

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

DE-FE0025193

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# Project Overview

## Project Objectives

Develop an enabling technology for simultaneous recovery of latent heat and removal of SO<sub>x</sub> and NO<sub>x</sub> 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

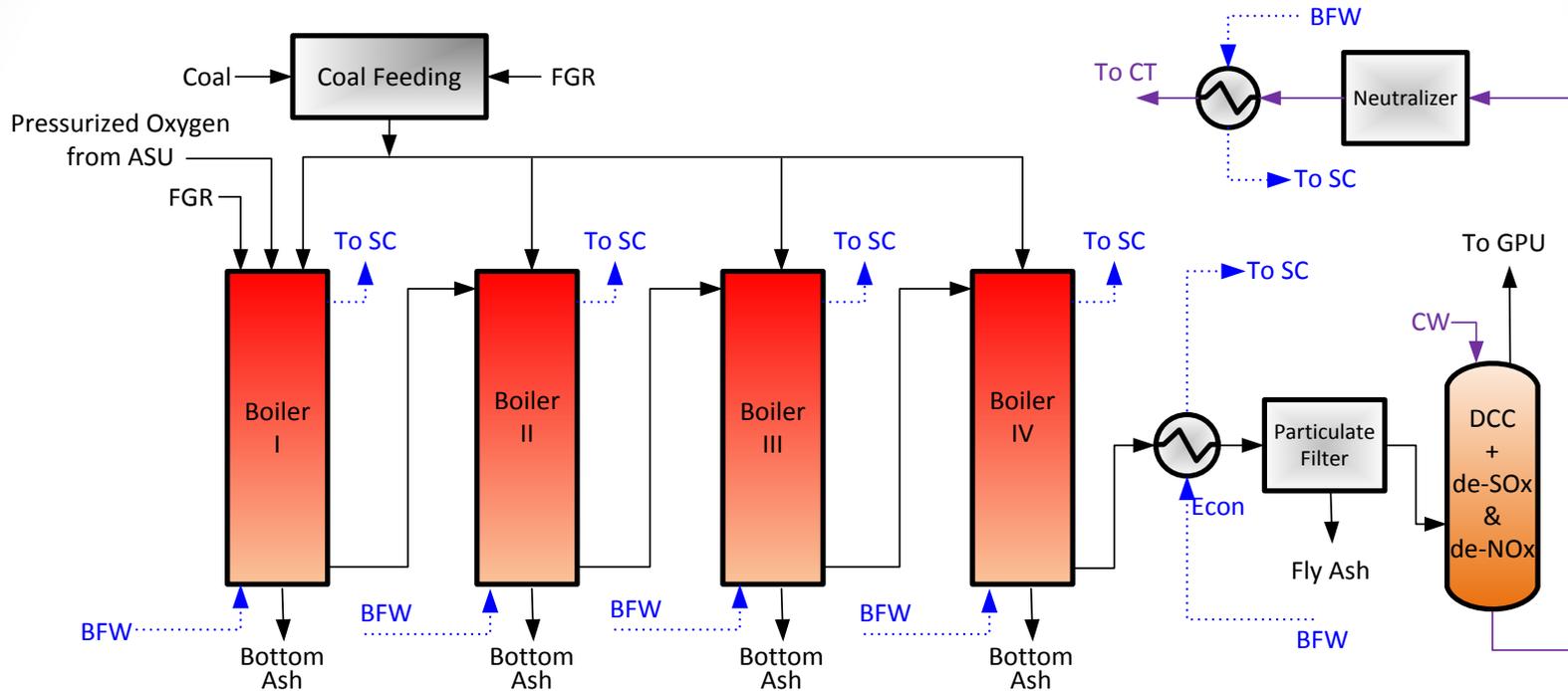
09/01/2015 - 08/31/2017

## Project Participants

Washington University

