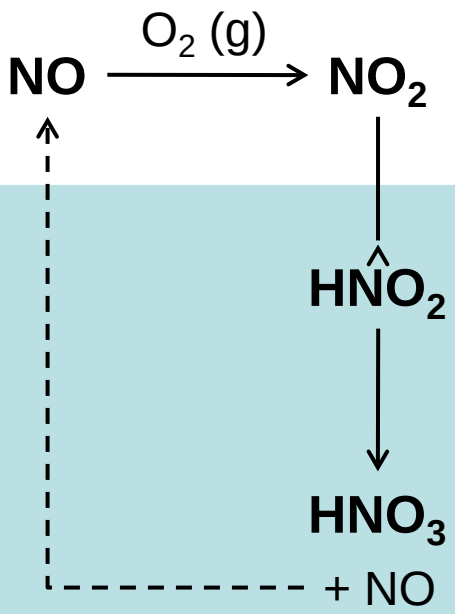
2nd Oxyfuel Combustion Conference, Yeppoon, Australia, 15th September 2011

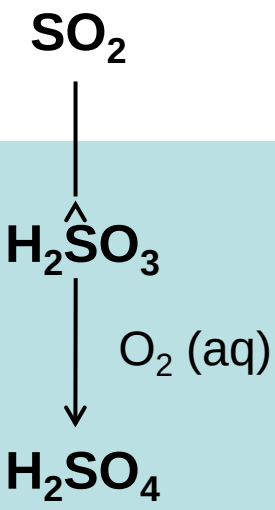
Sulphur and Nitrogen Chemistry in Pressurized Flue Gas Systems

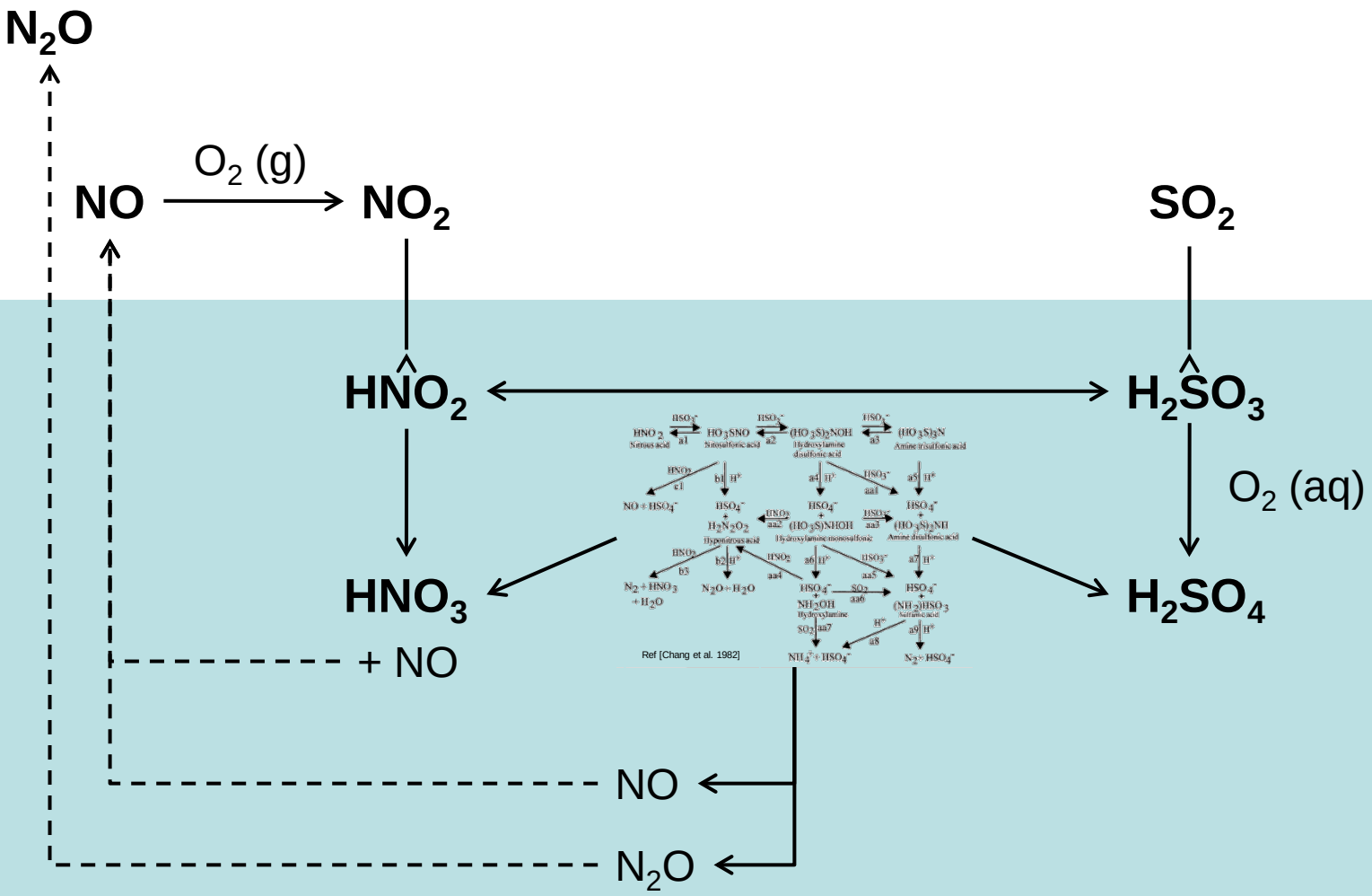
Tobias Pettersson, Fredrik Normann, Klas Andersson,
Chalmers University of Technology

