

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Chemistry and Process Design of Integrated Removal of Nitrogen and Sulfur Oxides  
in Pressurized Flue Gas Systems

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# Chemistry and Process Design of Integrated Removal of Nitrogen and Sulfur Oxides in Pressurized Flue Gas Systems

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## Abstract

Carbon capture and storage is vital to reach the climate goals to limit the increase in the global temperature. In two of the key carbon capture technologies, oxy-fuel and chemical looping combustion, a stream mainly containing carbon dioxide ( $\text{CO}_2$ ) and water is produced. However, the generated flue gas also contains contaminants such as nitrogen oxides ( $\text{NO}_x$ ) and sulfur oxides ( $\text{SO}_x$ ). The carbon dioxide is compressed and separated from water and impurities to achieve suitable conditions for transport and storage. In addition to storage and transport system requirements, separation of  $\text{NO}_x$  and  $\text{SO}_x$  during the  $\text{CO}_2$ -conditioning is required to avoid corrosion issues in various parts of the process. In addition to the emission control measures available for conventional power plants, there are new opportunities for control of  $\text{NO}_x$  and  $\text{SO}_x$  in pressurized flue gas systems of oxy-fuel and chemical looping combustion plants.

The work presented in this thesis evaluates the chemistry and process design of  $\text{NO}_x$  and  $\text{SO}_x$  removal during  $\text{CO}_2$ -conditioning in oxy-fuel and chemical looping combustion systems. The primary goals of this thesis are to expand the current understanding of  $\text{NO}_x$  and  $\text{SO}_x$  chemistry, and, to identify favorable conditions for achieving cost-effective control processes. Analysis of the reaction system by a detailed mechanism uncovers the importance of pH conditions in the liquid for the selectivity of the integrated  $\text{NO}_x$  and  $\text{SO}_x$  removal process. Moreover, a reduced mechanism is also proposed for engineering calculations of the pressurized flue gas systems that captures the effect of pH and describes the relevant gas and liquid-phase chemistry. Process simulations, which utilize the reduced mechanism, enable evaluation of design of the integrated removal of  $\text{NO}_x$  and  $\text{SO}_x$  in pressurized flue gas systems. Technical evaluation of the integrated process reveals that removal rates of >98% for  $\text{SO}_2$  and >90% for  $\text{NO}_x$  may be achieved. Moreover, the efficiency of the  $\text{NO}_x$  removal can be improved by the presence of  $\text{SO}_x$  and increased concentration of  $\text{O}_2$  in the flue gas. A comparison of the economic performance of the integrated removal process and the conventional emission control measures, i.e., selective catalytic reduction and wet flue gas desulfurization with limestone, shows significantly lower costs of removal by the integrated process.

*Keywords:* oxy-fuel combustion, chemical looping combustion,  $\text{NO}_x$ ,  $\text{SO}_x$ ,  $\text{CO}_2$  purification, pressurized flue gas



## List of publications

This thesis is based on the work contained in the following papers:

- Paper I            Ajdari S., Normann F., Andersson K., Johnsson F. Modeling the Nitrogen and Sulfur Chemistry in Pressurized Flue Gas Systems. *Industrial & Engineering Chemistry Research*, 2015, 54 (4), 1216-1227.
- Paper II            Ajdari, S., Normann, F., Andersson, K., Johnsson, F. Reduced Mechanism for Nitrogen and Sulfur Chemistry in Pressurized Flue Gas Systems. *Industrial & Engineering Chemistry Research*, 2016, 55 (19), 5514-5525.
- Paper III            Ajdari, S., Normann, F., Andersson, K. Evaluation of Operating- and Design Parameters for Pressurized Flue Gas Systems with Integrated Removal of NO<sub>x</sub> and SO<sub>2</sub>, *Submitted for publication*, 2018.
- Paper IV            Ajdari, S., Garðarsdóttir S. Ó., Normann, F., Andersson, K. Techno-Economic Evaluation of Integrated NO<sub>x</sub> and SO<sub>x</sub> Removal in Pressurized Flue Gas Systems for Carbon Capture Applications, *Submitted for publication*, 2019.

Sima Ajdari is the principal author of all four papers. Associate Professor Fredrik Normann and Professor Klas Andersson have contributed with the discussions and the editing of all papers. Professor Filip Johnsson has contributed with the discussions and the editing of **Papers I** and **II**. Dr. Stefania Ósk Garðarsdóttir from SINTEF has contributed with the economic estimation in **Paper IV**. Part of the gas-phase experiments in Paper A were performed by Sima Ajdari. As the main focus of Paper A is outside the scope of this thesis, the paper is included in the *Appendix*.

- Paper A.            Johansson, J., Heijnesson Hultén, A., Ajdari, S., Nilsson, P., Samuelsson, M., Normann F., Andersson, K., Gas-Phase Chemistry of the NO-SO<sub>2</sub>-ClO<sub>2</sub> System Applied to Flue Gas Cleaning. *Industrial & Engineering Chemistry Research*, 2018, 57(43), 14347-14354.

Additional work has been carried out within the remit of the principal work, resulting in the publications listed below. These have not been included in the thesis, as the contents either overlap with the appended papers or are considered to be outside the scope of this thesis.

- a. Ajdari S., Normann F., Andersson K., Mun T.Y., Lee Y., Won Y. Formation and Control of NO<sub>x</sub> and SO<sub>x</sub> in Pressurized Oxy-Combustion Systems, 2015, Proceedings of Clearwater Clean Coal Conference, Florida, USA.
- b. Ajdari S., Normann F., Andersson K. Control of NO<sub>x</sub> and SO<sub>x</sub> in Chemical-Looping Combustion Plants: The Importance of Pressurized Flue Gas Systems, 2014, 3rd International Conference on Chemical Looping, Göteborg, Sweden.
- c. Hultén, A. H., Nilsson, P., Samuelsson, M., Ajdari, S., Normann, F., Andersson K. First Evaluation of a Multicomponent Flue Gas Cleaning Concept using Chlorine Dioxide Gas – Experiments on Chemistry and Process Performance, 2017, *Fuel*, 210, 885-891.

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January, 2019

Sima Ajdari



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# 1. Introduction

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Global warming resulting from the increased greenhouse gas (GHG) emissions caused by human activities is a major threat to the environment and humankind. As a response, a global effort (under the Paris Agreement) has been made to limit the increase in global temperature to well below 2°C above pre-industrial levels, with attempts to limit warming further to only 1.5°C being initiated. In 2017, human-induced warming was about 1°C higher than the pre-industrial era levels<sup>1</sup>.

A major contributor to GHG emissions is the combustion of fossil fuels, which results in emissions of carbon dioxide (CO<sub>2</sub>). In 2016, fossil fuels represented 81% of the world's primary energy consumption<sup>2</sup>. Global energy demand is expected to increase, mainly driven by the developing economies in Asia. Several measures have been proposed to reduce CO<sub>2</sub> emissions from power generation: energy efficiency improvements; fuel switching; and low-GHG energy supply technologies, such as renewable energy, nuclear power and carbon capture and storage (CCS).

CCS is an option that would substantially decrease CO<sub>2</sub> emissions from large point sources (fossil fuel-based and biomass-based), such as power plants and industries. In combination with bioenergy, carbon capture and storage may even achieve negative GHG emissions, a technique known as bioenergy with carbon capture and storages (BECCS). The contribution from CCS and/or BECCS, together with other mitigation options, is considered to be essential for reaching the global climate goals<sup>3-4</sup>.

CCS technologies involve capturing the CO<sub>2</sub> generated during combustion from large point sources and transporting it to a suitable geologic storage site. CO<sub>2</sub> capture technologies fall into the following categories: post-combustion; pre-combustion; oxy-fuel combustion; and chemical looping combustion. In oxy-fuel and chemical looping combustion systems, N<sub>2</sub> is removed from the air prior to combustion, resulting in a flue gas that mainly comprises CO<sub>2</sub> and water. The CO<sub>2</sub>-rich flue gas is thereafter processed so as to remove the water, increase its pressure, and decrease its temperature, in processes that prepare it for cost-effective transport and storage. However, contaminants such as nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>), which are byproducts of combustion will exist in the flue gas.

Controlling NO<sub>x</sub> and SO<sub>x</sub> emissions from power plants and industrial sources has been required since the implementation of legislation for the control of such emissions in the 1970's. NO<sub>x</sub> and SO<sub>x</sub> emissions to the atmosphere have adverse effects on human health and the environment through the formation, for example, of acid rain, particulate matter, and smog. The control of NO<sub>x</sub> and SO<sub>x</sub> levels in oxy-fuel and chemical looping combustion systems is necessary to meet emission limits and fulfill transport and storage system requirements. In addition, the avoidance of costly corrosion of equipment in various parts of the process is an important incentive for controlling the levels of NO<sub>x</sub> and SO<sub>x</sub>. In general, several conventional techniques are available for the emission control, including

primary measures that are applied during combustion (mainly  $\text{NO}_x$ ) and secondary measures downstream of the combustion process, which can be applied to oxy-fuel and chemical looping combustion systems. Alternatively, the conditions in the  $\text{CO}_2$ -conditioning (increased pressure and decreased temperature compared to a conventional power plant) present new opportunities for emission control, possibly at a reduced cost.

Previous research<sup>5-8</sup> on the formation and control of  $\text{NO}_x$  and  $\text{SO}_x$  emissions from oxy-fuel systems have identified the nitrogen and sulfur chemistry during the  $\text{CO}_2$ -conditioning as an important knowledge gap to develop cost-efficient oxy-fuel power plants. This thesis discusses the chemistry and emission control of  $\text{NO}_x$  and  $\text{SO}_x$  in oxy-fuel and chemical looping combustion systems during  $\text{CO}_2$ -conditioning.

## 1.1. Aims of the thesis

The principal aim of this thesis is to contribute new information regarding the development of cost-efficient oxy-fuel and chemical looping combustion power plants. More specifically, the objective is to expand our current understanding of  $\text{NO}_x$  and  $\text{SO}_x$  chemistry under pressurized conditions that is important in the design of  $\text{CO}_2$  conditioning units for oxy-fuel and chemical looping combustion systems. Given the complexity of the  $\text{NO}_x$  and  $\text{SO}_x$  chemistry, identifying the process conditions that are important for achieving both adequate levels of emissions control and corrosion prevention is critical. This thesis evaluates the integrated control of  $\text{NO}_x$  and  $\text{SO}_x$  levels in flue gases and identifies critical areas for future work in the following three areas:

- (i) Identification of the reaction mechanism for a  $\text{NO}_x/\text{SO}_x/\text{H}_2\text{O}$  system under conditions relevant for flue gases from oxy-fuel and chemical looping combustion systems (**Paper I**).
- (ii) Investigation of the reaction pathways of the  $\text{NO}_x$  and  $\text{SO}_x$  chemistry, so as to derive reduced reaction mechanisms that would enable engineering calculations for predictions of  $\text{NO}_x$  and  $\text{SO}_x$  behaviors in pressurized flue gas systems and for the design of integrated removal systems (**Paper II**).
- (iii) Establishment of important design and operating conditions for efficient implementation of a system for  $\text{NO}_x$  and  $\text{SO}_x$  removal and for estimations of the associated costs of removal (**Papers III and IV**).