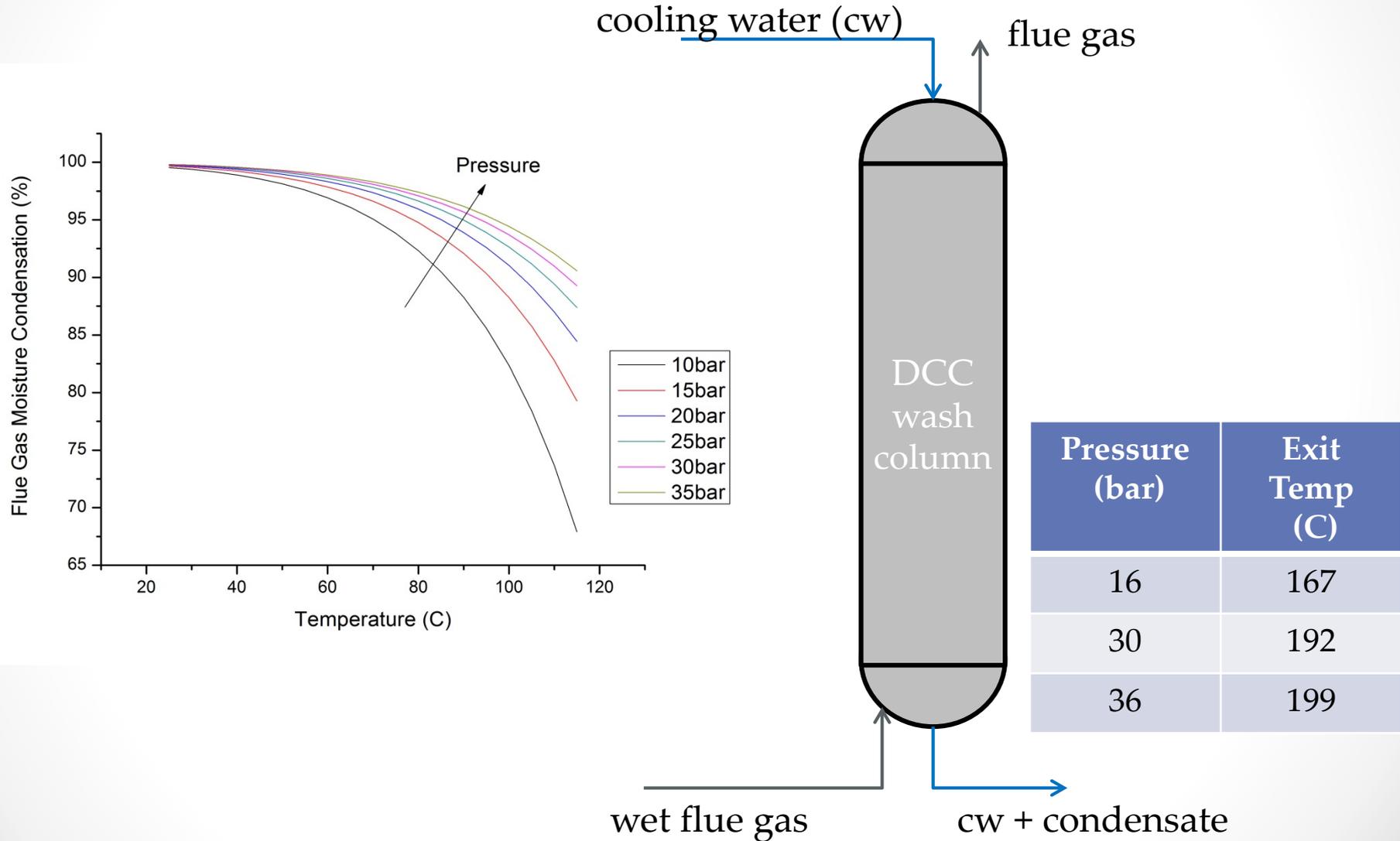
# Technology Background

# SPOC Process Flow Diagram

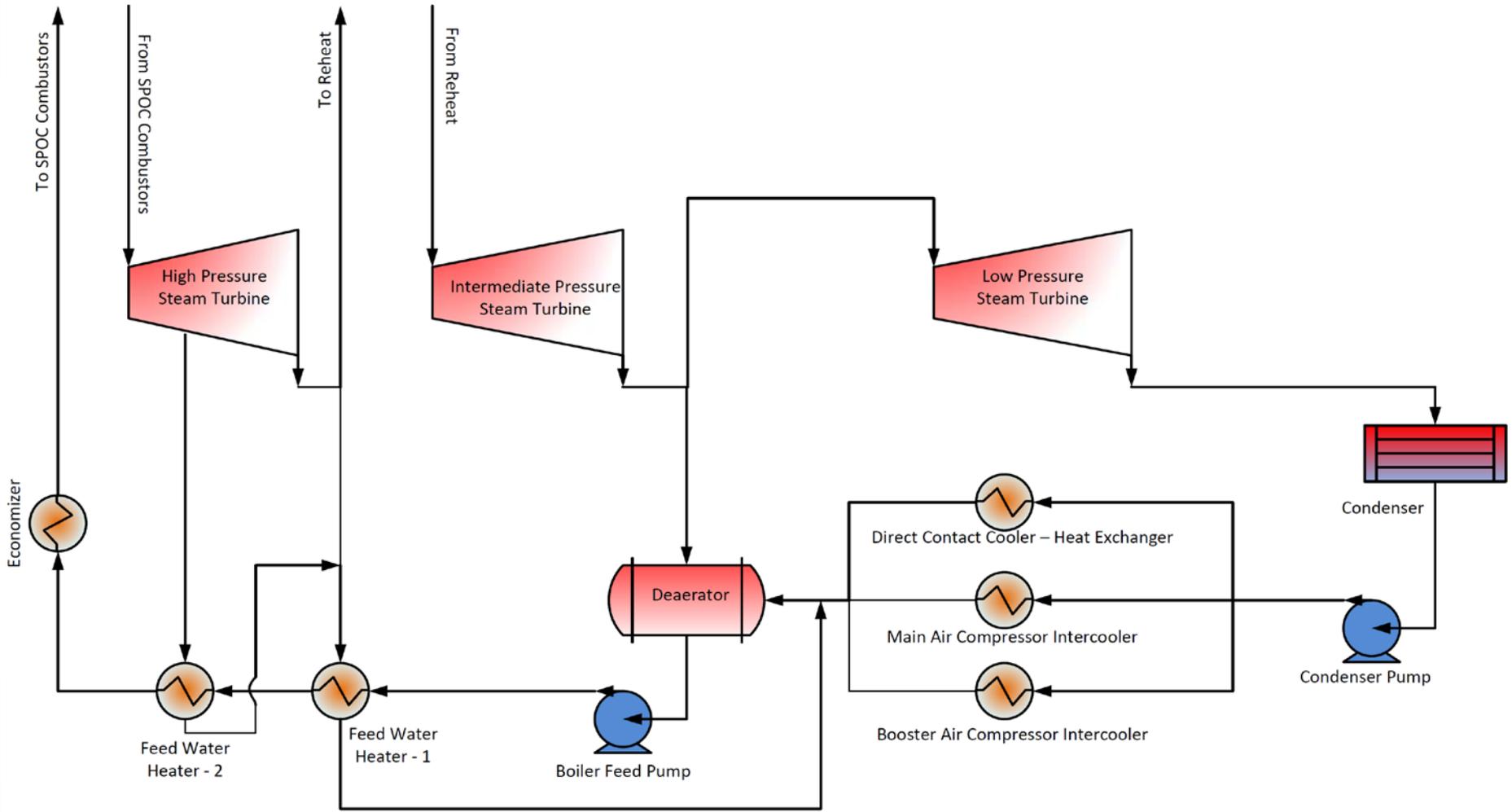


LEGEND				
ASU: Air Separation Unit	BFW: Boiler Feed Water	GPU: Gas Processing Unit	CT: Cooling Tower	CW: Cooling Water
DCC: Direct Contact Cooler	Econ: Economizer	SC: Steam Cycle	FGR: Flue Gas Recirculation	

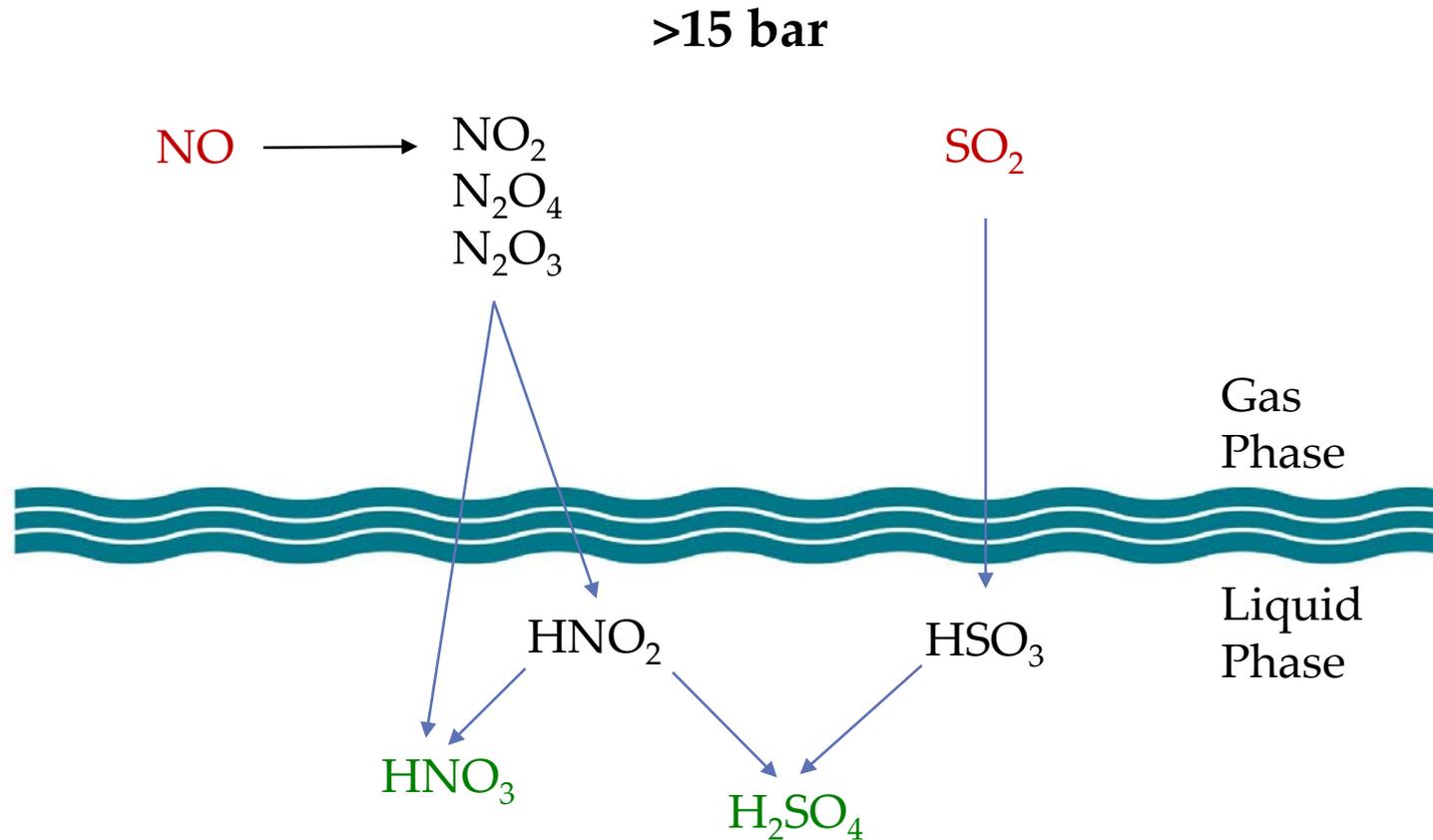
# Latent Heat Recovery – Direct Contact Cooler (DCC)