Linda Nylen, Marie Anheden*
Vattenfall Research and Development

*Marie Anheden currently works for Aker Clean Carbon


NO
O_2 (g)
NO_2
HNO_2
HNO_3
+ NO


SO_2
H_2SO_3
O_2 (aq)
H_2SO_4


N2O
NO
O2 (g)
NO2
SO2
HNO2
H2SO3
O2 (aq)
HNO3
H2SO4
+ NO
NO
N2O
Ref [Chang et al. 1982]

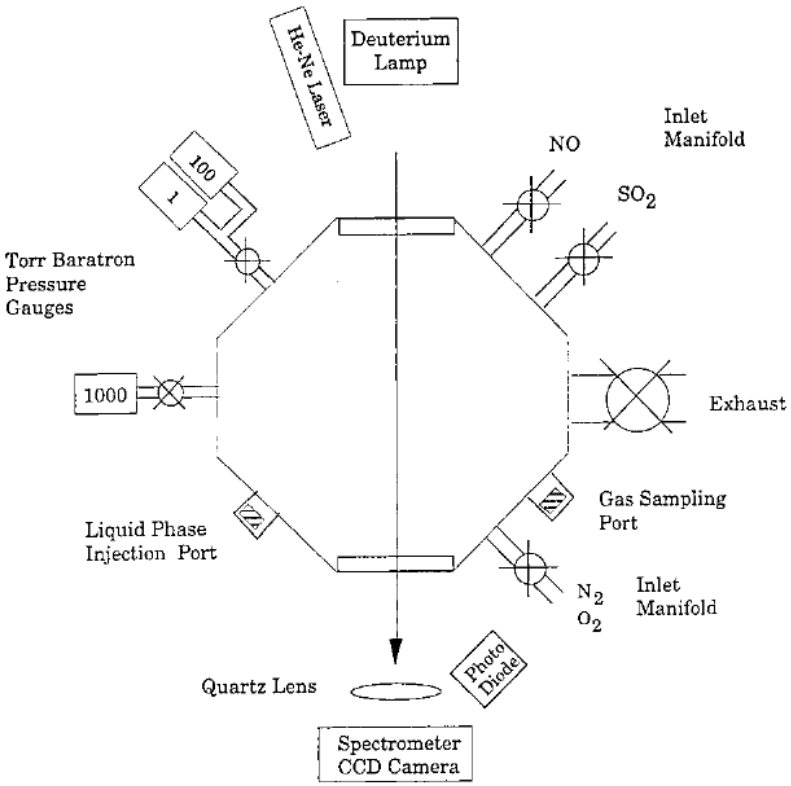
Aim

- Evaluate possible and probable reaction routes of NOx and SOx in the oxy-fuel flue gas train

As a way to:

- control SOx and NOx emission
- control acid formation and protect process equipment

Ecole Polytechnique Fédérale de Lausanne



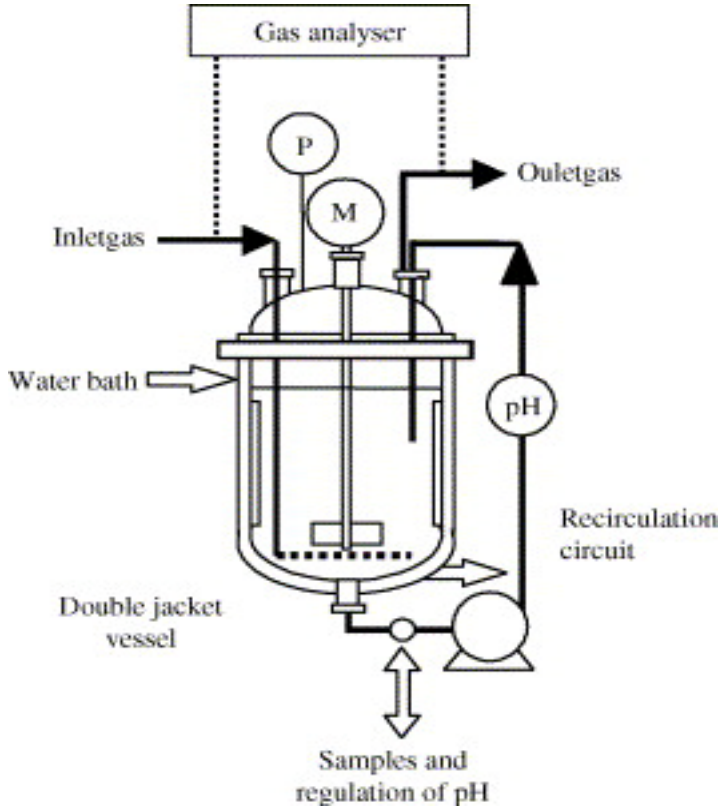
1 bar, 25-90ºC, 95% H_2SO_4 to pH 13

→ N_2O formed in the liquid at pH around 0

→ Complex dependence on the acidity

Refs: Pires and Rossi 1997.