## 1.2. Outline of the thesis

This thesis consists of an introductory essay and four appended papers. In the seven chapters of the essay, the appended papers are summarized, and the perspective and overall aims and methodologies of the thesis are presented. Chapter 2 provides background information on oxy-fuel and chemical looping combustion plants and describes the control of nitrogen and sulfur oxides in such plants. The methodologies are described in Chapter 3, with the specific methodological approach taken in each paper being introduced and related to the overall approach of the thesis. Thereafter, the results for the investigated chemistry and the design of the control system are summarized in Chapters 4 and 5, respectively. Finally, the conclusions and future outlooks are discussed in Chapters 6 and 7.

The appended papers cover the following topics:

- Paper I**                Reviews the current knowledge of the gas-phase and liquid-phase chemistries relevant to pressurized flue gas systems. A detailed-chemistry model and a reactor model are constructed to elucidate the important reaction pathways and significant operating parameters.
- Paper II**                Presents reduced mechanisms, based on the sensitivity analysis of the detailed chemistry model constructed in Paper I. A tool for mechanism evaluation based on a brute force method is developed. The reduced mechanisms are shown to be efficient for engineering and process simulation calculations of pressurized flue gas-cleaning systems.
- Paper III**               Performs process simulations of flue gas compression and integrated NO<sub>x</sub> and SO<sub>x</sub> removal in large-scale oxy-fuel and chemical looping combustion systems. The process simulation model is constructed in the Aspen Plus software and utilizes the reduced mechanism presented in Paper II. The paper evaluates the effects of process parameters on the efficiencies of removal of NO<sub>x</sub> and SO<sub>x</sub>.
- Paper IV**                Designs and estimates the cost of a large-scale flue gas compression system with integrated NO<sub>x</sub> and SO<sub>x</sub> removal based on the conclusions drawn in Paper III. The capital and operating costs of the integrated NO<sub>x</sub> and SO<sub>x</sub> removal are estimated from the basic design flowsheet and compared to those of conventional removal processes.

## 2. Background

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### 2.1. Oxy-fuel and chemical looping combustion technologies

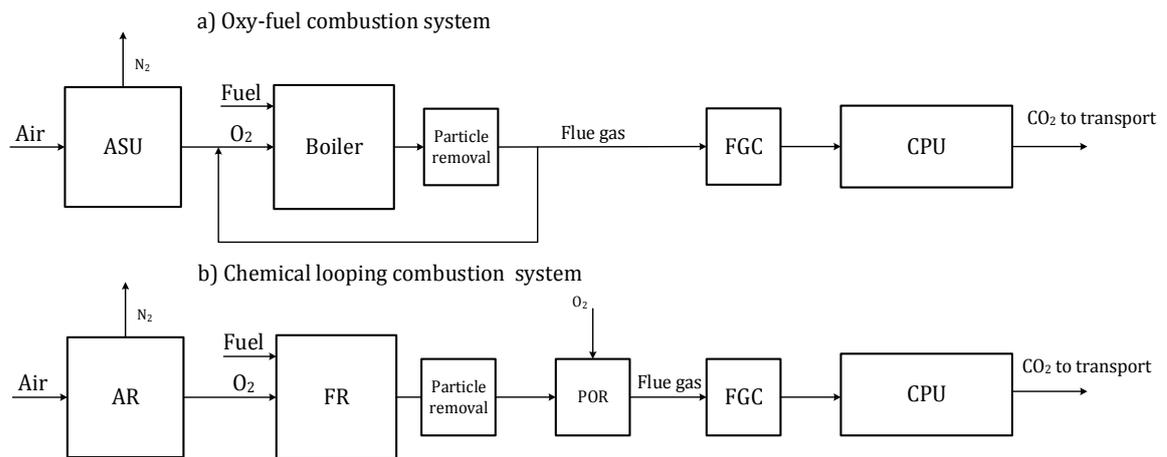
Extensive research on oxy-fuel combustion for CO<sub>2</sub> capture has been performed since the early 1990's. This research has resulted in a series of large full-chain pilot plants. Among these are the Vattenfall 30-MW<sub>th</sub> oxy-fuel pilot plant at Schwarze Pumpe, Germany, and the Callide 30-MW<sub>e</sub> oxy-fuel demonstration plant in Australia, which operated in the late 2000's and early 2010's. The results obtained from these pilot studies have been presented by Anheden et al.<sup>9</sup> and Komaki et al.<sup>10</sup>. The oxy-fuel process was, however, never commercialized, due to market and political circumstances, and the development was placed on hold. The development of a so-called 'second generation' of technologies with improved energy efficiencies of CO<sub>2</sub> capture has been initiated, including pressurized oxy-fuel combustion and chemical looping combustion. Pressurized oxy-fuel systems have demonstrated strong potential for energy efficiency improvements<sup>11-12</sup>. However, to date, they have only been tested in a number of small pilot plants<sup>13</sup>. The chemical looping combustion technology has been researched for CCS since the early 2000's. This technology has been tested in many small-scale pilot plants and a number of larger pilot plants (50 kW-3 MW), as reviewed by Adanez et al.<sup>14</sup> and Lyngfelt and Linderholm<sup>15</sup>.

Figure 2.1 shows a schematic of the oxy-fuel and chemical looping combustion power plants. Both combustion techniques have the objective of eliminating the airborne nitrogen from the flue gas to generate a stream of CO<sub>2</sub> and water vapor, which can be easily separated away. In oxy-fuel combustion, fuel is combusted with oxygen-and recycled flue gas instead of air. Oxygen is produced through cryogenic distillation in a so called air separation unit (ASU) at a considerable cost of energy. In a CLC system, the fuel is oxidized without mixing with air, and a metal oxide is instead used to transfer oxygen from air to fuel. The system consists of an air reactor and a fuel reactor. In the air reactor, the metal oxide is oxidized in air. The metal oxide is then transferred to the fuel reactor, where it is reduced by the fuel. The fuel is, thus, oxidized in the fuel reactor by the oxygen carried by the metal oxide.

Although the generated streams from combustion are rich in CO<sub>2</sub> and water vapor, they will also contain oxygen, nitrogen and argon from impurities in the oxygen, the excess oxygen for combustion, and air leakage into the system. In addition, contaminants such as nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>) will exist in the flue gas resulting from combustion of nitrogen and sulfur-containing fuels. The purposes of the flue gas trains in the oxy-fuel and chemical looping combustion systems are different from the conventional power plants in the sense that the focus is on CO<sub>2</sub>-conditioning rather than on the treatment of a vented gas, to meet the emissions regulations. The main differences between the CO<sub>2</sub> conditioning systems used for oxy-fuel and chemical looping flue gases is that chemical looping flue gas requires the use of a post-oxidation reactor (POR) for oxygen polishing, to ensure complete fuel conversion in the fuel reactor<sup>16</sup>. Particles are separated from the flue gas

downstream of the combustion chamber and upstream of the flue gas condenser (FGC, where water is separated from the flue gas). The CO<sub>2</sub>-rich flue gas is further purified in the CO<sub>2</sub> Processing Unit (CPU), if required. The exact requirement regarding the purity of the CO<sub>2</sub> stream is not fully clarified yet, and may vary depending on storage scenarios. According to the European Union’s directive on the geological storage of CO<sub>2</sub>, the storage gas should consist “overwhelmingly” of carbon dioxide<sup>17</sup>. To achieve cost-effective transportation and storage, the CO<sub>2</sub> is condensed and compressed in the CPU before it is discharged from the power plant. In order to transport efficiently large amounts of CO<sub>2</sub>, it should be transformed into a high-density form i.e. into a liquid, solid or supercritical phase.

Pipeline and ship transport are considered as viable transport alternatives. For ship transport, refrigerated liquid CO<sub>2</sub> (pressures in the ranges 7-8 bar and a temperature close to -50°C) is considered to be most feasible<sup>18</sup>. For pipeline transport, CO<sub>2</sub> must be compressed to high pressures in order to overcome the frictional- and static pressure drops. In addition, the pressure of CO<sub>2</sub> at the storage site should be higher than the critical pressure, to avoid a two-phase flow in the pipelines. The suggested conditions for the CO<sub>2</sub> stream at the delivery point are pressures in the range of 80-200 bar and temperatures in the range of 0-50°C<sup>19-20</sup>. However, pressures in the range of 100-120 bar and a temperature that is above the critical value (31.1°C) are reported to be favorable<sup>20</sup>.



**Figure 2.1.** Schematic of the oxy-fuel and chemical looping combustion systems. ASU, Air Separation Unit; AR, Air Reactor; CPU, CO<sub>2</sub> Processing Unit; FGC, Flue Gas Condenser, FR, Fuel Reactor; POR, Post Oxidation Reactor.

## 2.2. NO<sub>x</sub> and SO<sub>x</sub> removal in oxy-fuel combustion systems

Combustion of nitrogen and sulfur-containing fuels results in emissions of nitrogen oxides (NO<sub>x</sub>, NO and NO<sub>2</sub>) and sulfur oxides (SO<sub>x</sub>, SO<sub>2</sub> and SO<sub>3</sub>). In addition, NO<sub>x</sub> can be formed from molecular nitrogen that is present in the air. However, the latter is not expected to be significant in oxy-fuel systems<sup>6</sup> and is not considered relevant for chemical looping combustion systems. For oxy-fuel combustion, there exists considerable experience from laboratory- and pilot-scale plants regarding the formation of emission (see Normann<sup>6</sup>, Fleig<sup>5</sup>, and Wall et al.<sup>21</sup> and references therein). While considerable formation of emissions from chemical looping combustion systems have been shown<sup>22-24</sup>, but this area of research is not as developed as it is for the oxy-fuel systems. While most of the research on secondary measures for NO<sub>x</sub> and SO<sub>x</sub> control conducted to date has been on the development of the oxy-fuel technology, the knowledge acquired and experience gained are also applicable to chemical looping combustion systems. Thus, for the remaining part of this chapter, although results and experience for oxy-fuel combustion are mentioned, they are also applicable to chemical looping systems.