# SPOC Steam Cycle



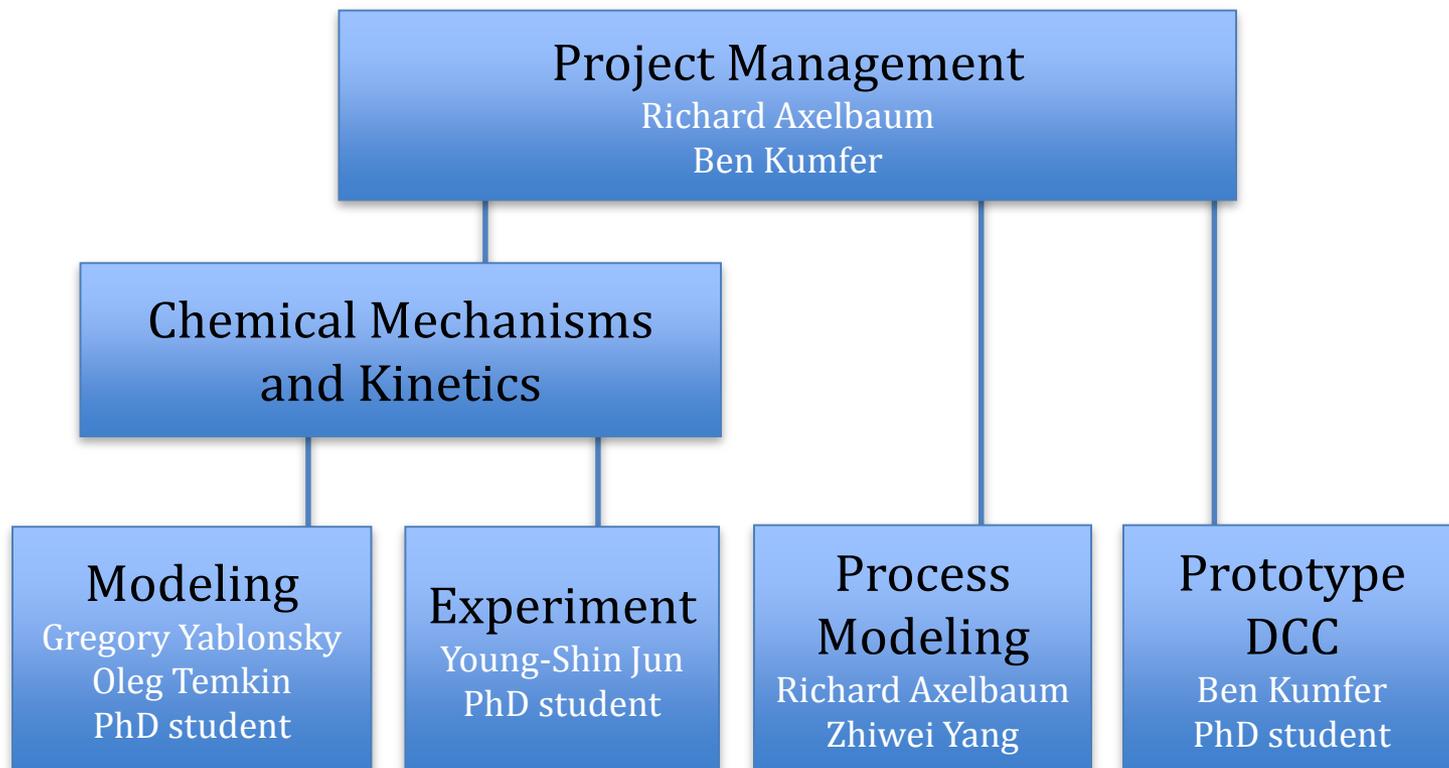
# SO<sub>x</sub> and NO<sub>x</sub> Removal Mechanism



