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

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CONSORTIUM FOR CLEAN COAL UTILIZATION

# Project Overview

## Project Objectives

Develop an enabling technology for simultaneous recovery of latent heat and removal of SOx and NOx 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

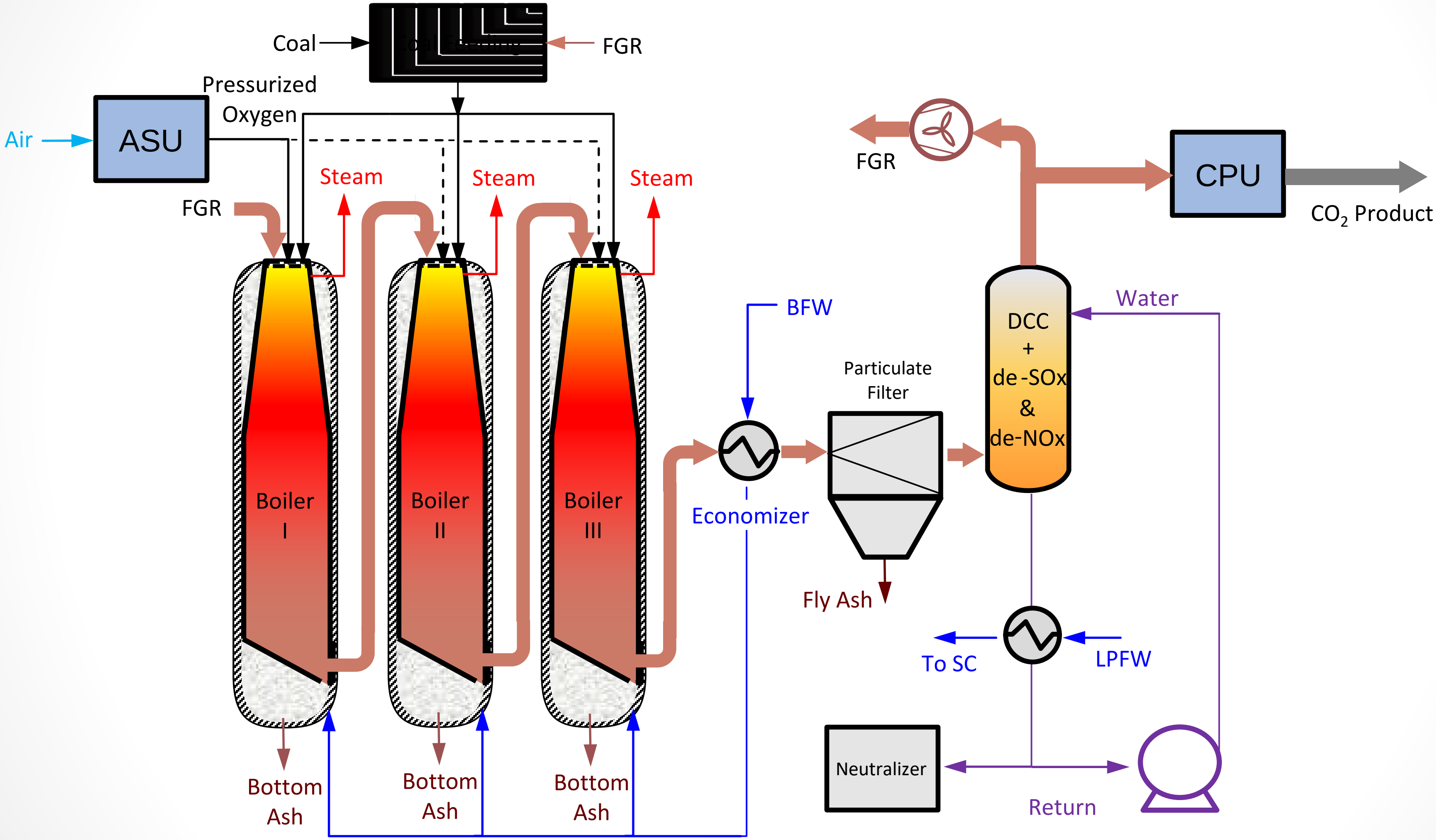
09/01/2015 - 08/31/2018 (extended)