The requirements for NO<sub>x</sub> and SO<sub>x</sub> removal in oxy-fuel and chemical looping combustion processes remain unclear. Although historically the limitations on NO<sub>x</sub> and SO<sub>x</sub> emissions have been set by the relevant pieces of legislation, in oxy-fuel and chemical looping power plants corrosion issues may impose even more stringent requirements. In the initial phase of the development of oxy-fuel technology, i.e., from the early 1990's until 2005, it was assumed that most of the NO<sub>x</sub> and SO<sub>2</sub> in the flue gas would be captured together with CO<sub>2</sub><sup>25</sup>. However, regulations and laws regarding storage sites are likely to be enacted. Since possible corrosion risks when NO<sub>2</sub> and SO<sub>2</sub> are present in the CO<sub>2</sub> even at low water vapor concentrations<sup>26-27</sup> and impacts of O<sub>2</sub>, NO<sub>2</sub> and SO<sub>2</sub> on some storage sites<sup>28</sup> have already been exhibited.

SO<sub>2</sub> and NO, which are the thermodynamically favored species at high temperatures, are the predominant SO<sub>x</sub> and NO<sub>x</sub> species in the flue gases generated from the combustion process. High pressure and low temperature of the CO<sub>2</sub>-conditioning affect the chemistry of nitrogen- and sulfur-containing species. Most important is the substantial increase in the rate of oxidation of NO to NO<sub>2</sub> in the high-pressure zones of the CO<sub>2</sub>-conditioning train by the oxygen present in the flue gas:



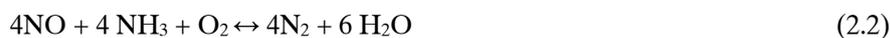
This activity is attributed to increases in the partial pressures of the reactants. The solubility of NO<sub>2</sub> in water is higher than that of NO in water (by about one order of magnitude). The NO<sub>2</sub> formed dissolves readily in water, which is either introduced to the process or formed during the condensation, compression, and cooling of the flue gas. NO<sub>2</sub> is highly reactive in aqueous solutions, reacting with water to form nitrous acid (HNO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>). The latter causes equipment corrosion problems. The presence of SO<sub>x</sub> in the system, significantly increases the number of reactions that can take place in the aqueous solution due to the interactions that occur between the nitrogen and sulfur species. These interactions may eventually lead to the oxidation of S(IV) into S(VI), i.e., the formation

of sulfates. On the one hand, this phenomenon implies that NO<sub>x</sub> and SO<sub>2</sub> can be removed efficiently through absorption processes. On the other hand, severe corrosion can occur if this process is not properly controlled. The formation of sulfuric acid and nitric acid has been observed in a number of oxy-fuel laboratory- and pilot-scale studies<sup>29-32</sup>.

NO<sub>x</sub> and SO<sub>x</sub> can be removed at various points in the process, using either conventional methods (available for air-combustion systems) or novel methods designed specifically for oxy-fuel systems. Compared to air-fired power plants, the flue gas volume is significantly lower in oxy-fuel and chemical looping combustion plants, due to the elimination of N<sub>2</sub> (downstream of the flue gas recycle, if present). The reduced volume flow leads to more compact systems, as compared to conventional power plants. However, the performances of the conventional methods in atmospheres with high concentrations of CO<sub>2</sub> is yet to be verified and the novel methods remain in the early-phase of development. Presented below are the most common measures for NO<sub>x</sub> and SO<sub>x</sub> removal (with the focus on secondary measures), as well as technologies proposed for simultaneous removal of these species in the high-pressure section of the flue gas train.

#### **Conventional methods for NO<sub>x</sub> removal**

A comprehensive review of the primary- and secondary measures applicable to the oxy-fuel technology has been provided by Normann et al.<sup>33</sup>. The most commonly used secondary measures in conventional air-fired power plants and industrial processes are selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). Selective reduction is based on the reaction of NO and ammonia (or urea) to form nitrogen and water:



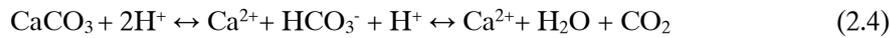
The reduction occurs in the temperature ranges of 800°-1100°C for SNCR and 300°-400°C for SCR. The effects of novel flue gas conditions on the performance of selective reduction or on the catalytic activity are yet to be demonstrated. Normann et al.<sup>33</sup> have predicted that although SNCR will have efficiency similar to those observed in air-fired systems, the increased concentration of CO<sub>2</sub> in the flue gas will change the operational temperature window, shifting to higher temperatures in oxy-fuel systems. Thus, SNCR must be placed in the recycle loop<sup>33</sup>.

The new conditions for the flue gas train in oxy-fuel and chemical looping systems, will allow for other possible locations for the SCR unit than what is seen for conventional flue gas systems<sup>6</sup>. As the cost of an SCR unit depends on the flue gas volume<sup>34</sup>, placing the SCR unit in the later stages of the CO<sub>2</sub>-conditioning might be economically favorable. Normann and co-workers<sup>33</sup> have suggested that the low-dust SCR option, i.e., downstream of the recycle loop and particle removal, might be favorable for oxy-fuel plants. Although Ritter et al.<sup>35</sup> tested the operation of an SCR unit in the pressurized flue gas train of an oxy-fuel plant and obtained satisfactory removal efficiencies, they claim that the pressurized SCR unit was not attractive in economic terms compared to alternatives. Another challenge faced by the application of SCR to oxy-fuel plants is the increased concentrations of SO<sub>2</sub>

and SO<sub>3</sub> in the flue gas, which reduce the performance of the SCR unit<sup>6,20</sup>. In addition, experiments by Fernández-Miranda and colleagues<sup>36</sup> have shown that a high concentration of CO<sub>2</sub> leads to a decreased efficiency of NO<sub>x</sub> removal through SCR.

### **Conventional methods for SO<sub>x</sub> removal**

The most commonly used flue gas desulfurization (FGD) process in large, air-fired combustion plants involves wet scrubbing using limestone (CaCO<sub>3</sub>)<sup>34</sup>. Similarly, the use of wet FGD with limestone for oxy-fuel power plants has been suggested and studied by several groups<sup>37-38</sup>. This process is based on the absorption of SO<sub>2</sub> by a limestone slurry, followed by oxidation according to the following reactions and the formation of gypsum as the final product:



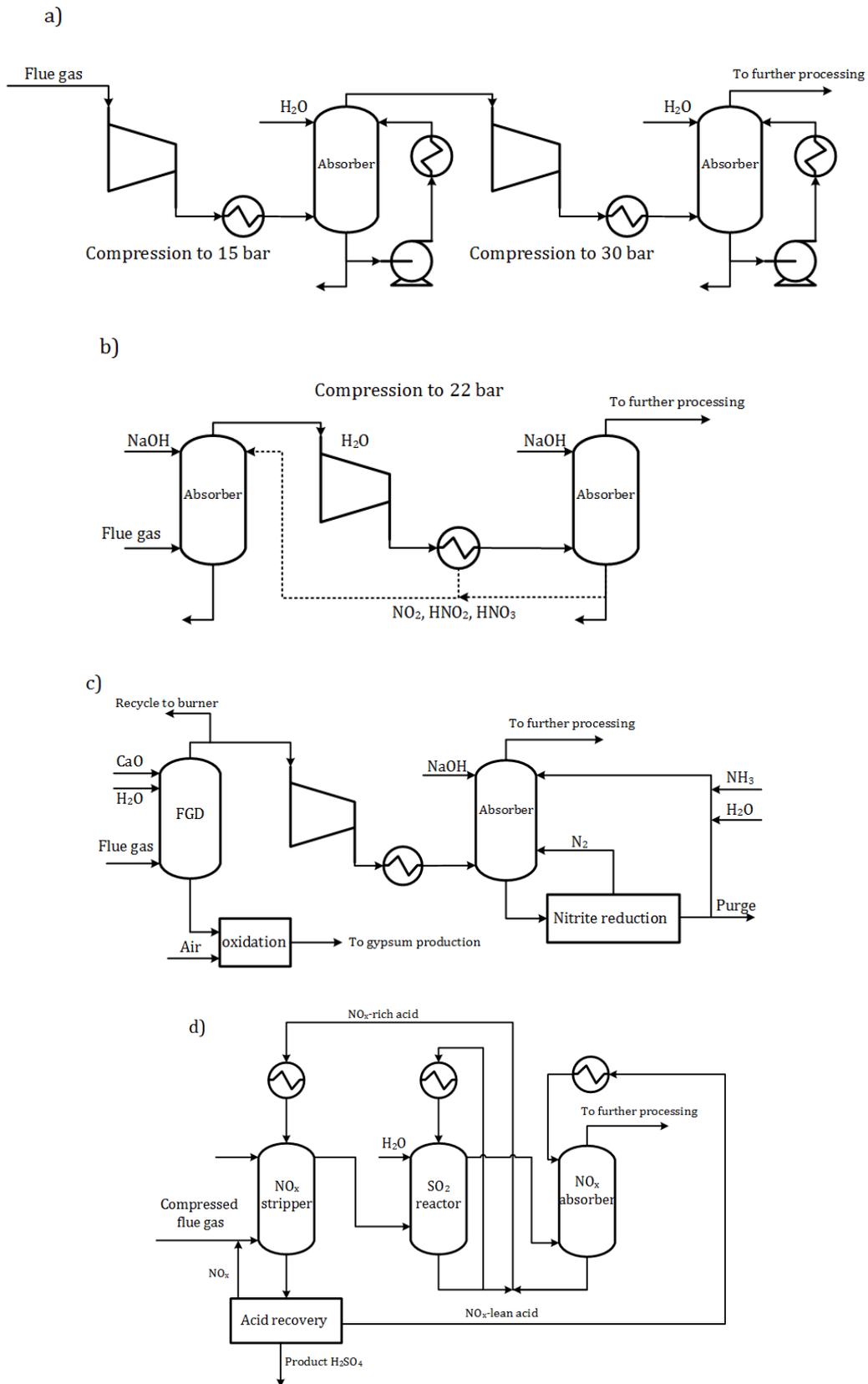
However, this system was originally designed to operate under air-fired conditions, and major differences exist in the composition of the flue gas (mainly in terms of CO<sub>2</sub>, acidic gas components such as SO<sub>2</sub> and SO<sub>3</sub>, and water vapor) between the oxy-fuel power plant and the air-fired power plant. In addition, in order to supply oxygen to the system for the oxidation of the hydrogen sulfite according to Reaction 2.5, air is added to the FGD unit in conventional power plants. This, however, can result in undesirable dilution of CO<sub>2</sub> with nitrogen. Alternatively, in oxy-fuel power plants, pure oxygen or a portion of the secondary recycle stream can be added to the desulfurization unit. An alternative is to add an external oxidation tank to avoid this problem, although the use of external oxidation tanks in wet FGDs applied to conventional power plants has certain disadvantages, related to plugging, scaling and lower efficiencies<sup>39</sup>.