Université Henri Poincaré



1 bar, 25ºC, Constant pH 0.77-5

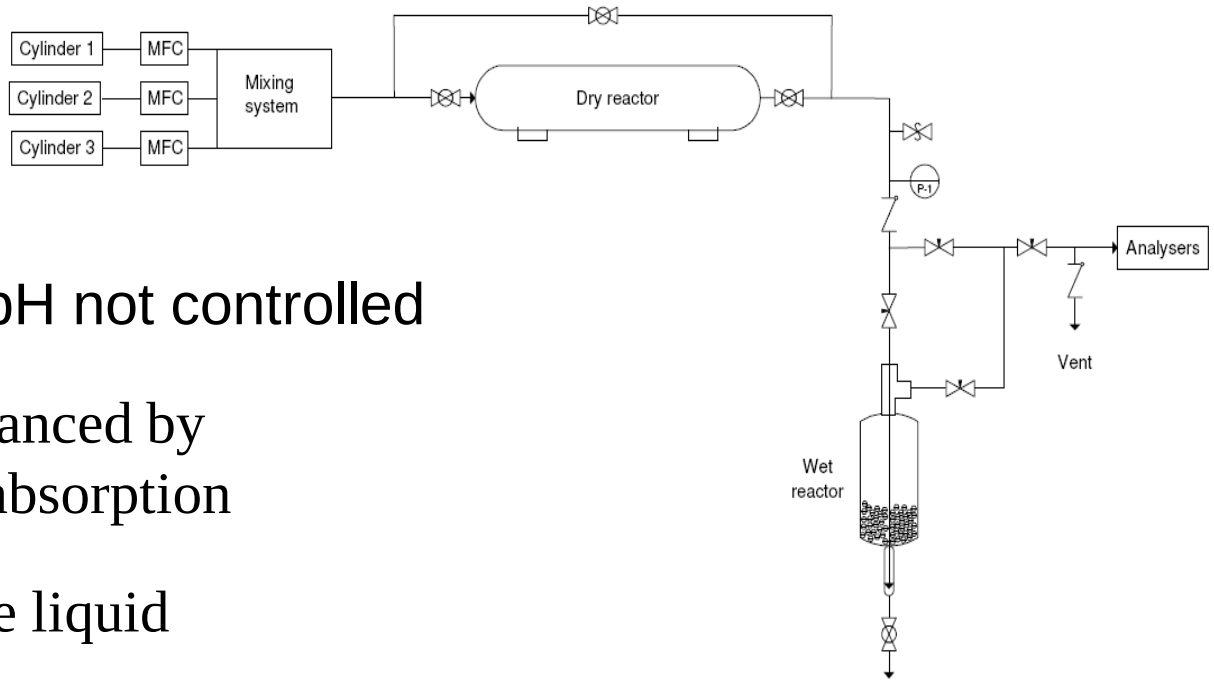
→ Important N_2O formation in the liquid at low pH

→ No N_2O formation for pH > 4

→ No formation of NO in liquid phase

Refs: Susianto et al. 2001 and Susianto et al. 2005.

Imperial College



1-15bar, 25-400ºC, pH not controlled

→ SO_2 absorption enhanced by simultaneous NO_2 absorption

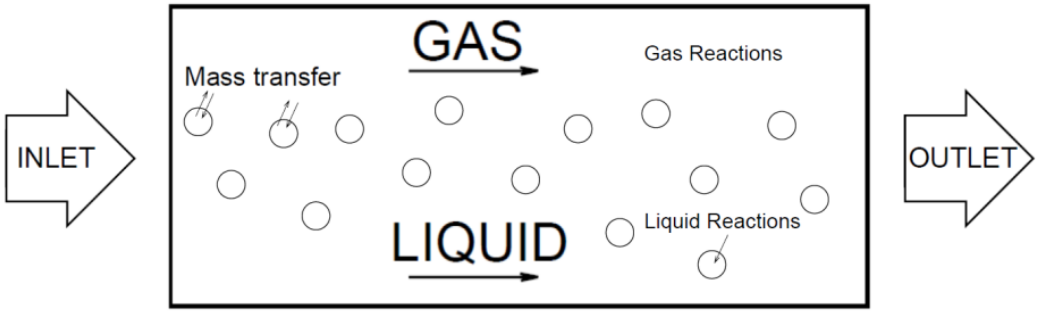
→ NO formation in the liquid

→ The pH is of high importance to the process

Refs: Torrente-Murciano et al. 2010, Torrente-Murciano et al. 2011.

