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

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Outline

- Technology Background
- Project Objectives
- Technical Approach
- Project Management

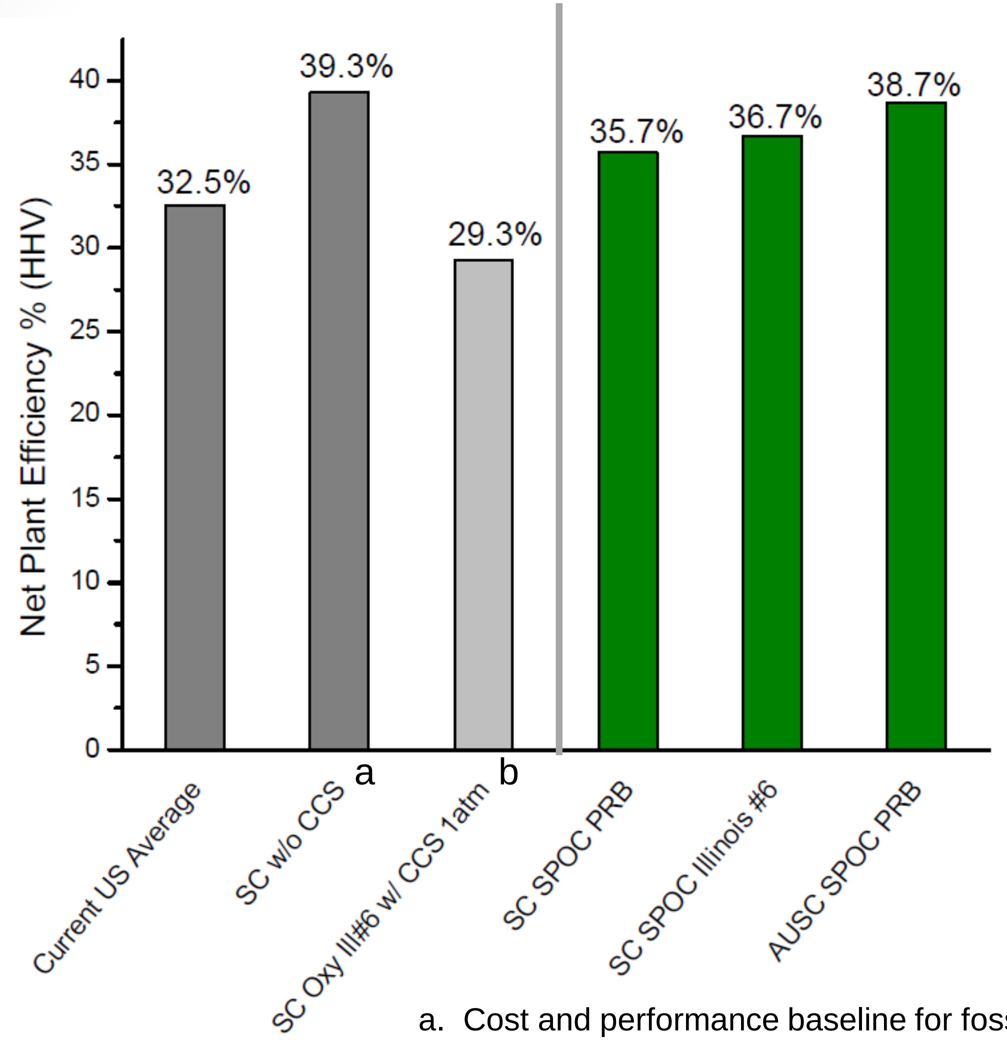
Technology Background

Pressurized Oxy-Combustion

- The requirement of high pressure CO_2 for sequestration enables pressurized combustion as a tool to increase efficiency and reduce costs.