The quality of produced gypsum should also be within certain specifications, so as to allow further utilization of the gypsum in, for example, the cardboard industry. A high partial pressure of the CO<sub>2</sub> in the flue gas could result in decreased dissolution of limestone in the solution, thereby increasing the amount of residual limestone in the gypsum<sup>38</sup>. Pilot-scale tests performed in the 30-MWth oxy-fuel power plant in Schwarze Pumpe have shown no major differences in quality of the gypsum compared to that produced under air-firing conditions<sup>37</sup>.

The performance of the wet desulfurization process under oxy-fuel conditions should be further investigated and verified. Studies performed to date in pilot- and laboratory-scale units have shown no significant change in and no fundamental problems with the performance of a conventional wet FGD scrubber<sup>38,40</sup>. This has been confirmed by the modeling work of Neveux et al.<sup>41</sup>.

## Pressurized flue gas cleaning

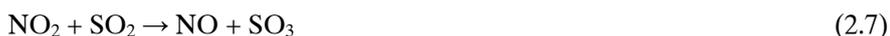
Concomitant with the development of the oxy-fuel technology, some absorption-based process concepts related to the pressurized flue gas systems have been put forward. Initially, Allam et al.<sup>42</sup> proposed the process of “sour compression” (Figure 2.2a), in which the flue gas comes in contact with water at two stages with operating pressures of at 15 bar and 30 bar, respectively, during the compression. According to Allam et al.<sup>42</sup>, SO<sub>2</sub> is expected to be removed primarily in the first stage, in the form of sulfuric acid, and NO<sub>2</sub> is removed in the second stage, in the form of nitric acid. Moreover, the use of alkaline sorbents in combination with sour compression has been suggested<sup>43</sup>. Trainer et al.<sup>44</sup>, have proposed a design in which an SO<sub>2</sub> scrubber is located prior to the compression and a pressurized absorber is used for NO<sub>x</sub> removal. Trainer et al.<sup>44</sup> have also proposed using NO<sub>2</sub> (and nitrogen acids) to enhance the SO<sub>2</sub> removal in the atmospheric scrubber. However, we found no published test results regarding the enhancing effects of N-S interactions. Subsequently, Liémans et al.<sup>45</sup> suggested the use in the scrubbers of acidic solutions that contain H<sub>2</sub>O<sub>2</sub>, to promote the formation of nitric acid and sulfuric acid. This concept is depicted in Figure 2.2b. An alternative concept presented by Winkler et al.<sup>46</sup>, called LICONOX (Figure 2.2c), is based on the removal of SO<sub>2</sub> prior to compression through conventional flue gas desulfurization (FGD) and NO<sub>x</sub> removal using ammonia in a pressurized alkaline scrubber. The nitrites formed as a result of selective absorption of NO<sub>2</sub> (through regulation of the pH level), is thereafter reduced to N<sub>2</sub> in a separate reactor. Winkler et al.<sup>46</sup> claim NO<sub>x</sub> removal rates  $\geq 90\%$ . Furthermore, Shah et al.<sup>47</sup> have presented a concept that is based on the use of sulfuric acid to remove NO<sub>x</sub> and SO<sub>x</sub> from a pressurized flue gas, with the eventual production of sulfuric acid and nitric acid, which is preferable for use with flue gases that contain high levels of SO<sub>x</sub> (around 1%)<sup>48</sup>. The process scheme is shown in Figure 2.2d. The compressed flue gas initially comes in contact with sulfuric acid in the NO<sub>x</sub>-stripper, so as to enrich the flue gas with the NO<sub>2</sub> that has been dissolved in the acid. The flue gas then enters the SO<sub>2</sub> reactor, where the SO<sub>2</sub> is to be converted to sulfuric acid. The authors claim that the sulfuric acid is produced via the “lead chamber process”. Finally, the remaining NO<sub>2</sub> is absorbed into sulfuric acid in the NO<sub>x</sub> absorber. The NO<sub>x</sub>-containing acid from the NO<sub>x</sub> absorber together and the sulfuric acid produced in the SO<sub>2</sub> reactor are recycled to the NO<sub>x</sub> stripper. The sulfuric acid from the NO<sub>x</sub> stripper is then fed into the acid recovery unit. Shah et al.<sup>49</sup> claim almost complete removal of SO<sub>x</sub> and around 75% NO<sub>x</sub> removal but have reported unsatisfactory performance from the NO<sub>x</sub> stripper.



**Figure 2.2.** Schematics of the proposed  $\text{NO}_x$  and  $\text{SO}_x$  cleaning concepts for a) Sour compression process (adapted from White et al.<sup>50</sup>); b) Process adapted from Trainer et al.<sup>44</sup>; c) LICONOX process, adapted from Winkler et al.<sup>46</sup>; d) Process adapted from Shah et al.<sup>47</sup>

### 2.3. Experimental research on pressurized flue gas cleaning

In the initial phase of the development of the oxy-fuel technology, i.e., from the early 1990's until 2005, it was assumed that most of the NO<sub>x</sub> and SO<sub>2</sub> in the flue gas would be captured together with CO<sub>2</sub><sup>25</sup>. In 2006, White et al.<sup>51</sup> presented a reaction pathway for the removal of NO<sub>x</sub> and SO<sub>x</sub> during flue gas compression. The proposed mechanism was based on the oxidation of NO to NO<sub>2</sub> by the O<sub>2</sub> in the flue gas (Reaction 2.1) and the eventual oxidation of SO<sub>2</sub> to SO<sub>3</sub> by NO<sub>2</sub>, which was considered to be a rapid reaction that lead to the formation of sulfuric acid:



In connection with this mechanism, Allam et al.<sup>42</sup> patented the sour compression concept, as described above. This concept prompted interest in experimental investigations of NO<sub>x</sub> and SO<sub>x</sub> behaviors in pressurized flue gas systems. These studies not only evaluated the potential for removal during compression<sup>32,52</sup> but also sought to identify corrosion issues<sup>27,53</sup> and the influences on downstream processes<sup>32,52</sup> experienced in the oxy-fuel combustion test facilities.

The sour compression concept was tested at the laboratory scale<sup>30</sup> and later at pilot scale using slip-streams from Doosan Babcock's 160-kW oxy-fuel pilot plant<sup>54</sup> and Vattenfall's 30-MW<sub>th</sub> oxy-fuel pilot plant in Schwarze Pumpe<sup>55</sup>. The laboratory-scale studies, published in 2011, showed that although the presence of NO<sub>2</sub> enhanced SO<sub>2</sub> removal, Reaction 2.7 was not significant in the absence of liquid water<sup>30</sup>. The pilot-scale studies, published in 2013, indicated that a significant level of oxidation of NO to NO<sub>2</sub> (around 50% for compression to 15 bar) could be achieved. Overall NO<sub>x</sub> removal efficiencies of >80% were reported<sup>55</sup>. The rate of SO<sub>2</sub> removal was found to be dependent upon the S/N ratio, and high rates of SO<sub>2</sub> removal (>80%) were achieved during flue gas compression. In addition, formation of N<sub>2</sub>O was observed at high S/N ratios—a phenomenon that could be neither explained nor controlled at the time.

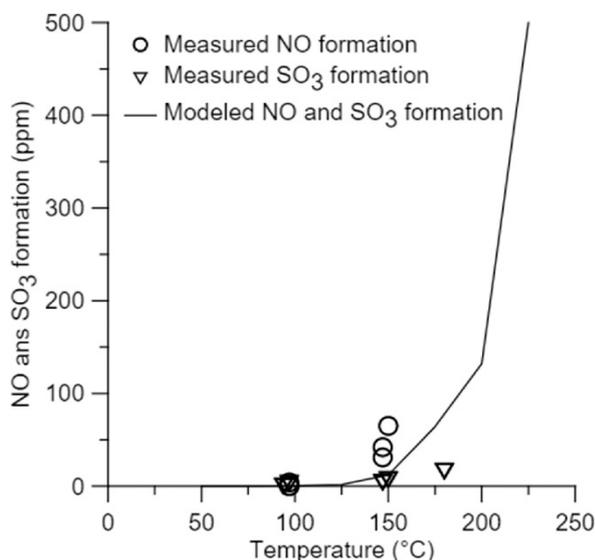
Starting in 2010, the LICONOX concept was tested in Vattenfall's 30-MW<sub>th</sub> oxy-fuel pilot plant in Schwarze Pumpe. Direct cooling of the compressors yielded 50% removal of NO<sub>x</sub> during compression to 18 bar. NO<sub>x</sub> removal rates of >90% were achieved in these tests at 15 bar<sup>46</sup>, although the rate of reduction to N<sub>2</sub> only reached around 23%<sup>35</sup>. A change in temperature within the range of 20°-50°C did not significantly affect the rate of removal of NO<sub>x</sub> in the absorber<sup>46</sup>.

Stanger and co-workers conducted series of experimental investigations at laboratory scale<sup>56</sup> and later using a slip stream from the Callide oxy-fuel pilot plant<sup>57</sup>, and examined the conversion of NO and absorption of NO<sub>x</sub> and the impacts on the SO<sub>2</sub> (and Hg) removal during compression, with the results being published in 2013<sup>56</sup> and 2015<sup>57</sup>. In general, increased pressure, prolonged residence time, and decreased temperature were identified as important factors for enhancing the rate of oxidation of NO to NO<sub>2</sub> and, consequently, the NO<sub>x</sub> capture rate. They observed a minor impact of SO<sub>2</sub> on the amounts of NO<sub>x</sub> captured during their tests, which suggests that the gas-phase

reaction of  $\text{SO}_2$  with  $\text{NO}_2$ , which would result in a reduction of  $\text{NO}_x$  capture (according to Reaction 2.7), is not important. They also observed enhanced capture of Hg as a result of the increase in the  $\text{NO}_2$  concentration during compression.

### Chalmers Experiments

In 2013, we performed gas-phase  $\text{SO}_2$ - $\text{NO}_2$  experiments (**Paper A**), to study the extent of oxidation of  $\text{SO}_2$  by  $\text{NO}_2$ . The results were compared to the modeling outcomes based on the available kinetics of Reaction 2.7 in the literature<sup>58</sup>. The oxidation of  $\text{SO}_2$  was shown to be negligible (<1%) even at temperatures up to 180°C, at high concentrations (10% inlet  $\text{NO}_2$  and  $\text{SO}_2$ , corresponding to about 3,300 ppm at 30 bar), and with residence times of minutes, as shown in Figure 2.3. Thus, the oxidation of  $\text{SO}_2$  in the presence of  $\text{NO}_2$  and water, as observed in the previous experiments<sup>30</sup>, takes place in the liquid phase.



**Figure 2.3.** Observed formation of NO and  $\text{SO}_3$  as products of the reaction between  $\text{SO}_2$  and  $\text{NO}_2$  in the gas-phase experiments (Ref: Paper A).