## Project Participants

Washington University

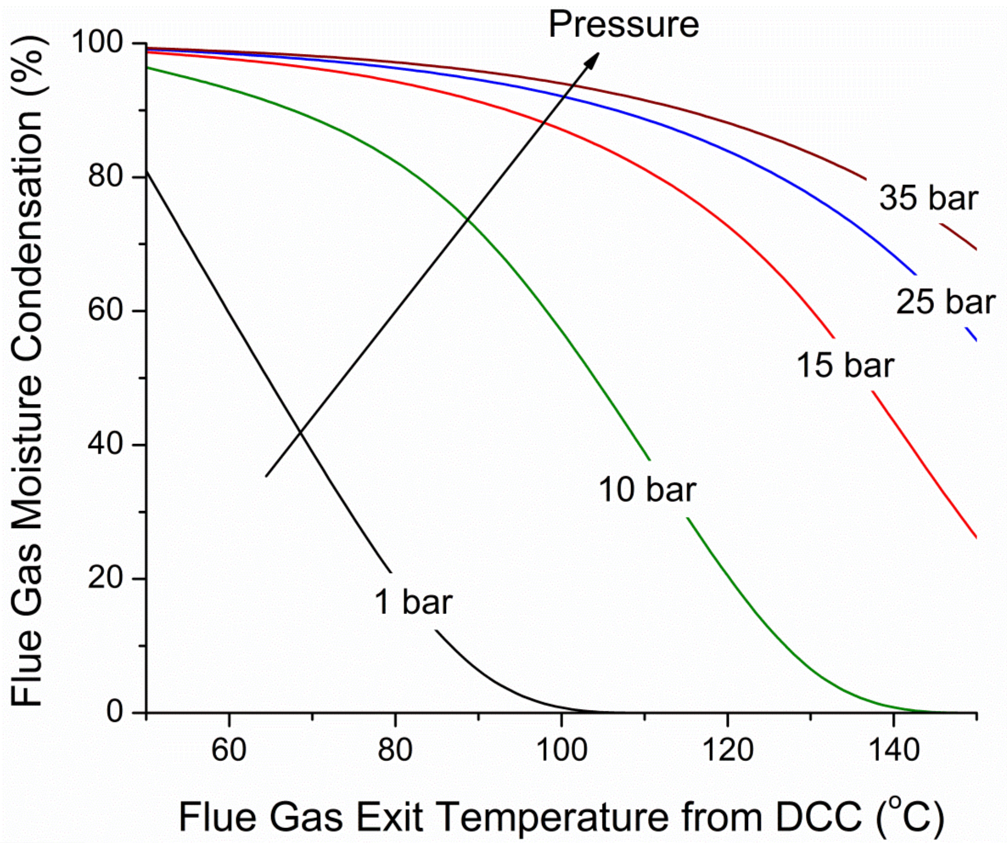
# Technology Background

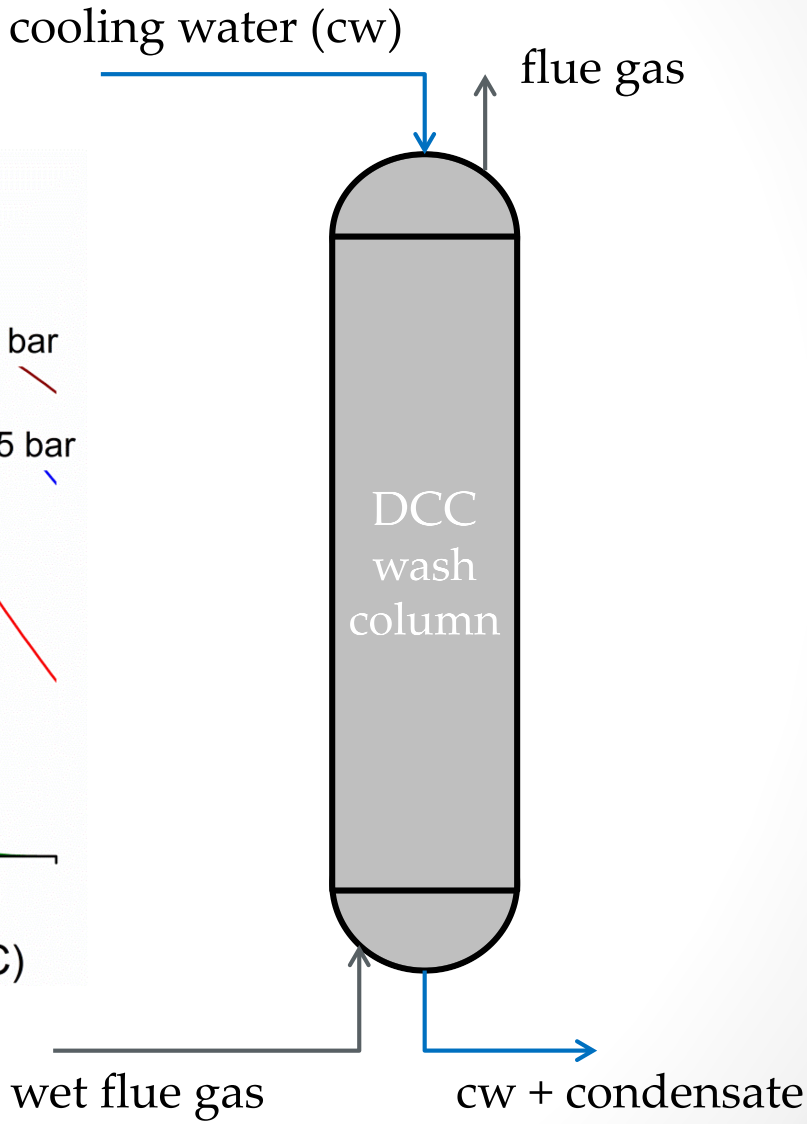
# SPOC Process



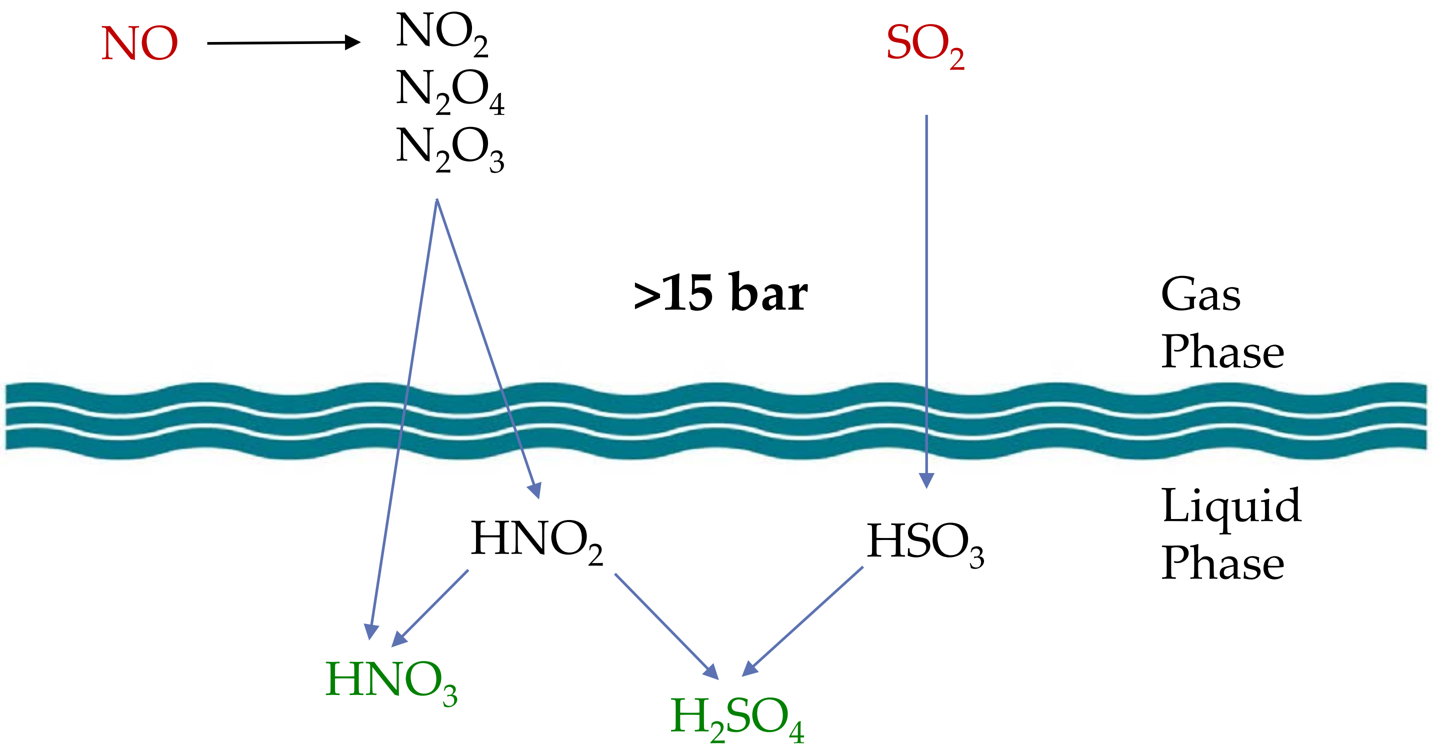
courtesy of Electric Power Research Institute

