Advanced Chemistry Modeling for SO2, SO3, and HCl Removal by Dry Sorbent Injection

Presented by: Guisu Liu, Ph.D., Director of Technology




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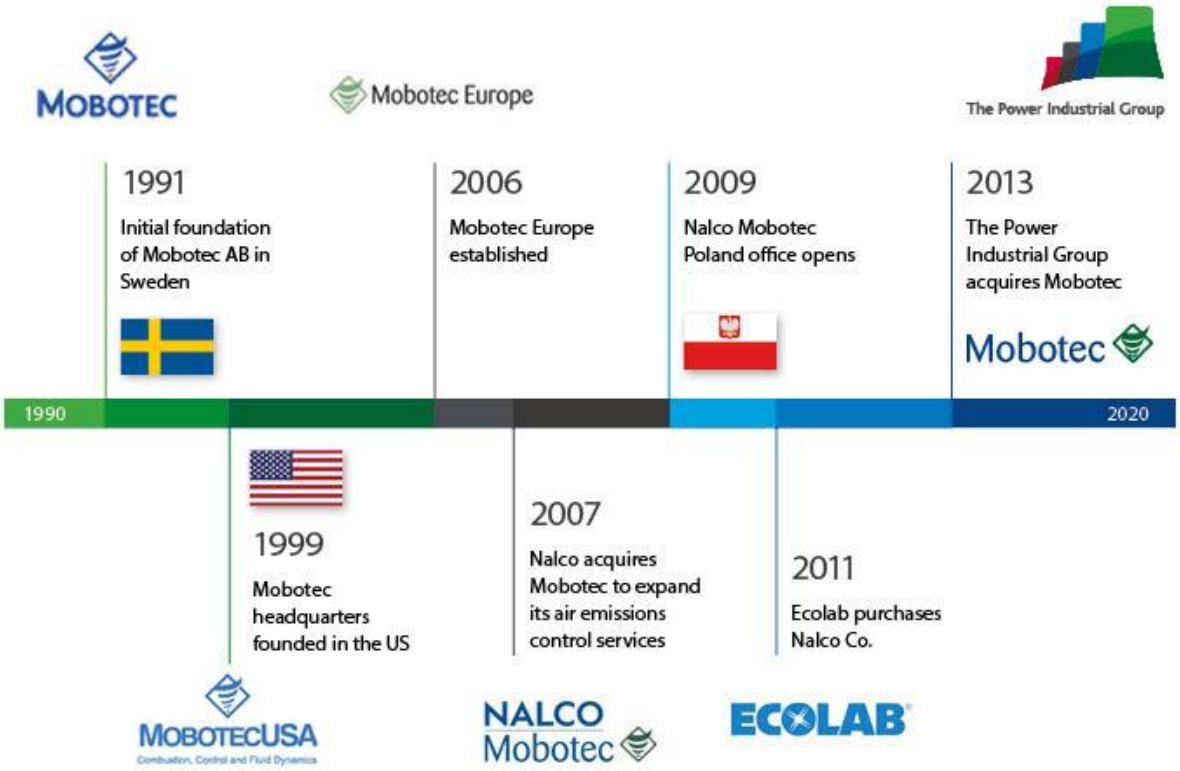
About Us – History

- The business has been delivering solutions for over 25 years' and is experienced in offering ranging applications with proven success



About Us – Core Technologies

ROFA®

Rotating Opposed Fire Air

- Up to 65% NOx reduction
- Combustion Optimization
- Tailored for upgradability
- Wide boiler applicability

ROTAMIX®

Rotating Opposed Fire Air

- 30-50% NOx Reduction
- 3rd Generation SNCR
- Tailored for upgradability
- Wide boiler applicability

SORBMIX®

Lance-less sorbent injection

- Sorbent neutral
- Performance up to 25%
- Reduced sorbent up to 40%
- Tailored for upgradability

Biomass Conversion

- Cost-effective solutions
- Ability to co-fire to 45%
- Ability to Convert 100%
- Low impact of operations

Low capital cost solutions meeting high performance requirements

Multi-pollutant control for NOx, SO2, SO3, HCl, Hg, CO2, LOI

In-House CFD, Engineering & Combustion Tuning services

Upgrade systems for enhanced performance

Improved Boiler Operation / Efficiency

Reducing Operational Costs

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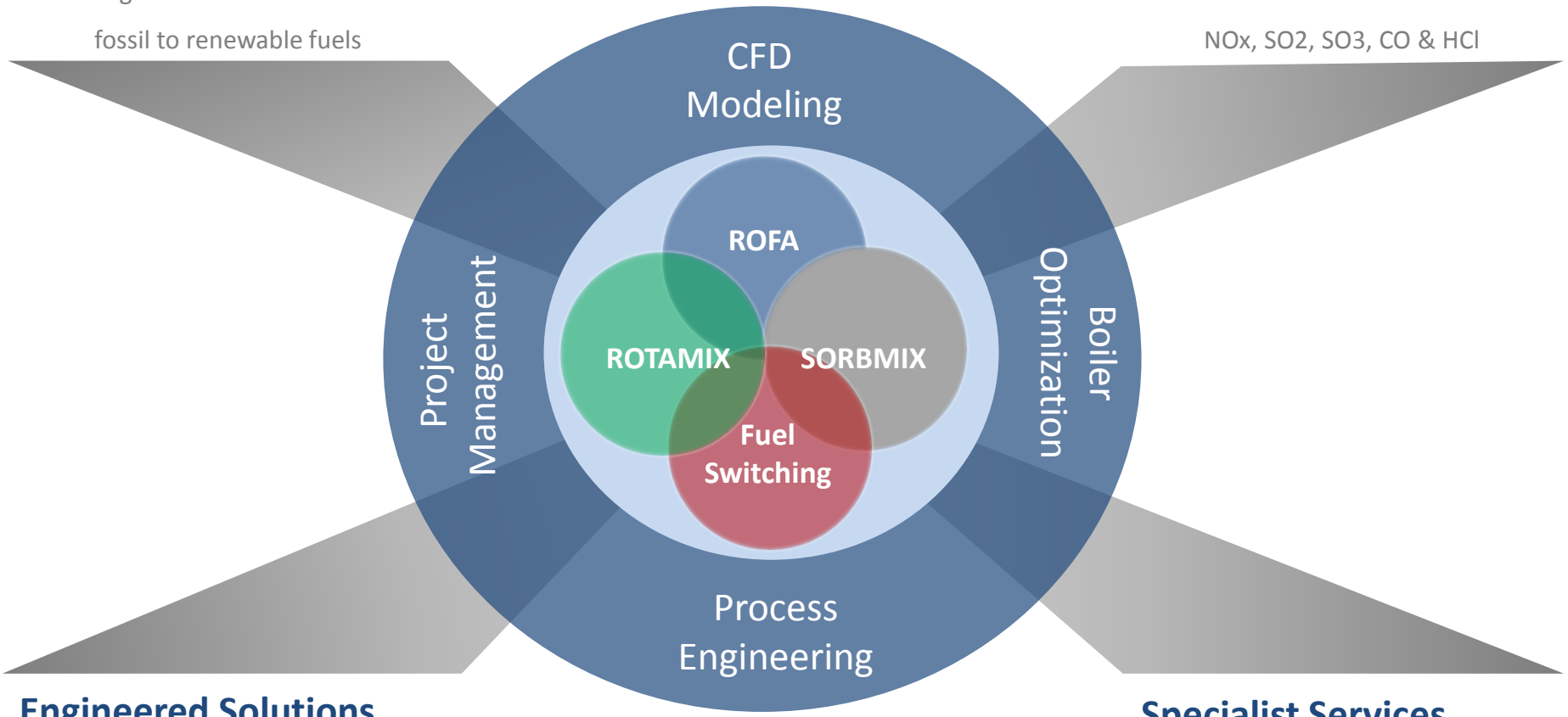
About Us – Application Diversity