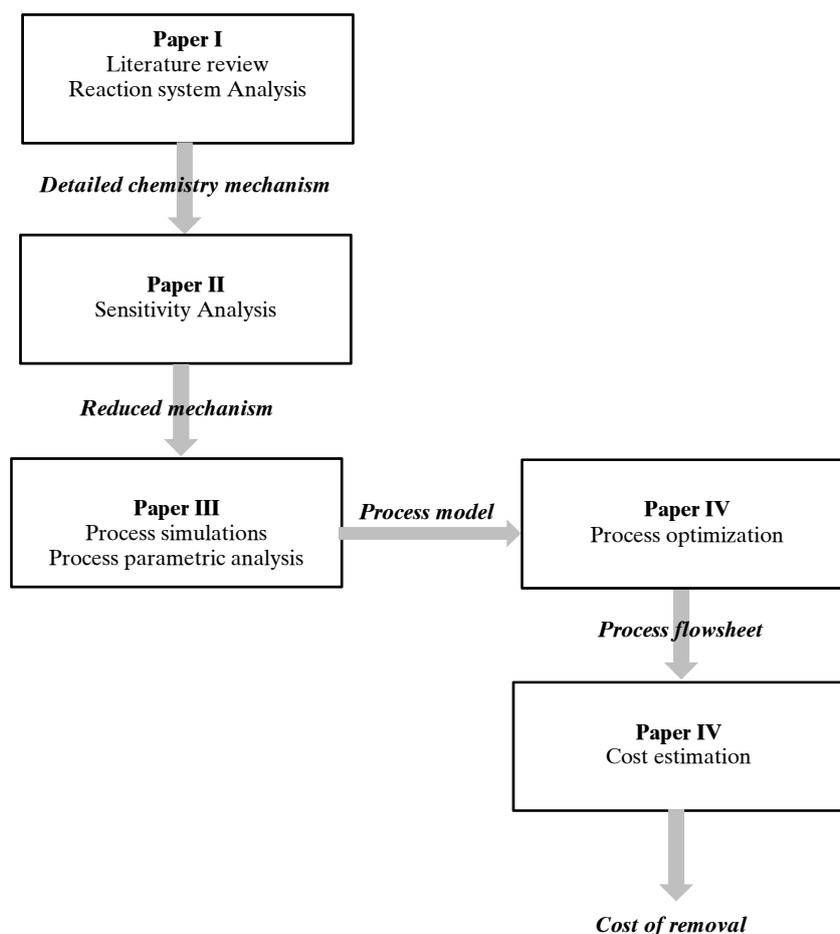
In summary, the experimental studies conducted at the laboratory and pilot scales show that substantial oxidation of NO to  $\text{NO}_2$  during flue gas compression (up to 30 bar) is possible. Pressure and residence time are identified as the main factors affecting the extent of oxidation. The simultaneous presence of  $\text{SO}_x$  and  $\text{NO}_x$  in the flue gas in contact with water allows interactions between the nitrogen and sulfur species, leading to the formation of sulfuric acid and  $\text{N}_2\text{O}$ , as observed in the previous experimental studies<sup>29</sup>. The interaction between  $\text{SO}_x$  and  $\text{NO}_x$  takes place in the liquid phase. It may also be concluded that the important interaction between  $\text{SO}_x$  and  $\text{NO}_x$  takes place in the liquid phase, which motivates the objective of this thesis to extend the understanding of the liquid-phase interactions between nitrogen and sulfur to be able to design efficient  $\text{CO}_2$  conditioning for oxy-fuel and chemical-looping combustion processes.



### 3. Methodology

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This thesis evaluates the chemistry, process performance, and design of the integrated removal of  $\text{NO}_x$  and  $\text{SO}_x$  in pressurized flue gas systems for oxy-fuel and chemical looping combustion systems. Figure 3.1 gives an overview of the methods applied in this work. The initial focus of the work is on the details of the chemistry with subsequent consideration of how flowsheets for the removal process can be established based on the knowledge gained in the previous steps. Initially, a detailed evaluation is carried out of the chemistry of the nitrogen and sulfur species based on literature review and analysis of all possible reactions (**Paper I**). The detailed chemistry model elucidates the possible interactions between the sulfur and nitrogen species when  $\text{NO}_x$  and  $\text{SO}_x$  are simultaneously absorbed into water. Thus, the reaction pathways of importance and the resulting products are identified. In addition, important factors that affect the formation of desirable products are pinpointed. In **Paper II**, further evaluation of the chemistry using a sensitivity analysis to provide insights into the relative levels of importance of the reactions generates reduced mechanisms, which facilitate the implementation of the chemistry in the process modeling tools with a more sophisticated description of mass transfer. In **Paper III**, important operating and design parameters for absorption-based removal systems in large scale oxy-fuel and chemical looping combustion systems are studied based on the mechanisms developed in **Paper II**. In **Paper IV**, all the acquired knowledge of process performance is integrated for evaluating a removal concept and its economic and technical performances, to provide novel perspectives on the practical issues related to commercialization of the integrated system for the removal of  $\text{NO}_x$  and  $\text{SO}_x$ . This chapter provides an overview on the modeling methods and assumptions applied in each paper. The modeling approaches are discussed in detail in each paper.



**Figure 3.1.** An overview of the methods applied in the thesis related to the topics covered in the appended papers

### 3.1. Development of reaction mechanisms

The detailed chemistry model, includes a complete set of possible homogeneous gas- and liquid-phase reactions for nitrogen and sulfur species for a  $\text{NO}_x/\text{SO}_x/\text{O}_2/\text{H}_2\text{O}$  system under conditions relevant to  $\text{CO}_2$ -conditioning in oxy-fuel and chemical looping combustion systems. A reactor model framework containing the kinetic reaction mechanism and a simplified description of mass transfer, shown in Figure 3.2, was developed using the MATLAB software. The gas- and liquid phases are modeled as two separate perfectly mixed batch reactors with equilibrium at the interface according to Henry's law. The mass transfer description is simplified at this stage of the work, as the mass transfer characteristics would be specific to the design of separation equipment. Nevertheless, the simplified description of mass transfer enables one to draw general conclusions as to the relative importance of the gas-phase and liquid-phase reactions, separately. In addition, sensitivity analysis of the reaction system based on the brute force method is applied to the reactor modeling framework for evaluation and simplification of the mechanism.

The kinetics of the reactions that are included in the reaction mechanism are compiled from well-established and experimentally validated data in the literature. The evaluations based on this reaction mechanism are, thus, qualitative compared to the experimental and demonstration studies on pressurized flue gas cleaning that were discussed in Chapter 2. An extensive literature review of the gas-phase and liquid phase chemistries of NO<sub>x</sub>-only and SO<sub>x</sub>-only systems forms the basis for the mechanism. The gas-phase chemistry of nitrogen oxides, as well as the absorption mechanisms of these gases in water, has been widely studied<sup>59-60</sup>. Similarly, the chemistry and absorption mechanisms of SO<sub>2</sub> are well-studied<sup>61-62</sup>. The presence of SO<sub>x</sub> in the system significantly increases the number of reactions that can occur due to interactions between nitrogen and sulfur species in the liquid phase. The N-S interactions in the liquid phase have previously been studied under atmospheric pressure in relation to atmospheric chemistry,<sup>63-65</sup> in relation to the effect of NO<sub>x</sub> on sulfur scrubber chemistry,<sup>66-68</sup> and with respect to the design of processes for the simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub><sup>69</sup>. A review of the current knowledge of the gas- and liquid-phase chemistry relevant to pressurized flue gas systems are presented in **Paper I**.

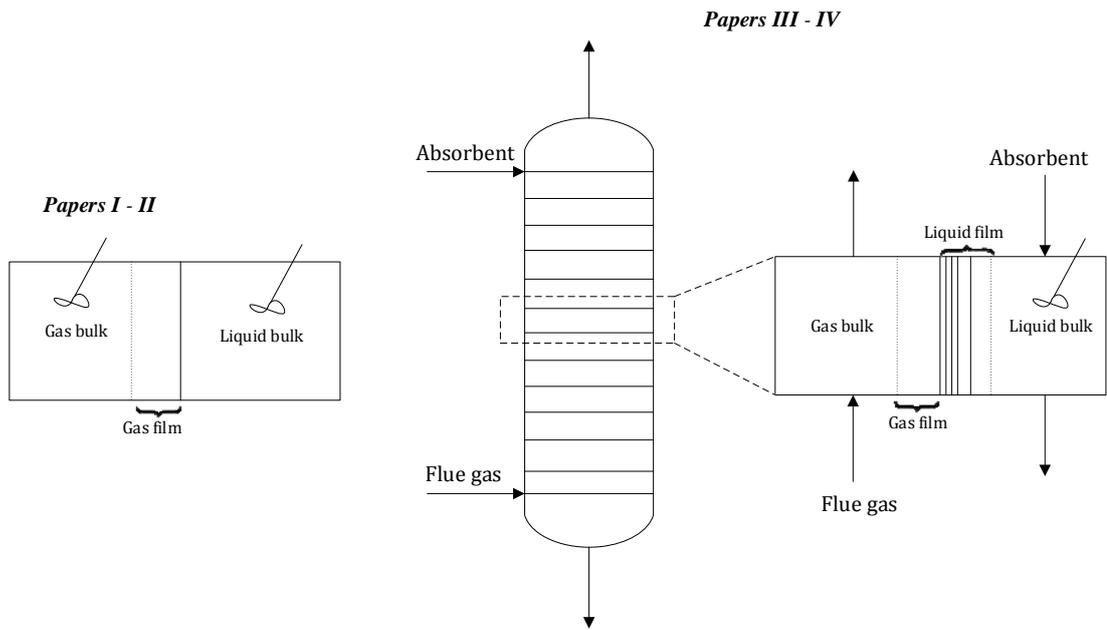
To facilitate the use of the advanced chemistry discussed in **Paper I** in engineering calculations for the design of integrated NO<sub>x</sub> and SO<sub>x</sub> removal processes, where implementing more sophisticated mass transfer descriptions is necessary, reduced reaction mechanisms are developed in **Paper II**. The reduced mechanisms are derived for specific pH levels by identifying the dominating reaction paths and rate-limiting reactions in the detailed chemistry model using sensitivity analysis. The rate-limiting and necessary reactions for the formation of the key products (identified in **Paper I**) at a specific pH were identified. The mechanism reduction was performed in steps: 1) Insignificant reactions and species revealed by the sensitivity analysis were omitted from the detailed mechanism to form the general reduced mechanism that is valid for the entire pH range (pH < 7). 2) Same as step 1 but for the identified pH ranges (i.e.  $1 \geq \text{pH}$ ;  $1 < \text{pH} < 4$ ;  $4 \leq \text{pH} \leq 5$ ;  $5 \leq \text{pH} < 7$ ) with significant differences in reaction chemistry to form the pH-specific reduced mechanisms. 3) Reactions were combined to form global reactions when possible.

