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Emission control at pulp mills

A case study on the implementation of combined SO_x and NO_x removal technology

Master's thesis in Sustainable Energy Systems

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Abstract

In this study the implementation of a combined NO_x and SO_x scrubber at pulp mills are evaluated using Södra´s site in Mönsterås as a case study. The study aimed to evaluate how the current process would be impacted by implementing the scrubber when achieving the same emission reduction as the current best available technology for large combustion plants in regard to chemical consumption, needed process modifications and possibility to treat the scrubber effluent with the current wastewater treatment system. To achieve this a scrubber was designed and modelled using Aspen Plus investigating different sulfite oxidation rates and flue gas data was collected from the site. From the results it was concluded that the impact on consumption of chemicals was of low significance except for NaOH and oxidised white liquor and that the effluent should not be treated in the current wastewater treatment plant due to large amounts of sulfate in the effluent which if not removed can affect the wastewater treatment negatively. In regard to process modifications this depends on which oxidising agent is used, for H_2O_2 the right temperature conditions can already be achieved but for ClO_2 the temperature needs to be further decreased which could be achieved through flue gas condensation.

Keywords: SO_x, NO_x, pulp mills, recovery boiler, lime kiln, sulfite oxidation, wastewater treatment.

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Samuel Myrberg, Gothenburg, June 2024

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

SCR	Selective catalytic reduction
SNCR	Selective non catalytic reduction
BAT	Best available technology

Nomenclature

Below is the nomenclature of chemical compounds and gathering names of different chemical species.

Chemical compounds

SO_2	Sulfur dioxide
Na_2SO_3	Sodium sulfite
HSO_3^-	Bisulfite ion
SO_3^{2-}	Sulfite ion
$Na_2S_2O_3$	Sodium thiosulfite
$S_2O_3^{2-}$	Thiosulfate ion
SO_4^{2-}	Sulfate ion
HSO_4^-	Bisulfite ion
NO_2	Nitrogen dioxide
NO	Nitrogen monoxide
HNO_2	Nitrous acid
NO_2^-	Nitrite ion
HNO_3	Nitric acid
NO_3^-	Nitrate ion
HADS	hydroxylamine disulfonic acid
HCO_3^-	Bicarbonate ion
CO_3^{2-}	Carbonate ion
ClO_2	Chlorine dioxide
H_2O_2	Hydrogen peroxide
HCl	Hydrochloric acid
Na_2S	Sodium sulfid
NaOH	Sodium hydroxide

Gathering names

S(IV)	Gathering name for HSO_3^- and SO_3^{2-}
S(VI)	Gathering name for HSO_4^- and SO_4^{2-}
N(III)	Gathering name for HNO_2 and NO_2^-
N(VI)	Gathering name for HNO_3 and NO_3^-
Carbonates	Gathering name for HCO_2^- and CO_2^{2-}

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Introduction

Nitrogen oxides also known as NO_x is a pollutant well associated with high temperature combustion. About 95 % of the total NO_x formed during combustion is in the form NO while the other 5 % is NO_2 [1]. When reaching the atmosphere NO interacts with other gases in the atmosphere to form NO_2. NO_2 then contributes to impaired atmospheric visibility, climate change, radical build up in the troposphere and has a significant effect on the tropospheric ozone concentration through photochemical ozone formation as well as effects on human health. Other effects of NO_x emissions include acidification and eutrophication.

In the EU, measures are taken to improve air quality to reduce the negative impacts on human health and environment [2]. As part of these measures, emissions reduction commitments for the period 2020-2029 and 2030 and forward have been implemented which increases the regulations on emissions of NO_x and SO_x within the EU member states. In Sweden the emission reduction commitments for the period 2020-2029 have been achieved for both NO_x and SO_x as well as the 2030 and forward commitment for SO_x. However, to be able to comply with the 2030 and forward commitments for NO_x a further reduction of 40 % compared to the emissions in 2021 is needed cumulatively over all relevant sectors [3]. As a consequence of this it has been proposed that recovery boiler which previously have been excluded from the NO_x fee should be included and crediting should be reduced from 100 to 60 % which would mean increased costs for the pulp and paper industry [4]. Due to these possible changes in regulations Södra is looking to evaluate the possibility of implementing NO_x reduction measures to reduce the emissions from the lime kiln and recovery boiler.

The Swedish Environmental Protection Agency (Naturvårdsverket) have suggested multiple secondary measures to reduce NO_x emissions from the pulp and paper industry including selective catalytic reduction (SCR), selective non catalytic reduction (SNCR) and wet flue gas treatment with oxidation of NO to NO_2 [5]. SCR and SNCR are well established technologies for large combustion plants but have shown to be difficult to apply to recovery boilers [6]. Wet flue gas treatment with oxidation of NO to NO_2 is an emerging technology which have seen promising results for NO_x removal and is applied within the pulp and paper industry in Asia [7]. In Sweden this technology has been tested at pilot scale at a pulp and paper mill in which 90 % of the NO_x was removed from the flue gas [5]. The process is also well studied in terms of the oxidation of NO to NO_2 and the chemistry taking place during the absorption process [8–11]. There are also studies which have studied the

techno economical performance of the technology and it has also been evaluated at pilot scale at a waste to energy plant where it was also investigated if the scrubber effluent could be treated by incineration [12] [13]. All these studies have studied the general applicability of the technology but to be able to validate the technology even further, more case specific studies have to be performed which take into consideration the site specific conditions.

1.1 Aim

The aim of this study is to use Södra´s site in Mönsterås as a case study to investigate the performance of the scrubber technology given the conditions at the site. This will include identifying limitations and possible process modifications that needs to be done to be able to implement the technology in an efficient manner. Hence, the relationship between NO_x and SO_x in the flue gas will be investigated as well as the dimension of the scrubber or scrubbers needed to achieve adequate emission reduction from the combustion processes at the site. It will also be investigated how the scrubber will affect the current consumption of process chemicals relative to today's consumption. Also, the possibility to treat the scrubber effluent using the current wastewater treatment process at the site will be discussed. The consumption and needed conditions for efficient oxidation of NO for two oxidising agents, ClO_2 and H_2O_2, will also be discussed as well as where in the processes these conditions can be achieved.

1.2 Background

In this section the company Södra is introduced along with the general measures that are used for NO_x and SO_x removal and the current best available technology for NO_x and SO_x removal within the pulp and paper industry. At the end of this section the wet flue gas treatment with NO oxidation is also further introduced.

1.2.1 Södra Cell Mönsterås

Södra is one of the largest cooperative companies in Sweden which operates in the forestry and wood industry with over 50 000 forest-owners, providing the forestry raw material. The company is divided into four business areas Södra Skog, Södra Wood, Södra Cell and Södra Innovation. Production ranges from a broad set of products and services such as sawn wood products, building systems, pulp, liquid bio-products, and renewable energy. The company's total turnover was approximately 33.4 billion SEK year 2022. There are three pulp mills within Södra Cell located in Värö, Mönsterås and Mörrum. These pulp mills are world leading producers of mainly paper pulp, but also textile pulp with a total annual production of 1.9 million tons. The pulp is chemically produced from both softwood and hardwoods, which can later be used to make high-quality products such as tissue or writing paper [14].

This project will be carried out at Södra Cell Mönsterås which is a kraft paper pulp mill located on the eastern coastline of Sweden. The pulp mill has a production capacity of 750,000 tons of coniferous and leafy wood per year. Besides paper pulp, green electricity is produced together with a recently integrated bio-methanol plant. The paper mill also provides municipal district heating, extraction of tall oil and terpentine [15].