# Latent Heat Recovery – Direct Contact Cooler (DCC)





# SOx and NOx Removal



Knowledge Gaps:

- There are discrepancies about the role of $N_2O_3$ and $N_2O_4$ in $NO_x$ dissolution
- Aqueous phase kinetics and mechanism remain unclear

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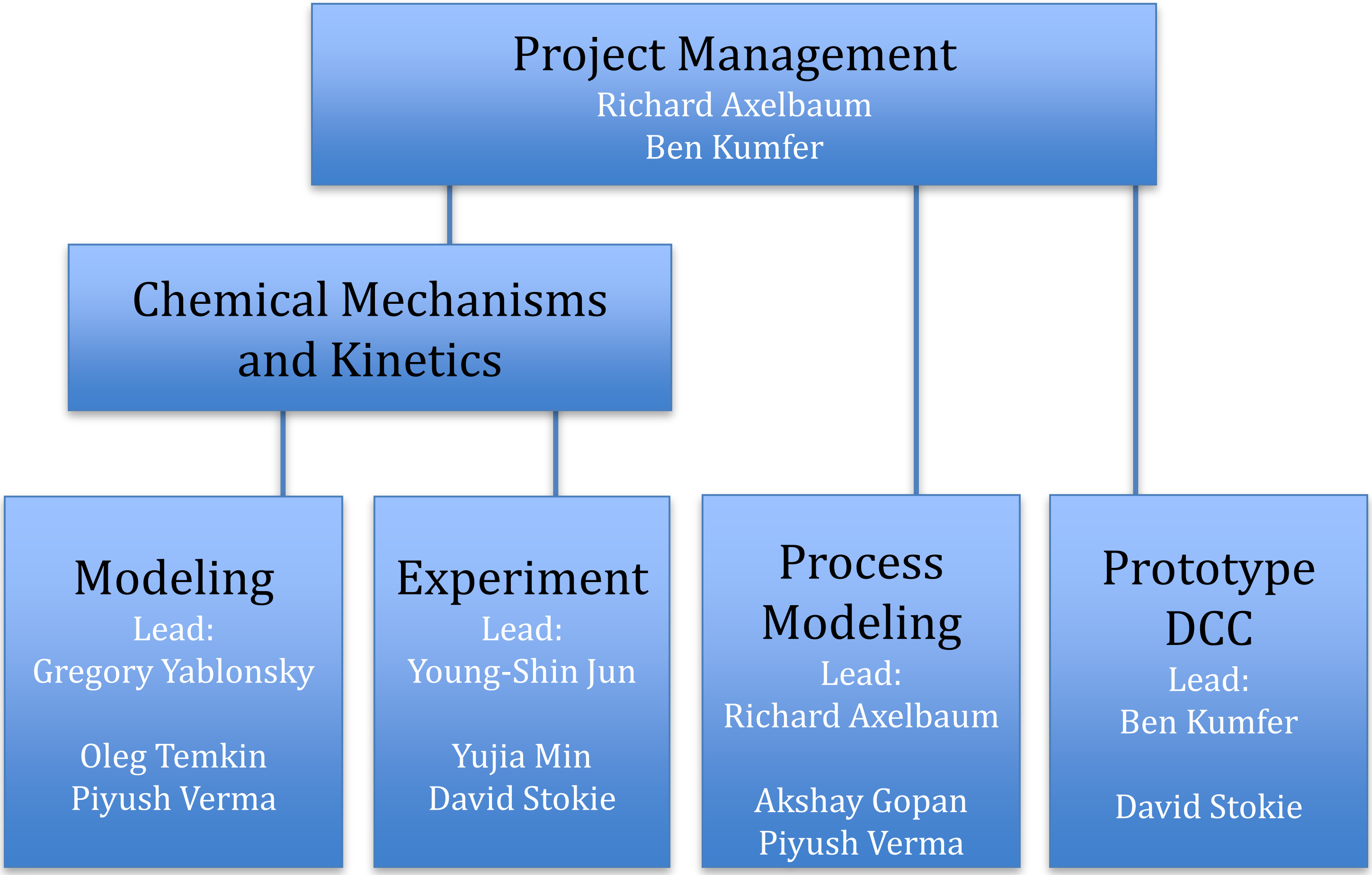
# Questions

- What is the optimum design for the DCC for pressurized oxy-combustion?
- What is the expected removal efficiency at the proposed operating conditions for SPOC?
- What are the optimal operating & inlet conditions for the DCC?
  - Inlet NOx/SOx ratio
  - pH
  - Temperature
- What are the critical and rate limiting reactions?
- Can faster/more efficient capture be achieved using catalysts?
- Is one column sufficient?

# Project Objectives

- Develop a predictive model for reactor design & operation.
- Experimentally determine critical reactions and rates.
- Design, build and test prototype DCC for 100 kW pressurized combustor at WUSTL.
- Conduct parametric study to optimize process.
- Estimate capital and operating costs of the DCC for a full-scale SPOC plant.

# Project Organization



**Project Management**
Richard Axelbaum
Ben Kumfer

**Chemical Mechanisms and Kinetics**

**Modeling**
Lead:
Gregory Yablonsky

Oleg Temkin
Piyush Verma

**Experiment**
Lead:
Young-Shin Jun

Yujia Min
David Stokie

**Process Modeling**
Lead:
Richard Axelbaum

Akshay Gopan
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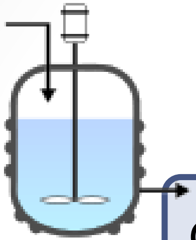
**Prototype DCC**
Lead:
Ben Kumfer

David Stokie

# Technical Approach/Project Scope

# Technical Approach



Continuously stirred tank reactor - CSTR (bench-scale)

Prototype DCC

(100 kW)

100 kW SPOC Facility

kinetic data

design

**Experiment**

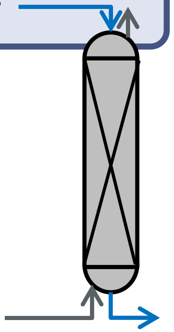
results

**Modeling**

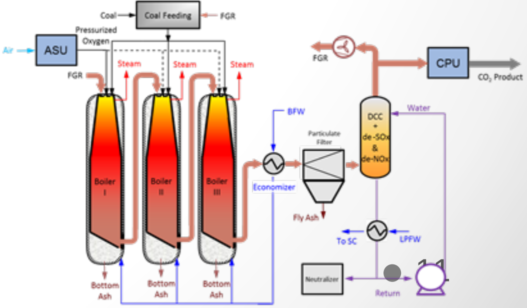
**Scale**

Kinetic model & reduced mechanism development

DCC model w/ chemistry & transport



SPOC process & econ. model (550 MWe)



# Technical Approach:

# Mechanism and Kinetics

# Reaction Mechanism & Kinetic Model

- Normann et al. proposed a detailed mechanism containing 34 reactions. (Intern. J. of Greenhouse Gas Control, V. 12, January 2013, pp.26-34.)
  - contains many intermediates
  - produces large discrepancies with experimental data in the literature (up to 700%)
  - kinetic expressions need verification

- A reduced model has been constructed.