Method

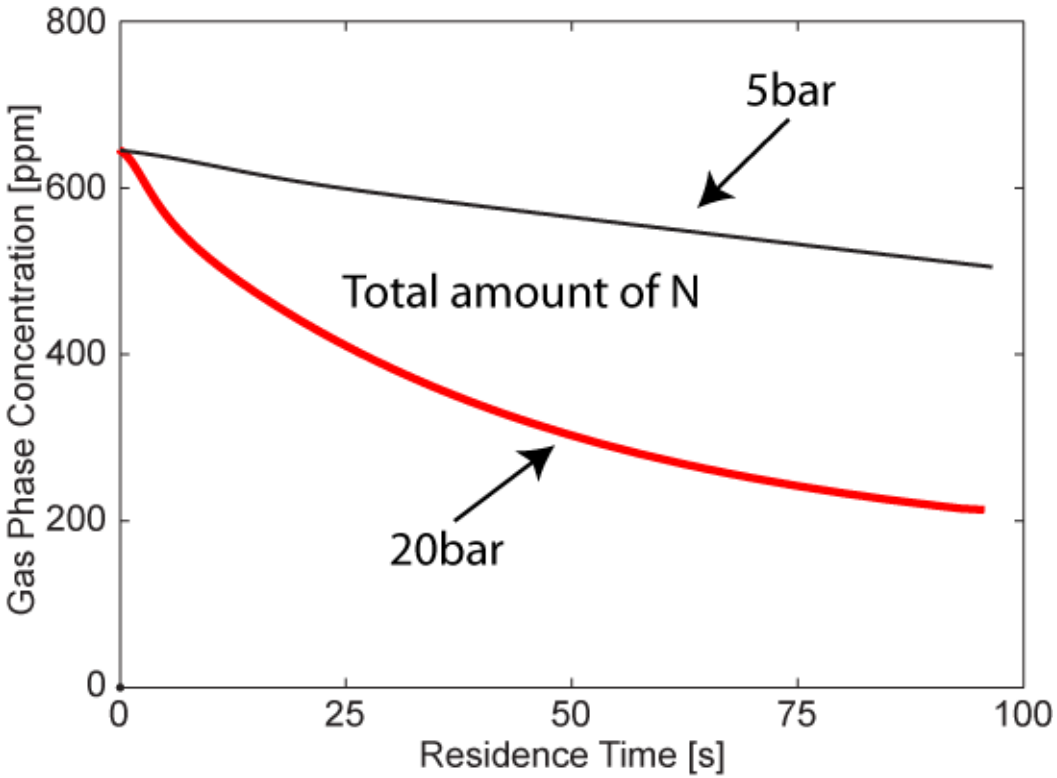
- Constructed reaction mechanism (Pettersson et al. 2011)
  - 10 gas phase reactions
  - 18 liquid phase reactions
- Mass transfer between gas and liquid phase
  - two-film theory
- Plug-flow reactor



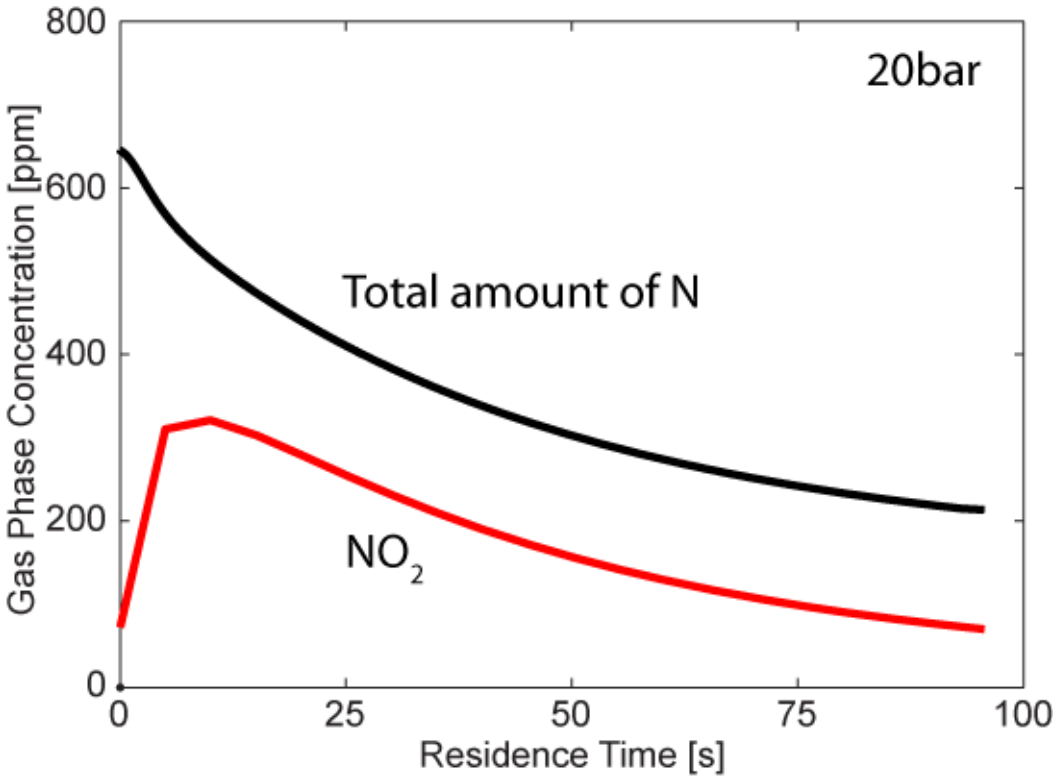
Method

Parameter	Reference case value	Sensitivity analysis
SO_2	3000ppm	0-3000ppm
NO_2	65ppm	0-650ppm
NO	585ppm	0-650ppm
O_2	5%	-
H_2O	Saturated	-
CO_2	Ballance	Ballance
Temperature	298K	298-338K
Pressure	20bar	1-30bar
Liquid/gas	$0.003 m^3/m^3$	$0.001-0.3\ m^3/m^3$
Residence time	100s	25-100s