1.2.2 General overview of NO_x reduction measures

In this section general NO_x emission reduction measures will be discussed both on a primary level and secondary level. On a primary level the techniques discussed are air staging, flue gas recirculation, fuel staging, lowering the excess air, reduce air preheat, water/steam injection and installation of low NO_x burners. For secondary measures the technologies discussed are SCR and SNCR.

Air staging is a technique in which NO_x emissions reduction is achieved by introducing two or more combustion zones where the stoichiometric relationship between fuel and air is varied between the zones. In a system with two combustion zones the primary zone would have a substoichiometric relationship between fuel and air to limit the conversion of fuel bound molecular nitrogen to NO_x as well as limiting the formation of thermal NO_x by lowering the combustion temperature. While in the secondary zone the relationship between fuel and air is over stoichiometric conditions to achieve burn out of the fuel while also increasing the volume of gas resulting in a lower temperature and reduced thermal NO_x formation [16].

Flue gas recirculation is a technique in which NO_x formation is reduced by recirculating flue gas into the combustion zone. This limits the availability of oxygen while also reducing the temperature of the flame which reduces the conversion of fuel bound NO_x and formation of thermal NO_x [16].

Fuel staging is a technique similar to air staging in which the stoichiometric relationship between fuel and air is altered. The objective of this is technique is on the contrary not to limit the formation of NO_x but rather the conversion of formed NO_x back to molecular nitrogen. This is done through the creation of three combustion zones, in the primary zone a majority of the fuel is burnt out with excess air. In the secondary zone more fuel is added which creates a substoichiometric atmosphere in which hydrocarbon radicals are formed which in turn react with NO_x and reduces the NO_x back to molecular nitrogen. The combustion of the fuel is then completed in the third zone by supplying excess air [16].

Other measures that can be taken to reduce NO_x emissions are performing the combustion with low excess air, reduce the air preheat, water/steam injection and installing low NO_x burners. Lowering the amount of excess air to the minimum need for complete combustion reduces the NO_x emissions by limiting the oxygen available, thereby reducing the amount of fuel bound nitrogen converted to NO_x and to some extent the formation of thermal NO_x. Reducing the air preheat or injecting water/steam into the combustion chamber reduces the flame temperature and thereby reduces the amount of thermal NO_x formed. Low NO_x burners applies the principles of either, air staging, flue gas recirculation, fuel staging or a combination of the three mentioned techniques to achieve reduced NO_x emissions [16]. Selection of fuel can also be used as a measure to reduce NO_x emissions by selecting a fuel with low nitrogen content meaning there is less fuel bound nitrogen that can be converted to NO_x and choosing a fuel with limited combustion temperatures to reduce thermal NO_x formation [6].

SCR is a technique in which a reducing agent, ammonia or urea, is used to reduce NO_x back to molecular nitrogen in the presence of a catalytic bed. The reducing agent is injected into the flue gas before entering the catalytic bed and the reaction takes place on the surface of the catalyst. Optimum operating temperature is in the range between 300-450 °C [16].

SNCR is a similar technique to SCR where a reducing agent, ammonia or urea, is used to reduce NO_x back to molecular nitrogen but without the presence of a catalyst. The reducing agent is injected directly into the flue gas where the reaction takes place. Due to there being no catalyst present SNCR operates at a higher temperature window between 800-1100 °C [16].

1.2.3 Current best avialable technology for pulp and paper industry

The techniques that are regarded as the best available technology (BAT) for NO_x reduction in the lime kiln are selection of fuel, optimised combustion and operation or installation of low NO_x burners [6]. Where optimised combustion includes good mixing between fuel and air as well as other measures like air staging, controlling the amount of excess air and optimising the temperature of the secondary air [6]. In addition to these, optimising flame shape, position and temperature profile is also included in optimised combustion. In regard to optimised operation the parameters included are controlling the lime mud flow as well as optimising the kiln speed, feed

rate and fuel rate [6].

The recommended measures for SO_x removal in the lime kiln is to use a fuel with low sulfur content to limit the amount of sulfur that can be converted to SO_x and ensuring enough excess oxygen to achieve complete burnout of the fuel. Other measures that can be taken that is not related to the choice of fuel is installation of alkaline flue gas scrubbers which have the possibility to remove >90 % of the flue gas SO_2 content [6].

For reducing the emissions from the recovery boiler the current best available technology is computerised combustion control with good mixing of fuel and air while also implementing a staged air system [6]. Other techniques like selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) has also been proposed as possible NO_x reduction measures but are seen as emerging technologies and not best available technology [6].

SNCR have shown a potential to reduce NO_x emissions in between 30-50%. To implement SNCR in existing recovery boilers the boiler would have to be retrofitted with the addition of injection ports for ammonia in the upper part of the boiler to create a chemical reactor. The limitations of SNCR can be associated with the narrow temperature band and the varying load of the recovery boiler which move the position of the optimal operational window causing varying efficiency of NO_x reduction. Parameters that affect the efficiency is the mixing between ammonia and air as well as being able to provide enough residence time in the optimal operational window. Operating outside this window might also cause other problems including ammonia slip if the temperature is to low and if the temperature is to high, ammonia is oxidised to NO_x [6].

Based on performance of the technique in other sectors SCR has the potential to reduce the NO_x emissions between 70-90% in a recovery boiler with higher efficiency in regard to reducing agent compared to SNCR. The limitation of the technique is ensuring a low dust flue gas with low SO_x content to not affect the durability of the catalyst [6].

The recommended measures for SO_x removal from the recovery boiler is to increase the dry solid content of the black liquor as well as installing wet scrubbers as discussed for the lime kiln. Increasing the dry solid content of black liquor reduces the SO_x emissions by increasing the temperature of the combustion which allows more sulfur to react with sodium to form Na_2SO_4 and by driving away sulfur from the black liquor before it enters the recovery boiler, decreasing the sulphidity of the black liquor. By decreasing the sulphidity of the black liquor the amount of sulfur in relation to sodium decreases and ensure that a majority of sulfur present can react with sodium which reduces the amount of SO_x that can be formed [6]. There are, however, some adverse effects of increasing the dry solid content as higher temperatures might cause increased emissions of NO_x [6].

1.2.4 Combined NO_x and SO_x removal technology

Recent studies indicates that coabsorption of SO_x and NO_x techniques with NO oxidation can achieve >90% NO_x removal with >99% SO_x removal. In this technique

an oxidising agent such as O_3, H_2O_2 or ClO_2 is injected into the flue gas to make the nitrogen oxides more soluble in water by oxidising NO to NO_2. SO_2 is adsorbed spontaneously to water with solubility being limiting. When dissolved, SO_2 reacts with water to form bisulfite which forms sulfite through a dissociative equilibrium reaction which is weighted towards sulfite under alkaline conditions. Sulfite then interacts with the dissolved NO_2 through hydralization which take place at a comparable rate to that of SO_2 absorption to water, allowing for efficient coremoval of NO_x and SO_x in a wet scrubber like equipment used for SO_x removal [10]. This method is heavily dependent on the coexistence of sulfur and nitrogen in the flue gas to achieve high removal efficiency of NO_x. In the case of combustion of sulfur deficient fuel, Na_2SO_3 can be added in the scrubber liquid to increase the removal efficiency of NO_x, however, this is associated with increased operational cost [10].