# Proposed Mechanism

## **$NO_x$ Reactions**

*Gas Phase*

1. $2NO\ (g) + O_2(g) \rightarrow 2NO_2\ (g)$
2. $2NO_2(g) \leftrightarrow N_2O_4(g)$
3. $NO(g) + NO_2(g) \rightarrow N_2O_3(g)$

*Gas + Liquid Phase*

4. $2\ NO_2\ (g) + H_2O\ (g, aq) \rightarrow HNO_2\ (aq) + HNO_3\ (aq)$
5. $N_2O_4(g) + H_2O\ (g, aq) \rightarrow HNO_2\ (aq) + HNO_3\ (aq)$
6. $N_2O_3(g) + 2H_2O\ (g, aq) \rightarrow 2\ HNO_2\ (aq)$
7. $3\ HNO_2\ (aq) \rightarrow HNO_3\ (aq) + 2\ NO\ (g, aq) + H_2O\ (g, aq)$

## **$SO_x$ Reactions**

8. $SO_2\ (g) + H_2O\ (g, aq) \rightarrow HSO_3^-\ (aq) + H^+\ (aq)$

## **$SO_x$ + $NO_x$ Reactions**

9. $HNO_2\ (aq) + HSO_3^-\ (aq) + H^+\ (aq) \rightarrow H_2SO_4\ (aq) + \frac{1}{2}\ N_2O\ (g) + \frac{1}{2}\ H_2O\ (aq)$
10. $2\ HNO_2\ (aq) + HSO_3^-\ (aq) + H^+\ (aq) \rightarrow 2NO\ (g) + H_2SO_4\ (aq) + H_2O\ (aq)$

# Technical Approach:

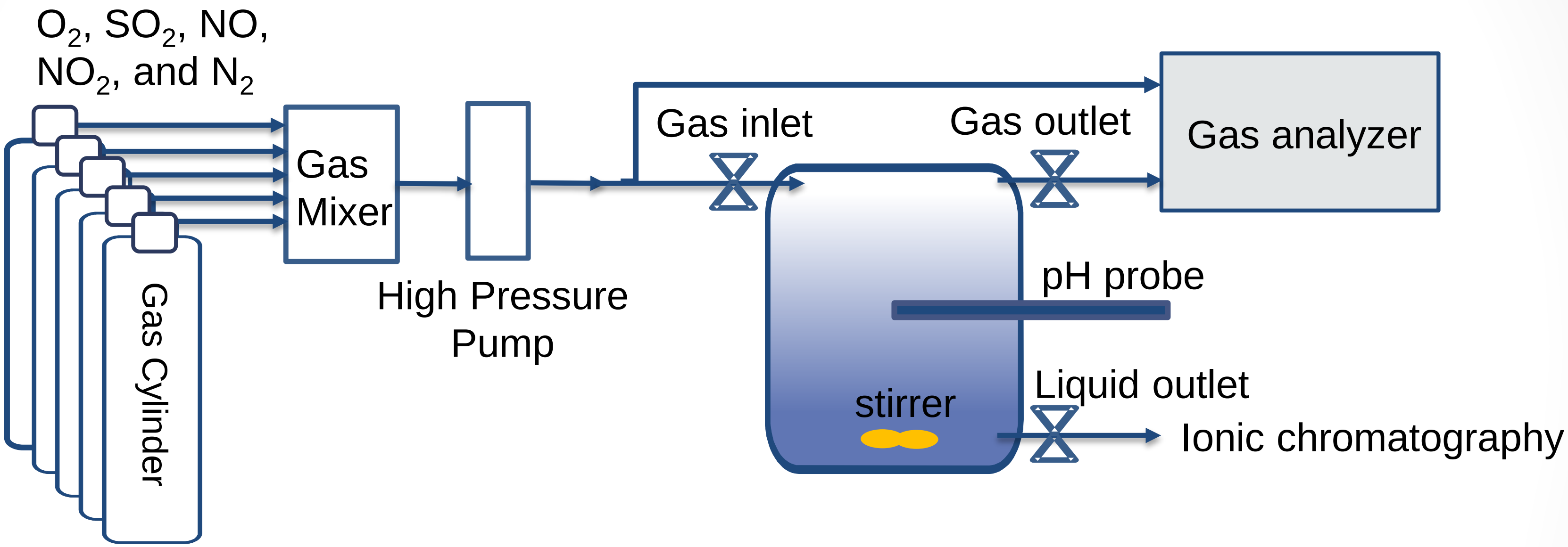
# Bench-Scale Experiments

# Objectives of bench scale experiments

- Determine contributions of different routes, and identify the key reactions and rates
- Justify or eliminate (add) steps from the hypothesized mechanisms
- Obtain estimates of optimal parameters (initial composition and pH, temperature) for the DCC operation