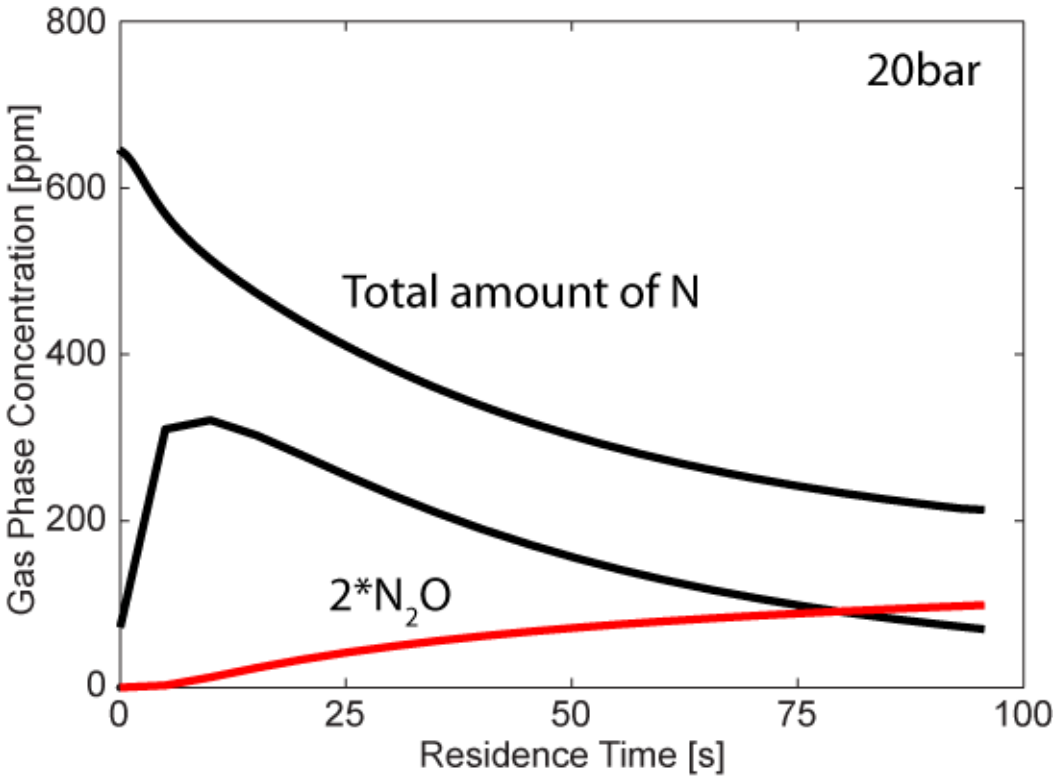
Simulation Results



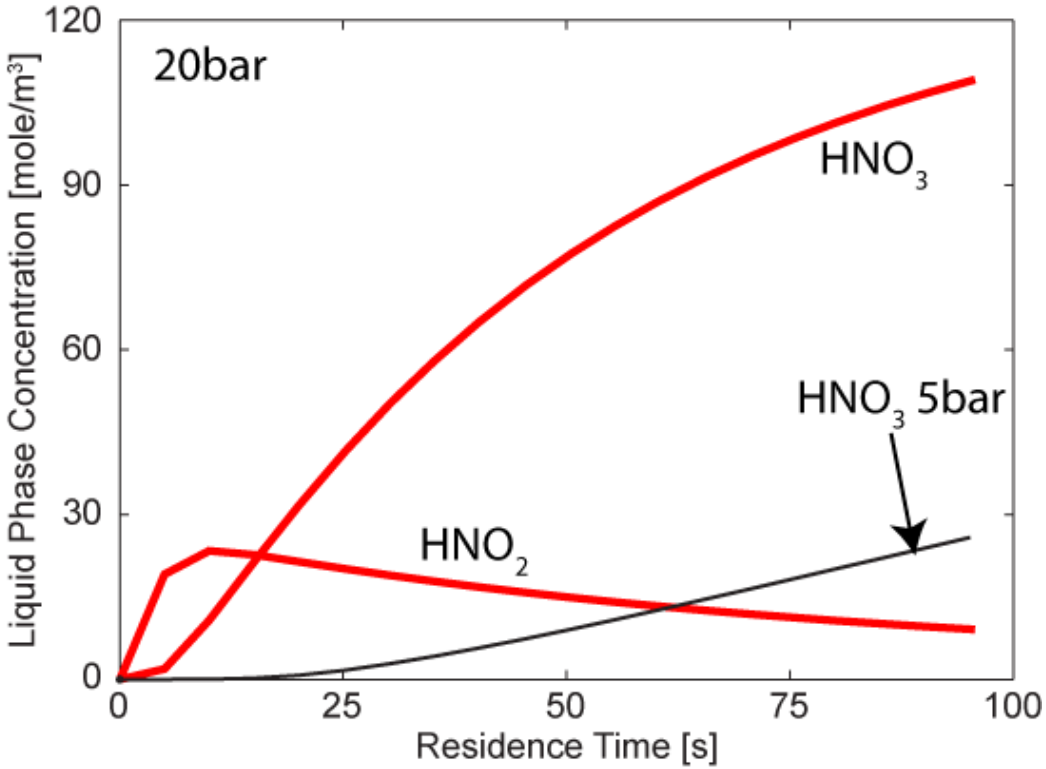
Simulation Results



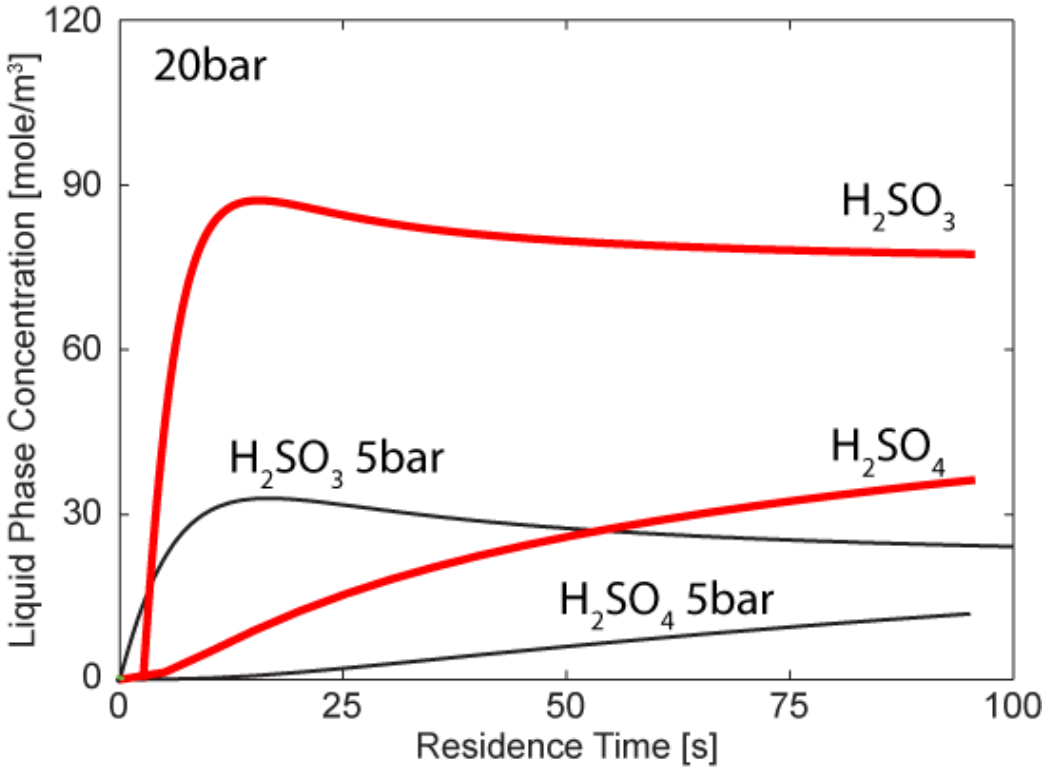
Simulation Results



Simulation Results

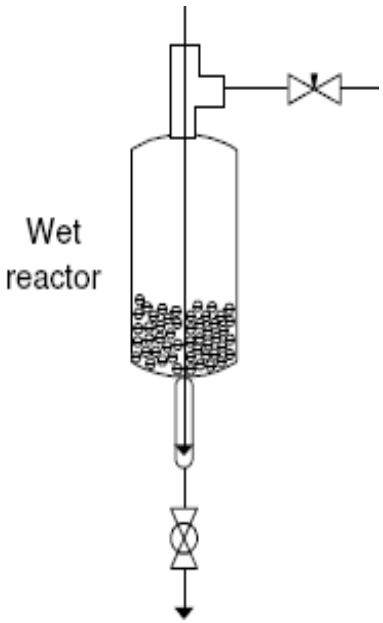