- Benefits of Pressurized Combustion
  - Recover latent heat in flue gas
  - Latent heat recovery can be combine with integrated pollution removal
  - Reduce gas volume
  - Avoid air-ingress
  - Fuel flexibility
  - Controlled radiation heat transfer

ASPEN Plus Results – Plant Efficiency

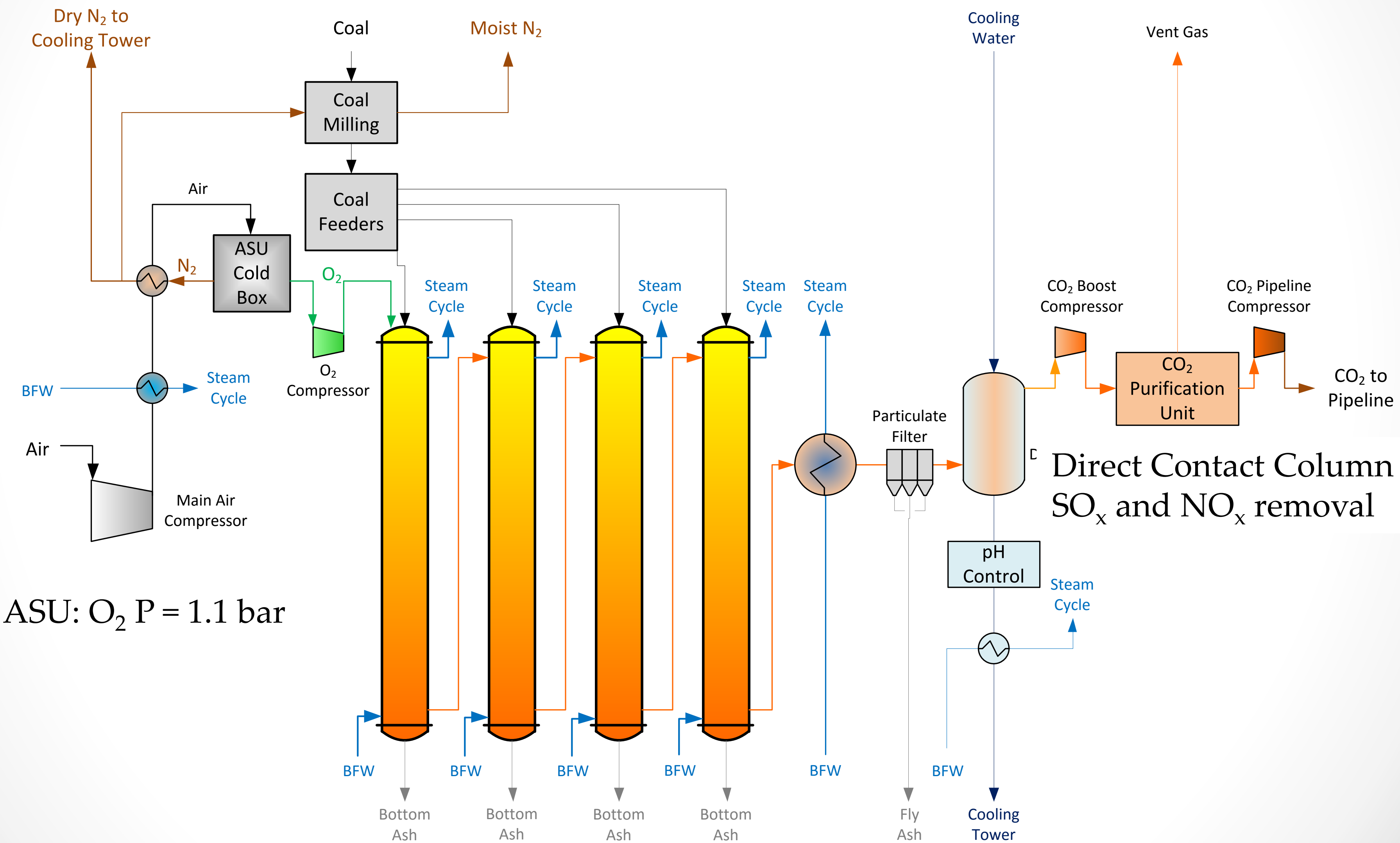


Gopan A, et al. *Applied Energy*, 125, 179-188 (2014)

a. Cost and performance baseline for fossil energy plants volume 1: bituminous coal and natural gas to electricity. DOE/NETL-2010/1397, rev. 2