# Experiment to Obtain Kinetic Data

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



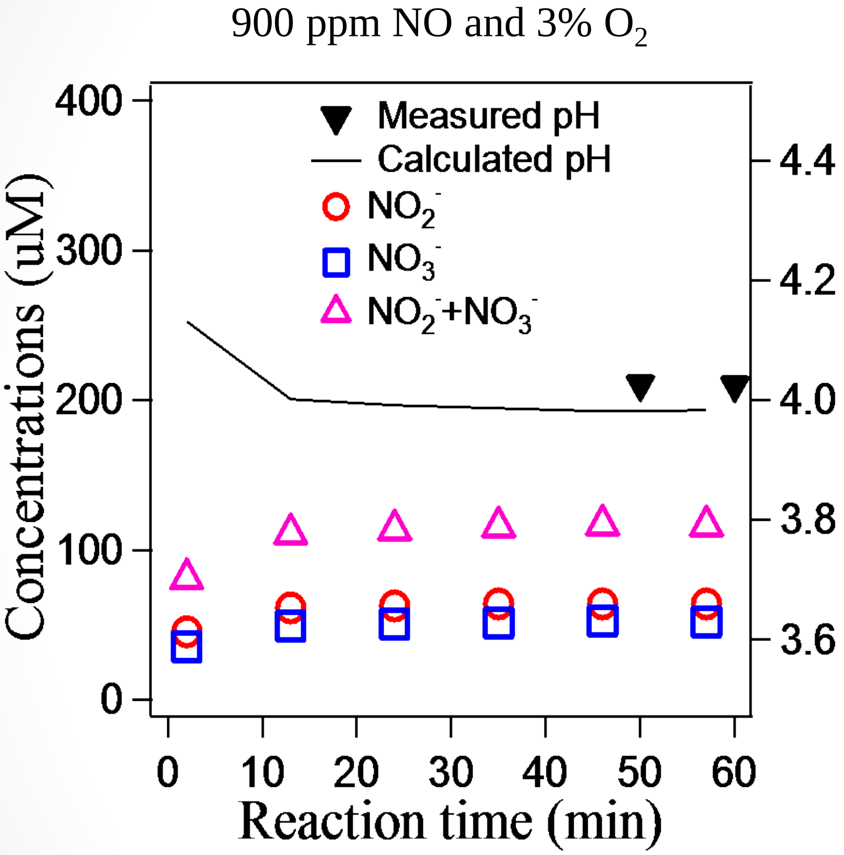
*In situ* pH measurements under high pressure/temperature conditions

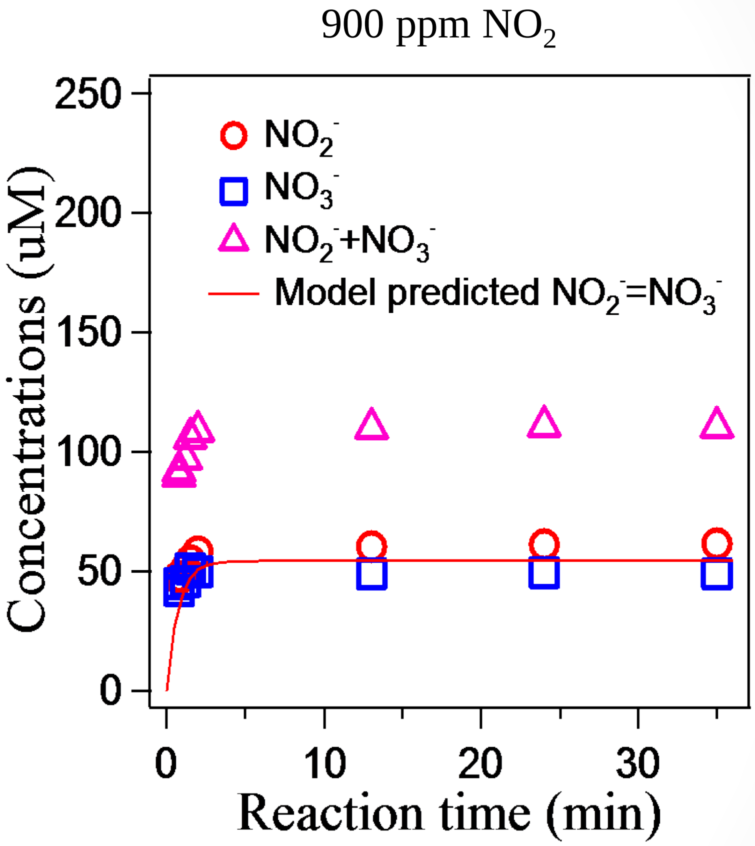
**<u>Tests:</u> A) 900 ppm $NO_x$ ; B) 450 ppm $SO_2$ ; C) $NO_x/SO_x$ ratio of 2**

- **25 °C** (this presentation); will increase to 150 °C in future
- **Pressure of 15 bar,** high enough for $NO_x$ and $SO_x$ removal and latent-heat recovery.

# NO(g) and $NO_2$ (g) dissolution in water

**Aqueous analysis:** 50 mL gas mixtures reacted with 250 mL water at 25°C and 15 bar


900 ppm NO and 3% $O_2$


900 ppm $NO_2$

**$NO_2^-/NO_3^-$ close to 1:1**

# Revisit NOx reactions

*Gas Phase*

1. $2NO\ (g) + O_2(g) \rightarrow 2NO_2\ (g)$ → NO quickly oxidized to $NO_2$
2. $2NO_2(g) \leftrightarrow N_2O_4(g)$
3. $NO(g) + NO_2(g) \rightarrow N_2O_3(g)$ → $N_2O_3$ is not significant

*Gas + Liquid Phase*

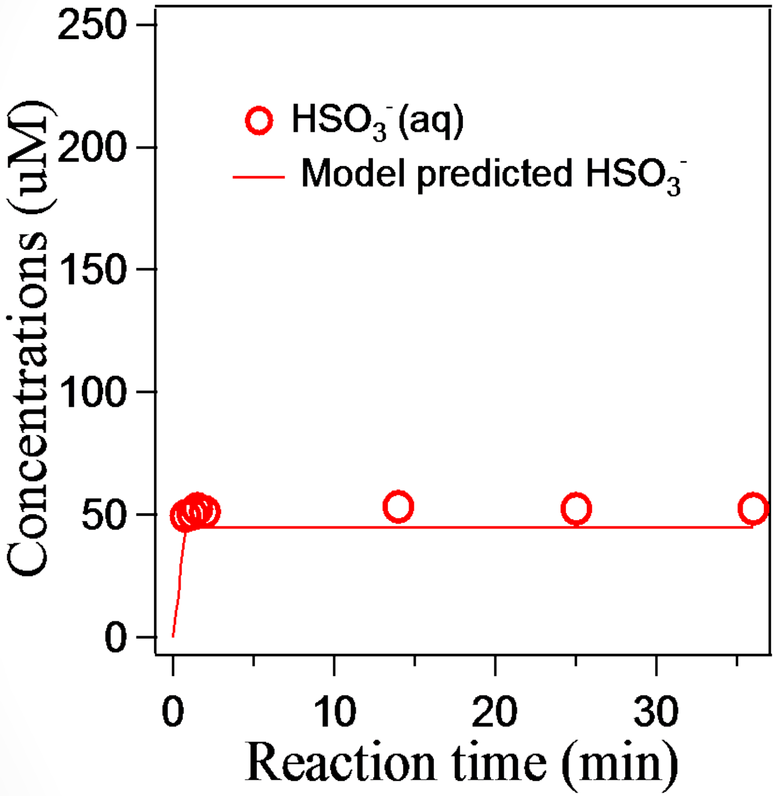
4. $2\ NO_2\ (g) + H_2O\ (g, aq) \rightarrow HNO_2\ (aq) + HNO_3\ (aq)$ ] Dominant
5. $N_2O_4(g) + H_2O\ (g, aq) \rightarrow HNO_2\ (aq) + HNO_3\ (aq)$ ]
6. $N_2O_3(g) + 2H_2O\ (g, aq) \rightarrow 2\ HNO_2\ (aq)$ → Not significant
7. $3\ HNO_2\ (aq) \rightarrow HNO_3\ (aq) + 2\ NO\ (g, aq) + H_2O\ (g, aq)$