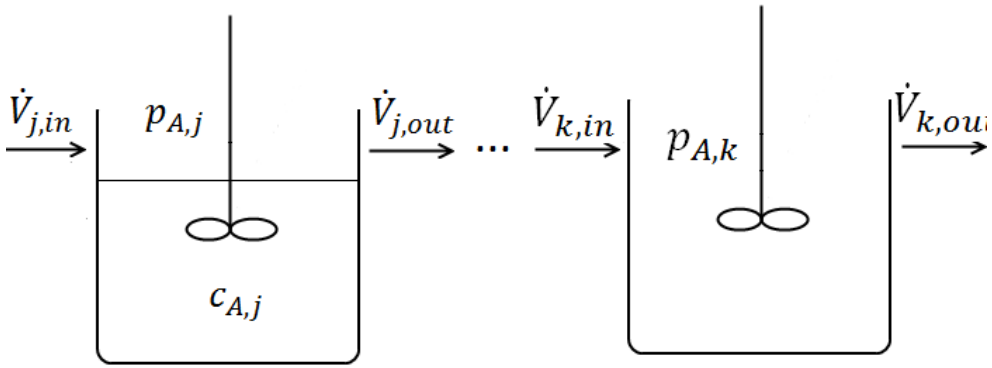
Simulation Results



Comparison to Imperial College Measurements

- The experiments by Imperial College is modelled
- Tank in series
- Assumed gas-liquid contact area, mass transfer coefficients



