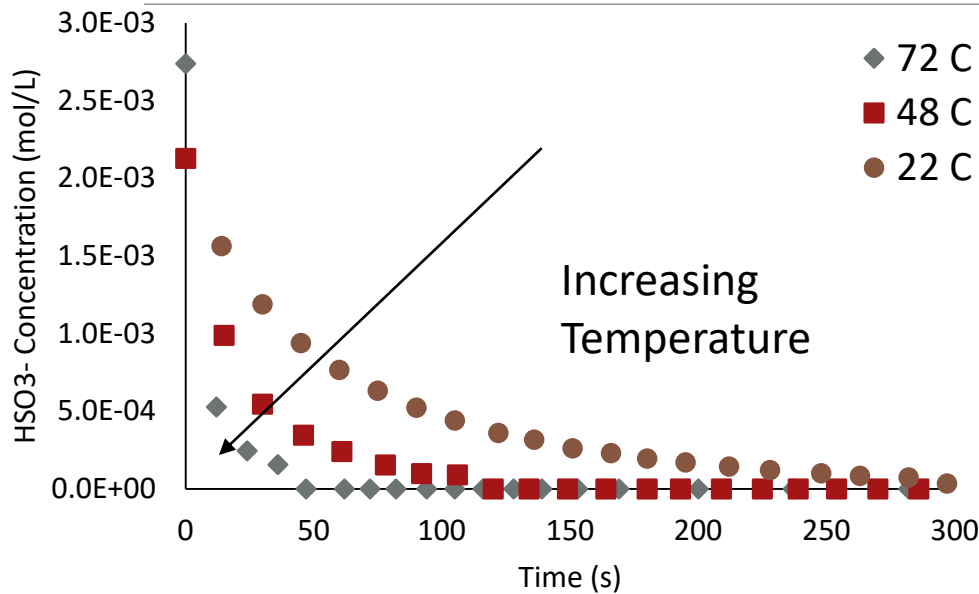
Liquid Chemistry



When compared to previous models, the overall trends are the same however our model fits better to the experimental data

Petrisans et. al. (2001)

The effect of temperature and pH

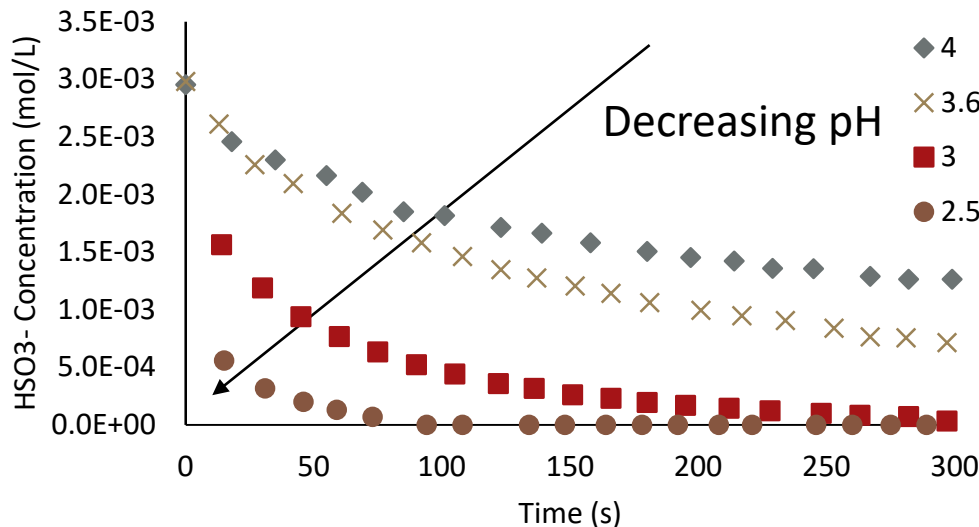


Increase in temperature results in an increased rate of HSO₃⁻ consumption, however the proportionality of H₂SO₄ to [HADS] is similar

Decrease in pH results in an increase H₂SO₄ formed

Addition of 0.03 M of HCO₃⁻/CO₃²⁻ results in no observable change in reaction rates or concentrations

At 72 C additional reactions are observed



Progress and Current Status

PROTOTYPE DIRECT CONTACT COOLER (DCC)

DCC Prototype

Features:

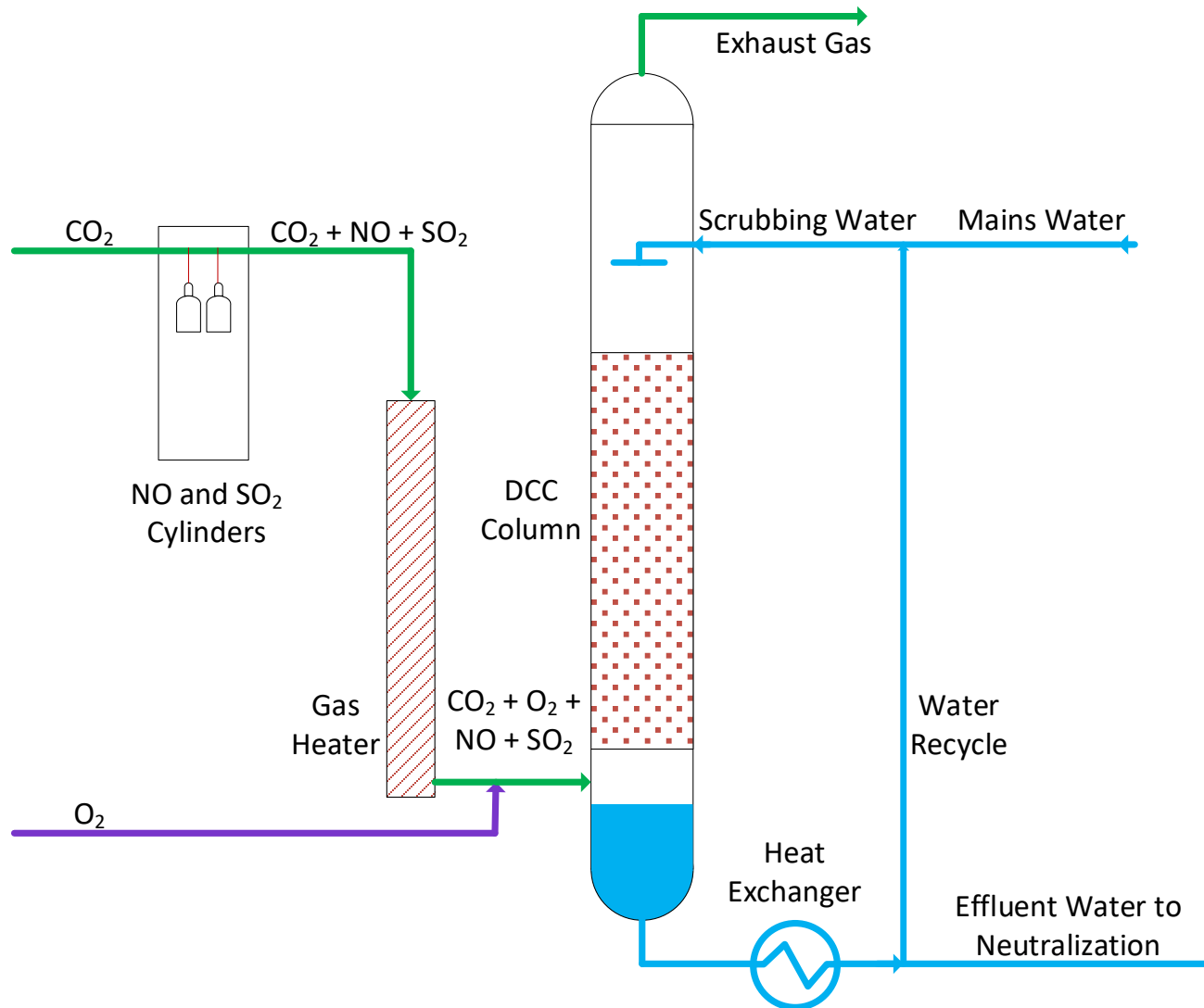
- 100 kW_{th} SPOC facility integration
- Simulated flue gas capability
- Liquid recycle and pH control

Parameters:

- Vapor residence time: ≤ 120 seconds
- pH range: 2 – 7
- L/G ratio: 3 – 80 (L/m³)
- 1 -30 bar maximum operating pressure
- Flue Gas Temperatures: < 350 °C