→ Not significant

- $NO_2^-/NO_3^-$ close to 1:1 is consistent with dissolution of $NO_2$ ($N_2O_4$)
  → Reaction 4 and 5 is dominant and reaction 6 is not significant
- In $NO_2$ experiment, after 1 hour reaction, we did not observed any change of $HNO_2$ (aq)/$HNO_3$(aq) ratio or NO (< 2ppm) in gas phase.
  → Reaction 7 is not important

# $SO_2$(g) dissolution in water

**Aqueous analysis**: 50 mL of 450 ppm $SO_2$ reacted with 250 mL water at 25°C and 15 bar



Rapid dissolution

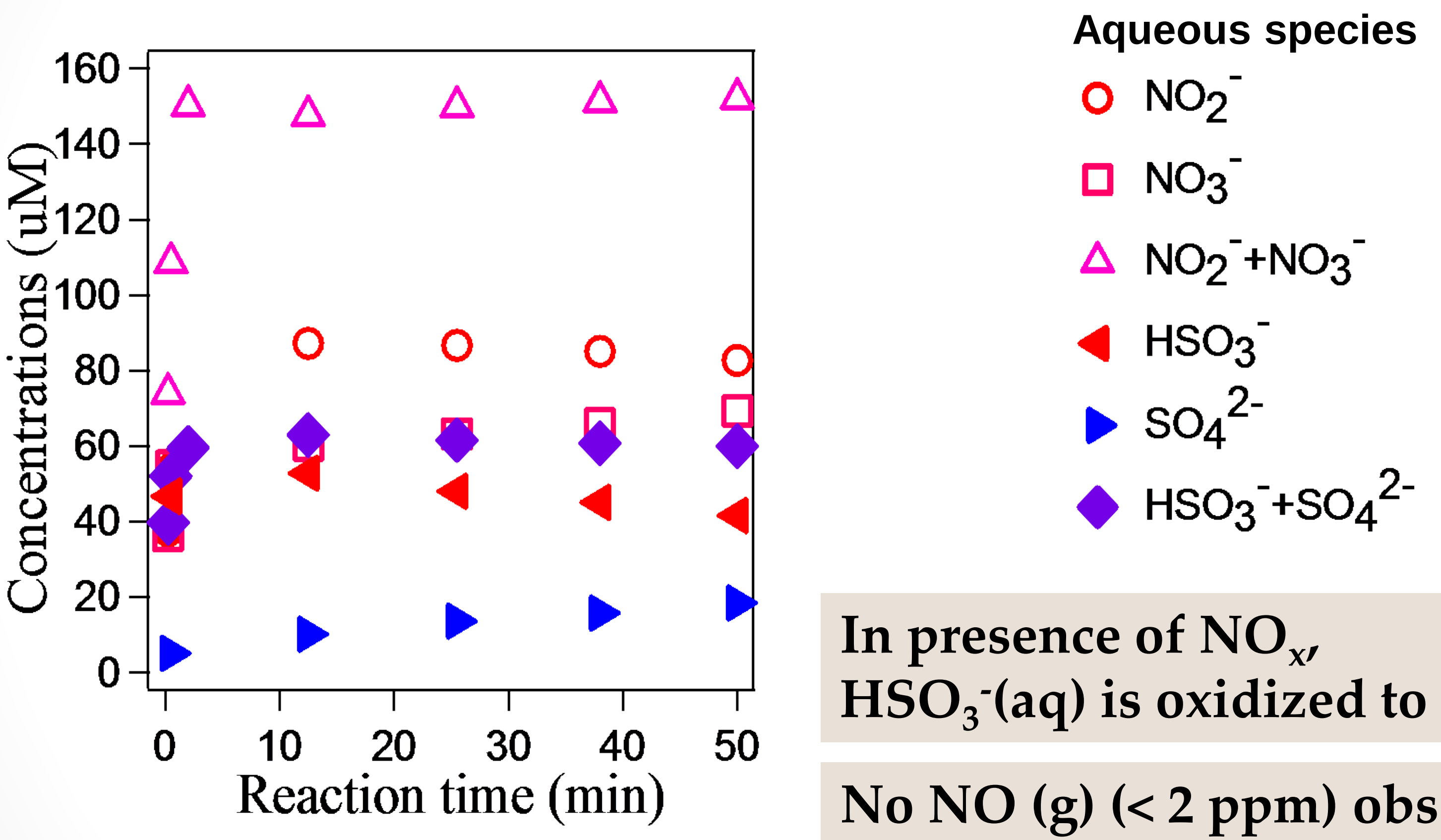
**No significant amount of $SO_4^{2-}$ (aq) (< 2.5 uM)**

**$SO_x$ Reactions**

8. $SO_2$ (g) + $H_2O$ (g, aq) → $HSO_3^-$ (aq) + $H^+$ (aq)

# $NO_2$(g) + $SO_2$(g) dissolution in water

**Aqueous analysis**: 50 mL of 1066 ppm $NO_2$ + 659 ppm $SO_2$ reacted with 250 mL water at 25°C and 15 bar



**In presence of $NO_x$, $HSO_3^-$(aq) is oxidized to $SO_4^{2-}$(aq)**

**No NO (g) (< 2 ppm) observed**

**$SO_x$ + $NO_x$ Reactions**

**9. $HNO_2$ (aq) + $HSO_3^-$ (aq) + $H^+$ (aq) → $H_2SO_4$ (aq)+ ½ $N_2O$ (g) + ½ $H_2O$ (aq)**

10. 2 $HNO_2$ (aq) + $HSO_3^-$ (aq) + $H^+$ (aq) → 2NO (g) + $H_2SO_4$ (aq) + $H_2O$ (aq)