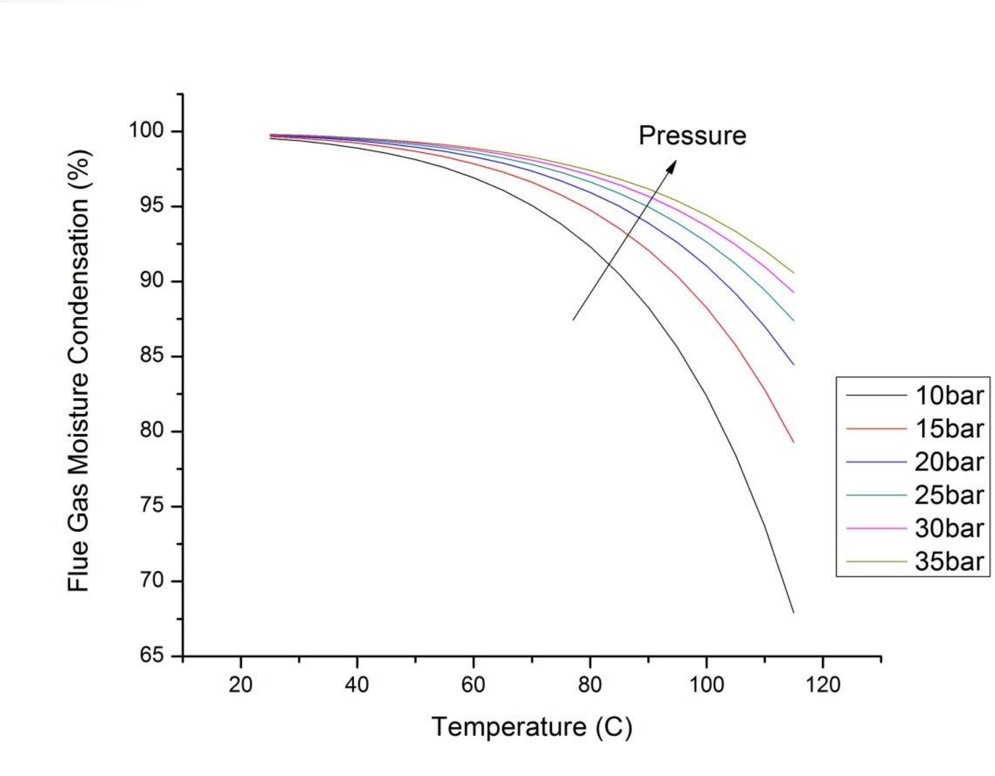
b. Advancing Oxycombustion Technology for Bituminous Coal Power Plants: An R&D Guide. DOE/NETL - 2010/1405