# Project Objectives

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

# Project Organization

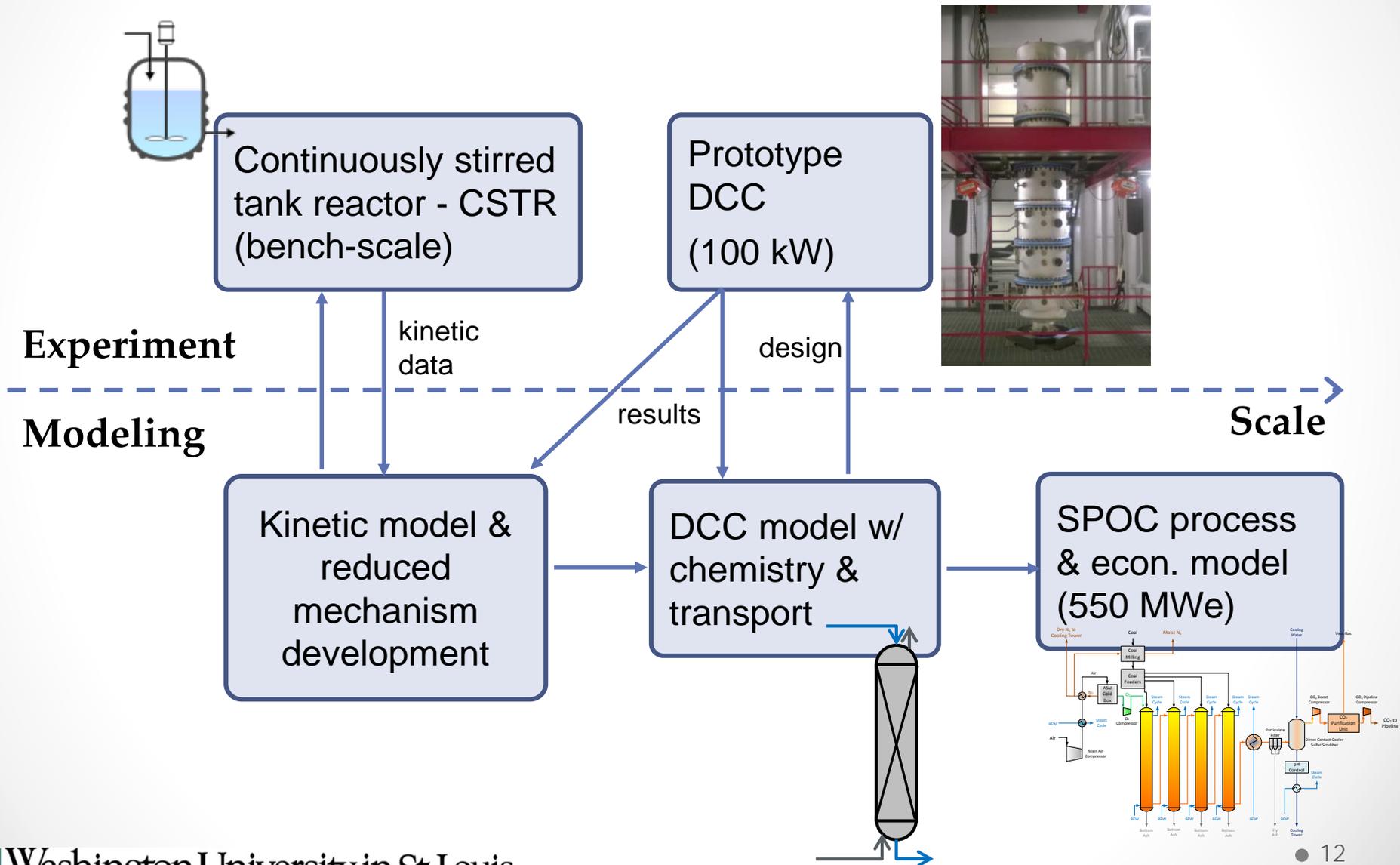


# Questions

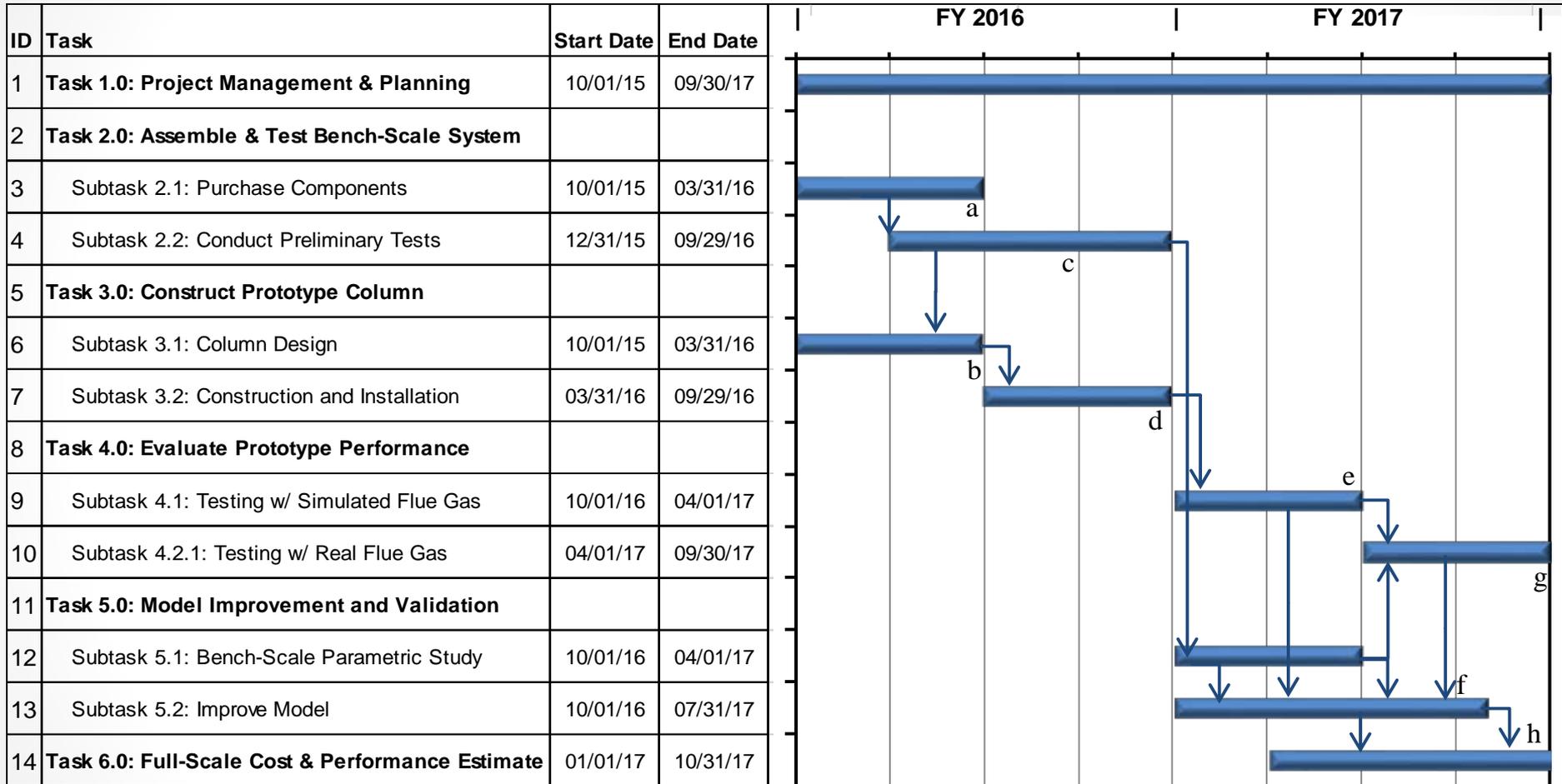
- What is the optimum design for the DCC for pressurized oxy-combustion?
- What is the expected removal efficiency at the proposed operating conditions for SPOC?
- What are the optimal DCC operating & inlet conditions?
  - Inlet NO<sub>x</sub>/SO<sub>x</sub> ratio
  - pH
  - Temperature
- What are the critical and rate limiting reactions?
- Can faster/more efficient capture be achieved using catalysts?
- Is one column sufficient?

# Technical Approach/Project Scope

# Technical Approach



# Schedule



# Knowledge Gaps and Challenges

1. **Mechanisms and kinetic parameters** of consumption/generation of different NO<sub>x</sub>- and SO<sub>2</sub>-species **in the gas phase is well understood.**
  - Mechanism for the NO- and SO- containing species in the **liquid phase remains unclear**, and some of the kinetic parameters are highly uncertain.
2. Literature regarding **influence of pH** on capture effectiveness is limited and sometimes contradictory. Because the pH changes as the reaction occurs, it is difficult to predict which mechanism is dominant.
  - To date, experimental systems have not controlled or directly measured the experimental pH values.
3. No systematic studies of the **effects of acid-base catalysts**, e.g., ion-exchange catalysis, on this gas-liquid process have been conducted.
4. **Difficult to experimentally measure** the concentrations of certain **key intermediate species.**
  - Lack of experimental data on the concentrations of critical species makes it challenging to obtain accurate kinetic data for key chemical reactions in such high pressure, high temperature systems.

# Technical Approach: Mechanism and Kinetics

# Expected Outcomes of Model Development

- New kinetic data on the absorption and conversion reactions of NO, NO<sub>2</sub>, and SO<sub>2</sub> under high temperature and pressure conditions with controlled pH.
  - This will be the first study to conduct experiments under well-characterized *in situ* pH conditions.
  - Catalyst performance will be evaluated.
- An experimentally-validated chemical mechanism
- A simplified but reliable kinetic model with experimentally-obtained kinetic parameters.
- Recommendations on the optimal working regime, i.e., reactant concentrations, temperature and pH.

# 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
  - cannot explain some experimental data in the literature
  - kinetic expressions need verification
  
- A reduced model has been constructed.

# Proposed Mechanism

## ***I. N (nitrogen) -block***

1.  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{NO}_2(\text{g})$
2.  $2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$
3.  $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_3(\text{g})$
4.  $2\text{NO}_2(\text{g} \rightarrow \text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{HNO}_2(\text{aq}) + \text{HNO}_3(\text{aq})$
5.  $\text{N}_2\text{O}_4(\text{g} \rightarrow \text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{HNO}_2(\text{aq}) + \text{HNO}_3(\text{aq})$
6.  $\text{N}_2\text{O}_3(\text{g} \rightarrow \text{aq}) + 2\text{H}_2\text{O}(\text{aq}) \rightarrow 2\text{HNO}_2(\text{aq})$
7.  $3\text{HNO}_2(\text{aq}) \rightarrow \text{HNO}_3(\text{aq}) + 2\text{NO}(\text{g}, \text{aq}) + \text{H}_2\text{O}(\text{aq})$

## ***II. S (sulfur) -block***

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

## ***III. S&N -block***

9.  $2\text{HNO}_2(\text{aq}) + \text{H}^+(\text{aq}) + \text{HSO}_3^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{aq}) + 2\text{NO}(\text{g}) + 2\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
10.  $2\text{HNO}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{HSO}_3^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{aq}) + \text{N}_2\text{O}(\text{g}) + 4\text{H}^+(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq})$

# Modeling to guide experiments

## ➤ NO<sub>x</sub> in gas phase

- Literature: contradictory statements about whether N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>3</sub> are important,
- Modeling results: NO and NO<sub>2</sub> are the major species; [NO<sub>2</sub>] >> [N<sub>2</sub>O<sub>4</sub>] > [N<sub>2</sub>O<sub>3</sub>].
- Gas-phase experimental data will be obtained.