2

Theory

In this chapter the kraft pulping process is introduced along with general information about the recovery boiler and lime kiln which both have an important role in the kraft process. Also presented in this section, is the formation of emissions such as NO_x, SO_x and HCl in these units and an introduction to the wastewater treatment process used at Södras site in Mönsterås. Lastly the scrubber used for combined SO_x and NO_x removal is introduced in higher detail regarding the oxidation and absorption process.

2.1 The kraft process

The kraft process that is performed at Södra is a method of transforming wood into wood pulp. Wood pulp mainly consists of cellulose fibers and is the main component in paper production. The process is known for its ability to break down the wood chips into pulp by the use of a mix of white liquor and water. White liquor is a solution that consists of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) [17].

The process includes a series of steps, and the main parts are preparation of wood chips, cooking, washing, bleaching, and drying. The wood chip preparation is the start of the process where the wood, softwood or hardwood, are debarked and chipped into small pieces. The cooking stage takes place in the pulp digester, where the white liquor and steam are added. The purpose is to break the bonds between lignin, hemicellulose, and cellulose in the wood and remove the lignin by dissolution. After cooking, the pulp is washed to remove the spent cooking chemicals and lignin. The washing plant is also considering chemical recovery, chemical demand in subsequent bleaching steps as well as obtaining a clean product. The product is then bleached to further remove color and improve brightness. Various chemicals like chlorine, chlorine dioxide, hydrogen peroxide, or oxygen can be used in this step. When the desired result is obtained the pulp needs to be dried to achieve the right moisture content. The final wood pulp product can then be used to manufacture paper and other cellulose-based products [17].

Furthermore, one of the key features in the Kraft process is the high chemical recovery efficiency. Figure 2.1 shows a simplified flowsheet of the kraft recovery process that includes the cooking chemical cycle and the lime cycle. This stage of the process enables recycling of pulping chemicals (NaOH and Na_2S), which minimize chemical consumption, and also creates energy generation due to the combustion of black liquor in the recovery boiler [18].

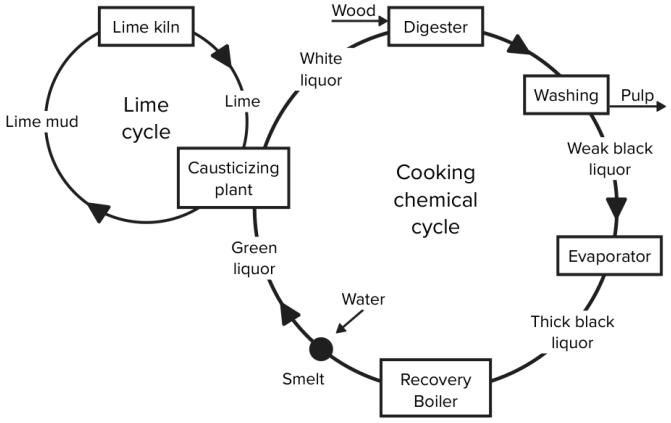


Figure 2.1: The kraft recovery process.

In figure 2.1, it can be shown that when cooking in the digester, black liquor formation occurs that contains dissolved lignin, spent cooking chemicals, and other by-products. When washing the pulp the weak black liquor is separated from the pulp and enters the multi-effect evaporators to remove water content and obtain thick black liquor. The recovery boiler burns the black liquor which generates heat and releases sodium compounds consisting mainly of sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S) which forms the so-called char bed or molten smelt. The smelt is then extracted from the recovery boiler and enters a smelt dissolver tank where the sodium compounds are dissolved in water to form green liquor [19]. The green liquor then enters the causticizing plant. Here, the burned lime (CaO) from the lime kiln reacts with water to form $Ca(OH)_2$, also known as 'slaked lime'. The calcium hydroxide is then mixed with the green liquor (Na_2CO_3) in causticization vessels and the reaction forms NaOH and $CaCO_3$ as can be seen in Equation (2.1) [20].

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3 \tag{2.1}$$

Calcium carbonate is separated from the white liquor and rewashed before being fed back into the lime kiln for reburning, closing the lime cycle. Na_2S as being part of the green liquor goes through the whole causticizing process and ends up in the white liquor makeup together with the sodium hydroxide. The white makeup liquor is returned to the digester for reuse in pulping [20].

As mentioned, the recycled lime ($CaCO_3$) from the white liquor preparation enters the rotary lime kiln together with makeup lime mud. The lime sludge is then heated to a high temperature and reburnt into calcium oxide which can be fed back to the causticizing plant. The reaction that takes place in the lime kiln can be seen in Equation (2.2).

$$CaCO_3 \rightarrow CaO + CO_2 \tag{2.2}$$

The causticization process requires approximately 250 kg of calcium oxide per tonne of pulp produced. Therefore, the lime cycle is a very important part of the pulp mill

process and is essential to avoid expensive costs of makeup lime [20].

2.1.1 The lime kiln & recovery boiler

In general, the lime reburning process is divided into four stages: drying, heating, calcination, and cooling. The cylindrical rotary lime kiln is fed with lime mud at the feed end and the lime flows towards the burner end of the kiln due to the tilting of the kiln. The kiln is equipped with a burner at the lower end which combust biomass. The combustion gases moves counter-currently toward the feed end, heating the kiln, and the moisture of the lime evaporates. The calcination begins when the temperature exceeds approximately 820 °C and the reaction is greatly accelerated by temperature increase. The appropriate temperature for calcination is approximately 1100 °C. The flue gases exit the kiln from the feed end, where the concentration of CO_2 is as highest. Lastly, the burned lime (CaO) is cooled before leaving the kiln [21].

The purpose of the recovery boiler, other than recovering cooking chemicals, is to use thick black liquor as a source of fuel to produce steam. Heat released from the combustion of the organic matter of the lignin can be recovered as super-heated steam with high temperature and pressure. The super-heated steam can further be used for providing various processes in the pulp with high pressure steam, electricity by expanding the steam through a steam turbine and after expansion of the steam it can either be used in process or to supply district heating. The thick black liquor, having a dry solid content of 65-85 %, is obtained from the evaporation steps and sprayed into the lower part of the recovery boiler. The molten smelt containing mainly Na_2CO_3 and Na_2S is formed due to combustion in flight when the black liquor is burned in an oxygen deficient environment. The air supply to the recovery boiler is regulated at different sections of the boiler through primary, secondary and tertiary air nozzles to ensure optimal combustion conditions [19]. According to the International Flame Research Foundation, a mixture of 90 mole% Na_2CO_3 and 10 mole% Na_2S has a melting point of 760 °C and is fully molten at 830 °C [22].

In general, the flue gas composition from both the recovery boiler and lime kiln has some similarities as they operate by the same air combustion principle. These flue gases consists mainly of CO_2, CO, nitrogen and sulfur oxides and total reduced sulfur compounds (TRS) [21]. However, some compound formations differs a bit comparing the two unit operations. For example the make-up lime does not purely consist of $CaCO_3$. Approximately 5% dry content of lime mud are impurities where the highest concentrations are Na_2O followed by MgO, SO_3, P_2O_5 , SiO_2, Al_2O_3, Fe_2O_3, and K_2O. Na_2O and K_2O represent the total alkali content of the lime and the sodium compounds together with SO_3 reacts into Na_2SO_4 through the lime burning. The sodium sulphate is easily extracted from the kiln to the causticizing plant due to its low melting point. Note that the composition of lime mud varies from mill to mill depending on which wood species is used and on the efficiencies of the process units in the lime cycle and more [23].

