

Gas Phase Oxidation of SO₂ by NO₂ in Pressurized Flue Gas Systems - An Experimental Investigation

Sima Ajdari, Fredrik Normann, Klas Andersson, Filip Johnsson
Combustion and Carbon Capture Technologies Group
Chalmers University of Technology

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Outline

- Background
- Motivation
- Objective
- Method
 - Experimental setup
 - Modeling of the gas phase chemistry
- Results
- Conclusions
- Future focus

Background

- CO₂-rich stream from oxy-fuel and chemical looping combustion systems contaminated with NO_x and SO_x
- Pressure and temperature have direct influence on the chemistry of nitrogen- and sulfur-containing species
- Process conditions of CO₂ capture schemes
 - New opportunities for NO_x and SO_x removal
 - Corrosion issues during compression

Background

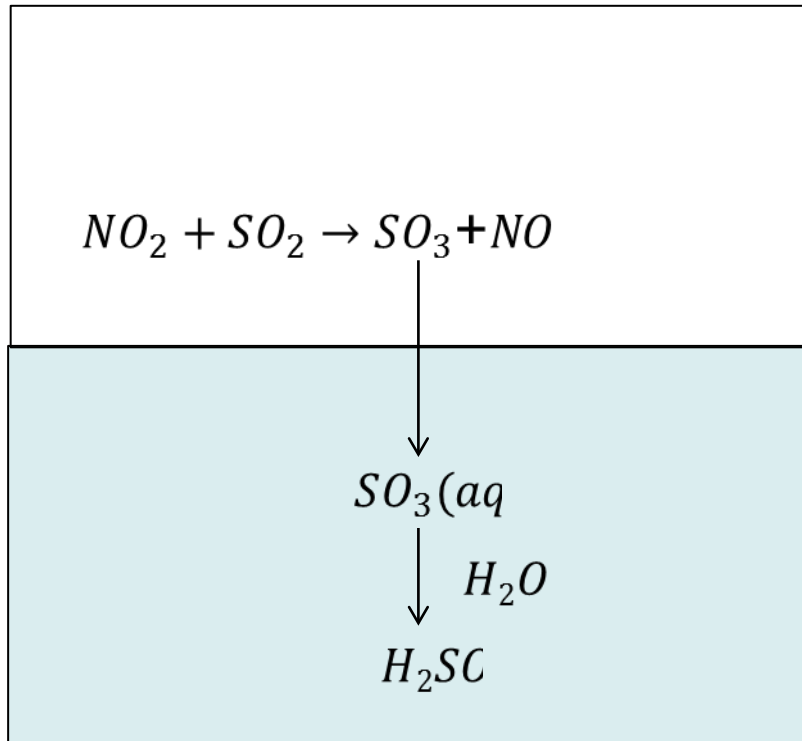
- NO_x and SO_x content of flue gases from combustion process: mainly NO and SO_2
- Elevated pressure and low temperatures in the flue gas train in favor of increased oxidation of NO to NO_2
- NO_2 high solubility in water : potential for removal by water
- Present understanding of the chemistry of the system
 - Gas phase chemistry of nitrogen oxides and absorption mechanisms widely studied and well understood: HNO_3 and HNO_2 as main products of absorption
 - The challenge: presence of SO_x increases number of possible reactions