## ➤ Mass transfer limited or kinetically limited

- Literature: contradictory conclusions about which is limiting,
- Modeling: better agreement with experimental data of Ting et al obtained when a higher mass transfer coefficient is used

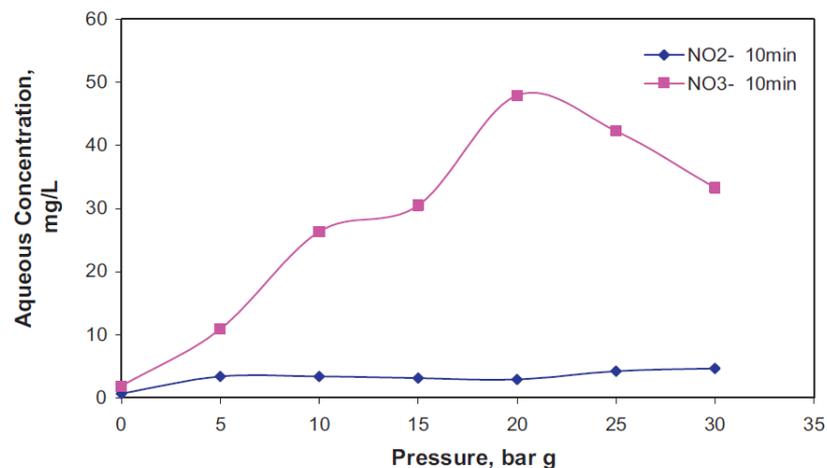
$$R_{\text{dissolution}} \approx R_{\text{liquid reaction}}.$$

- We can change circulation rate, stirring, and residence time in our experiment, to determine which one is limiting.

# Modeling to guide experiments

➤ Explain the difference between  $\text{HNO}_3$  and  $\text{HNO}_2$  concentration dependencies on pressure (Ting et al)

- Modeling results: both concentrations increase with pressure.
- Possible reason for the difference in acids concentrations: decomposition of  $\text{HNO}_2$  (Reaction 7)
- Decomposition of  $\text{HNO}_2$  may need to be faster in model.
- In future experiments, possible difference in acids concentrations has to be analyzed to obtain more accurate kinetic data.



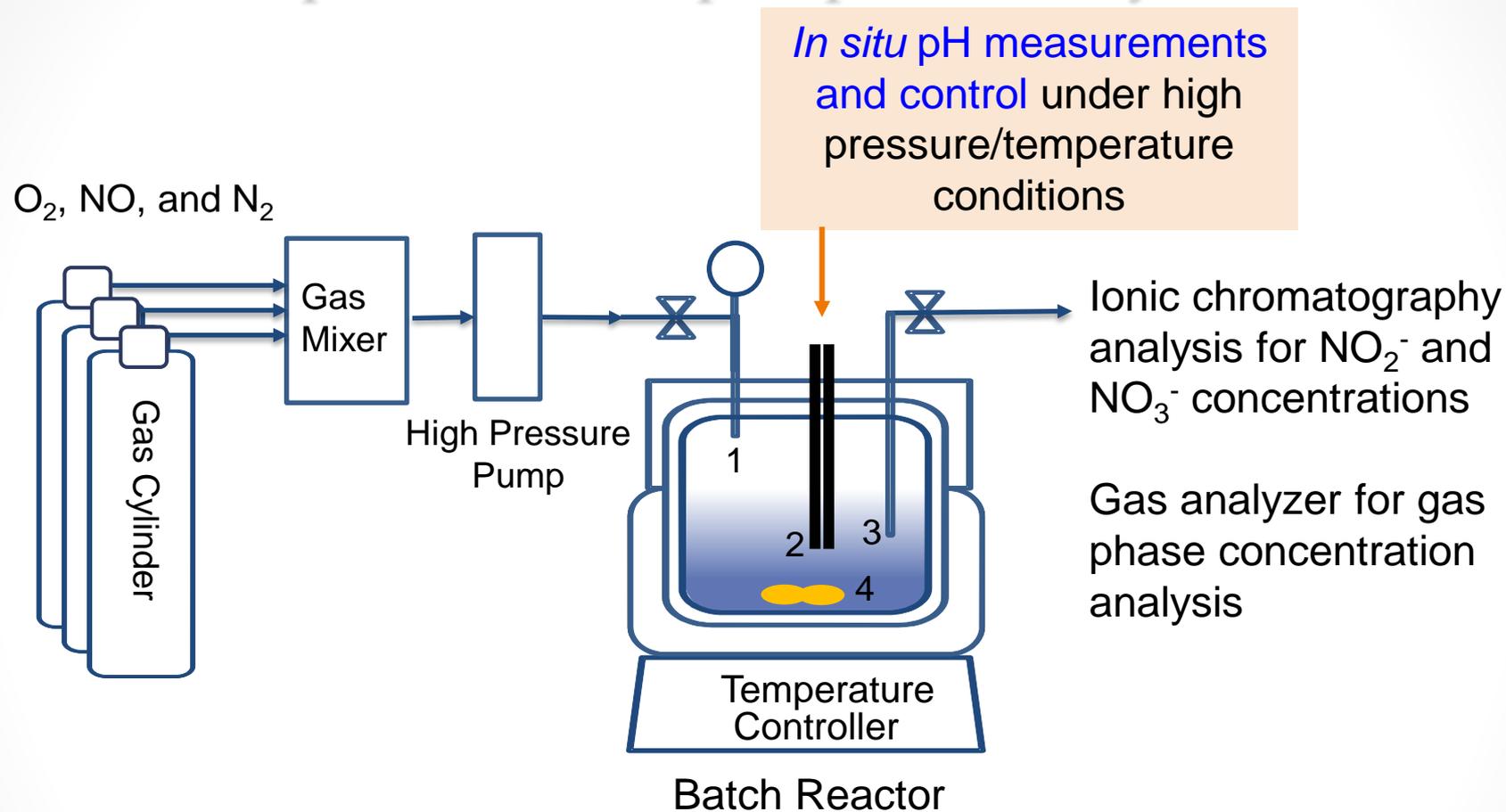
Initial analysis of nitrate/nitrite in solution after 10 min of bubbling contacting with gaseous  $\text{NO}_x$  at different pressures. Standard analysis performed by professional laboratory up to 2 weeks after experiment.