During lime burning, mud ring formations occurs as CaO and reacts with high concentrations of CO_2 inside the kiln and is re-carbonated into $CaCO_3$. This hardening of ring deposits on the surface of the kiln is strongest at temperatures

around 750 ℃. Hardening of $CaSO_4$ may also occur with higher concentrations of SO_2 and SO_3 when temperatures exceeds 900 ℃, but at normal kiln operating conditions this is not as common. Ring formation is one of the most troublesome problems with kiln burning and requires extensive kiln shutdowns for ring removal [23].

The elemental composition of the kraft black liquor is a share of approximately 2/3 organic compounds and 1/3 inorganic compounds when producing pine and birch kraft paper [17]. The organic part refers to the residual lignin and hemicellulose removed from the pulping process and the inorganic part consists mainly of sodium salts, Na_2SO_4 and NaOH, but also solid sulfur. These sodium and sulphur compounds can be added as make-up chemicals to the black liquor to better utilize the reduction of sodium for green liquor formation. Smaller fractions of potassium, chloride, nitrogen, calcium and magnesium salts are also present in the black liquor [24].

2.1.2 Wastewater treatment plant

The water treatment facility at Södra Mönsterås consists of three sedimentation steps and two oxygenating steps. Before entering the waste water treatment plant the waste streams are cooled to a temperature around 37 °C. In the first sedimentation step course particles such as fibers are separated from the liquid, the waste water then continues to the ANOX basin. Before entering the ANOX basin the pH of the wastewater is adjusted to be within the band of 6.5-8.5 and phosphoric acid is added to the wastewater to supply phosphorus as a macro-nutrient due to phosphor deficiency within the waste water treatment plant. When entering the ANOX basin the waste water is aerated which allows the microorganisms to decompose organic materials. After the ANOX basin the waste water continues to the LUZON basin where the waste water is further aerated and the organic matter further decomposed.

In the process of decomposing these materials the microorganisms clump together through flocculation which allows them to also trap fine particles and form a sludge. The waste water with the formed sludge then enters the second sedimentation step where the sludge settles and is separated from the liquid. Some of the sludge from the second sedimentation step is then recirculated to the LUZON basin to continue participating in the cleaning process while some sludge is removed to maintain a good balance between microorganisms and available organic matter. This removed sludge is then dewatered in a sludge press and later on combusted in the bark or recovery boiler. The water from the second sedimentation steps continue to the third and last sedimentation step where most of the remaining particles are allowed to settle before the water exits the waste water treatment plant. In Figure 2.2 the complete waste water treatment proccess can be seen.

Figure 2.2: Södra Mönsterås water treatment system.

This is how the waste water treatment operates during the current conditions at Södra Mönsterås where they use chlorine free treatment of the pulp. If they where to start treating the pulp with chlorine dioxide the operation of the waste water treatment system would change to also be able to handle chlorate. In this case the ANOX basin would no longer be aerated to be able to reduce chlorate.

2.1.2.1 Microorganisms in the wastewater treatment plant

The active microorganism in the wastewater treatment process are heterotrophs which obtain carbon from decomposing organic compounds. Based on whether the specie use organic or inorganic compounds the hetrotrophs are further divided into the groups organotrophs and chemohetrotrophs respectively. In the case when the specie use both organic and inorganic compounds they are refereed to as chemoorganoheterotrophs, which is the group that most bacteria belong to. These organisms can either decompose organic compounds through fermentation, respiration or anaerobic respiration. Fermentation takes place when organic compounds are decomposed in the absence of oxygen and respiration when oxygen is present. Anaerobic respiration is when organisms use other substances than O_2 for respiration like NO_3^- or SO_4^{2-} to obtain oxygen [25].

2.2 Exhaust gas composition

In this section theory behind the formation of NO_x, SO_x and HCl in the recovery boiler and lime kiln is presented.

2.2.1 Nitrogen oxides

There are three main routes of nitrogen oxide formation during combustion, these three routes are thermal, fuel and prompt NO_x. Thermal NO_x is primarily formed at high temperatures in a fuel lean environment where there is a high availability of oxygen. The formation of thermal NO_x can be described by the Zeldovich mechanism as in reactions 2.3 to 2.5 [26] and is thought to be the main route for NO_x formation in lime kilns [21].

$$N_2 + O \rightleftharpoons NO + N \tag{2.3}$$

$$N + O_2 \rightleftharpoons NO + O \tag{2.4}$$

$$N + OH \rightleftharpoons NO + H \tag{2.5}$$

Fuel NO_x is formed due to the reducing environment surrounding a fuel particle or droplet which lead to formation of volatile nitrogen compounds. These volatile compounds are then readily oxidised when reaching an oxygen rich environment which leads to the formation of NO. If however given sufficient residence time and high enough temperature the volatile compounds can be reduced to molecular nitrogen. Prompt NO_x is formed when hydrocarbons react with molecular nitrogen in a reducing environment. This cause the formation of volatile nitrogen compounds which then similarly to the formation of fuel NO_x is oxidised when reaching an oxygen rich environment [26]. In Figure 2.3 a schematic representation of the NO_x formation routes can be found.

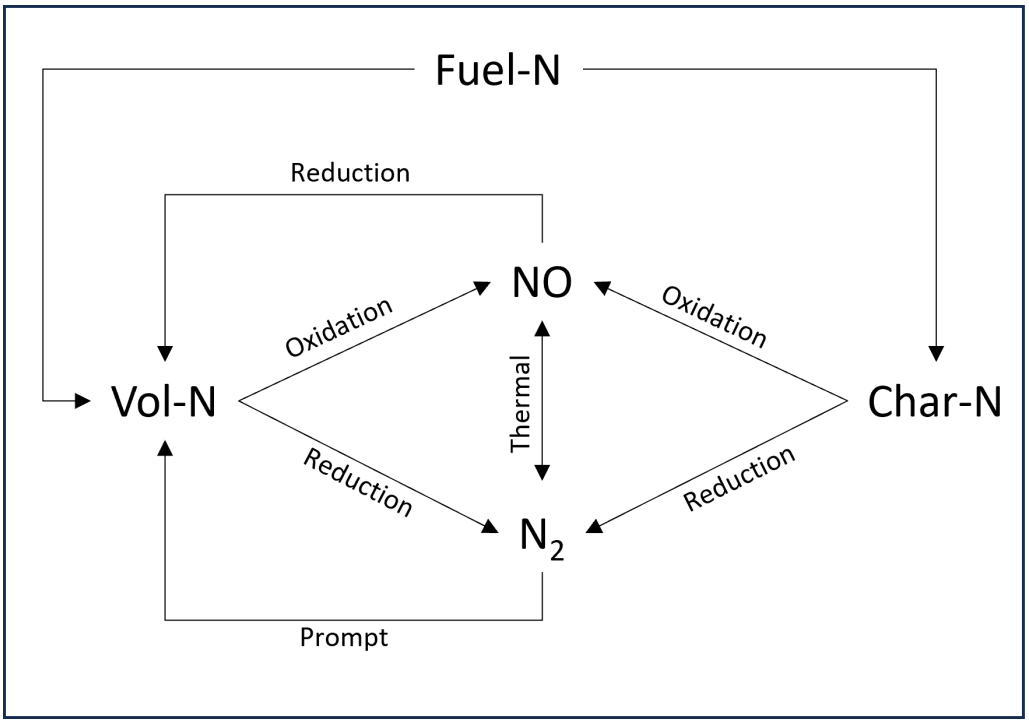


Figure 2.3: Reaction paths for NO_x formation during combustion.