### 3.2. Process simulations

Process simulations are performed in the Aspen Plus software for the design of the flue gas compression and integrated removal of NO<sub>x</sub> and SO<sub>x</sub> in **Papers III** and **IV**. The simulations considerations for the flue gas compressor are presented in **Paper III**. The general considerations for simulations of the absorber, which is the main unit in the integrated removal process, are presented below.

#### **Absorber model**

In order to design and predict the performances of integrated NO<sub>x</sub> and SO<sub>x</sub> removal processes in terms of the rate of absorption of NO<sub>x</sub> and SO<sub>2</sub> and the products formed in the liquid phase, a process model (steady-state) based on the reduced mechanism and a detailed description of the mass transfer is developed. Figure 3.2 illustrates the modeling strategy used. The absorber is divided into theoretical stages modeled with a rate-based approach<sup>70</sup>, which considers the rates of multicomponent mass transfer and chemical reactions. Mass transfer between the gas phase and the liquid phase is described by the concept of the two-film theory<sup>71</sup>, which is widely used in modeling gas absorption. This model assumes that the resistance to diffusion in each phase lies entirely in a thin layer adjacent to the phase interface and the mass transfer through these films occurs by steady-state molecular diffusion. Outside the films, in the gas and liquid bulk, the mixing is assumed to be sufficiently high so that there is no concentration gradient i.e. perfect mixing. The two-film model, although rather simple from a physical standpoint compared to the alternative models i.e. penetration theory and surface renewal theory, results in fairly similar prediction of the steady-state behavior<sup>72</sup> and is widely used in modeling the gas absorption processes. The multicomponent diffusion in the films is described by the Maxwell-Stefan approach<sup>73</sup> which takes into account the diffusional interactions between the components. The binary-diffusion coefficients are calculated based on the Chapman-Enskog theory (Chapman-Enskog-Wilke-Lee model)<sup>74</sup> for the gas components and Nernst-Hartley and Wilke-Lee models for the ionic and molecular species in the liquid phase, respectively. Properties such as mass transfer coefficients, interfacial area, volumetric gas and liquid holdup are estimated based on experimentally obtained correlations specific to the column internals. These correlations take into account the mass transport dependence on the physical properties and hydrodynamics of the process. Reactions in the liquid film, as well in the liquid and gas phases are considered.



**Figure 3.3.** Schematic overview of the modeling strategies for the absorber column used in the papers.

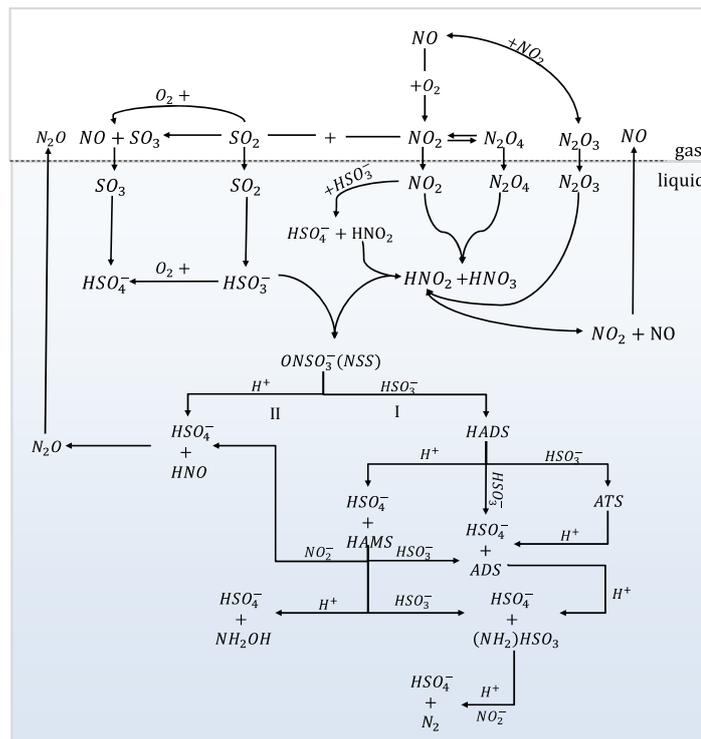
### 3.3. Process design and evaluation

Design of a compression and integrated NO<sub>x</sub> and SO<sub>x</sub> removal unit for large scale oxy-fuel and chemical looping combustion power plants was evaluated in **Paper IV**. The evaluation was based on technical aspects including removal efficiencies, and quality and amount of wastewater generated in addition to cost estimations. The comprehensive models of the absorber and the compressor were completed with a basic design flowsheet including the utilities and supporting equipment required. The obtained detailed equipment list provided the basis for the investment cost estimation of the integrated removal process. A detailed description of the process schematics and assumptions are presented in **Paper IV**. The primary criteria for the technical design of the integrated removal process was to attain removal rates similar to those commonly achieved using the “Best Available Techniques”(BAT)<sup>34</sup>, i.e. selective catalytic reduction and wet flue gas desulfurization using limestone.

Study-level cost estimations (typical accuracy of ±30%) are performed in **Paper IV** for different design alternatives that are applicable to coal- and biomass-based oxy-fuel and chemical looping combustion plants. The capital cost estimations use a bottom-up approach based on the main components in the flowsheet, which are estimated using the Aspen In-Plant Cost Estimator. The capital cost estimations use a bottom-up approach based on the main components in the flowsheet, which are estimated using the Aspen In-Plant Cost Estimator. The remaining associated costs, i.e., installation costs (based on individual units), process contingencies, and indirect costs are estimated based on the equipment costs. The operating costs are divided into: electricity; chemicals; process water; cooling water; maintenance; and labor. The total plant costs (TPCs), which included the costs for equipment, materials, construction labor, home office expenses, process contingencies, and project contingencies, are derived. Moreover, the specific cost of NO<sub>x</sub> and SO<sub>x</sub> removal is calculated.

## 4. Chemistry of NO<sub>x</sub> and SO<sub>x</sub> in pressurized flue gas systems

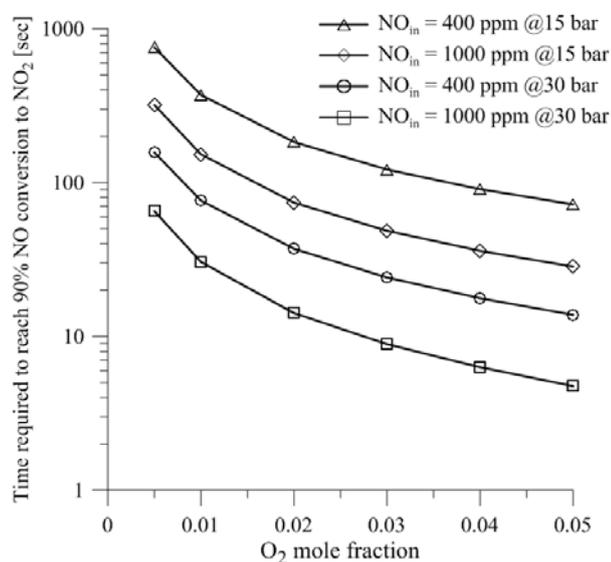
The chemistry of NO<sub>x</sub> and SO<sub>x</sub> in a pressurized flue gas system, which also contains O<sub>2</sub> and H<sub>2</sub>O, is presented in Figure 4.1 and discussed here. Findings of the present work regarding the reaction mechanisms (**Papers I and II**) and the important factors affecting the chemistry, as well as the implications for the design of oxy-fuel and chemical looping combustion power plants are presented.



**Figure 4.1.** Schematic overview of the reactions included in the detailed chemistry model which was developed in Paper I

#### 4.1. Gas-phase chemistry

The substantial gas-phase oxidation of NO to NO<sub>2</sub> that occurs under pressurized conditions is the most important gas-phase reaction for the pressurized flue gases and the most important difference from atmospheric systems. This reaction initializes the interactions between nitrogen and sulfur species in the liquid phase, as NO<sub>2</sub> dissolves readily in water and forms acids. At concentrations up to 2,000 ppm and even at pressures up to 30 bar, other species, such as N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>3</sub>, are not expected to be formed to any significant extent; thus, NO<sub>2</sub> is the main species that diffuses into the water. The gas-phase oxidation of NO to NO<sub>2</sub> is favored by increases in pressure and decreases in temperature. The kinetics of this reaction is well-studied over a wide range of temperatures and partial pressures, and there is general agreement between the kinetics reported by different groups. The validity of the kinetics for the pressurized flue gases has also been confirmed<sup>56</sup>, implying that the extent of NO oxidation in pressurized flue gas systems can be predicted with high confidence. The concentration of O<sub>2</sub> and the residence time are additional important factors influencing the rate of oxidation of NO to NO<sub>2</sub>. The effect of the O<sub>2</sub> concentration is of special relevance for the design of a CLC system, as more O<sub>2</sub> is added downstream of the fuel reactor to complete fuel conversion. As shown in Figure 4.2 and discussed in **Papers III** and **IV**, higher concentrations of O<sub>2</sub> (e.g., around 4%) are beneficial in terms of the cost effectiveness of the removal process, and O<sub>2</sub> concentrations <1% are not feasible for the pressurized removal of NO<sub>x</sub>.



**Figure 4.2.** Effects of O<sub>2</sub> concentration and pressure on the time required to achieve 90% conversion of NO to NO<sub>2</sub> for NO inlet concentrations of 400 ppm and 1000 ppm.