Fuel Flexibility

Co-Firing & 100% Conversions from fossil to renewable fuels

Emissions Control

Multi-Pollutant Control solutions for NOx, SO2, SO3, CO & HCl



Engineered Solutions

Bespoke engineered solutions and to meet specific requirements

Specialist Services

Engineered solutions and tuning support to optimize combustion

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About Us – Mobotec Offering

Capital Projects

Proven cost-effective solutions to meeting multi-pollutant compliance requirements

- ROFA® - Rotating Opposed Fire Air
- ROTAMIX® - Advanced SNCR
- SORBMIX® - Sorbent Injection

Upgrade Solutions

Increased performance and reduced costs over traditional installed equipment

- 'Boosting' existing Over-Fire Air systems
- Improving effectiveness of installed SNCR
- Reducing sorbent usage in DSI & FSI systems

Fuel Flexibility

Working in conjunction with the client to deliver a cradle to grave solution

- Feasibility & FEED Study evaluations
- Biomass Co-Firing (up to 45%)
- Full coal-to-biomass conversions

Specialist Services

Leading solutions provider, with unique capabilities and proven experience to deliver

- CFD Modeling
- Engineering Studies
- Combustion Tuning

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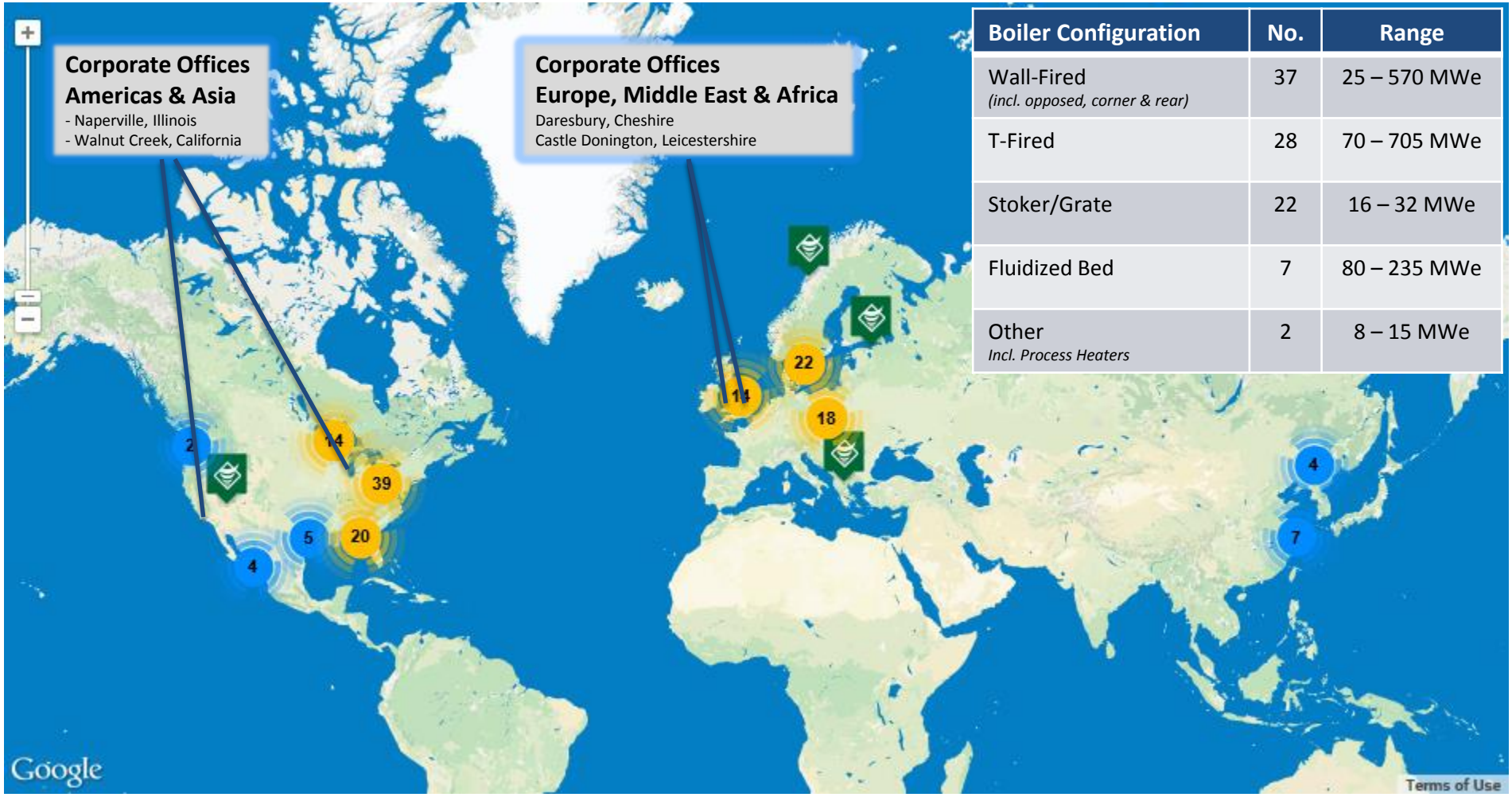
About Us – Global Experience

- Through offices across North America & Europe, Mobotec has completed nearly 100 major projects worldwide

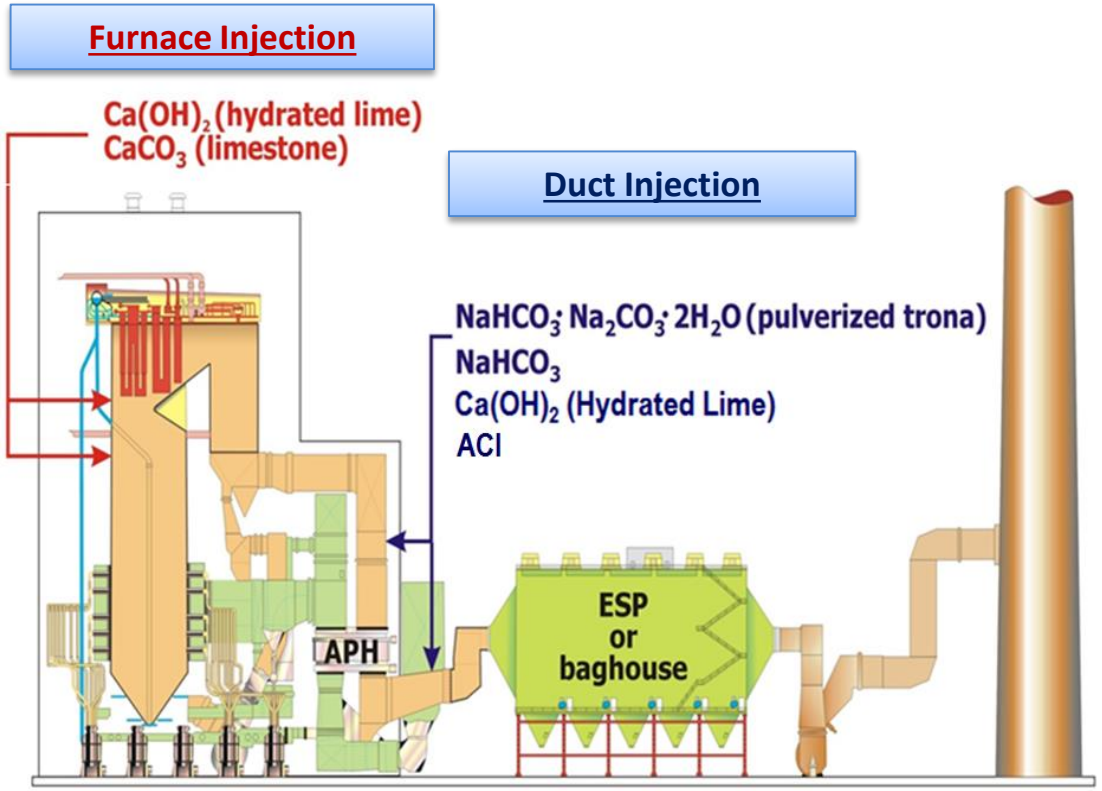


Boiler Configuration	No.	Range
Wall-Fired *(incl. opposed, corner & rear)*	37	25 – 570 MWe
T-Fired	28	70 – 705 MWe
Stoker/Grate	22	16 – 32 MWe
Fluidized Bed	7	80 – 235 MWe
Other *Incl. Process Heaters*	2	8 – 15 MWe