The NO_x emissions from the recovery boiler originates mainly from the nitrogen in the black liquor (fuel NO_x) where the dry black liquor content can contain up to 0.15 wt% nitrogen. The nitrogen in the black liquor is volatilised into N_2 and NO through oxidation by the combustion, where the nitric oxide is further oxidised into NO_2 with the presence of oxygen as it reaches the atmosphere [27]. Approximately 95% or more of the nitrogen oxides formed is NO and the rest is NO_2. It is stated that only a minor part of the NO emissions is "thermal NO" formed from oxidation of nitrogen in the combustion air [28].

The black liquor nitrogen is mainly in the form of ammonia where oxidation yields NO as the the liquor droplets are devolatilised when sprayed in into the recovery boiler. This devolatilisation, or pyrolysis, occurs in the oxidising zone of the recovery boiler which also has been referred to as "combustion in flight" previously. In the initial devolatilisation, approximately 2/3 of the nitrogen is released as volatile nitrogen compounds, either N_2 or NH_3. The remaining 1/3 of the total nitrogen is bound in the char carbon matrix as the sodium compounds in the bed are reduced during the combustion. In general, small portions of the nitrogen in the char bed is released forming NO when in contact with oxygen during the reducing phase, but most of this nitrogen exits the recovery boiler along with the green liquor. Also, NH_3 in the oxidising zone can either form N_2 or NO. Therefore, the total nitrogen emissions from the recovery boiler is mainly in the form of NO [28]. In Figure 2.4 the fate of black liquor nitrogen can be seen.

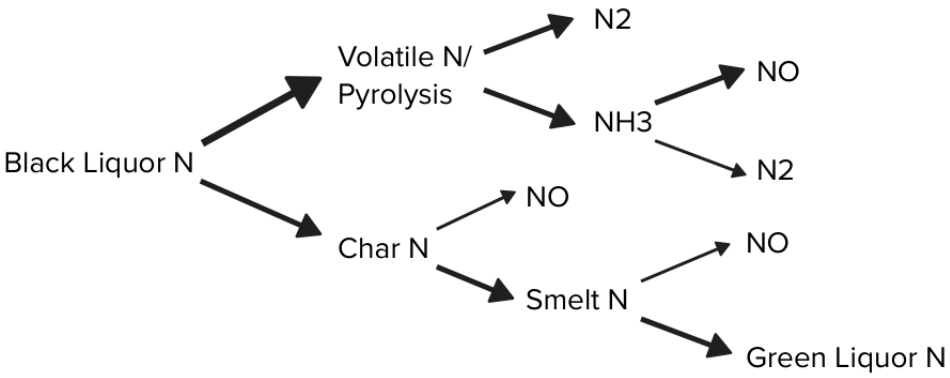
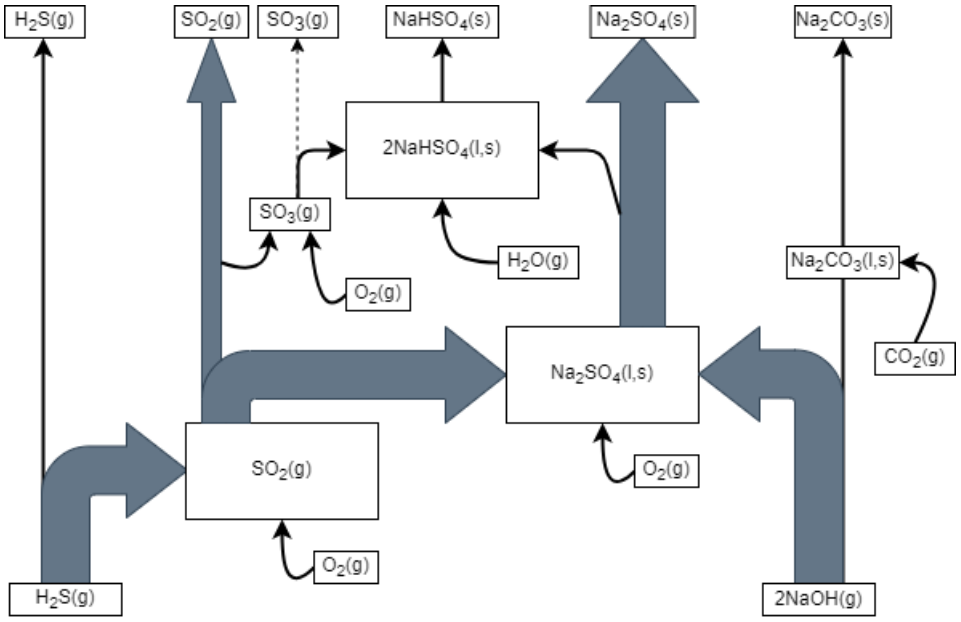


Figure 2.4: NO_x formation routes in the recovery boiler.

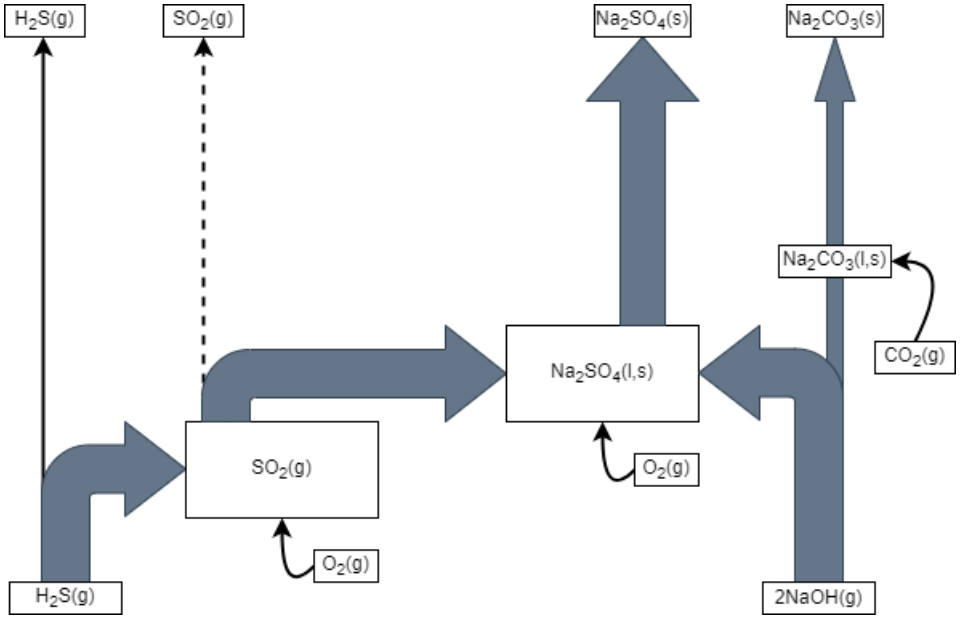
2.2.2 Sulfur oxides

SO_x emissions mainly stem from oxidation of fuel bound sulfur and the most prevalent specie of SO_x is SO_2 [16]. Other sulfur related emissions includes emissions of total reduced sulfur (TRS) which stem from incomplete combustion [6]. In the presence of oxygen TRS will be oxidised to SO_2.