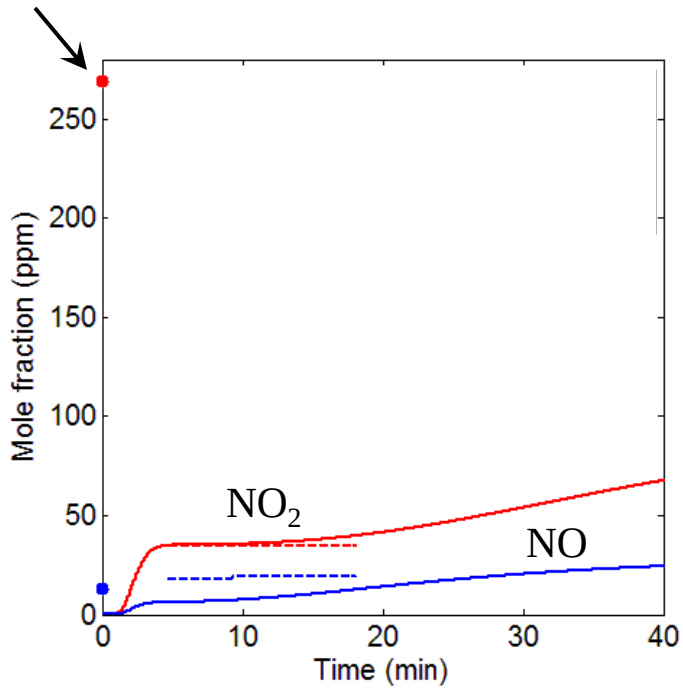


Refs: Torrente-Murciano et al. 2011, Torrente-Murciano et al. 2010.

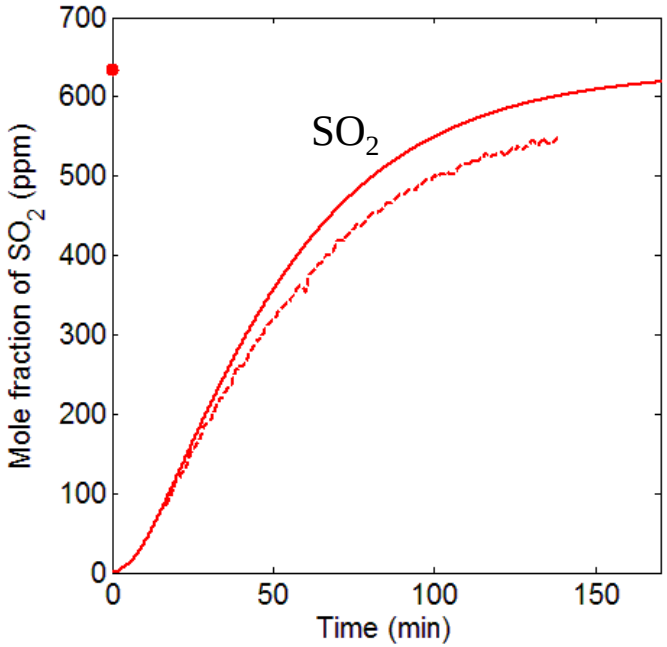
NO_x Absorption and SO_x Absorption

------ Measured
—— Calculated

Inlet concentration



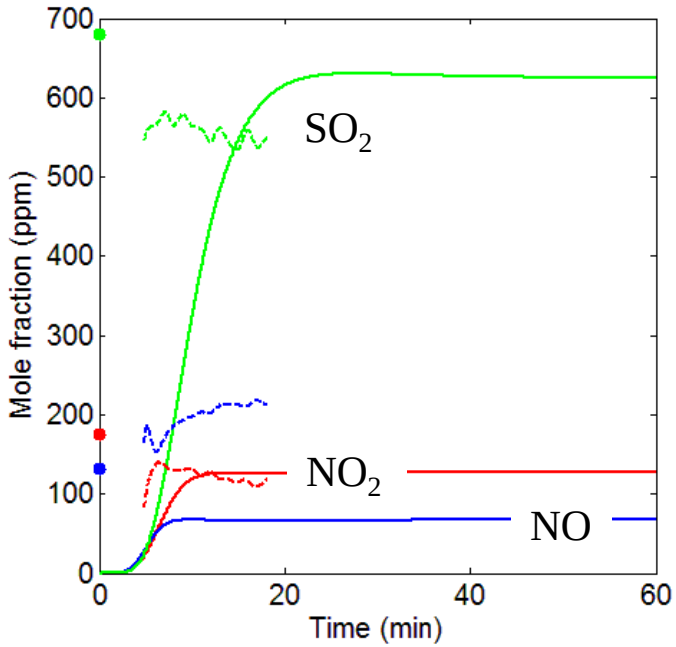
p = 15 bar, • = 143 s
300 mL prefilled water