Sorbent Injection Overview

Multi-pollutant SO2, SO3, HCl, Hg Control

- Understanding mixing is key to developing mixing strategy
- Expertise on both furnace injection and duct injection
- Chemistry well understood
- Strong CFD modeling expertise on both mixing and chemistry
- Understanding how furnace combustion affects sorbent technology and performance



Experience with Sorbent Injection

- **Furnace Sorbent Injection (FSI) experience**
  - 13 installations around the world
  - Projects ranging from 30 - 350 MWe
  - Utilizing a variety of limestone and hydrate lime sorbents
  - Primarily for the reduction of SO2

- **Dry Sorbent Injection (DSI) experience**
  - 3 trials in the United States
  - Projects ranging from 190 - 621 MWe
  - Utilizing a variety of Trona, SBC, hydrate lime sorbents
  - Primarily for the reduction of SO2, HCl, SO3

Understanding Sorbent Chemistry is Critical

Chemistry is captured into various chemistry sub-models that have been developed and incorporated into in-house CFD codes

- Sorbent thermal decomposition
- Sorbent sintering characteristics and impact
- Sorbent physical property and its impact (Size, Surface area, Porosity)
- Absorption chemistry and kinetics
  - CaO reacts with SO2, SO3, HCl
  - Trona reacts with HCl, SO2, SO3
- Temperature impact
- Sorbent dispersion and mixing impact

Mobotec's in-house modeling tools are unique and very useful to evaluate a furnace or duct injection system prior to installation

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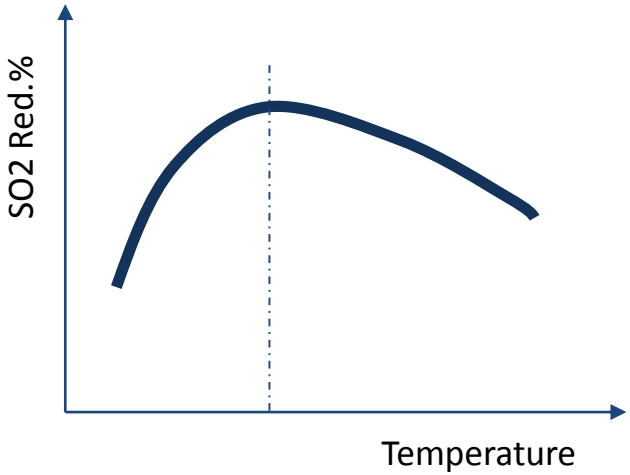
Ca-Based Sorbent Furnace Injection for SO2 Control

Fundamentals of Lime-Based Sorbent with SO2

- Physical and chemical process of limestone or hydrate lime-SO2 in furnace
  - Calcination: CaCO3/Ca(OH)2 -> CaO + CO2/H2O
    - High level of calcination at higher temperatures
    - Resulting in high surface area
  - Sintering
    - Sintering occurs at high temperatures
    - Resulting in reducing surface area and porosity
  - Sulfation: CaO + SO2 + 0.5 O2 -> CaSO4
    - Diffusion controlled process
    - Porosity decreases as sulfation degree increases
    - Shrinking core model
  - Diffusion
    - Bulk duffusion
    - Molecular diffusion
    - Knudsen diffusion



- All mechanisms are implanted as User-Defined Function in C++ language, and coupled with Fluent CFD code.

- Model can evaluate the factors affecting sulfation rate
  - Sorbent quality and size
  - Injecting temperature
  - Mixing between particles and SO2 in gas phase
  - Residence time

Milne, C.R., Silcox, G.D., Pershing, D.W., Kirchgessner, D.A., Ind. Eng. Chem. Res. 29:P2192-2201,1990
Milne, C.R., Silcox, G.D., Pershing, D.W., Kirchgessner, D.A., Ind. Eng. Chem. Res. 29:P139-149,1990
Milne, C.R., Silcox, G.D., Pershing, D.W., Kirchgessner, D.A., Ind. Eng. Chem. Res. 29:P2201-2214,1990

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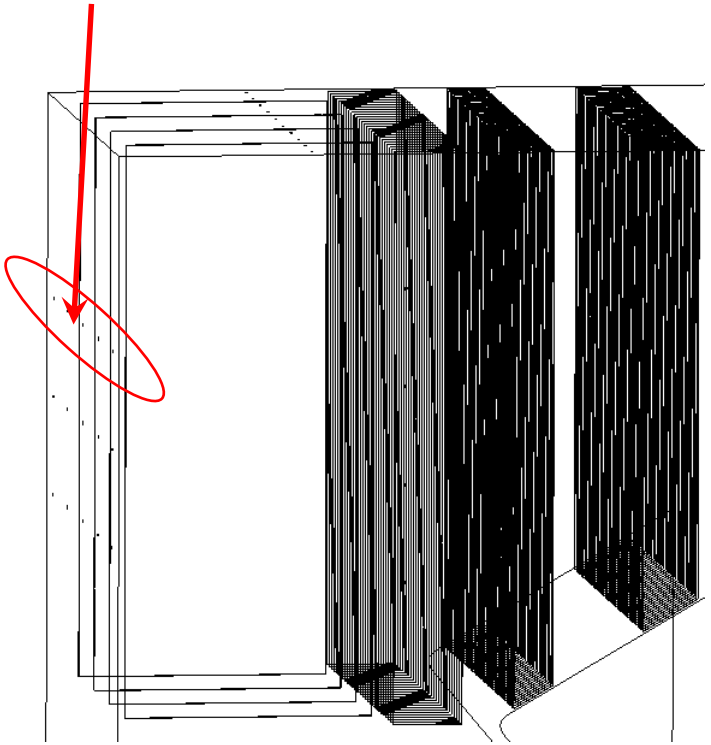
SORBMIX® Injection Locations

5 ports on front wall



- SORBMIX® is a patented sorbent injection system that does not use traditional injection lances.
  - Consists of a small boosted ambient air fan, air duct, air injection nozzles, and dampers.
  - Can be applied to DSI, FSI or ACI systems
- Benefits of SORBMIX® injection system:
  - Reduced sorbent usage
  - Improved pollutant reduction
  - Reduced operating cost
  - No in-furnace/duct lance
  - Reduced maintenance costs
  - Reduced injectors required