In the recovery boiler sulfur enters through the black liquor in which it mainly exists as inorganic sulfur compounds with the dominating forms being sulfide and sulfate. Other inorganic forms that are present to a minor extent includes thiosulfate, sulfite and polysulfates. About 30-40 % of the sulfur present in black liquor exists as organosulfur compounds [29]. The sulfate that ends up in the bed of the furnace is reduced by reducing gases (H_2 or CO) or char in the bed to sodium sulphide or vaporised in the form of H_2S or COS and is carried away by the flue gas. The release of sulfur from the bed to the flue gas is heavily dependent on the temperature with a decreasing release corresponding to higher temperatures. In the lower furnace in which there are reducing conditions sulfur exists mainly as hydrogen sulfide and as it moves toward the upper part of the furnace where there is oxidising conditions it reacts with oxygen to form SO_2. Depending on the ratio S/Na_2 (sulfidity) in the upper part of the furnace the release of SO_2 varies significantly. In cases with a sulfidity above one a substantial part of the SO_2 is released to the atmosphere and another substantial part is further oxidised to sulfate which interacts with sodium compounds to form sodium sulfate. A minor part of the SO_2 is oxidised to SO_3 of which some is emitted to the atmosphere while some interacts with water and sodium sulfate to form sodium bisulfate. In cases with a sulphidity less than one the majority of the SO_2 is oxidised to sulfate and interacts with sodium compounds to form sodium sulfate with small emissions of SO_2 into the atmosphere [24]. Figure 2.5 gives a schematic representation for the fate of sulfur during both these operating conditions.



(a) The fate of sulfur during operation with high sulfidity.



(b) The fate of sulfur during operation with low sulfidity.

Figure 2.5: The fate of sulfur in the flue gas from the recovery boiler at high and low sulfidity [24].

2.2.3 Hydrogen chloride

Other emissions from the recovery boiler includes emissions of HCl which stem from the chloride content of the black liquor. The chloride content of black liquor varies between 0.2-2 % of the black liquor mass and is mostly present as either NaCl or KCl. One of the parameters that have been found to be closely related to the HCl emissions is the concentration of SO_2 in the flue gas. The correlations that have been observed is that HCl emissions increases with increased SO_2 concentration. HCl is

formed through reactions where NaCl or KCl reacts with H_2O, O_2 or SO_4^- where the reaction rate is significantly higher if the salt is in vapour state. Most of the NaCl and KCl evaporated from the smelt bed reacts according to reaction 2.6 [30].

$$SO_2 + 2\,ACl(l,g) + \frac{1}{2}O_2 + H_2O(g) \rightarrow A_2SO_4 + HCl \tag{2.6}$$

One important parameter regarding HCl formation is temperature as the amount of NaCl and KCl evaporated from the lower furnace and char bed increases almost exponentially with increasing temperature, which increases the amount of NaCl and KCl that is available to form HCl. Simultaneously as previously discussed increasing the temperature is also associated with increased release of sodium vapours from the lower furnace as well as reducing the amount of sulfur vapours. This increases the competition for SO_2 which decreases the amount available for HCl production [30].

2.3 Secondary wet exhaust gas cleaning

In this section theory regarding the gas phase oxidation of NO and the absorption process is presented.

2.3.1 Gas phase oxidation

To be able absorb NO_x from the flue gas in which NO is the dominant specie, NO needs to be further oxidised to achieve efficient absorption due to its low solubility. At atmospheric conditions NO can be completely oxidised according to reaction 2.7 due to NO_2 being thermodynamically favored at lower temperatures [9].

$$2\,NO + O_2 \rightleftharpoons NO_2 \tag{2.7}$$

However, the rate of oxidation in reaction 2.7 is to low to be of relevance in a flue gas cleaning system. Therefore, to enhance the NO oxidation an oxidising agent is used to increase the rate of oxidation. In this study ClO_2 and H_2O_2 will be investigated as possible oxidising agents as studies have shown that these efficiently can oxidise NO while also being common chemicals within the pulp and paper industry used for bleaching [9].

2.3.1.1 NO oxidation with ClO_2

Decomposition of ClO_2 in the atmosphere takes place according reactions 2.8-2.10 [9].

$$ClO_2 + h\nu \rightarrow Cl + O_2 \tag{2.8}$$

$$Cl + ClO_2 \rightarrow 2\,ClO \tag{2.9}$$

$$ClO + ClO \rightarrow Cl_2 + O_2 \tag{2.10}$$

Chlorine can then become fully reduced to HCl through reactions 2.11 and 2.12 in a

humid environment [9].

$$Cl \rightarrow Cl_2 \tag{2.11}$$

$$Cl_2 + H_2O(g) \rightarrow 2\,HCl + O \tag{2.12}$$

Under dry conditions oxidation of NO by ClO_2 can take place according to reaction 2.13 and 2.14 [9].

$$NO + ClO_2 \rightarrow NO_2 + ClO \tag{2.13}$$

$$NO + ClO \rightarrow NO_2 + Cl \tag{2.14}$$

NO_2 is then in equilibrium with its dimer N_2O_4 according to reaction 2.15 or can react with NO to form N_2O_3 according to reaction 2.16. Both these species are highly soluble in water [9].

$$NO_2 + NO_2 \rightleftharpoons N_2O_4 \tag{2.15}$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \tag{2.16}$$

If the environment is humid gaseous HNO_3 can also be formed according to reaction 2.17 [9].

$$3\,NO_2 + H_2O(g) \rightarrow 2\,HNO_3(g) + NO \tag{2.17}$$

Another specie that also can be formed if the oxidation take place in a humid environment is HNO_2 which can be formed according to reaction 2.18 [9].

$$NO + NO_2 + H_2O(g) \rightarrow 2\,HNO_2(g) \tag{2.18}$$

The complete reaction for when Cl is fully reduced during wet conditions can be seen in reaction 2.19 [10].

$$5\,NO + 3\,ClO_2 + 4\,H_2O \rightarrow 5\,HNO_3 + 3\,HCl \tag{2.19}$$

In experiments it has been found that close to complete oxidation of NO can be achieved with a molar ratio between ClO_2 to NO above 0.6 for a range of humidity levels between 0-30 % given a residence time of 2 s. This ratio is comparable to the stoichiometric ratio 0.5 for dry conditions and 0.4 for wet conditions. The oxidation has also been shown to be insensitive to temperature in the span of 100-180 °C with a high selectivity towards NO_2 [9].

2.3.1.2 NO oxidation with H_2O_2

By injecting H_2O_2 into a hot gas thermal decomposition of H_2O_2 can be achieved according to reaction 2.20-2.23 [31].

$$H_2O_2 \rightarrow OH + OH \tag{2.20}$$

$$H_2O_2 \rightarrow HO_2 + H \tag{2.21}$$

$$H_2O_2 \rightarrow H_2O + O \tag{2.22}$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \tag{2.23}$$

When H_2O_2 decomposes radicals are formed which can react with NO to achieve oxidation according to reactions 2.24-2.27 [31] [32].

$$NO + OH \rightarrow HONO \tag{2.24}$$

$$HONO + OH \rightarrow NO_2 + H_2O \tag{2.25}$$

$$NO + HO_2 \rightarrow OH + NO_2 \tag{2.26}$$

$$HO_2 + NO \rightarrow HNO_3 \tag{2.27}$$

In experiments the optimum temperature band for NO oxidation by H_2O_2 has been determined to be between 400-650 °C. The maximum conversion of NO to NO_2 during these experiments was 97 % at a molar ratio between H_2O_2 to NO of 2.6:1 with a temperature of 500 °C given a residence time of 0.7 s. Worth noting is that this ratio deviates significantly from the stoichiometric relationship of 1 H_2O_2 per NO which can be derived from reactions 2.20 to 2.27 if all H_2O_2 is consumed during oxidation of NO. This is thought to have been due to radical destruction at the reactor wall and wick during the experiments. Therefore, the ratio between H_2O_2 and NO in large scale application should be lower than the achieved one in experiments as these surface effects should be of much lower significance [31].