Motivation

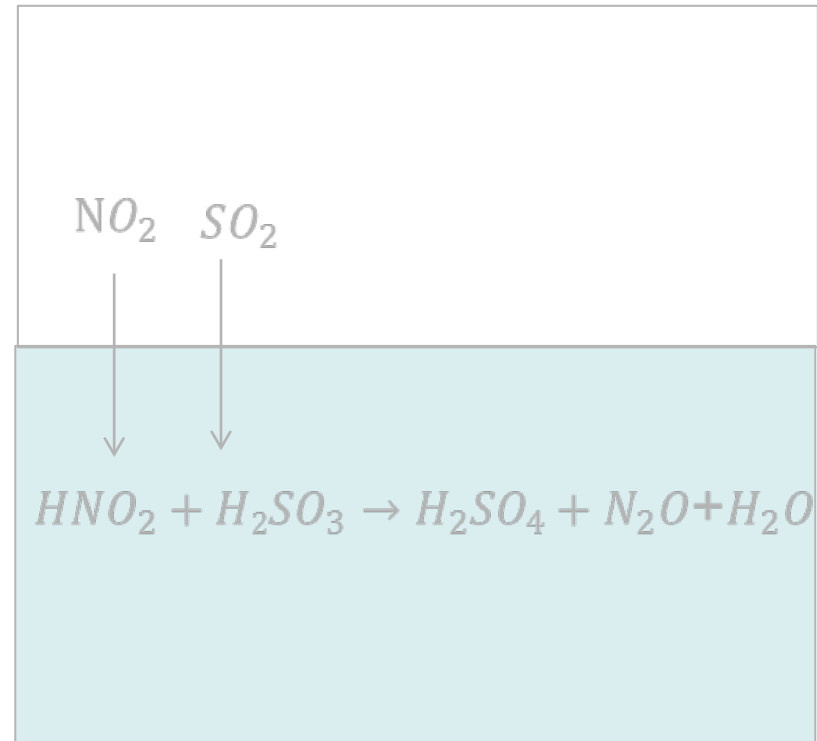
- Formation of Sulfuric acid and nitric acid during the compression of flue gases in oxy-fuel systems the condenser water in number of experimental investigations (Zanganeh et al., 2011 and White et al., 2010, etc.) and predicted in a modelling study by Normann et al. (2013)
- Increased concentration of NO_x enhances the removal of SO_2 from the gas phase (White et al., 2010)

Motivation

- The mechanism for the formation of sulfuric acid not fully exploited, two main reaction paths proposed:
- Path 1