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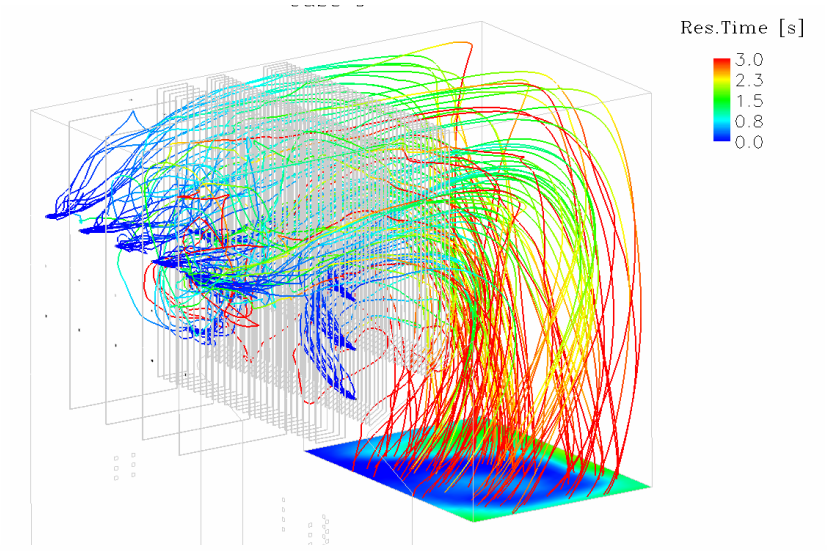
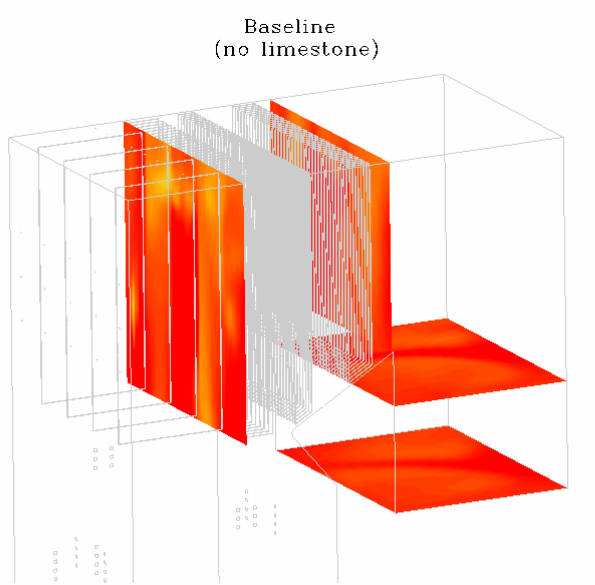
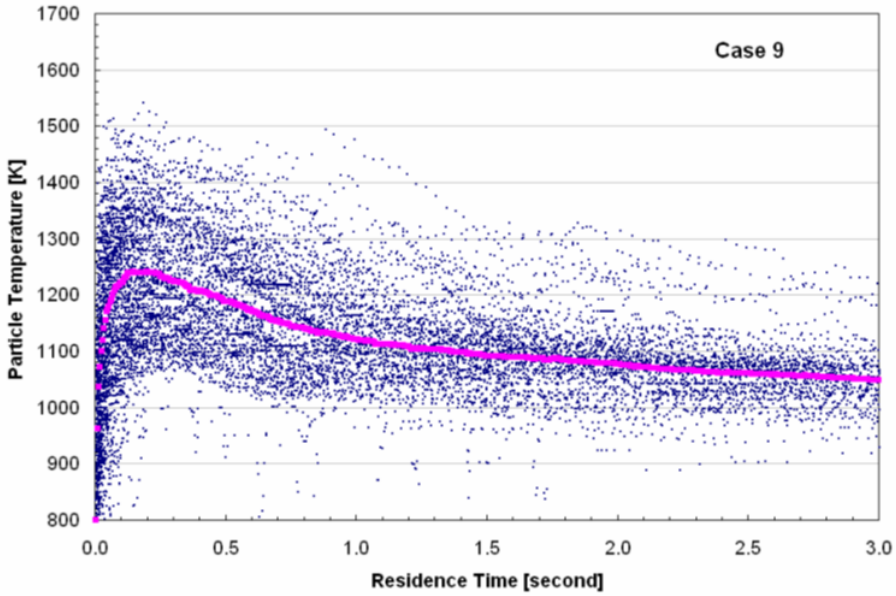
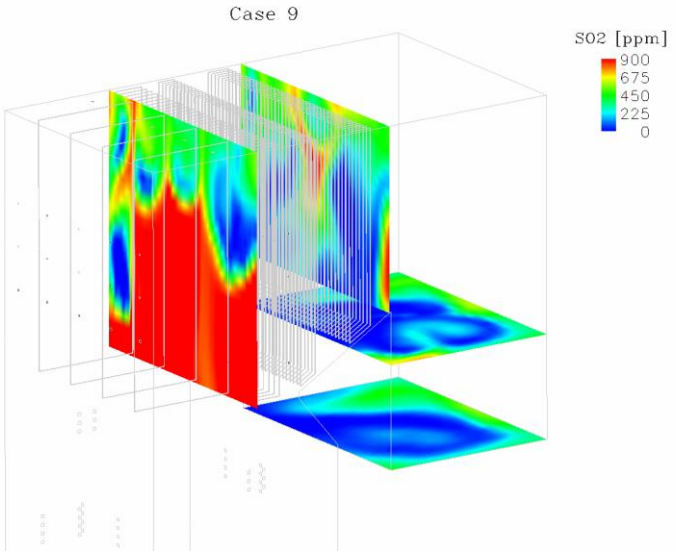
Particle Dispersion and SO2 Reduction





Baseline SO2





SORBMIX® SO2

Full-Scale Application and Model Validation

Plant Details:

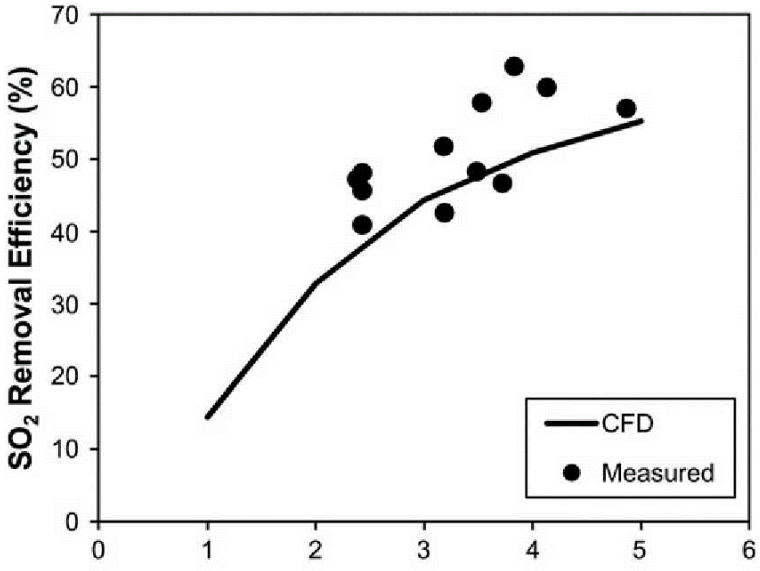
- **Client:** Hoosier Energy
- **Plant:** Ratts Station
- **Boiler:** Wall-fired furnace
- **Capacity:** 126 MWe
- **Fuel:** Eastern bit. Coal
- **Coal N%:** 1.14%ar
- **Coal S%:** 1% ar