## 4.2. Liquid-phase chemistry

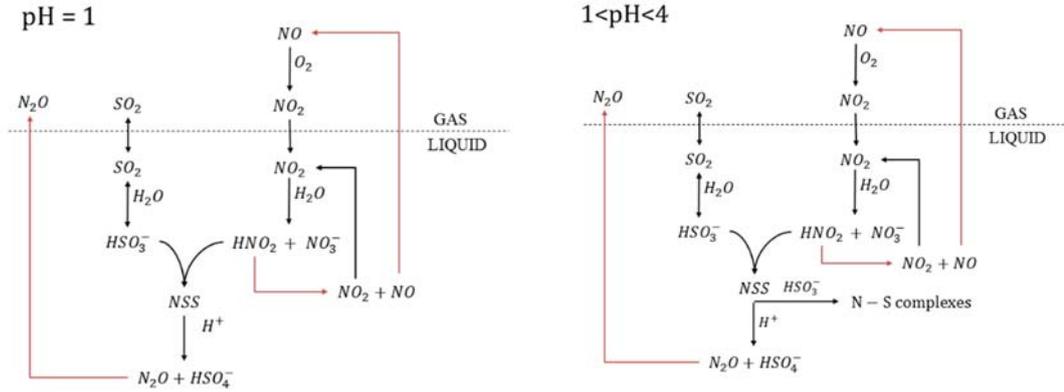
Once the NO<sub>2</sub> and SO<sub>2</sub> in the flue gas are dissolved into the liquid phase, various reactions may occur. Nitrous acid (HNO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>) form as a result of the kinetically controlled reaction of NO<sub>2</sub> with water:



The reaction of SO<sub>2</sub> in water is instantaneous and reversible, with the pH level having a strong effect on the dominating species:

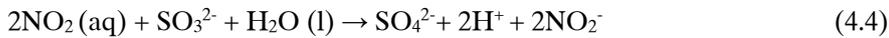
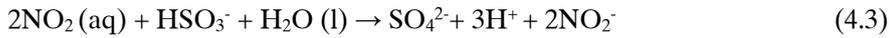


In the liquid phase, two types of interactions between nitrogen and sulfur species are possible: interactions between HNO<sub>2</sub> and HSO<sub>3</sub><sup>-</sup>; interactions between dissolved NO<sub>2</sub> and S(IV) (HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup>). The types of liquid-phase products and the reactions of importance are highly dependent upon the pH level in the liquid phase. Figure 4.3 presents the important reaction mechanisms for pH < 4 which were identified in **Paper II**. The differences in the reaction routes and products formed highlight the importance of pH for attaining high removal rates for NO<sub>x</sub> and SO<sub>x</sub>, as well as for avoiding the formation of unwanted products. Under very acidic conditions (pH ≤ 1), NO<sub>x</sub> may eventually be converted to N<sub>2</sub>O, and SO<sub>2</sub> may be oxidized to sulfuric acid, with the degree of conversion depending on the nitrogen-to-sulfur (N/S) ratio in the flue gas and the residence time. In addition to the formation of N<sub>2</sub>O, the decomposition of nitrous acid at low pH is undesirable with respect to the efficiency of NO<sub>x</sub> removal. Moreover, a large fraction of the absorbed SO<sub>2</sub> will be in the dissolved form [i.e., SO<sub>2</sub>(aq)] and in equilibrium with the gas phase according to Reaction (4.2). As a result, the liquid phase is unstable, in the sense that SO<sub>2</sub> can desorb to the gas phase upon any change in either the pH level or the partial pressure of SO<sub>2</sub>(g). This pH condition is particularly interesting in the context of the handling of the condensates formed during the multi-stage compression and cooling of flue gases. As the acid gases in the flue gas i.e., NO<sub>2</sub> and SO<sub>2</sub> dissolve into the condensate upon its formation, the pH level in the liquid drops. The pH value of the condensate depends on the amount of acid gases dissolved and the liquid-to-gas (L/G) ratio. A pH ≤ 1 is probable for the condensate from a pressurized flue gas system, as indicated by the results in **Paper IV**. This implies that upon depressurization, N<sub>2</sub>O, NO, and SO<sub>2</sub> are released from the condensate. For a pH level in the range of 1–4, two competing pathways will be active, one of which will result in the formation of N-S complexes, while the other will result in the formation of N<sub>2</sub>O and sulfate. The degree of competition between these two pathways depends on the pH level and the N/S ratio. This pH condition is mainly relevant for condensate handling systems and not for NO<sub>x</sub> and SO<sub>x</sub> removal processes, as high removal rates cannot be achieved.



**Figure 4.3.** Reaction mechanisms of importance for the pressurized flue gas systems for pH 1 and  $1 < \text{pH} < 4$ . The red lines indicate undesirable reaction routes. Note that  $\text{HNO}_2$  represents  $\text{HNO}_2 + \text{NO}_2^-$ . NSS refers to nitrososulfonic acid ( $\text{ONSO}_3^-$ ). The N-S complexes are mainly HADS, hydroxylamine disulfonic acid [ $\text{HON}(\text{SO}_3)_2^{2-}$ ], and HAMS, hydroxylamine monosulfonic acid ( $\text{HONHSO}_3^-$ ). Adapted from **Paper I**.

When the solution is mildly acidic, i.e.,  $\text{pH} > 4$ , high rates of  $\text{SO}_2$  absorption can be achieved and the formation of  $\text{N}_2\text{O}$  can be avoided. The N-S complexes are the main products of the N-S interactions. At  $\text{pH} > 5$ , reactions of  $\text{NO}_2$  and S(IV) become important:



This is of great importance for the removal process, as the rates of Reactions 4.3 and 4.4 are higher than the rate of  $\text{NO}_2$  reaction with water (Reaction 4.1). This means that the presence of sulfur can increase the absorption rate of  $\text{NO}_2$  via these reactions. It is known that the rates of the reactions between  $\text{NO}_2$  and S(IV) increase with increasing pH level, most probably due to increases in the  $\text{SO}_3^{2-}/\text{HSO}_3^-$  ratio, given that Reaction 4.4 is faster than Reaction 4.3<sup>75-77</sup>.

The N-S complexes (mainly hydroxylamine disulfonic acid (HADS) in the case of removal processes) can react further to drive the formation of hydroxylamine ( $\text{NH}_2\text{OH}$ ) or reduction of  $\text{HNO}_2$  to  $\text{N}_2$  and oxidation of S(IV) to sulfates, although the reaction system is complex. In addition, the residence times required to achieve these products are very long (in the order of hours for formation of  $\text{NH}_2\text{OH}$  for concentrations in pressurized flue gas systems) and the reduction to  $\text{N}_2$  is not expected even within days. Thus, the main N-S complex for the removal processes is hydroxylamine disulfonic acid (HADS), although hydroxylamine monosulfonic acid (HAMS) may form in the waste treatment system when the pH value is  $\leq 2$  and the residence times are in the order of hours, as shown in **Paper IV**.

## Uncertainties

As discussed in **Papers I** and **III**, a source of uncertainty in this work is the rates of Reactions 4.3 and 4.4. First, these reactions have not been studied at pH values <5, at which pH levels the interactions between HNO<sub>2</sub> and S(IV) are significant, thereby complicating the reaction analysis. Second, the reported kinetics of these reactions are discrepant in the literature. The pH-dependent rates reported for Reactions 4.3 and 4.4 by Clifton et al.<sup>75</sup> were used in the detailed chemistry model and the reduced mechanism. The values reported by Lee and Schwartz<sup>63</sup> and Shen and Rochelle<sup>67</sup> were about one order of magnitude lower than the values defined by Clifton et al.<sup>75</sup> The significance of the effect of the discussed uncertainty in relation to Reactions 4.3 and 4.4 on the design of a pressurized NO<sub>x</sub> and SO<sub>x</sub> absorber column, depends on the N/S ratio in the flue gas. The sensitivity of the estimated height of absorber, an important factor in the cost of the absorber, to a decrease in the rates of Reactions 4.3 and 4.4 is higher for a flue gas with a N/S ratio closer to 1. For instance, using the kinetics reported by Lee and Schwartz<sup>63</sup> in the reduced mechanism, results in a 5% higher cost of absorber for a flue gas with a N/S ratio of 1 and a 110% higher cost of absorber for a flue gas with a N/S ratio of 0.4 for achieving 90% NO<sub>x</sub> removal.

Another source of uncertainty in this work is the rate of oxidation of HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> by dissolved O<sub>2</sub> in the liquid phase, as described by:



The oxidation of S(IV) by O<sub>2</sub> in the flue gas, if significant, would decrease the enhancing effect of S(IV) on NO<sub>2</sub> absorption, which is important for the sizing of the absorber for simultaneous removal of NO<sub>x</sub> and SO<sub>x</sub>, as shown in **Paper III**. Although these reactions have been studied for various pH ranges, they are not fully understood. The reported kinetics are not in agreement, due to the high sensitivity of the reaction to the presence of impurities<sup>78</sup>, and it has not been established how the concentration of O<sub>2</sub> affects the rate of oxidation. In this context, the kinetics reported by Connick et al.<sup>79</sup> is not dependent upon the O<sub>2</sub> concentration, whereas Shen<sup>77</sup> has reported an increase in the rate of oxidation concomitant with an increase in the O<sub>2</sub> concentration. Although these reactions were not originally included in the models described in **Papers I** and **II**, the effect of including these reactions in the mechanism used in **Paper III** have been discussed briefly. The oxidation of S(IV) by the O<sub>2</sub> in the flue gas, as predicted by the rate reported by Connick et al.<sup>79</sup>, would not change the required packing height of the pressurized NO<sub>x</sub>-SO<sub>x</sub> absorber for a flue gas with inlet NO<sub>x</sub> =400 ppm and inlet SO<sub>2</sub>=400 ppm, while the required packing height will increase by 33% for a flue gas inlet NO<sub>x</sub> =400 ppm and inlet SO<sub>2</sub>=1000 ppm. The latter results in increased investment cost of the absorber by 5%. As several ionic species (such as ions of iron, manganese, and copper, in addition to chloride) and the ionic strength in the solution affect the rate<sup>79</sup>, the extent of oxidation should either be validated for a specific condition or chemicals that inhibit the oxidation process should be added to avoid this problem.

## 5. Design of the integrated NO<sub>x</sub> and SO<sub>x</sub> removal process

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### **Compression and intercooling**

For a full-scale multistage compressor with intercooling between stages, the rate of oxidation of NO into NO<sub>2</sub> depends on the design of the compression process-pressure levels, residence times in the intercoolers and the intercooling temperature. Due to the very short residence times in the compressors and high temperatures, the oxidation of NO to NO<sub>2</sub> is expected to occur in the intercoolers-more specifically the last intercooler with the highest pressure. A compressor design with active cooling is not considered suitable as it might trigger acid formation and corrosion inside the compressor. In **Paper III**, order-of-magnitude estimations of the residence times in the intercoolers were determined by designing the intercoolers as shell-and-tube heat exchangers. Evaluations in **Paper III**, revealed that the maximum 50% NO conversion can be reached during the multi-stage compression and cooling, with the degree of conversion strongly dependent on the O<sub>2</sub> concentration, as discussed earlier. In addition, although the pressurized NO<sub>x</sub> removal process would benefit from longer residence times in the intercoolers which could for example be attained by lower number of stages, as the compressor constitutes the major part (>85%) of the total cost of CO<sub>2</sub>-conditioning, the optimization of the compressor efficiency and cost is of higher priority. It was shown in **Paper III** that allocating residence time to the flue gas to enhance the NO oxidation prior to the absorber is needed to ensure BAT level efficiencies achieved by the process.