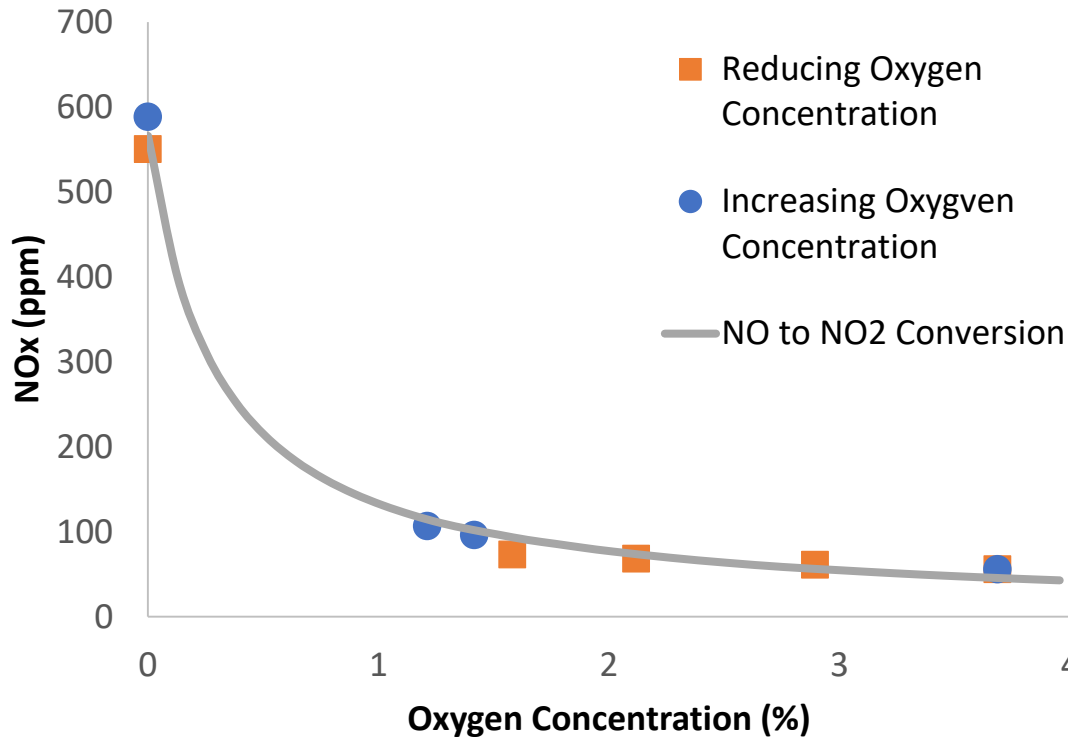


DCC Test Facility



The effect of O₂ concentration on NO_x conversion

Full SO_x conversion



Conditions:

Pressure : 13.5 bar (abs)