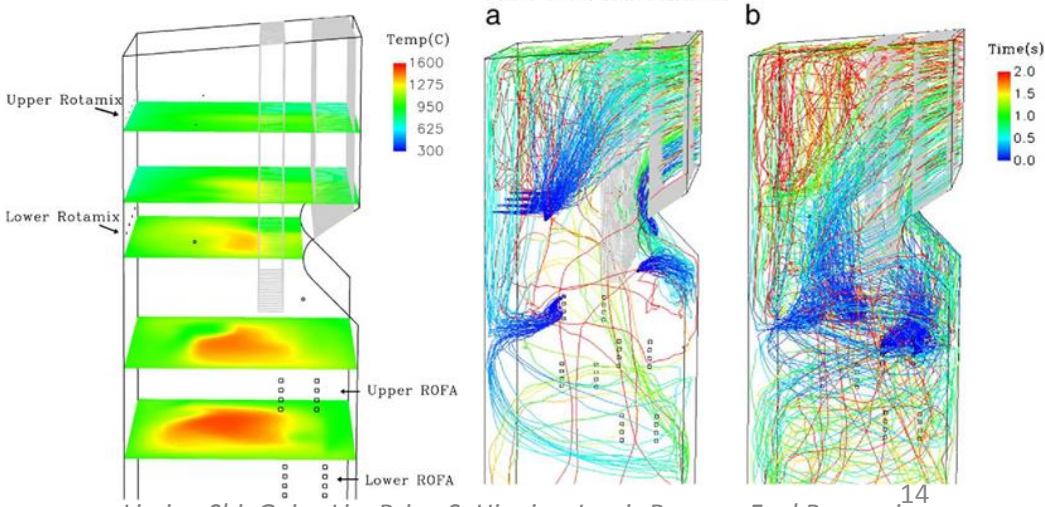
NOx Solution:

- ROFA®/ROTAMIX® (Anhydrous Ammonia)

SO2 Solution:

- SORBMIX® FSI (Hydrate Lime)





Liming Shi, Guisu Liu, Brian S. Higgins, Lewis Benson, Fuel Processing Technology 92 (2011) 372–378

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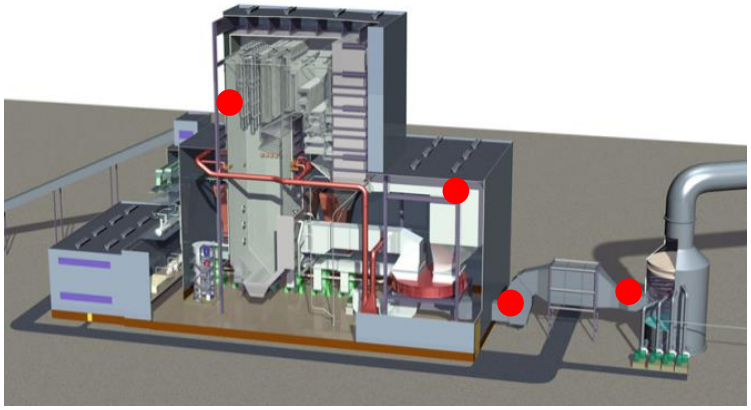
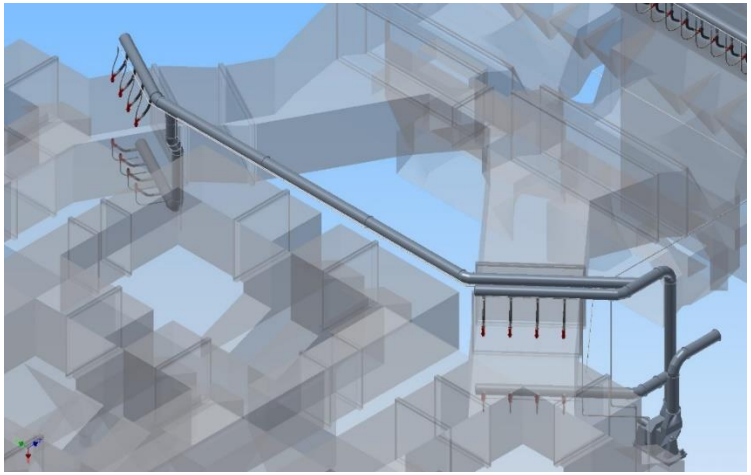
DSI Sorbent Injection for SO3 Control

SO3 Control by Sorbent Injection

- Multiple injection locations
  - In furnace
  - Before air pre-heater
  - Before electrostatic precipitator or fabric filter
  - Before flue gas desulfurization

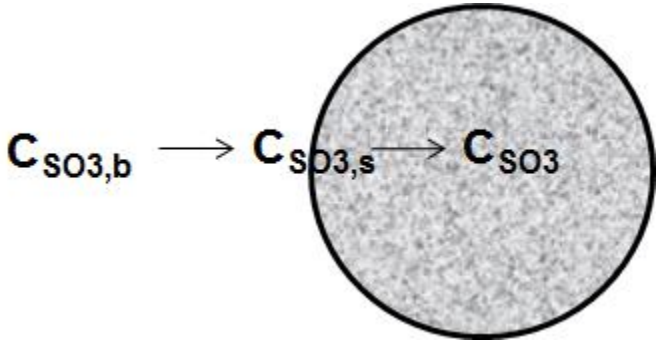


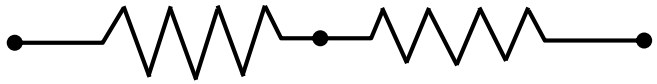
- Various sorbents
  - Ca-based: Hydrated lime
  - Na-based: Trona, Sodium bicarbonate
  - Mg-based: Magnesium hydroxide



SO3 Absorption Chemistry

- SO3 or H2SO4 transport from bulk flow to particle surface
- SO3 or H2SO4 diffuse inside sorbent particle
- Reactions
  - SO3 + Ca(OH)2 = CaSO4 + H2O
  - H2SO4 + Ca(OH)2 = CaSO4 + 2H2O