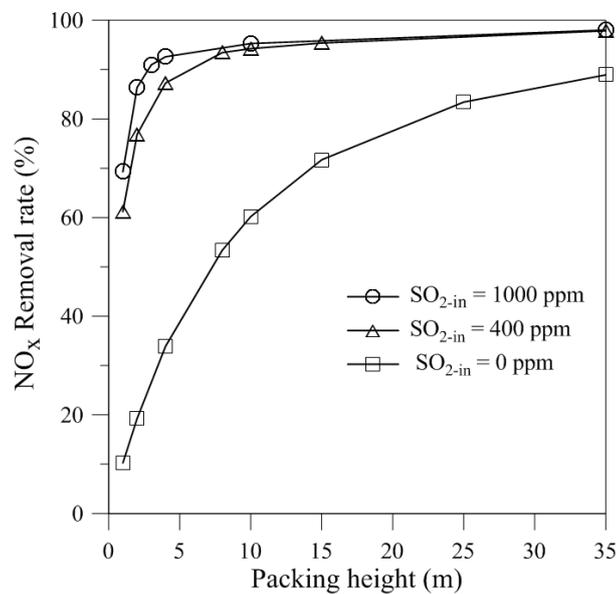
### **Absorption column: performance and cost**

The absorber column is the essential unit of the removal process. Using process simulations, suitable operating conditions are suggested and discussed. The evaluation is based on technical and economic aspects. This chapter includes results from **Papers III** and **IV**.

In the absorber, flue gas is introduced from the bottom of the column where it is counter-currently contacted with the absorbing solution which is fed from the top and distributed over a packing material. The primary role of the absorber is to absorb as much as possible NO<sub>x</sub> and SO<sub>2</sub> while avoiding the formation of N<sub>2</sub>O and consuming as little absorbing solution as possible. The latter is desirable both in terms of operating costs associated with the chemicals and costs of water treatment. In **Papers I** and **II**, pH was shown to significantly affect the selectivity and removal efficiencies of NO<sub>x</sub> and SO<sub>x</sub>. Thus, a caustic solution (NaOH; 50% w/w) is used to regulate the pH levels in the absorber. The absorber is operated in a closed-loop scheme i.e. a major part of the bottom liquid from absorber is recirculated after conditioning with NaOH and make-up water, so as to maintain the desired pH level and concentrations of reacting species.

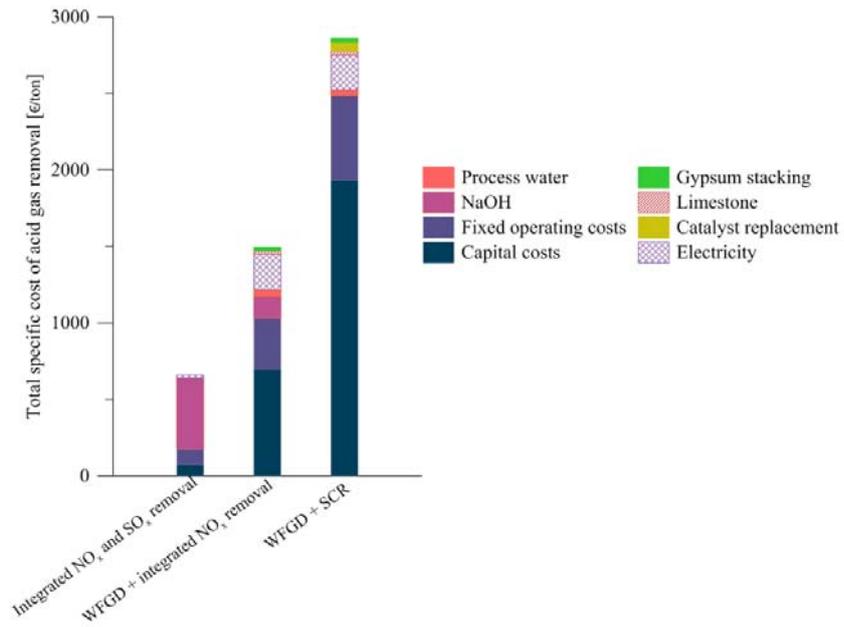
For a sulfur-containing flue gas, SO<sub>2</sub> absorbs completely if pH>4 and sufficient residence time for overcoming the mass transfer resistances is provided, as SO<sub>2</sub> is highly soluble in water and the

reactions of  $\text{SO}_2$  and water are instantaneous. The absorption of  $\text{NO}_2$  on the other hand, is much slower but is enhanced in case sulfur is present, either as  $\text{SO}_2$  in the flue gas or as added S(IV) in the absorbing solution e.g. by adding  $\text{Na}_2\text{SO}_3$ . Figure 6.1 shows the effect of packing height for varying  $\text{SO}_2/\text{NO}_2$  ratio in the flue gas with  $\text{NO}_2/\text{NO}_x = 90\%$  on the  $\text{NO}_x$  removal rate in a pressurized absorber. In absence of sulfur, much longer residence time (higher packing) is required due to much slower reactions in the liquid phase and the effect of packing height on the  $\text{NO}_x$  removal efficiency is more noticeable due to its effect on the  $\text{NO}_2$  absorption, while almost complete  $\text{NO}_2$  absorption may be achieved with a 4 m packing for a flue gas with  $\text{SO}_{2,\text{in}} = 1000$  ppm and the remaining effect of increased height is on the increased rate of oxidation of NO. On the other hand, only 90%  $\text{NO}_2$  removal is achieved with a 35 m packing for a flue gas with no  $\text{SO}_2$ . This implies an almost 200% difference in the installed cost of the absorber for these cases.



**Figure 5.1.** Effect of packing height on the rate of removal of  $\text{NO}_x$  at 30 bar for a flue gas with 4%  $\text{O}_2$ , 400 ppm  $\text{NO}_x$ ,  $\text{NO}_2/\text{NO}_x = 90\%$ . Adapted from **Paper III**.

**Paper IV** evaluates the costs associated with the integrated  $\text{NO}_x$  and  $\text{SO}_x$  removal and flue gas compression of oxy-fuel and chemical looping combustion systems. Figure 5.2 presents the total specific cost of acid gas (counted as  $\text{SO}_2$  and  $\text{NO}_2$ ) removal for the integrated removal concept, WFGD + integrated  $\text{NO}_x$  removal, and WFGD + SCR. The integrated removal processes have significantly lower costs of emission control compared to conventional  $\text{NO}_x$  and  $\text{SO}_x$  removal systems. On a  $\text{CO}_2$  capture cost basis, the cost for the integrated removal concept is around 5 €/tonne  $\text{CO}_2$  captured lower than the cost for a conventional flue gas system with WFGD and SCR. Assuming a total capture cost of around 50 €/tonne  $\text{CO}_2$ , the implementation of the integrated  $\text{NO}_x$  and  $\text{SO}_x$  removal would decrease the  $\text{CO}_2$  capture cost with around 10%. Thus, it is of great concern to consider the nitrogen and sulfur chemistry of pressurized flue gas systems to design cost efficient carbon capture with the oxy-fuel and chemical looping combustion technologies.



**Figure 5.2.** Total specific cost of acid gas (counted as SO<sub>2</sub> and NO<sub>2</sub>) removal for the integrated removal concept, WFGD + integrated NO<sub>x</sub> removal, and WFGD + SCR. The costs were calculated for a flue gas corresponding to 350 MW<sub>e</sub> with an electrical efficiency of 39%. It should be noted that the costs of associated with wastewater treatment, which is of importance for the integrated removal and WFGD systems, are not included in the cost estimations.

## 6. Conclusions

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The chemistry of NO<sub>x</sub> and SO<sub>x</sub> in pressurized flue gas cleaning systems were investigated. A detailed-chemistry model, with the main focus on the liquid-phase chemistry, was developed to uncover the reaction mechanism and the important parameters affecting the chemistry. Reduced mechanisms based on the essential and/or rate-limiting reactions in the detailed reaction mechanism were developed to facilitate engineering-related calculations of pressurized flue gas systems. The reduced mechanisms enable technical and economic evaluations of units for integrated removal of NO<sub>x</sub> and SO<sub>x</sub> with compression of flue gases in oxy-fuel and chemical looping combustion systems. The most important contributions of the work are:

- Identification of reaction pathways of NO<sub>x</sub> and SO<sub>x</sub> in the pressurized flue gas systems, which extends our understanding of the active chemistries in the system. The main findings are: 1) pH level has a significant effect on the selectivity of the liquid-phase chemistry, and 2) the areas in which additional research is required to boost confidence in the evaluation and design of integrated processes for the removal of NO<sub>x</sub> and SO<sub>x</sub> species. (**Paper I**)
- The reduced reaction mechanisms that capture the pH-dependency of the liquid-phase chemistry while taking into account the most important gas-phase and liquid-phase reactions while being applicable for engineering calculations and design. The reduced mechanism enables process evaluations of integrated NO<sub>x</sub> and SO<sub>x</sub> removal systems (**Paper II**).
- The extent of NO<sub>x</sub> control is identified as the defining factor for the process design of the removal process. The rates of NO<sub>x</sub> removal may be improved considerably by the presence of SO<sub>2</sub> in the flue gas (**Paper III**).
- Integrated removal of NO<sub>x</sub> and SO<sub>x</sub> together with flue gas compression achieves efficiencies as high as those of conventional cleaning processes, i.e., wet flue gas desulfurization with limestone and selective catalytic reduction, albeit with significantly lower costs for the removal process – the CO<sub>2</sub> capture cost (€/tonne) is reduced with around 10% with the integrated removal compared to a system with conventional emission control techniques (**Paper IV**).



## 7. Outlook

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We have developed a model that can be used for technical evaluations of new techniques for the simultaneous removal of  $\text{NO}_x$  and  $\text{SO}_x$  from the flue gases of combustion systems. Although the focus has been on pressurized systems, the enhancement of understanding of the liquid-phase chemistry and the developed model are valuable for the evaluation of atmospheric removal systems, for example, processes that apply an oxidizing agent prior to absorption. Considering the work and results presented in this thesis, the following key areas with respect to the understanding and design of flue gas trains for oxy-fuel and chemical looping combustion systems are proposed as topics for future investigations:

- Experimental investigations of the extent of oxidation of S(IV) in the liquid phase by the  $\text{O}_2$  present in the flue gas, as well as the  $\text{NO}_2$ -S(IV) reactions that take place under conditions relevant for pressurized flue gas systems. These will be important for accurately predicting and designing the integrated removal processes.
- To confirm the accuracy of the predictions made by the modeling, validation of the model for the operation of a technical-scale absorber is necessary.
- Techno-economic evaluations of the processes for treatment of the wastewater from the integrated process will be a determining factor in the commercialization of the integrated removal process.
- In order to improve the cost efficiencies of oxy-fuel and chemical looping plants, comprehensive optimization of flue gas cleaning, encompassing the boiler, downstream  $\text{CO}_2$  compression, the purification processes, and the transport and storage systems is needed.



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