Temperature : 24 °C

L:G Ratio : 1 kg:kg

Residence Time : 120 seconds

Inlet SO₂ ppm : 421 ppm

Inlet NO_x ppm : 550 ppm

L:G Ratio based on water flow for heat transfer requirements

O₂ concentration range similar to oxyfuel outlet conditions

SO₂ and NO_x ppm similar to oxyfuel outlet conditions

Progress and Current Status

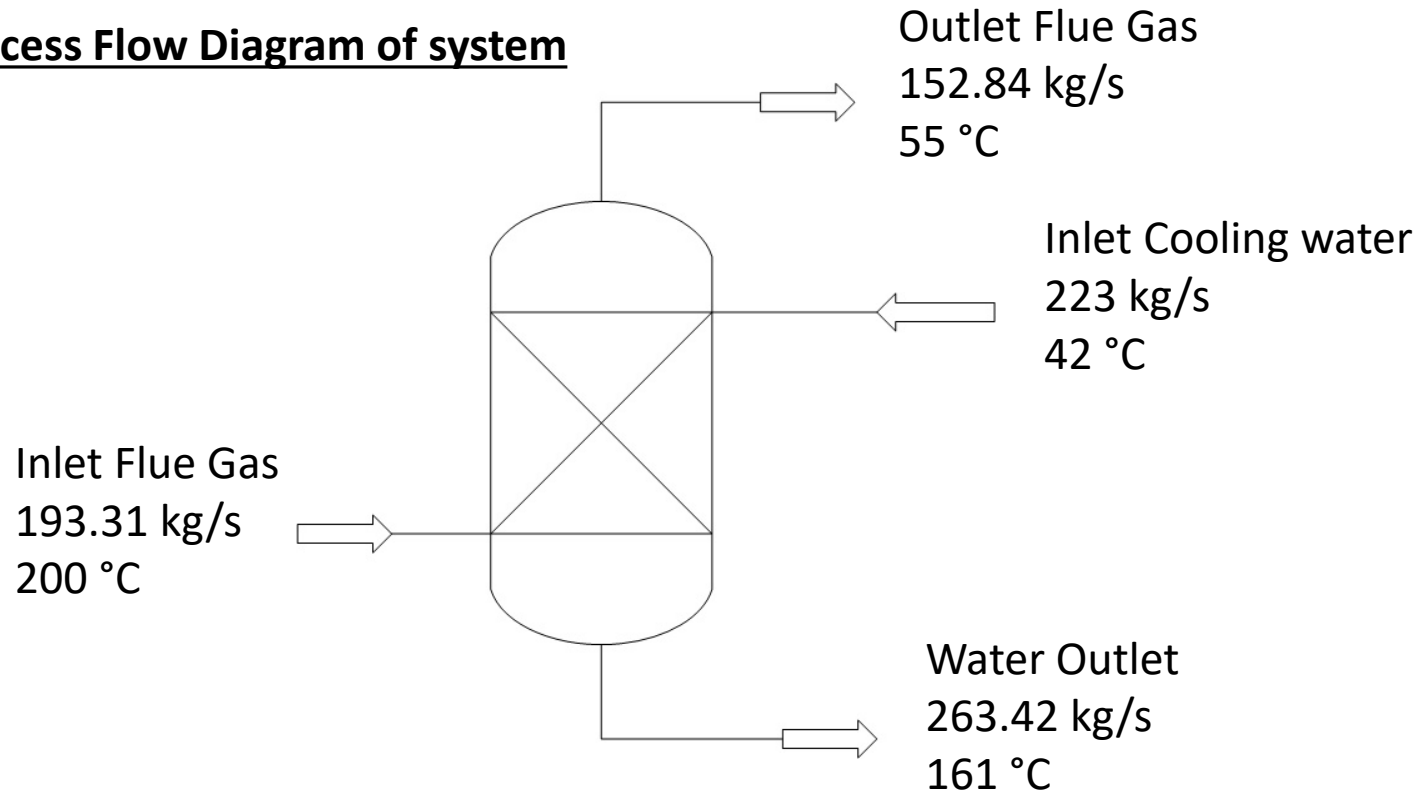
FULL-SCALE DCC MODELING USING
IMPROVED MODEL OF CHEMISTRY

DCC Full Scale Modeling.

Objectives:

1. Capturing latent heat from the flue gas
2. Removal of SO_x

Process Flow Diagram of system



Modeling Parameters

Assumption for Modelling:

- Packed Column is used with Raschig metal rings.
- Cooling water flow rate was determined based on the flue gas outlet temperature
- Height is calculated based on an outlet SO_x concentration of less than 15 ppm.

Two configurations were studied for the process:

Option A : Single DCC	Option B: Two DCCs in parallel
Diameter is sized based on total gas flow rate with an approach to flooding velocity of 80%.	Diameter was fixed at 4 m because of ease of transportation. The total gas flow rate is split in two parts.
Approach to flooding velocity is 80%	Approach to flooding velocity is 71%

DCC Full-scale Modeling

Inlet Flue gas Composition

	O2	H2O	NO	NO2	SO2	SO3
Mole Fraction	3%	39%	700 (ppm)	250 (ppm)	700 (ppm)	250 (ppm)

Outlet Gas Results

	H2O concentration	SOx Removal	NOx Removal
Single Column	< 1.5% v/v	> 99%	75.8%
Two Columns	< 1.5% v/v	> 99%	71.8%

Column Design Specification

	Diameter	Length	Residence time
Single Column	5 m	60 m	80.4 s
Two Columns	4 m	45 m	77.1 s

Future Work

- Operate lab-scale DCC at elevated flue gas temperature, up to 200 °C. Validate model under these conditions.
- Optimize the design of a full-scale DCC and feed this information into the techno-economic model being developed by EPRI, Doosan Babcock and Air Liquide (next talk).

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