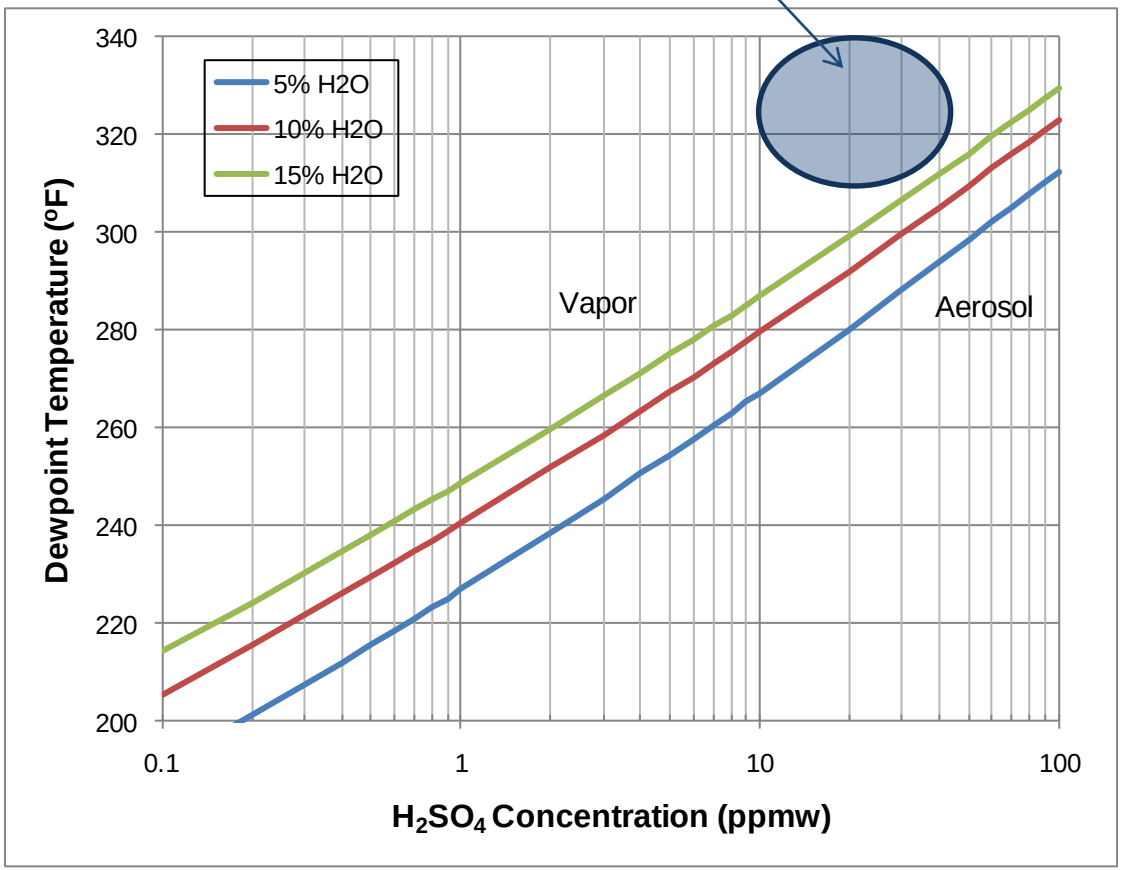
External resistance

Internal resistance

Operating Parameters

- Operating conditions
  - Sorbent injection rate
  - Inlet SO_3 concentration
  - Residence time
  - Temperature
- Sorbent properties
  - Pore volume
  - Specific surface area
  - Particle size

Modeled operating conditions



Verhoff, F.H., Banchero,J.T. Chemical Engineering Progress, 1974, 70, 71-72.

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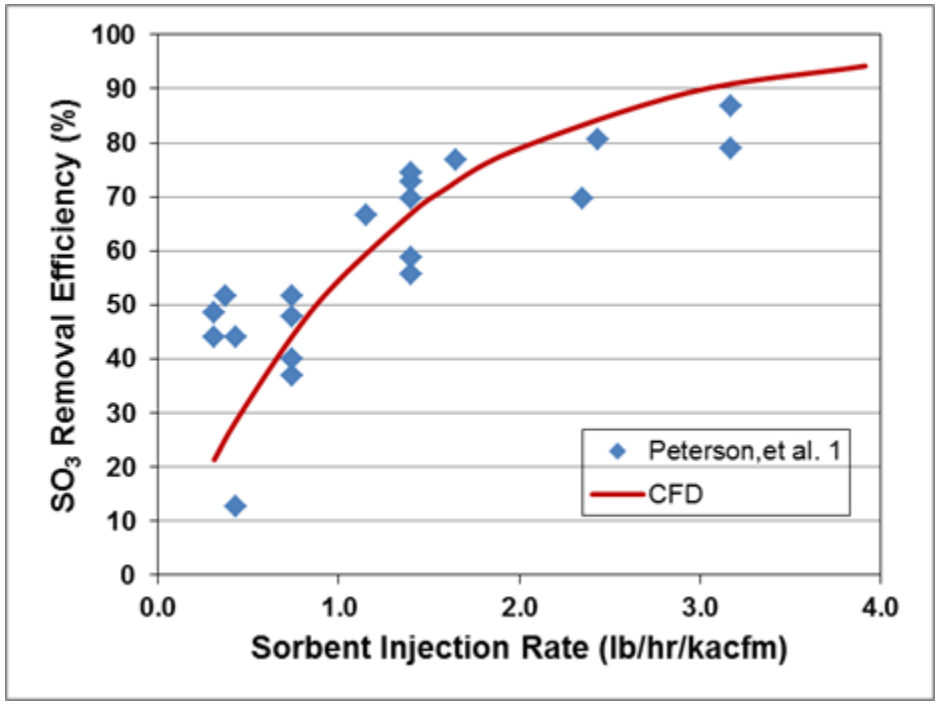
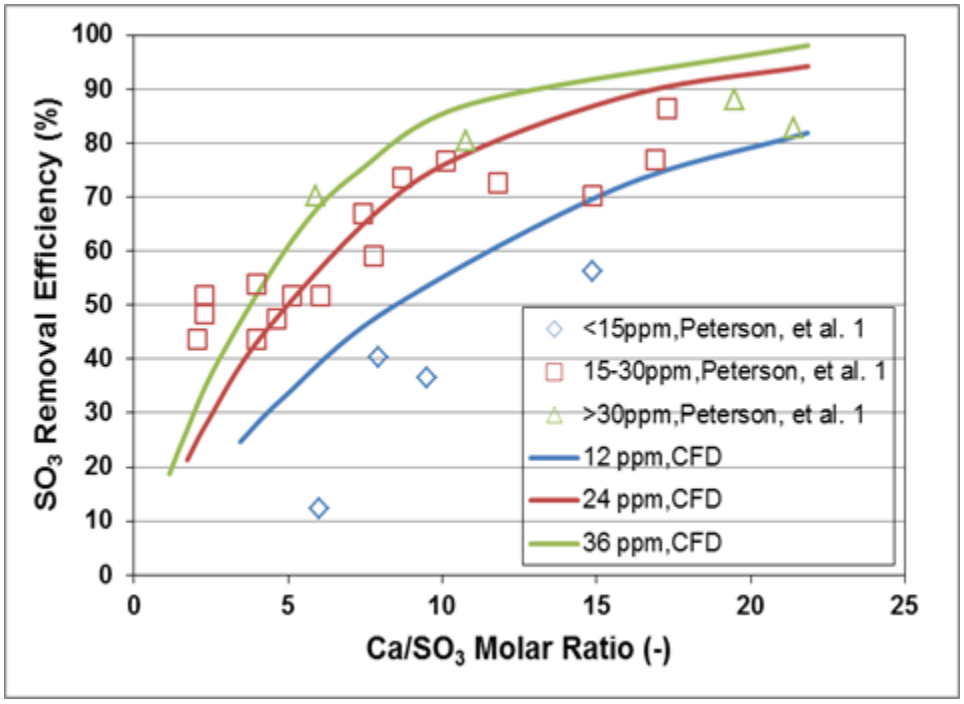
Model Validation





Liming Shi, Guisu Liu, Lewis Benson, "An Enhanced CFD Based Chemistry Model for SO3 Mitigation by Dry Sorbent Injection", Paper #117, MEGA Symposium, Baltimore, MD, September 2012