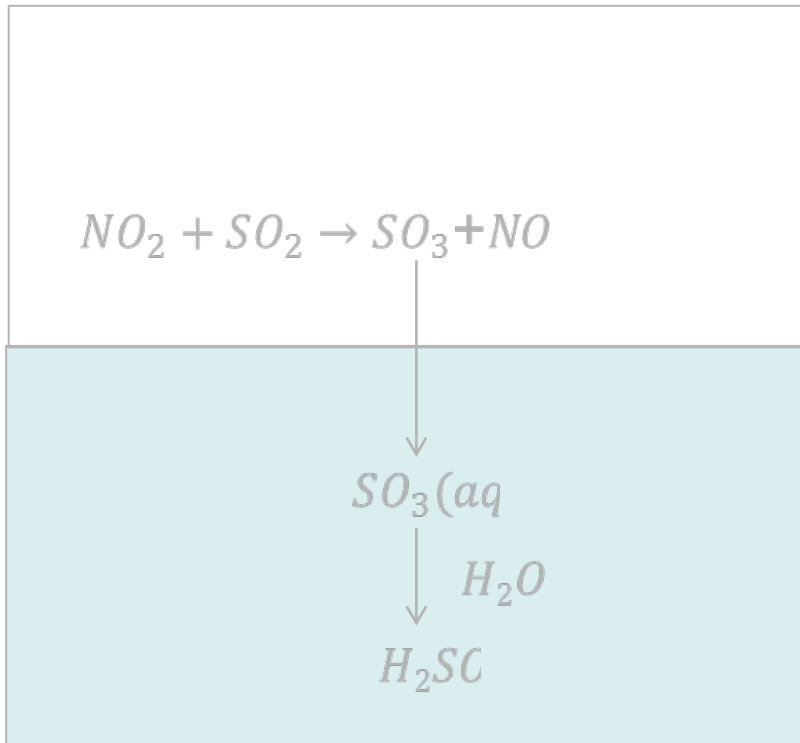
Path 2



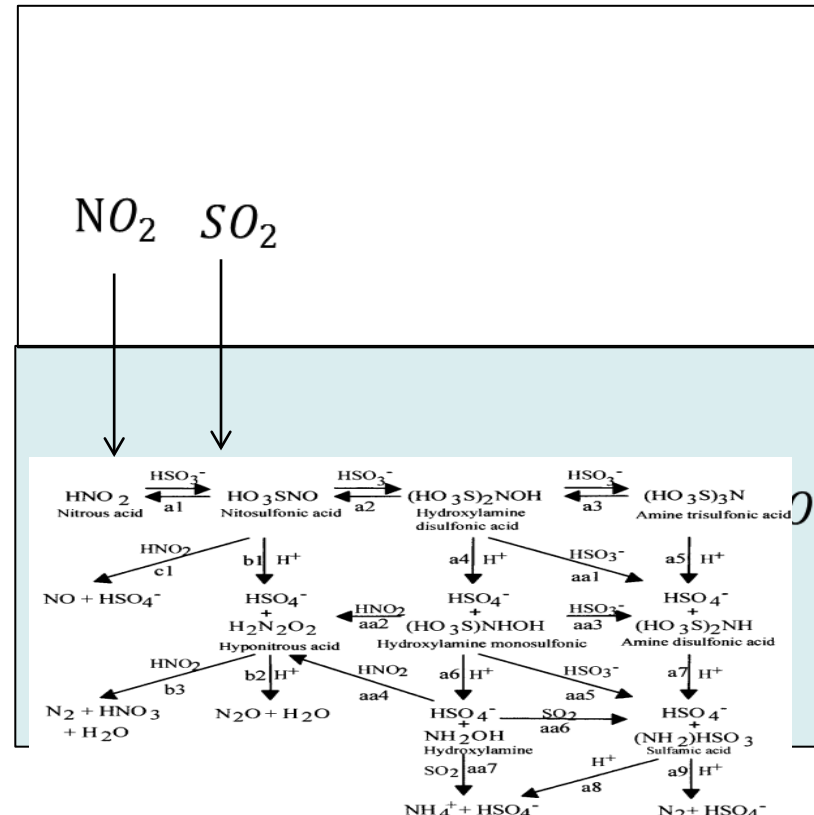
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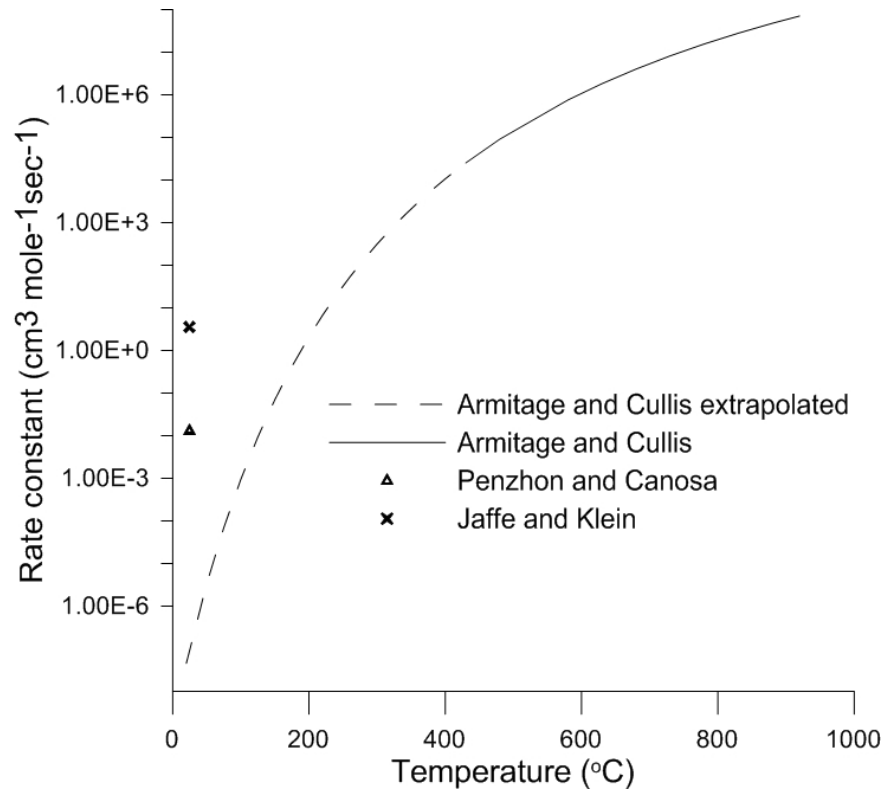
Path 2