Ting et al, 2013

# Technical Approach:

## CSTR Experiments

# Experiment setup of preliminary tests



1. Gas inlet and pressure gauge;
2. High pressure/temperature pH electrodes;
3. Liquid outlet; and
4. Mechanical stirrer

# Experimental variables used in preliminary tests

## Testing NO<sub>x</sub> Reactions

Variables	Conditions
Pressure (bar)	15
Temperature (°C)	25
NO concentration	0.9%
O <sub>2</sub> gas concentration	8%
Reaction time (min)	10 and 60
Stirring rate (rpm)	1200

### Gas Phase

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

Input and output gas

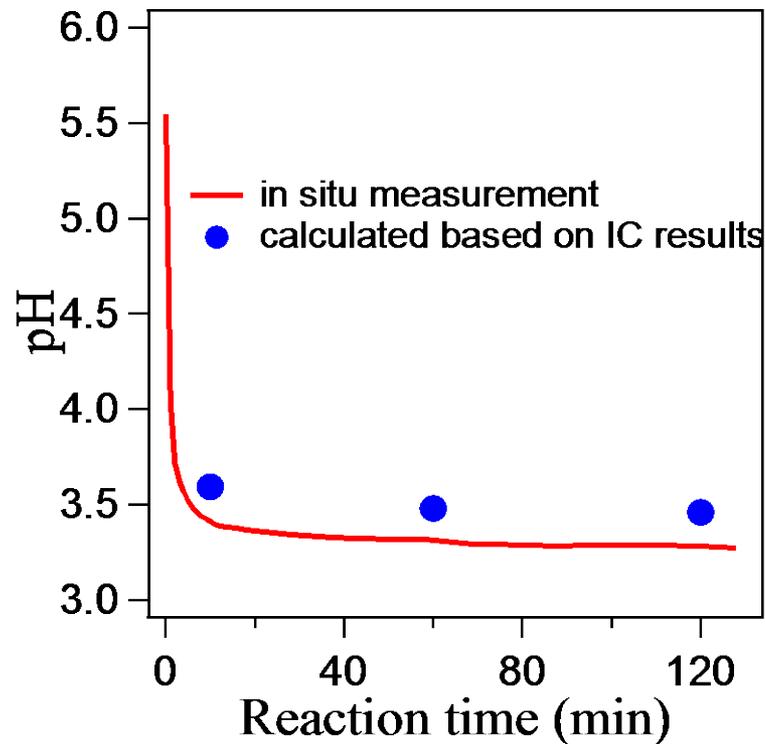
### Gas + Liquid Phase

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

Aqueous NO<sub>2</sub><sup>-</sup>  
and NO<sub>3</sub><sup>-</sup>  
concentrations  
and pH  
measurement

# *In situ* pH and ion chromatography-determined $\text{NO}_2^-$ and $\text{NO}_3^-$ concentration evolution during $\text{NO}_x$ gas dissolution

Reaction time (min)	$\text{NO}_2^-$ ( $\mu\text{M}$ )	$\text{NO}_3^-$ ( $\mu\text{M}$ )
10	194.5	121.0
60	257.5	168.7
120	272.6	178.2