# Proposed reduced mechanism

(After experiment)

## $NO_x$ Reactions

*Gas Phase*

1. $2NO\ (g) + O_2(g) \rightarrow 2NO_2\ (g)$
2. $2NO_2(g) \leftrightarrow N_2O_4(g)$ Equilibrium

~~3. $NO(g) + NO_2(g) \rightarrow N_2O_3(g)$~~

*Gas + Liquid Phase*

4. $2\ NO_2\ (g) + H_2O\ (g, aq) \rightarrow HNO_2\ (aq) + HNO_3\ (aq)$
5. $N_2O_4(g) + H_2O\ (g, aq) \rightarrow HNO_2\ (aq) + HNO_3\ (aq)$

Combined

~~6. $N_2O_3(g) + 2H_2O\ (g, aq) \rightarrow 2\ HNO_2\ (aq)$~~

~~7. $3\ HNO_2\ (aq) \rightarrow HNO_3\ (aq) + 2\ NO\ (g, aq) + H_2O\ (g, aq)$~~

## $SO_x$ Reactions

8. $SO_2\ (g) + H_2O\ (g, aq) \leftrightarrow HSO_3^-\ (aq) + H^+\ (aq)$ Equilibrium

## $SO_x$ + $NO_x$ Reactions

9. $HNO_2\ (aq) + HSO_3^-\ (aq) + H^+\ (aq) \rightarrow H_2SO_4\ (aq) + \frac{1}{2}\ N_2O\ (g) + \frac{1}{2}\ H_2O\ (aq)$

~~10. $2\ HNO_2\ (aq) + HSO_3^-\ (aq) + H^+\ (aq) \rightarrow 2NO\ (g) + H_2SO_4\ (aq) + H_2O\ (aq)$~~

# Future work

- **1. Examine the aqueous phase reactions between NO- and SO- containing species**
  - Effects of $NO_2/SO_2$ and pH
- **2. Simulate the actual temperature in the DCC**
  - Increase temperature from $25^oC$ to $150^oC$
- **3. Investigate effects of different catalysts**
  - e.g., Amberlyst, Amberlite, and activated carbon as catalysts

# Technical Approach:

# Prototype Direct Contact Cooler (DCC)

# Prototype DCC

**Technical Approach:**

The DCC was designed for both synthetic flue gas and flue gas taken from a 100 kWth pressurized oxy-combustion pilot facility

**Aims:**

Synthetic Flue Gas

- To demonstrate simultaneous capture of pollutants and latent heat
- To parametrically investigate $SO_x$/$NO_x$ capture efficiency

Pressurized Oxy-Combustion Flue Gas

- To determine the pollutant removal efficiency
- To determine the potential energy recovery

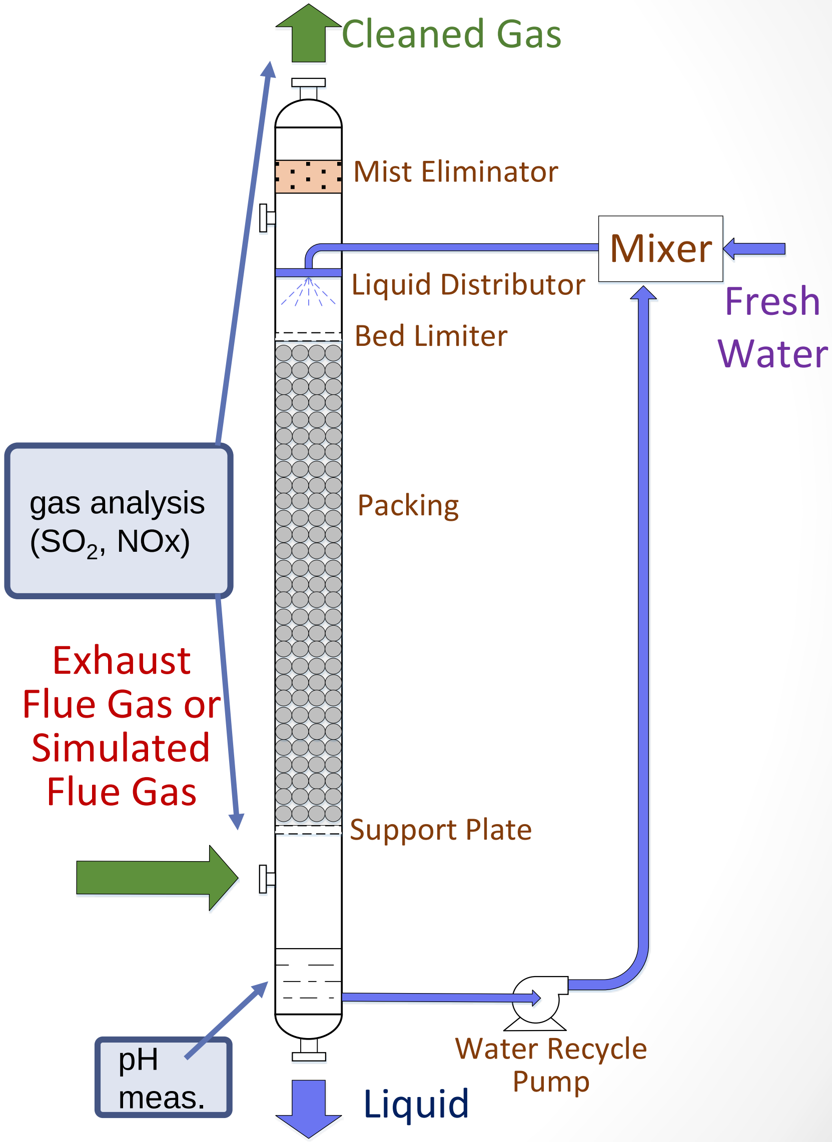
# Prototype DCC

**Features:**

- 316L column
- 30 bar vessel pressure rating
- Saddle ring packing
- Coupled to 100 kW pressurized combustion test facility
- Liquid recycle for pH control
- Reaction temperature control