Reaction diagram between nitrite and bisulfite ions proposed by Chang et al. (1982) taken from Petrissans & Zoulalian (2001)

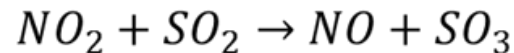
Motivation

- First path
- Available kinetic data for $NO_2(g) + SO_2(g) \rightarrow SO_3(g) + NO(g)$

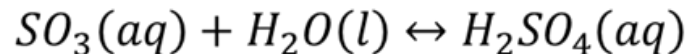
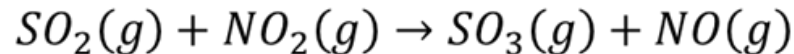


Objective

- To examine the significance of the homogeneous reaction of SO_2 and NO_2 under conditions relevant for pressurized flue gases from oxy-fuel combustion systems



- ✓ To clarify the mechanism that enhances SO_x absorption at increased pressure (clarification of the significance of the following path to the formation of sulfuric acid)

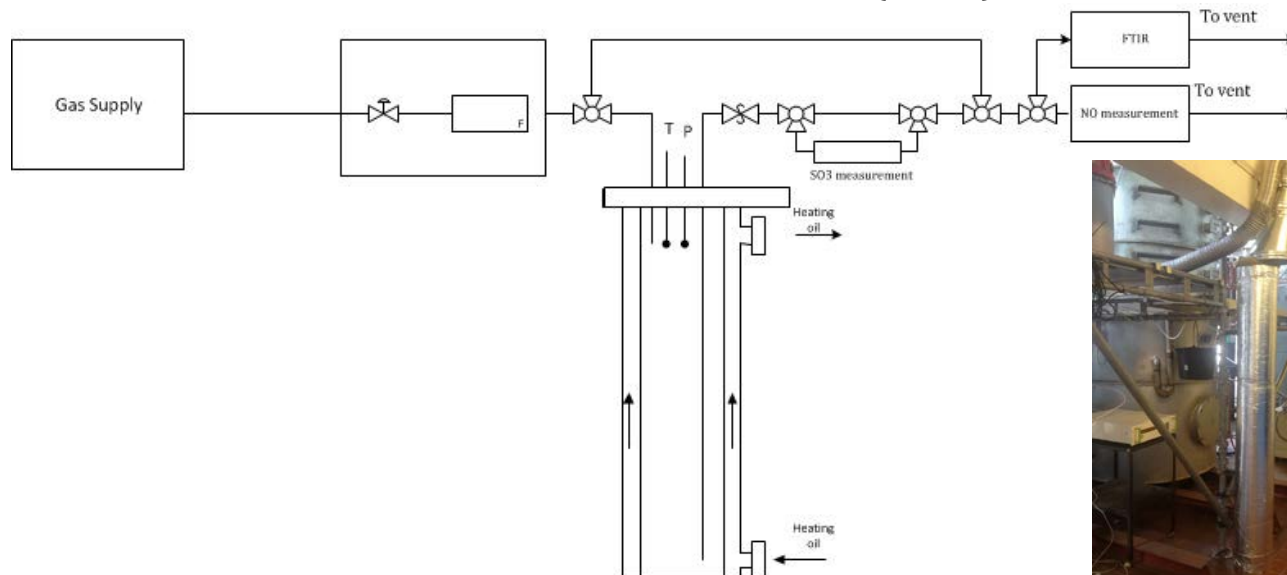


Method

- Experimental study of the reaction in a temperature-controlled reactor
- Modeling of the gas phase chemistry