2.3.2 Liquid chemistry of the absorption process.

After the oxidation step the flue enters the absorber. In the absorber SO_2 is directly absorbed into the liquid phase with the only limitation being solubility. As SO_2 enters the liquid phase of the scrubber it can react with H_2O according to reaction 2.28 to from bisulfite. Bisulfite is then in equilibrium with its dissociated form, sulfite, according to reaction 2.29 [10].

$$SO_2(aq) + H_2O(l) \rightleftharpoons H^+ + {HSO_3}^- \tag{2.28}$$

$${HSO_3}^- \rightleftharpoons H^+ + {SO_3}^{2-} \tag{2.29}$$

Sulfite and bisulfite can then be further oxidised by O_2 dissolved in the liquid phase

according to reaction 2.30 and 2.31 [10].

$$2{SO_3}^{2-} + O_2(aq) \rightarrow 2\,{SO_4}^{2-} \tag{2.30}$$

$$2\,{HSO_3}^{-} + O_2(aq) \rightarrow 2\,{SO_4}^{2-} + 2\,H^+ \tag{2.31}$$

Sulfate is then in equilibrium with its acid form through reaction 2.32 [8].

$${HSO_4}^{-} \rightleftharpoons H^+ + {SO_4}^{2-} \tag{2.32}$$

When NO_2 enters the liquid phase of the absorber it can react with H_2O according to reaction 2.33 to form nitric and nitrous acid. These two acids are then in equilibrium with their dissociated forms as in reactions 2.34 and 2.35. Nitric acid can also decompose according to 2.36 due to being unstable. This chain of reactions might also be initiated by the dimer N_2O_4 [10].

$$2\,NO_2(aq) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq) \tag{2.33}$$

$$HNO_2(aq) \leftharpoons H^+ + {NO_2}^{-} \tag{2.34}$$

$$HNO_3(aq) \leftharpoons H^+ + {NO_3}^{-} \tag{2.35}$$

$$2\,HNO_2(aq) \rightleftharpoons NO(aq) + NO_2(aq) + H_2O(l) \tag{2.36}$$

An alternative route for NO_x absorption is reaction 2.37 which favor a equimolar relationship between NO_2 and NO [10].

$$NO + NO_2 + H_2O \leftharpoons 2\,HNO_2 \tag{2.37}$$

When both sulfite species and NO_2 is present in the liquid phase another reaction route is possible in which NO_2 is hydrolysed instead of forming nitrous and nitric acid. Whether or not this hydrolysis takes place is dependent on the pH of the scrubber due to the dissociative reactions 2.29, 2.34 and 2.35. At a pH>7 sulfite is the dominant form of the sulfur species and this allows for hydrolysis through reaction 2.38 which has a higher reaction rate than reaction 2.33 [10].

$$2\,NO_2(aq) + {SO_3}^{2-} + H_2O(l) \rightarrow 2\,{NO_2}^{-} + {SO_4}^{2-} + 2\,H^+ \tag{2.38}$$

A similar route can be also achieved via bisulfite according to reaction 2.39 [10].

$$2\,NO_2(aq) + {HSO_3}^{-} + H_2O(l) \rightarrow 2\,{NO_2}^{-} + {SO_4}^{2-} + 3\,H^+ \tag{2.39}$$

Reaction 2.38 and 2.39 are the main contributors toward efficient NO_x absorption as the hydrolysis takes place at a similar rate to that of SO_2 absorption. The theoretical molar ratio between NO_2 and the sulfite species in reaction 2.38 and 2.39 is 2:1 but it has been seen in experiments that sulfite species are oxidised at a higher rate than

can be explained by these two reactions [10]. It has been proposed that this is due to an alternative reaction path than reaction 2.38 in which sulfite radicals are formed [33]. A reaction mechanism has been proposed [34] for this radical reaction chain which is supported by experimental results [11] and can be seen in reactions 2.40 to 2.49.

$$NO_2(aq) + {SO_3}^{2-} \rightarrow {NO_2}^- + {SO_3}^{\bullet -} \tag{2.40}$$

$${SO_3}^{\bullet -} + {SO_3}^{\bullet -} \rightarrow {S_2O_6}^{2-} \tag{2.41}$$

$${SO_3}^{\bullet -} + {SO_3}^{\bullet -} \rightarrow {SO_3}^{2-} + SO_3 \tag{2.42}$$

$$SO_3 + H_2O \rightarrow 2H^+ + {SO_4}^{2-} \tag{2.43}$$

$${SO_3}^{\bullet -} + O_2 \rightarrow {SO_5}^{\bullet -} \tag{2.44}$$

$${SO_5}^{\bullet -} + {SO_3}^{2-} \rightarrow {SO_5}^{2-} + {SO_3}^{\bullet -} \tag{2.45}$$

$${SO_5}^{\bullet -} + {SO_3}^{2-} \rightarrow {SO_4}^{2-} + {SO_4}^{\bullet -} \tag{2.46}$$

$${SO_4}^{\bullet -} + {SO_3}^{2-} \rightarrow {SO_4}^{2-} + {SO_3}^{\bullet -} \tag{2.47}$$

$${SO_5}^{2-} + H^+ \rightleftharpoons {HSO_5}^- \tag{2.48}$$

$${HSO_5}^- + {SO_3}^{2-} \rightarrow 2{SO_4}^{2-} \tag{2.49}$$

As can be seen in the proposed reaction mechanism more than four sulfite molecules can be oxidised per sulfite radical formed if oxygen is present in the solution. To reduce the sulfite oxidation through the radical reaction chain a radical scavenger can be introduced into the scrubber liquid such as thiosulfate which terminates the reaction chain and reduces sulfite oxidation [35]. This termination of the reaction chain have been proposed to take place through reactions 2.50 and 2.51. In experiments it has been found that by adding 5 mM thiosulfate to 10 mM of sulfite, the sulfite oxidation by O_2 can be almost completely inhibited [36].

$$R^{\bullet} + {S_2O_3}^{2-} \rightarrow R + {S_2O_3}^{\bullet -} \tag{2.50}$$

$${S_2O_3}^{\bullet -} + {S_2O_3}^{\bullet -} \rightarrow {S_4O_6}^{2-} \tag{2.51}$$

Thiosulfate can also hydrolyse NO_2 according reaction 2.52 [35]. It has been shown that by adding thiosulfate to water increases NO_2 absorption with 30 % compared to pure water [36].

$$NO_2 + {S_2O_3}^{2-} \rightarrow NO_2^- + {S_2O_3}^{\bullet -} \tag{2.52}$$

To obtain thiosulfate, sodium sulfide in white liquor can be oxidised by the addition of oxygen through reactions 2.53 and 2.54.

$$Na_2S + H_2O \rightarrow NaSH + NaOH \tag{2.53}$$

$$Na_2S + 2O_2 \rightarrow Na_2S_2O_3 + H_2O \tag{2.54}$$

The thiosulfate can then be further oxidised to sodium sulfate through reaction 2.55. Oxidised white liquor is commonly used within the pulp and paper industry as part of an oxygen delignification step which use is to reduce the consumption of bleaching chemicals [37]. In an oxygen based system for complete white liquor oxidation the conversion of sulfide into thiosulfate is between 98-99 % and the conversion of thiosulfate into sulfate up to 60 % [38].