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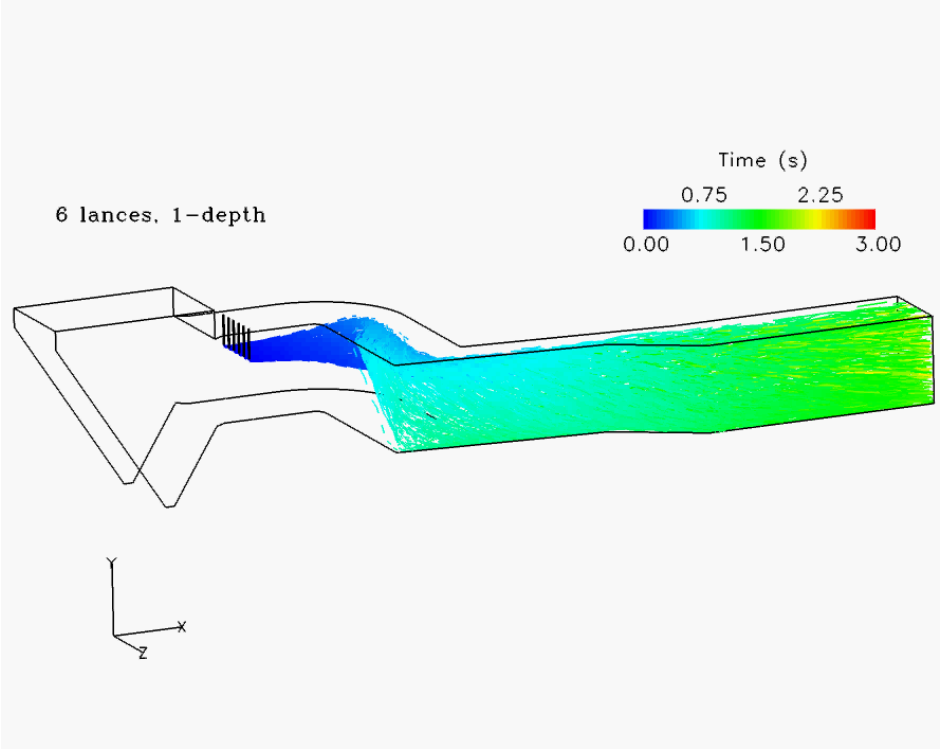
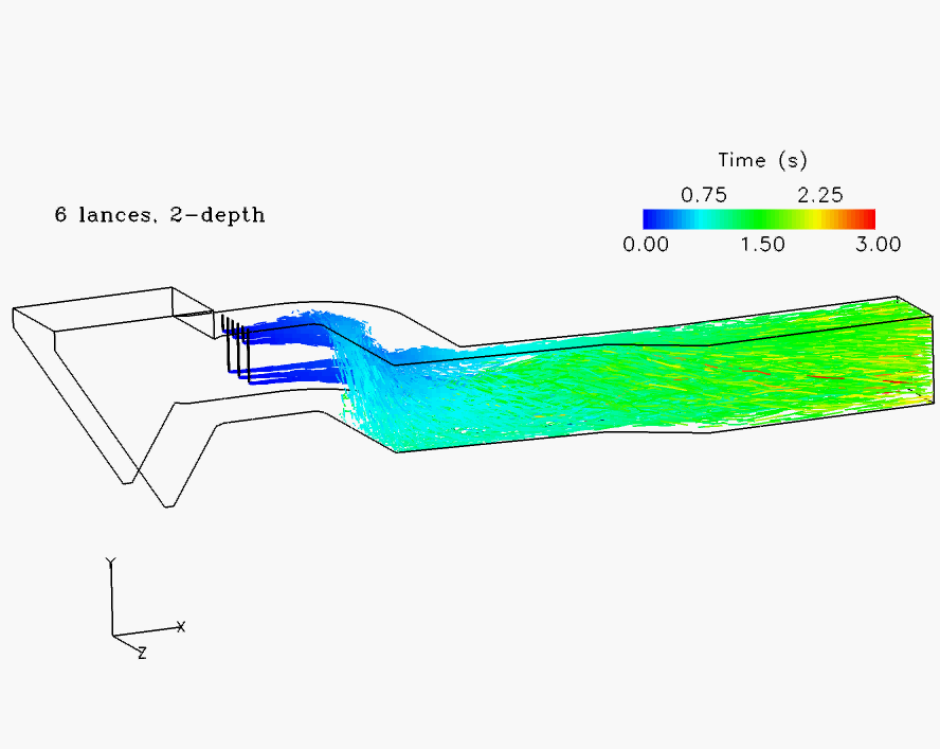
Industrial Applications

Evaluating Particle Dispersion for Different Injections





CFD model was used to evaluate the injection strategy and to predict the performance for DSI SO3 reduction system at a 450 MW unit.

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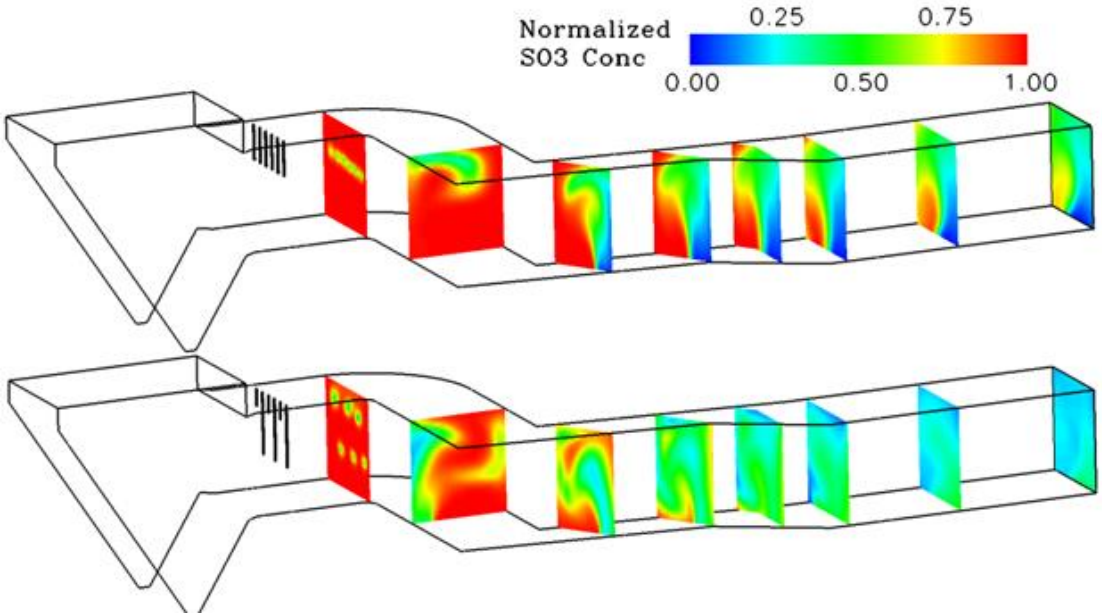
Predicting SO3 Reduction for Different Injections



Predicted SO3 Reduction

61%

75%

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Trona Injection for SO2/HCl Control through DSI

Fundamentals of Trona Reacting with HCl and SO2

- Trona calcination
  - $2Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O \leftrightarrow 3Na_2CO_3 + CO_2 + 5H_2O$
  - Resulting in high porous Na2CO3 particles
- Sintering
  - Sintering kinetics
  - Resulting in loss in surface area and porosity
- Global simultaneous reactions
  - $2HCl + Na2CO3 \leftrightarrow 2\ NaCl + CO2 + H2O$
  - $SO2 + 0.5O2 + Na2CO3 \leftrightarrow Na2SO4 + CO2$
- Reaction mechanisms
  - Chemical reaction kinetics
  - Diffusion (Pore diffusion/Knudson diffusion/boundary layer diffusion)

A. Ekmekyapar, H. Erşahan, S. Yapıcı. Ind. Eng. Chem. Res., 1996, 35, 258-262.
G.P. Maule, J.H. Cameron. The Institute of Paper Chemistry. 1989, Paper 317.
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C. Güldür, G. Doğu, T. Doğu. Chemical Engineering and Processing, 2001, 40, 13–18.
S. Kimura, J.M. Smith. AIChE Journal, 1987, 33, 1522-1532.