Method - Experimental Setup

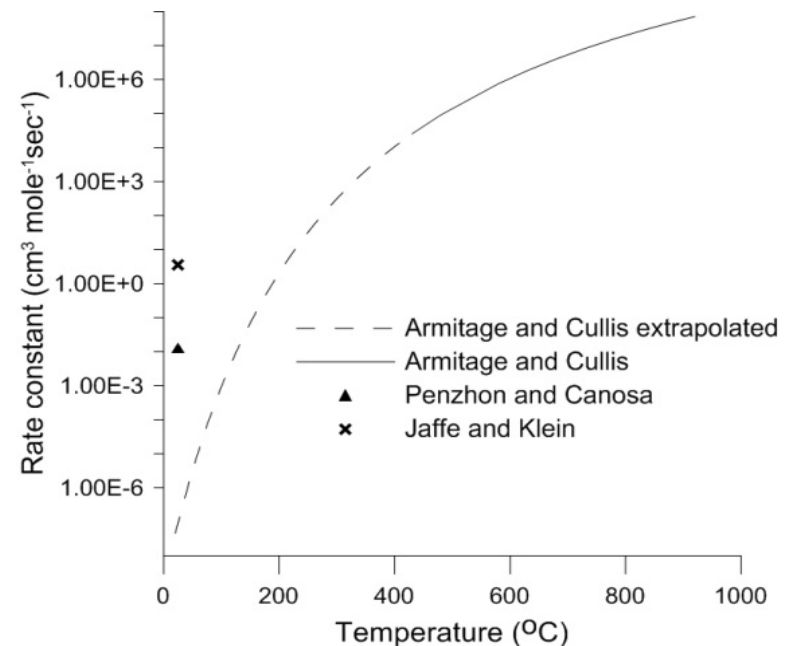
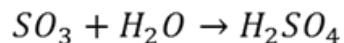
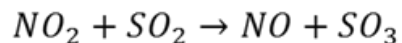
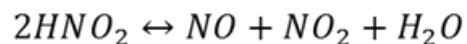
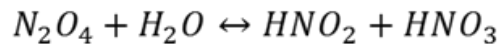
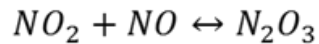
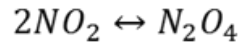
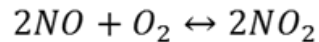
- Temperature-controlled reactor (up to 250°C)
- Atmospheric pressure and dry conditions
- Increased partial pressures of SO₂ and NO₂ to “simulate” pressurized conditions
- Feed gas: 10% NO₂ and 10% SO₂ (\cong 3300 ppm at 30 bar)
- Residence time: 4-8 minutes
- SO₃ measurement: salt method based on Vainio et al. (2013)



Simplified diagram of the experimental setup

Method- gas phase chemistry

- Plug flow reactor model
- Constructed reaction mechanism: gas phase reactions of importance in the flue gas during the compression and cooling