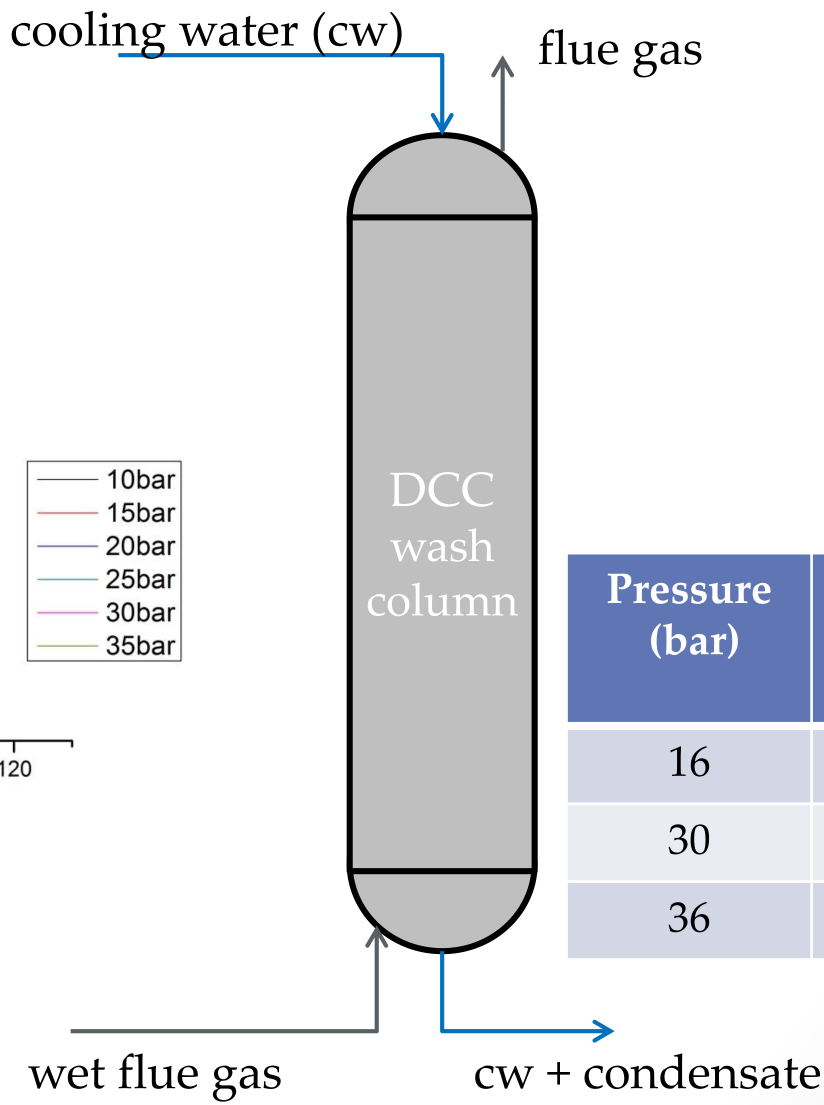
SPOC Process Flow Diagram



Std. ASU: O_2 P = 1.1 bar

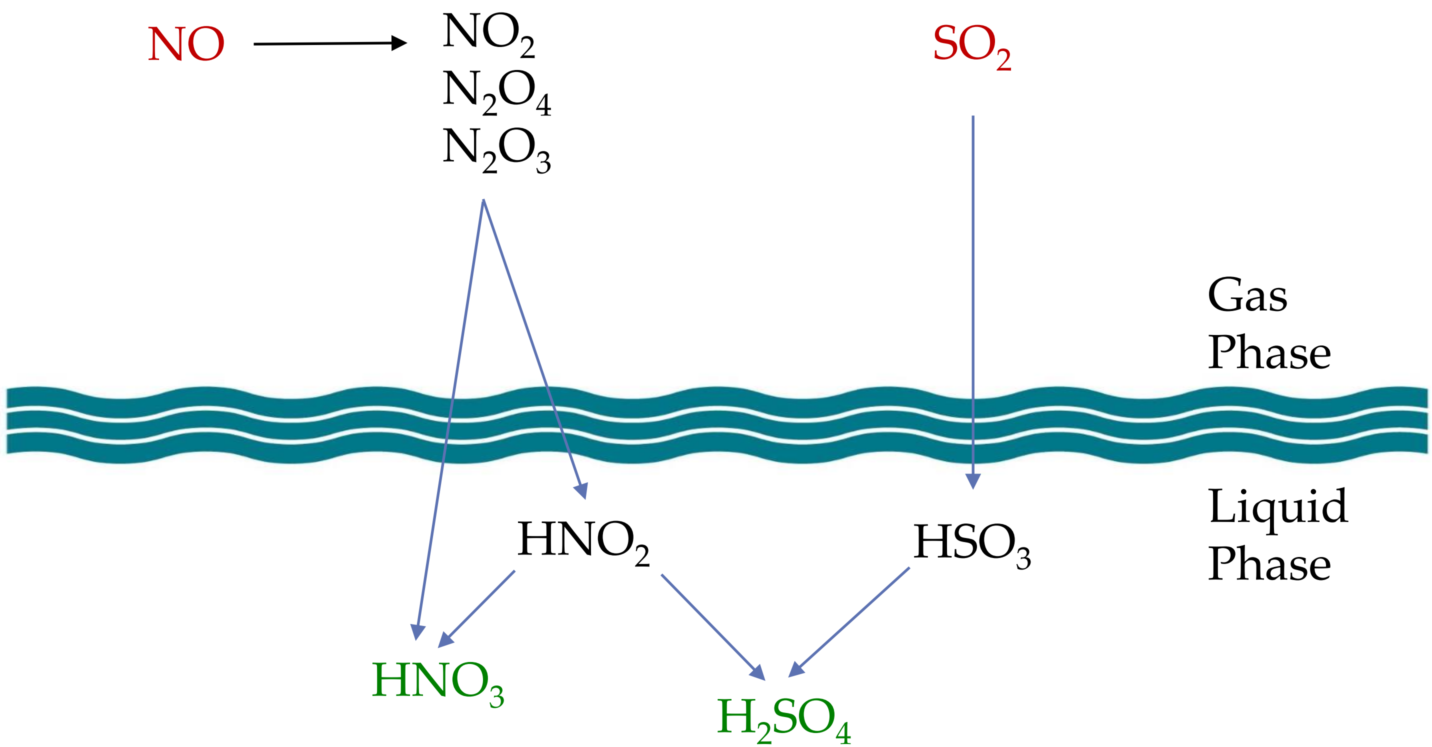
Latent Heat Recovery – DCC





Pressure (bar)	Exit Temp (C)
16	167
30	192
36	199

SOx and NOx Removal Mechanism



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 NOx/SOx ratio
  - pH
  - Temperature
- What are the critical and rate limiting reactions?
- Is one column sufficient?

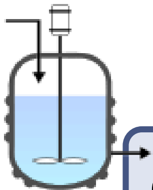
Project Objectives

Mission: to develop an enabling technology for simultaneous recovery of latent heat and removal of SOx and NOx from flue gas during pressurized oxy-coal combustion, so as to eliminate conventional FGD and de-NOx processes and minimize the COE.

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.

Technical Approach



Continuously stirred tank reactor - CSTR (bench-scale)

Prototype DCC

(100 kW)

kinetic data

design

results

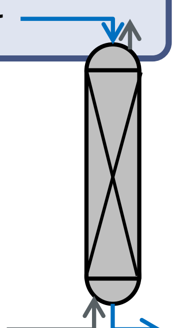
Experiment

Modeling

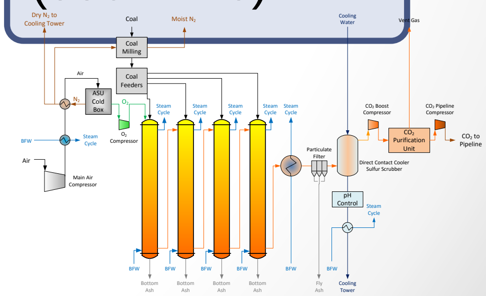
Scale

Kinetic model & reduced mechanism development

DCC model w/ chemistry & transport



SPOC process & econ. model (550 MWe)



Technical Approach:

Mechanism and Kinetics

Knowledge Gaps and Challenges: Reaction Mechanism & Kinetic Model

1. The earlier understanding of the chemistry (the so-called lead chamber process) has been shown to be insufficient but this chemistry is still often used to describe the process.

2. New chemical mechanisms have been proposed but these have been based on existing kinetic data developed under conditions different from this system.

3. A "rational" kinetic model is needed where
   - the level of complexity of the model is just sufficient to characterize the chemistry, and
   - the kinetic parameters in the mechanism are obtain by experiment.

Building blocks of the Mechanism

1. ***N (nitrogen) -block***
   - Gas-phase oxidation of NO into nitrogen oxides NO_2, N_2O_3 and N_2O_4
   - Liquid-phase dissolution of nitrogen oxides; production of nitrous and nitric acids (HNO_2, HNO_3)

2. ***S (sulfur) -block***
   - Liquid-phase dissolution of SO_2

3. ***S&N -block***
   - Liquid-phase interaction between S- and N-compounds.
   - Production of the sulfuric acid (H_2SO_4)

Development of the Mechanism

Mechanism reduction:

Based on the 33-step mechanism of Norman, et al.,
Intern. J. of Greenhouse Gas Control, V. 12, January 2013, pp.26-34.,

- A 10-step reduced mechanism has been constructed by Yablonsky and Temkin.