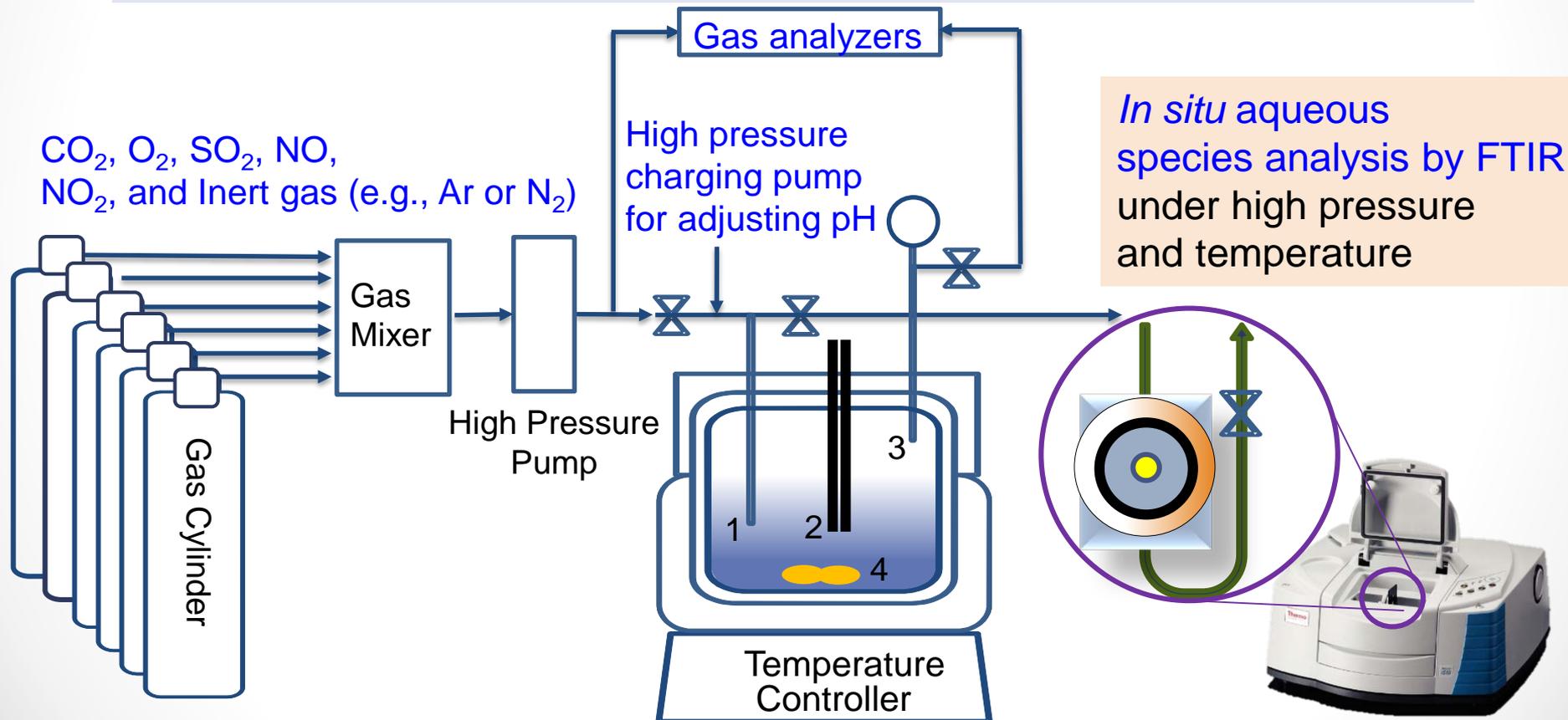


# Experiment setup to be used in future tests

Unique reactor design optimized for conducting experiments up to

- 325 °C
- 40 bar
- $pH = 0$

Coupled to *in-situ* FTIR measurements of aqueous species

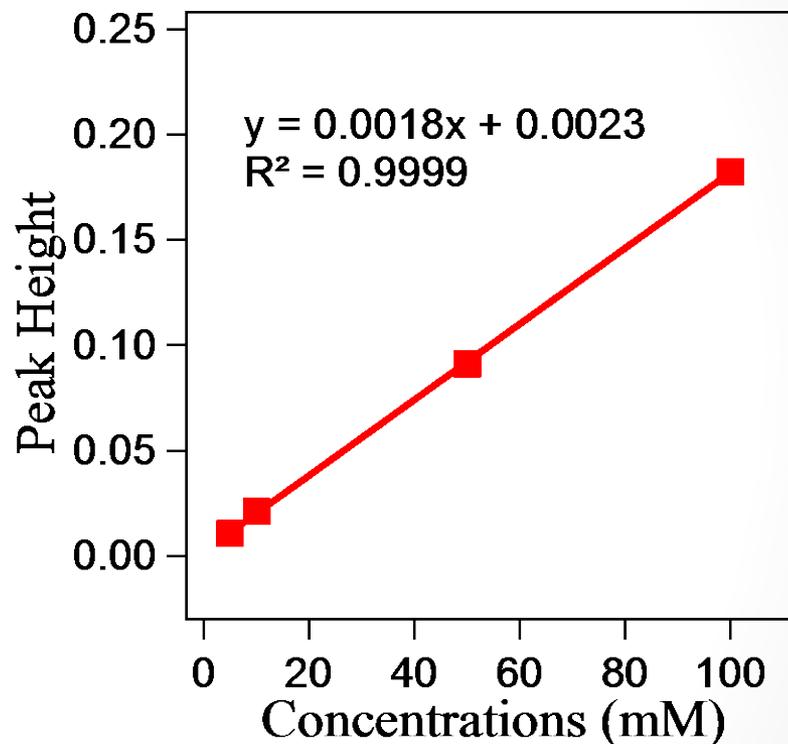
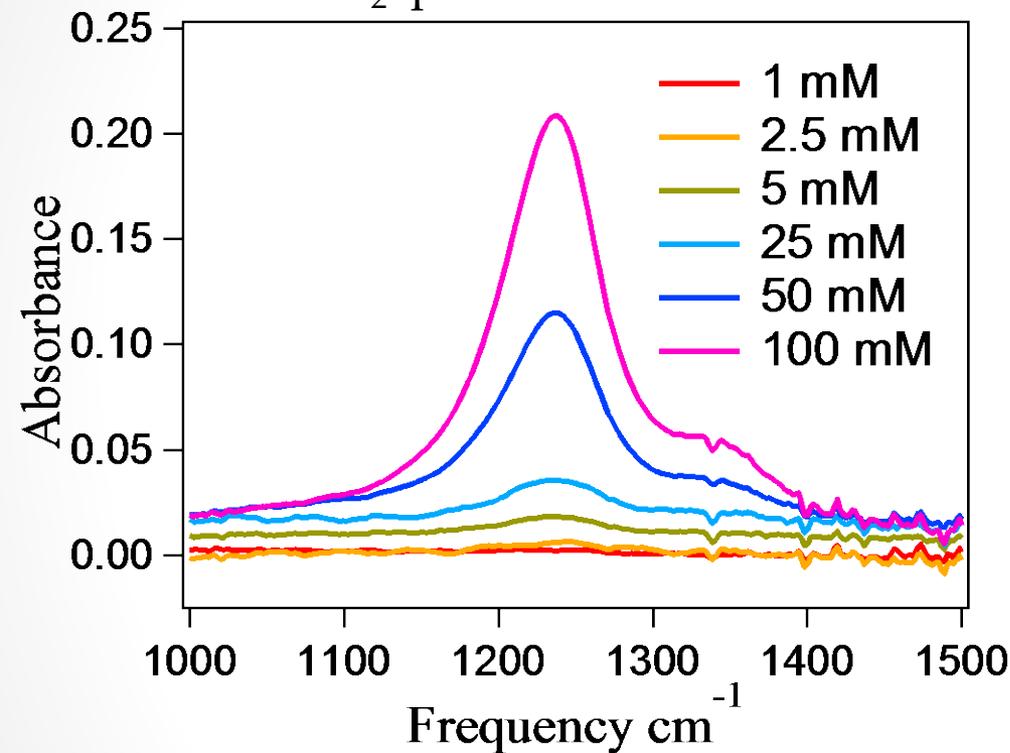


*In situ* aqueous species analysis by FTIR under high pressure and temperature



# High temperature and pressure FTIR for in situ analysis

$\text{NO}_2^-$  peak around  $1236\text{ cm}^{-1}$



**Detection limits and calibration  
have been performed for each species**

# Future plans for Bench scale experiments

- Obtain new kinetic data on the absorption and conversion reactions of NO, NO<sub>2</sub>, and SO<sub>2</sub> under high temperature and pressure conditions with controlled pH.
  - This will be the first study to conduct experiments under well-characterized *in situ* pH conditions.
  - Catalyst performance will be evaluated.
- Experimentally obtain kinetic parameters for validating reaction mechanisms and models
- Provide recommendations on the optimal working regime, i.e., reactant concentrations, temperature and pH.

# Accomplishments

- **Unique and new capabilities have been developed.**
  - *In situ* pH monitoring
  - *In situ* FTIR measurements of aqueous concentrations of nitrite or nitrate (> 2.5 mM) or sulfate (> 0.1 mM) or sulfite (0.025 mM)
  - *Ex situ* ion chromatography for lower concentrations of these species
    - *measure within a few minutes after sampling rather than long waiting time reported previous.*
- **All instruments have been purchased and set up.**
- **Safety protocols for experiments have been determined.**
- **Preliminary tests have been conducted.**

Technical Approach:

Prototype Direct Contact Cooler  
(DCC)

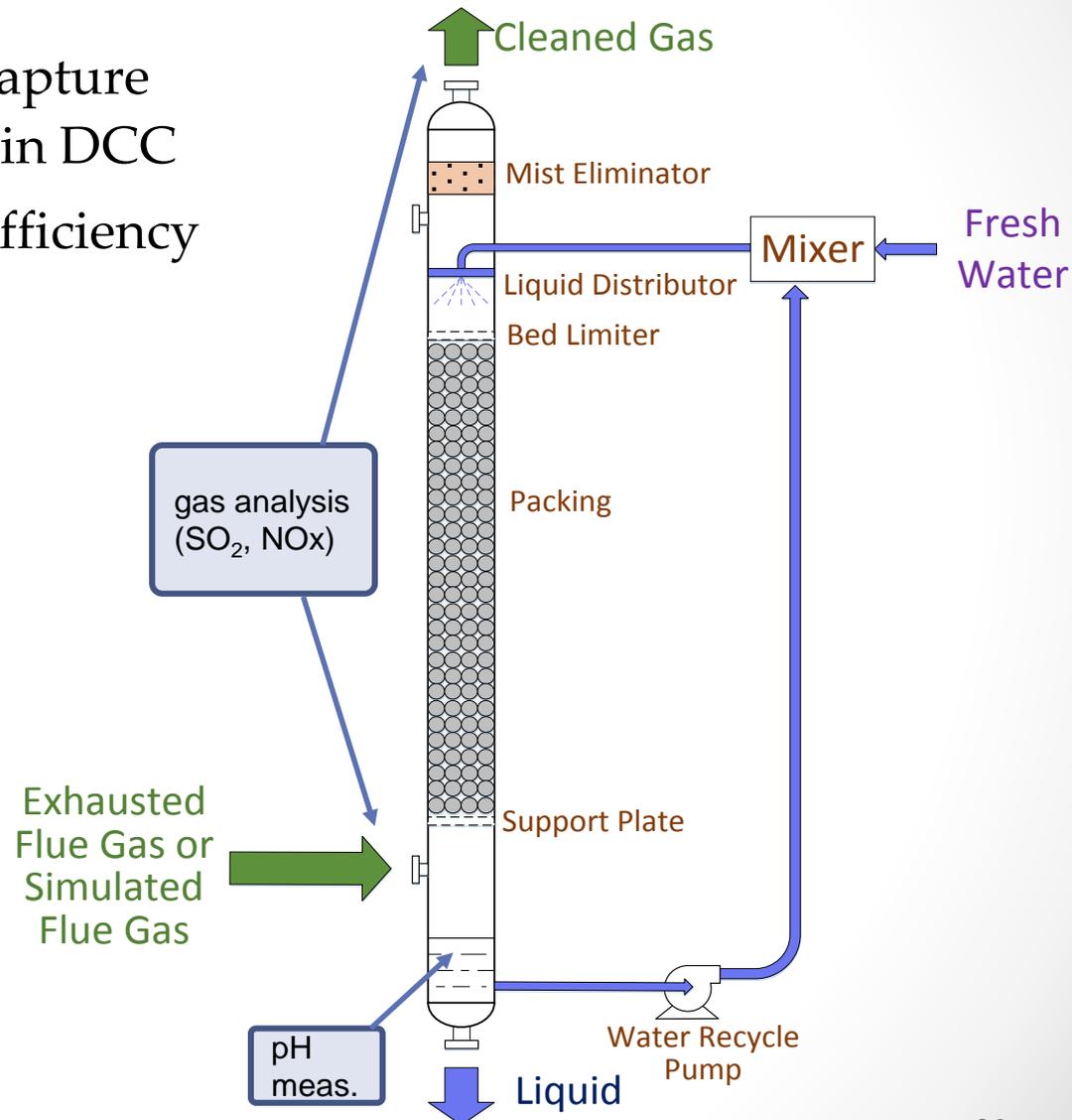
# Prototype DCC

## Aims:

- Demonstrate simultaneous capture of pollutants and latent heat in DCC
- Measure SO<sub>x</sub>/NO<sub>x</sub> capture efficiency vs. operating parameters