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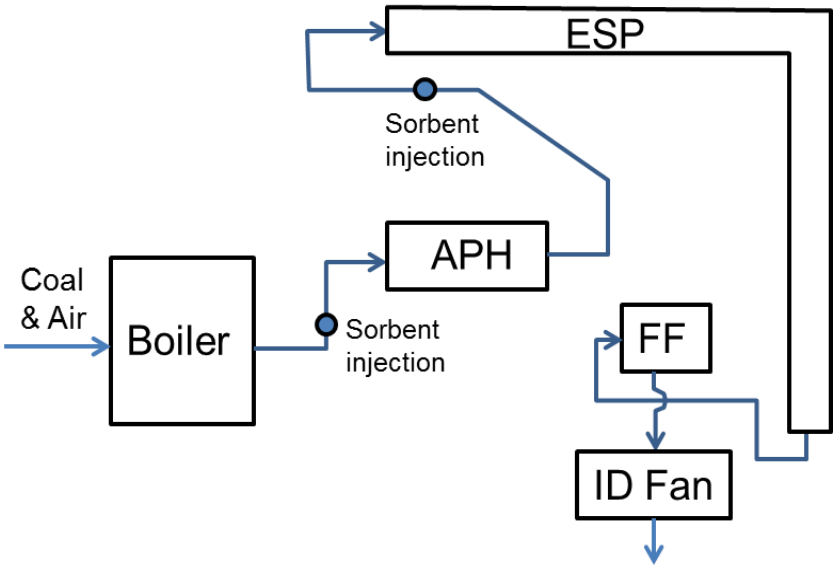
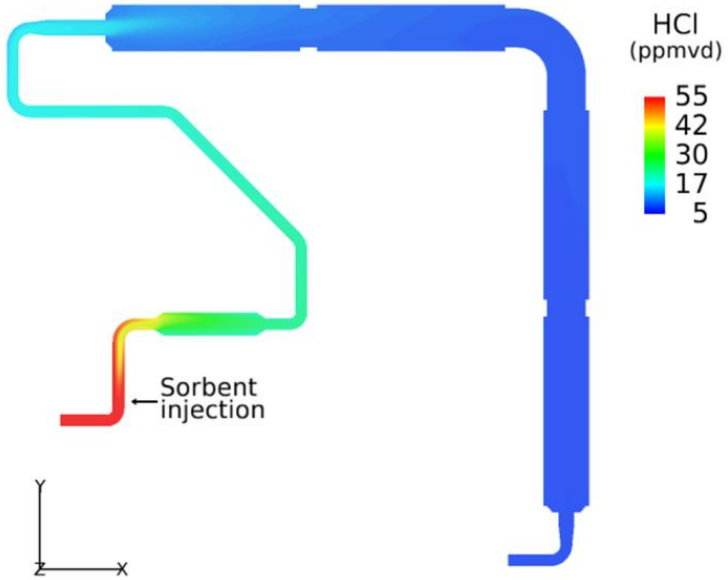
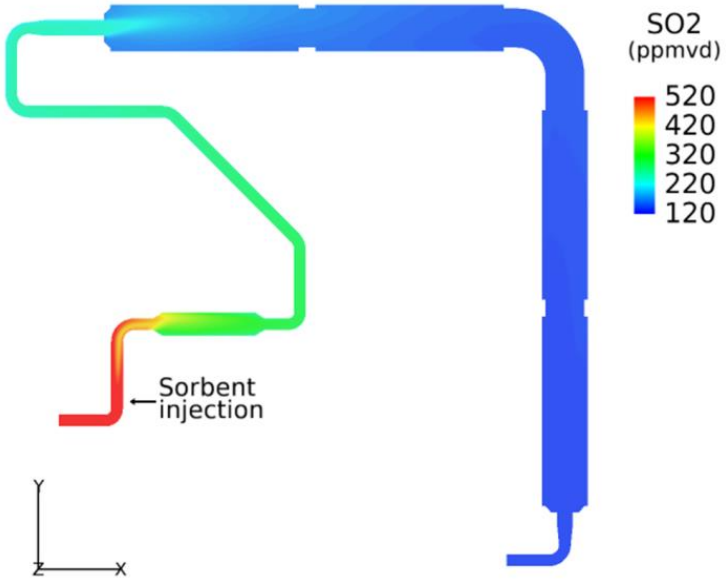
Pilot-Scale Testing Facility







- WRI CTF, 250,000 Btu/hr
- Backend includes APH, ESP, FF, ID fan
- Subbituminou coal
- HCl: 50-60 ppmv
- SO_2: 500-600 ppmv

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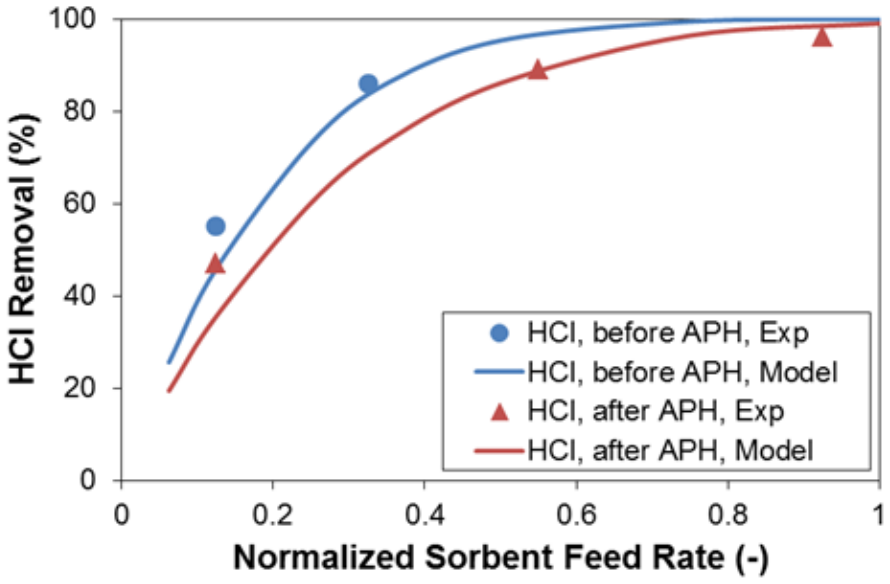
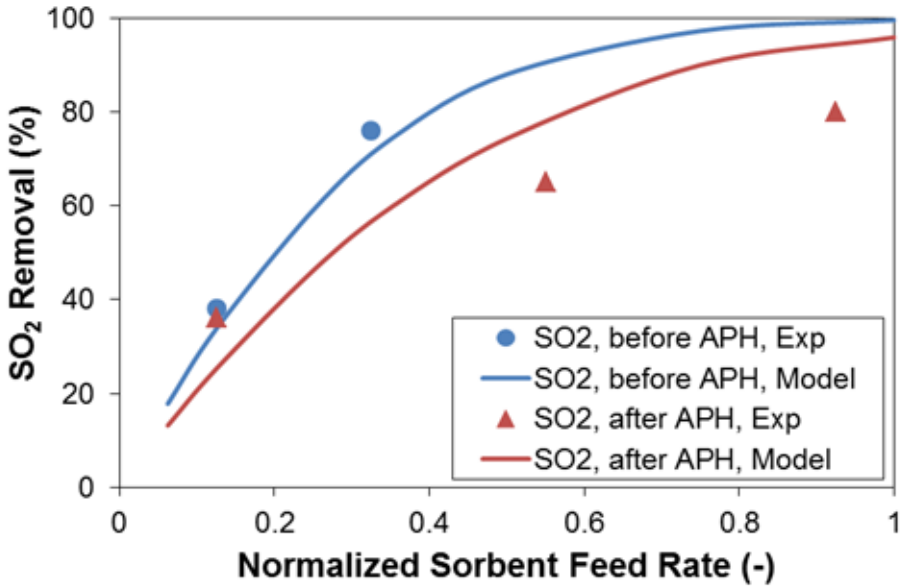
Model Validation





- Sensitivity analysis of parameters related with operating conditions and sorbent properties are completed.
- Competitive reaction of HCl and SO2 with sorbent is well predicted.
- Model predictions on the HCl and SO2 removal at WRI testing facility are in good agreement with measured values before APH and after APH injections.

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Summary

- Advanced chemistry sub-models have been developed for sorbent injection technologies including:
  - Ca-based sorbent for SO2 control in furnace
  - Hydrate lime injection for SO3 control
  - Trona injection for SO2/HCl control
- Fundamental kinetic data were implemented in the model, which was then coupled with CFD code through user-defined functions (UDFs).
- Each of these chemistry models have been validated against testing data. Incorporated with CFD, this validated advanced chemistry sub-models can be used as an important tool to optimize DSI/FSI injection system, as well as to predict sorbent usage for specific applications.

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