Rational 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. $SO_2\ (g) + H_2O\ (g, aq) = HSO_3^-\ (aq) + H^+\ (aq)$

$SO_x + NO_x$ Reactions

9. $HNO_2\ (aq) + HSO_3^-\ (aq) + H^+\ (aq) \rightarrow H_2SO_4\ (aq) + ½\ N_2O\ (g) + ½\ H_2O\ (aq)$
10. $2\ HNO_2\ (aq) + HSO_3^-\ (aq) + H^+\ (aq) \rightarrow 2NO\ (g) + H_2SO_4\ (aq) + H_2O\ (aq)$

Kinetic Modeling: Goals

1. Justify or eliminate (add) steps in the mechanism based on gas- and liquid-phase experimental data conducted in the domain of the anticipated operational conditions.

2. Estimate contributions of the different routes and accurately determine reaction parameters for the key reactions.

3. Obtain estimates of optimal parameters (initial composition and pH, temperature and residence times).

Technical Approach:

CSTR Experiments

Knowledge Gaps and Challenges: SOx and NOx Chemistry

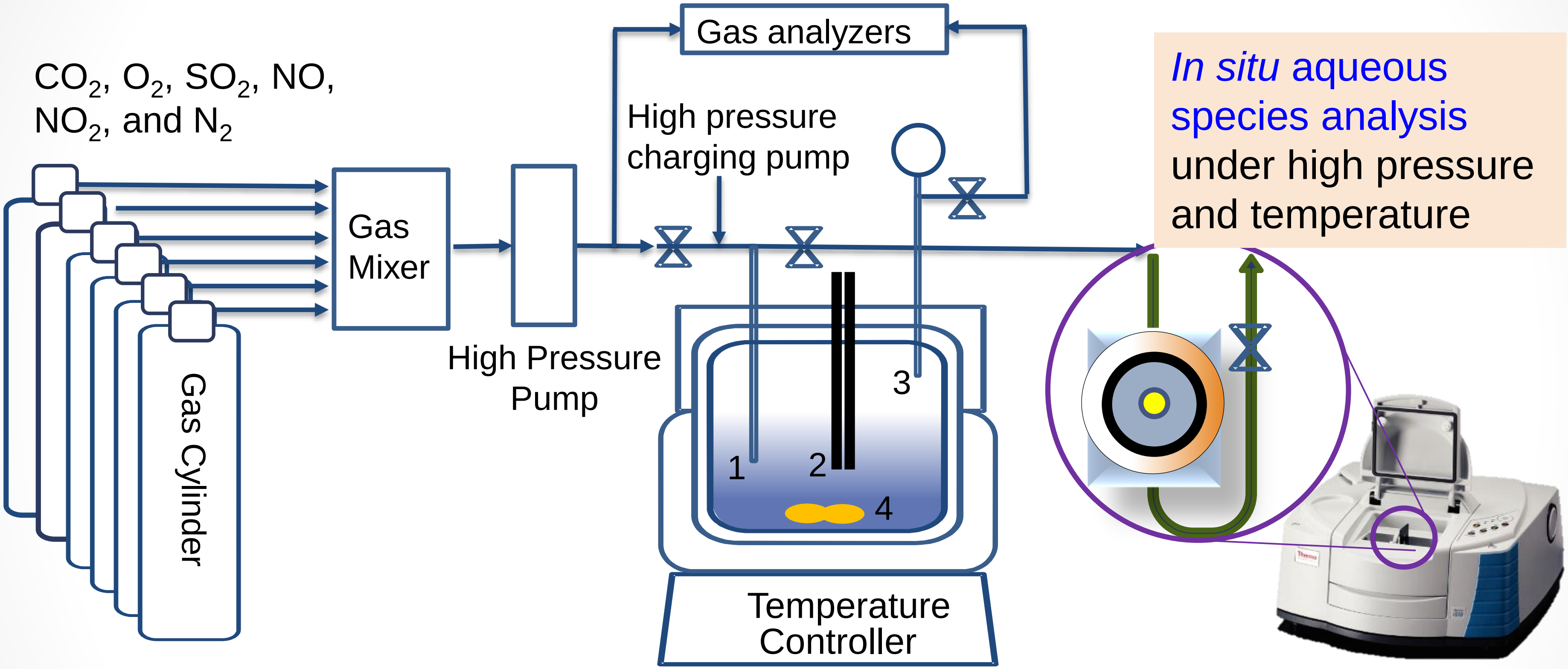
1. Mechanisms and kinetic parameters of consumption/generation of different NOx- and SO_2-species ***in the gas phase*** and their dissolution in water are well understood.
   - Kinetic mechanism for the NO- and SO- containing species ***in the liquid phase*** remains unclear, and some of the kinetic 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. 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.