## Features:

- Packed-bed column design
- Pressure up to 30 bar
- Coupled to 100 kW pressurized combustion test facility
- Both simulated and real flue gas will be used
- Liquid recycle for pH control

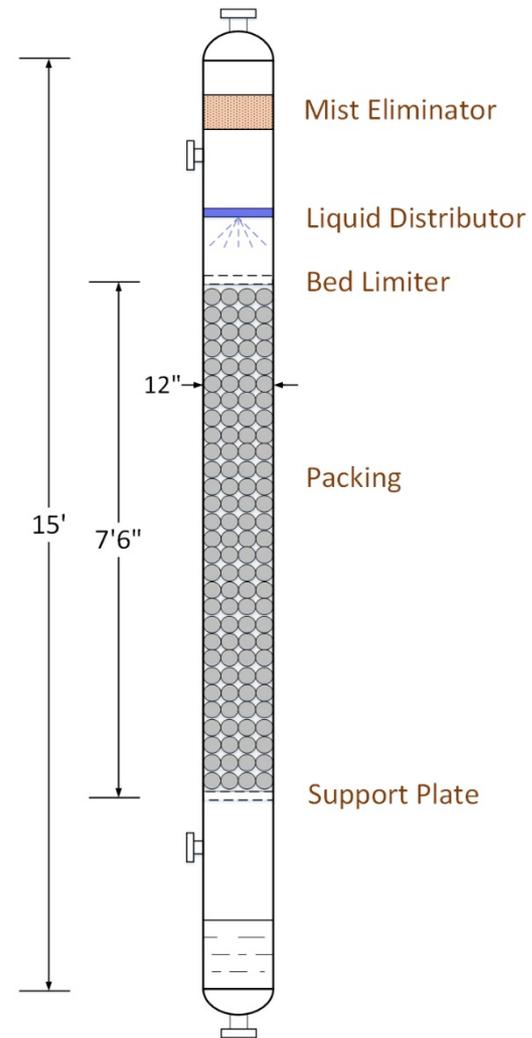


# Progress to Date

- **Vendors under contract:**
  - Progressive Recovery Inc. - vessel and system design and fabrication
  - Process Engineering Associates, LLC – reactor modeling, sizing, process design
- **Preliminary design completed:**
  - Reactor sizing, packing type, ancillary equipment specifications
  - Process flow sheet & piping and instrument diagram
  - Reactor model (CHEMCAD) with our detailed chemistry and transport developed
- **Detailed cost proposal under evaluation**
- **Construction to be completed Dec 2016**

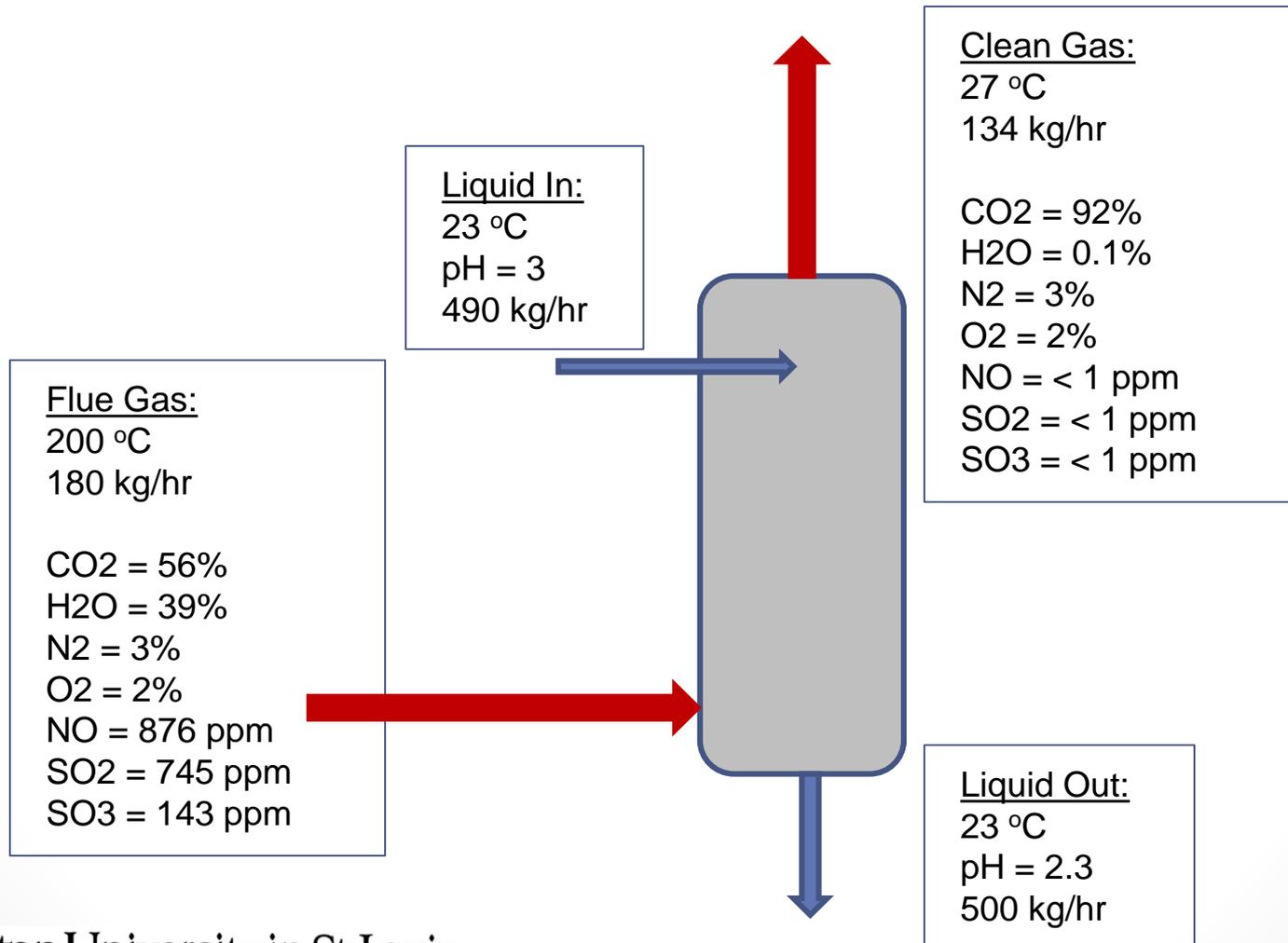
# Reactor Design Specifications

- Vapor residence time:  $\leq 120$  seconds
- pH range: 2.5 – 7
- L/G ratio: 3 – 80 (L/m<sup>3</sup>)
- Number of stages of packing: 5
- Packing type: random saddle ring
- Material of construction: 316 stainless steel



# Reactor Modeling for Preliminary Design

- SO<sub>x</sub> & NO<sub>x</sub> capture is sensitive to L/G
- Complete removal can be achieved



# Milestones

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
In progress	3.2	Construct Prototype	09/30/2016
	4.1	Performance Test w/ Simulated Flue Gas	03/31/2017
In progress	5.2	Complete Improved Model	06/30/2017
	4.2	Performance Test w/ Real Flue Gas	08/31/2017
	6	Full-Scale Cost & Performance Estimate	08/31/2017

# Acknowledgements

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