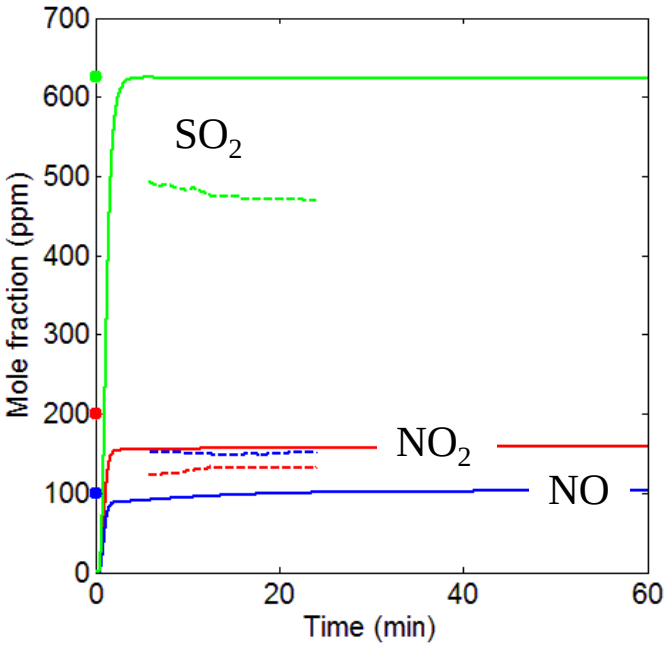
p = 5 bar, • = 143 s
300 mL prefilled 3M sulfuric acid

Simultaneous NO_x and SO_x Absorption

------ Measured
—— Calculated



p = 5 bar, • = 372 s
10 mL prefilled water

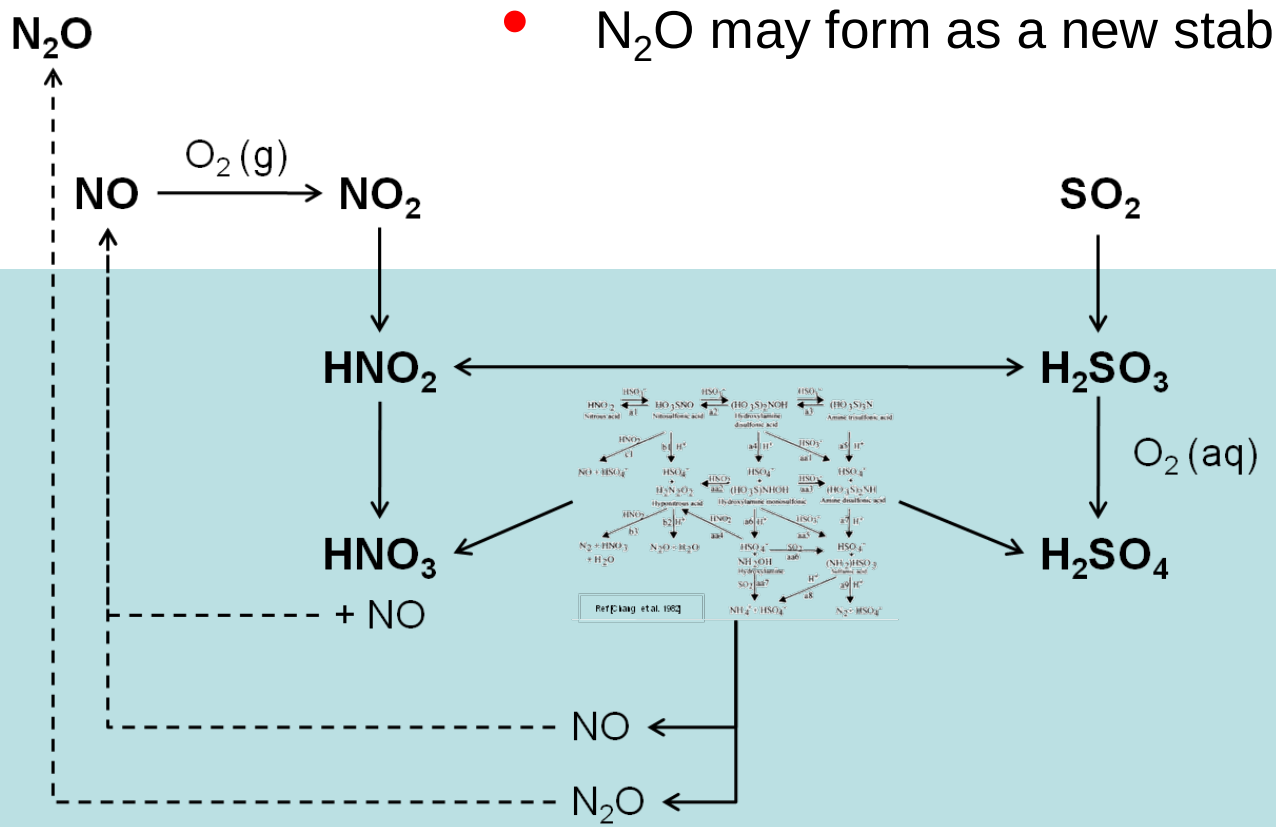


p = 5 bar, • = 62 s
10 mL prefilled 3M sulfuric acid

Conclusion

The interactions between HNO_2 and H_2SO_3 is crucial to the N-S reaction system

- NO_x and SO_x absorption is favoured
- pH controls the chemistry
- N_2O may form as a new stable product



2nd Oxyfuel Combustion Conference, Yeppoon, Australia, 15th September 2011

Sulphur and Nitrogen Chemistry in Pressurized Flue Gas Systems

Tobias Pettersson, Fredrik Normann, Klas Andersson,
Chalmers University of Technology

Linda Nylen, Marie Anheden
Vattenfall Research and Development