Novel bench-scale experiment setup to obtain kinetic data

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



In situ aqueous species analysis under high pressure and temperature

In situ pH measurements and control under high pressure/temperature conditions

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

Experimental variables to be used in bench scale studies

Variables	Conditions
Pressure (bar)	5, 10, 15, 30
pH	0.5, 1, 2, 3, 4, 5
Temperature (^oC)	25, 75, 125, 175, 225, 275, 325
NO_x/SO_2 ratio	0, 0.1, 0.2, 0.4, 0.8, ∞
SO_2 concentration	0.09 – 0.9%
O_2 gas concentration	0 – 3%

Expected Outcomes of Model Development

- New kinetic data on the absorption and conversion reactions of NO, NO_2, and SO_2 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.

- 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.

Prototype DCC Design & Testing

- Packed-bed column design
- Pressure up to 15 bar
- Coupled to 100kW pressurized combustion facility
- Test with both simulated and real flue gas
- Model using software, e.g. ASPEN and KG Tower

prototype DCC

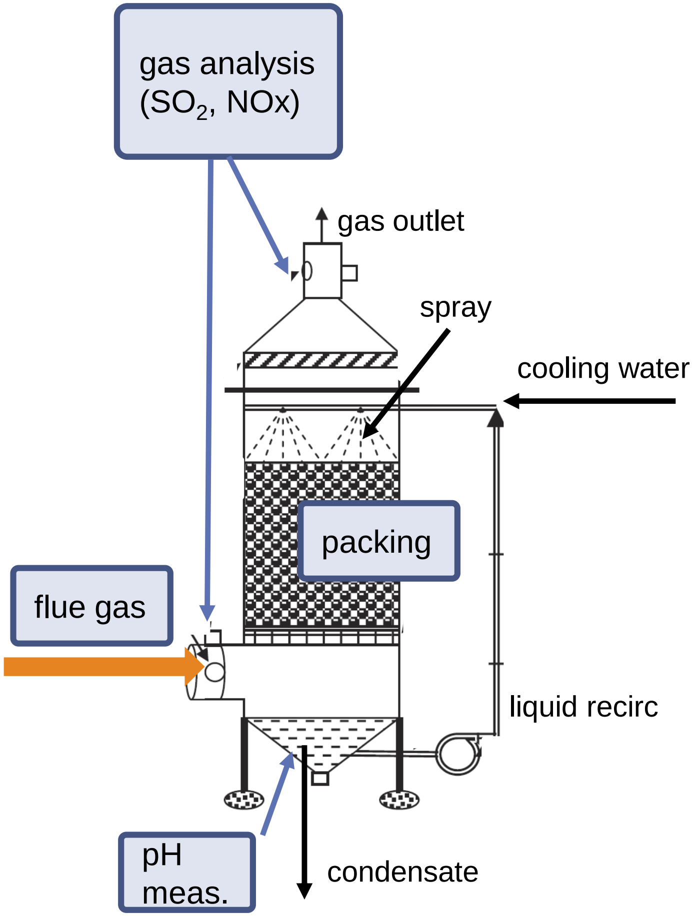
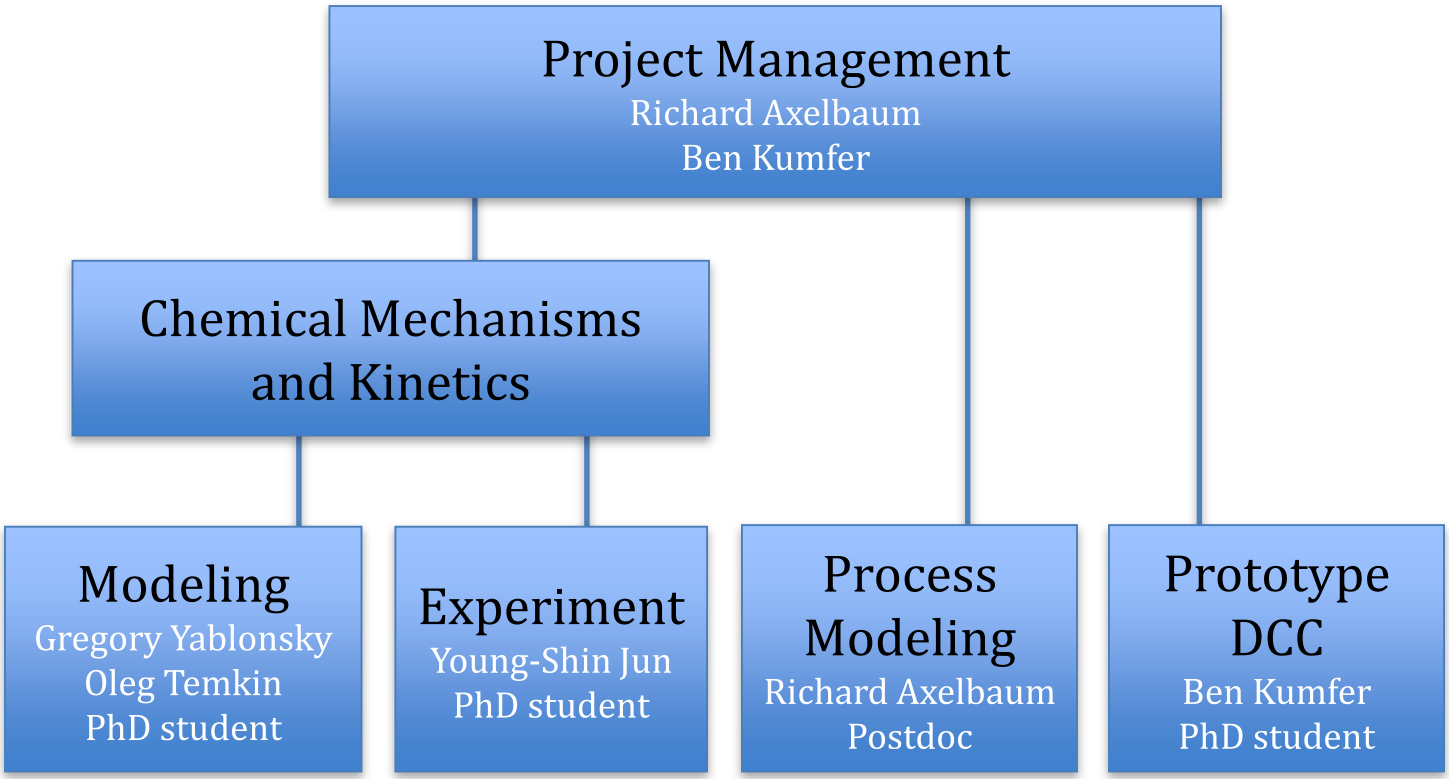


Figure adapted from: M. J. Jafari, *et al.*, Iranian J. Environ. Healt. 9(1) (2012) 20.

Milestones

ID	Budget Period	Task No.	Milestone Description	Planned Completion	Verification Method
a	1	2.1	Purchase Bench-Scale Equip.	03/31/2016	Quarterly Report
b	1	3.1	Schematic Prototype Column Design	03/31/2016	Quarterly Report
c	1	2.2	Preliminary Bench-Scale Tests Complete	06/30/2016	Quarterly Report
d	1	3.2	Construct Prototype	09/30/2016	Quarterly Report
e	1	4.1	Performance Test w/ Simulated Flue Gas	03/31/2017	Quarterly Report
f	1	5.2	Complete Improved Model	06/30/2017	Quarterly Report
g	1	4.2	Performance Test w/ Real Flue Gas	09/30/2017	Final Report
h	1	6	Full-Scale Cost & Performance Estimate	09/30/2017	Final Report

Project Organization



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