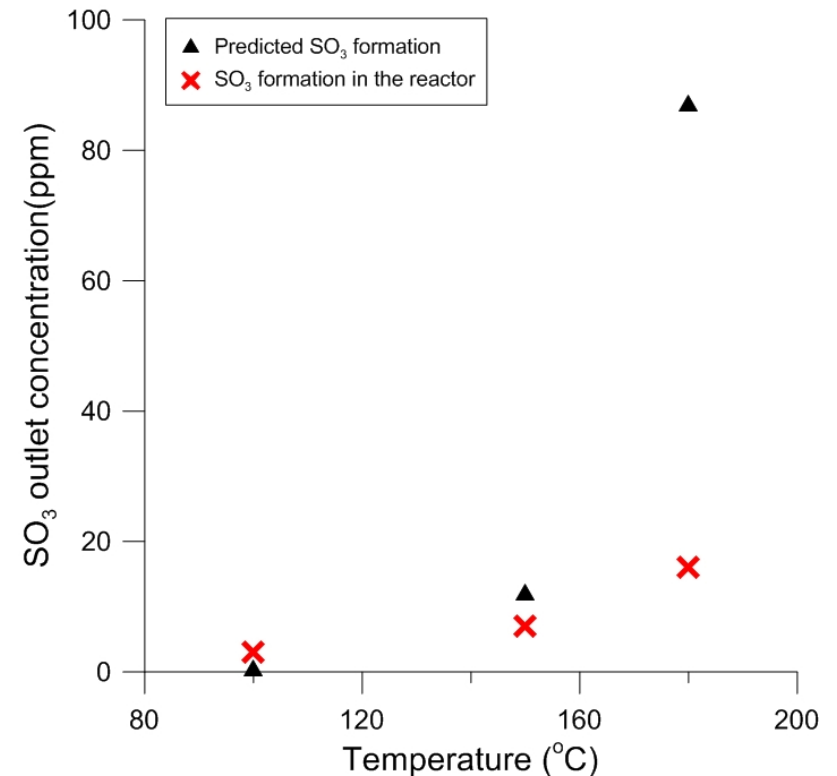
Results

- Conversion of SO_2 to SO_3 in the reactor

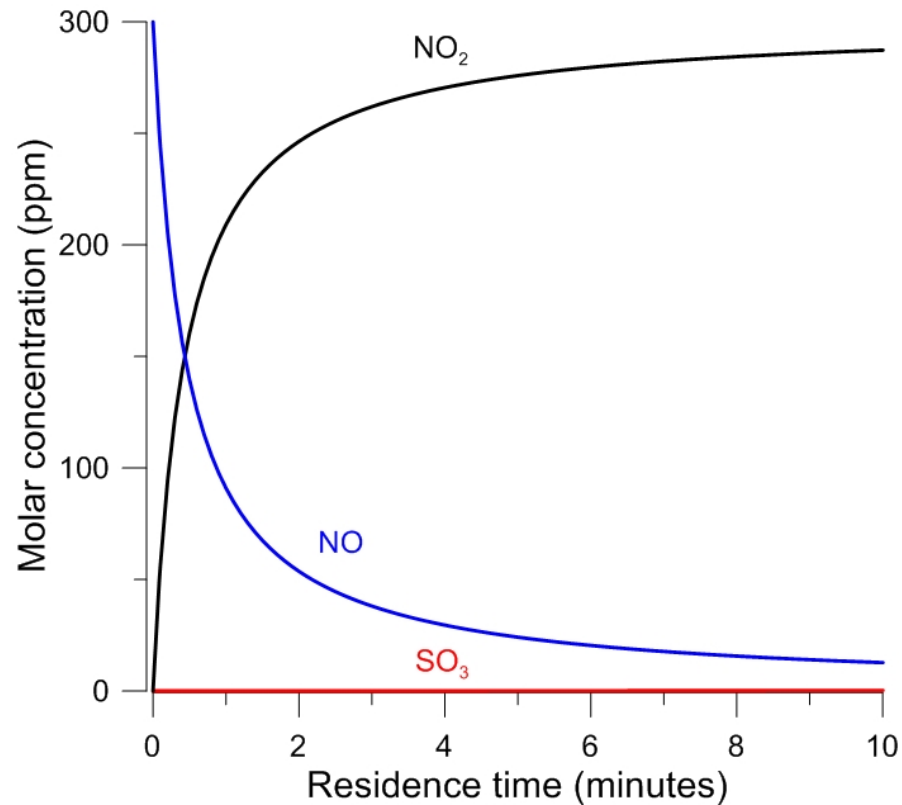
Initial concentrations			Temperature ($^{\circ}\text{C}$)	SO_2 to SO_3 conversion (%)
NO_2	SO_2	SO_3		
10%	10%	0	180	0.2
10%	10%	0	150	<0.1
10%	10%	0	100	0

Results

- Predicted NO and SO₃ formation based on the gas phase chemistry model vs. experimental results for SO₃ formation



Results



Conversion of SO₂ and NO in the gas phase at 200°C for a flue gas containing 300 ppm NO and 2000 ppm SO₂ and 3% O₂ at 30 bar, calculated based on the kinetics reported by Armitage and Cullis(1971) for the oxidation of SO₂ by NO₂ and Atkinson et al.(1997) for the oxidation of NO by O₂

Conclusions

- Oxidation of SO_2 by NO_2 in the gas phase is insignificant at dry conditions and up to 180°C
- The results are in agreement with the modeling predictions based on the available kinetics for the $\text{NO}_2 + \text{SO}_2$ reaction
- Evaluation of the effect of temperature and residence time on the composition of a dry flue gas at pressurized conditions: formation of SO_3 is not significant: oxidation by NO_2 is not the main pathway for the formation of sulfuric acid in the compression section

Future Focus

- Modeling of the liquid phase chemistry , study of the possible products depending on the operating conditions
- Gas-liquid experiments to verify the developed model

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Sima.ajdari@chalmers.se

<http://www.chalmers.se/en/projects/Pages/forbrannings--och-koldioxidinfangningstekniker.aspx>



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