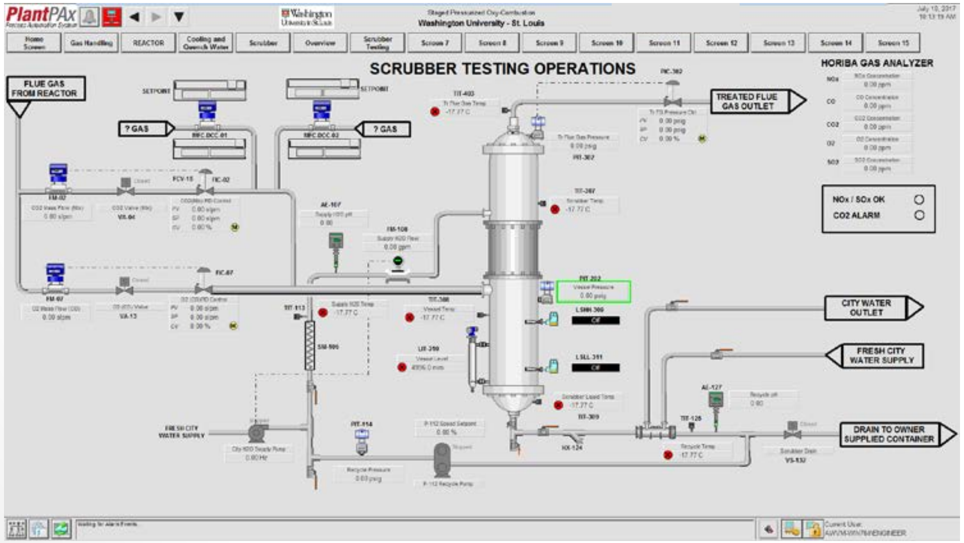
**Operational Conditions:**

| | |
|---|---|
| pH: | 3.5 – 6 |
| Liquid/Gas ratio: | 3 – 80 (L/$m^3$) |
| Pressure: | 1 – 15 bar |
| $SO_x$, $NO_x$ Concentration: | 300 – 2200 ppm |
| $NO_x$: $SO_x$ Ratio: | 0.5 – 2.0 |
| Liquid Temperature: | 15 – 50 °C |
| Gas Temperature: | 15 – 300 °C |



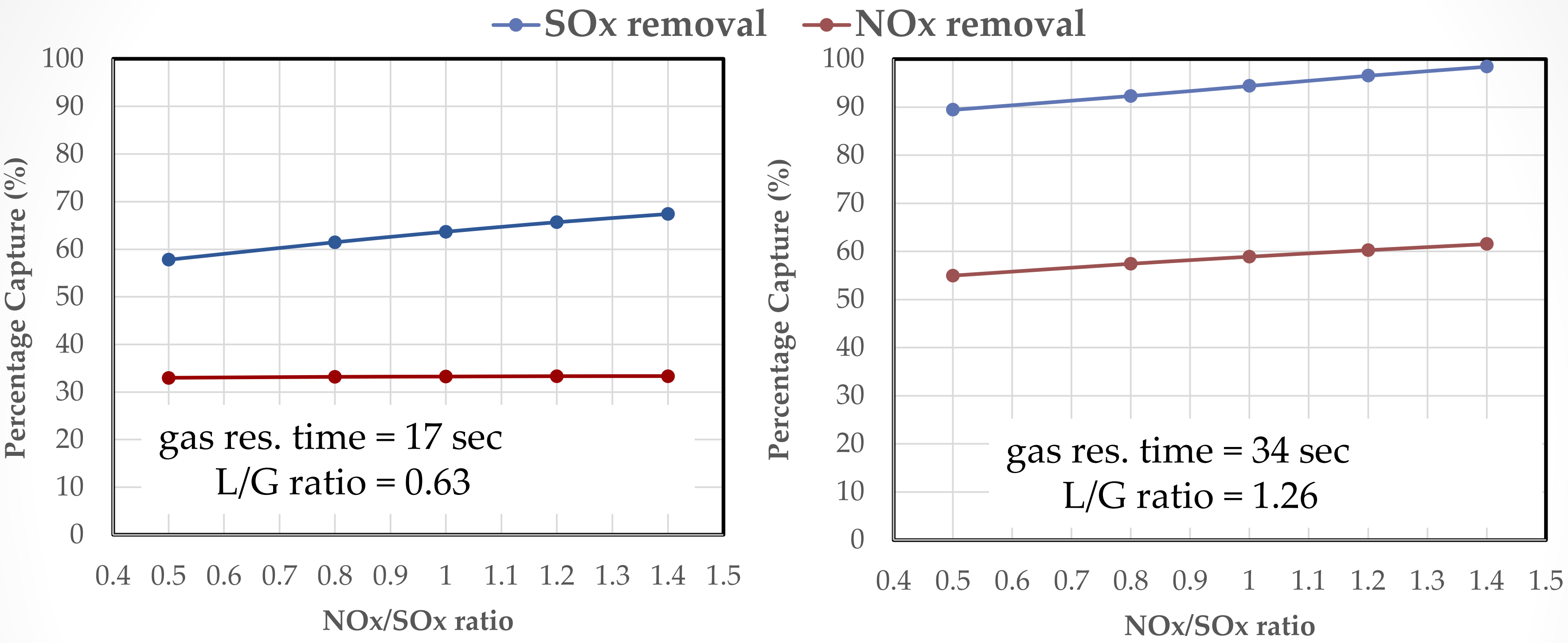
# Progress to Date

- The DCC column has been designed, fabricated, and hydro-tested by Progressive Recovery Inc.
- An experimental procedure and matrix has been established based on modeling.
- Integration into the laboratory infrastructure complete.  Commissioning **September 2017**.
- The automated control system designed: installation **September 2017**.



# DCC Model Results:

## Effect of NOx/SOx and residence time on removal



**Conditions:**

Operation – Single pass

Inlet Water Temp – 18°C

Inlet Gas Temp – 300°C

**Flue gas inlet composition:**

$NO_2$ – 225 to 630 ppm

NO – 225 to 630 ppm

$SO_2$ – 450 ppm

$SO_3$ – 450 ppm

$O_2$ - 1.6%(v)

# Milestone Log

| Status | Task No. | Milestone Description | Planned Completion |
|---|---|---|---|
| Complete | 2.1 | Purchase Bench-Scale Equip. | 03/31/2016 |
| Complete | 3.1 | Schematic Prototype Column Design | 03/31/2016 |
| Complete | 2.2 | Preliminary Bench-Scale Tests Complete | 06/30/2016 |
| Near Comp. | 3.2 | Construct Prototype | 08/31/2017 |
| Beginning | 4.1 | Performance Test w/ Simulated Flue Gas | 03/31/2018 |
| In progress | 5.2 | Complete Improved Model | 06/30/2018 |
|  | 4.2 | Performance Test w/ Real Flue Gas | 08/31/2018 |
|  | 6 | Full-Scale Cost & Performance Estimate | 08/31/2018 |

# Acknowledgements

## U.S. Department of Energy:

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NETL Project Manager: Arun Bose

## Consortium for Clean Coal Utilization:

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### U.S. DOE Disclaimer