$$Na_2S_2O_3 + 2O_2 + 2NaOH \rightarrow 2Na_2SO_4 + H_2O \tag{2.55}$$

Another unwanted reaction that increases the consumption of sulfite is the formation of hydroxylamine disulfonic acid (HADS) through reaction 2.56 [8]. However, this reaction is of little importance at a pH>7 since ${SO_3}^{2-}$ is the dominant form of sulfite in this pH range and this reaction takes place through ${HSO_3}^-$.

$$HNO_2 + 2{HSO_3}^- \rightarrow HADS + H_2O \tag{2.56}$$

Other reactions that also takes place in the liquid phase of the scrubber is the formation and dissociation of carbonic acid through reaction 2.57 and the dissociation of water through reaction 2.58.

$$CO_2 + H_2O \rightleftharpoons {HCO_3}^- + H^+ \tag{2.57}$$

$$H_2O \rightleftharpoons OH^- + H^+ \tag{2.58}$$

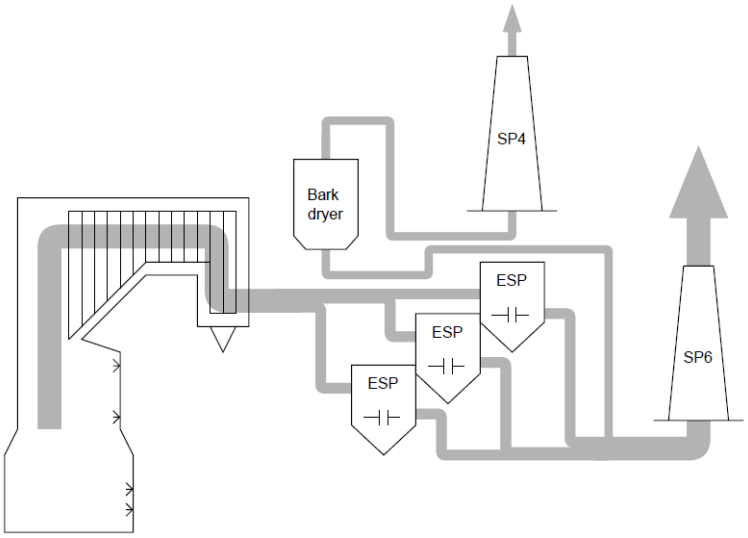
3

Methods

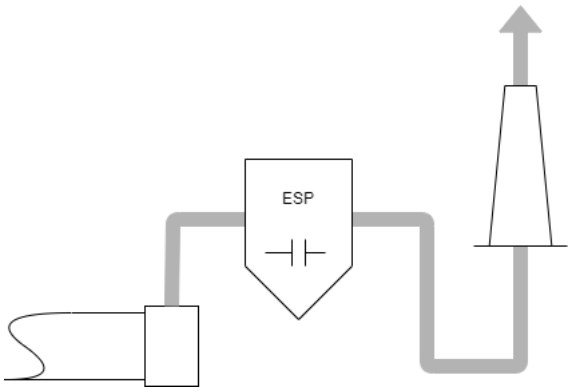
In this study process data regarding flue gas flows, flue gas compositions and temperature was gathered from Södra's site in Mönsterås. Based on these data a case study was performed in which process modifications needed for implementation of the scrubber equipment was identified. To determine the size and performance of the scrubber for combined NO_x and SO_x removal, simulations were carried out in Aspen Plus. Based on the resulting flows from the simulations the need for process chemicals was estimated as well as the possibility to send the scrubber effluent to the wastewater treatment plant.

3.1 Mapping of emission sources

The emission sources considered in this paper are the emissions from the recovery boiler and the two lime kilns at the site. The recovery boiler has two chimneys as some of the flue gas is diverted and pulled through the bark dryer at the site. Due to this, these two chimneys are considered as separate emission sources where the non diverted flue gas flow will be refereed to as SP6 while the diverted flue gas flow is refereed to as SP4. In Figure 3.1a the flue gas path is visualised after the flue gas has exited the combustion chamber and convective section of the boiler. The two lime kilns will be refereed to as MU1 and MU2 and the flue gas path for these two units can be seen in Figure 3.1b. To map the emissions from these sources data based on a 14 hour long measuring campaign done by an independent company [39] using FTIR during what is claimed to be normal operating conditions except for MU2 where there was a stop the day before. From this data the flue gas flow and temperature in SP4 and SP6 could be gathered as well as the flue gas composition regarding H_2O, CO_2 and O_2. As no measurements in regard SO_2, NO_2 and NO was performed in SP4 it was assumed that the flow of these gases were unchanged after passing through the bark dryer. Similarly the composition and temperature for MU1 and MU2 was gathered from this data but the flue gas flow was gathered from Södra´s own measurement equipment as the yearly average.



(a) Flue gas path for the recovery boiler.



(b) Flue gas path gas path for both lime kilns.

Figure 3.1: Flue gas path for the recovery boiler and the two lime kilns at Södra´s site in Mönsterås.

In Table A.1 the input data used in the model based on the information gathering can be seen. All the flue gas parameters that are presented are measured in the chimneys meaning that the flue gas has passed all other units in the flue gas path before being measured.

3.2 Estimation of chemical consumption

To be able to oxidise NO to NO_2 using H_2O_2 efficiently it is assumed that it is possible to inject H_2O_2 directly into the convective section for the lime kilns and the recovery boiler at the correct temperature span and that sufficient residence time is achieved. It is assumed that a ratio of 2.6:1 is sufficient to achieve complete oxidation of NO and that the flow of the injection is small enough to not have any significant effect on the temperature. For ClO_2 the flue gas is first cooled through flue gas condensation before ClO_2 is injected into the flue gas stream. It is assumed that

a molar ratio 0.5:1 is sufficient for complete oxidation and that sufficient residence time is achieved. For both H_2O_2 and ClO_2 it is also assumed that NO_2 is the only product of oxidation. When simulating the flue gas in Aspen it was assumed that the flue gas streams SP4 and SP6 were mixed before entering the scrubber and the same was done for the lime kilns.

Implementation of the scrubber technology will also affect the consumption of process chemicals including NaOH, oxidised white liquor, H_2O_2 and water. In Table A.2 the current consumption of these chemical during normal operation can be seen. As Södra´s site in Mönsterås is a totally chlorine free mill there is currently no facility for production or consumption of ClO_2. Therefore, to be able to estimate the impact on consumption of ClO_2, if it were to be used for bleaching, it was assumed that 15 kg per ton produced pulp was needed [40]. Current

3.3 Model

In Figure 3.2 a schematic overview of the scrubber process can be seen after the oxidation of NO to NO_2. The oxidised flue gas first enters a quench where the gas is cooled to its saturation temperature. In the quench chlorides are also removed from the flue gas and the height of the quench is therefore designed to allow for complete removal of chlorides to reduce the risk of corrosion in the scrubber equipment. To maintain the pH of the quench liquid NaOH is added. The flue gas then enters the scrubber which is designed to remove 90 % of the incoming NO_x which corresponds to the highest NO_x reduction by secondary measures for large combustion plants [16]. To achieve this NO_x removal Na_2SO_3 is added until 90 % removal is achieved. The operating pH of the scrubber was optimised to minimise the consumption of Na_2SO_3 as this has been identified as the major cost of the scrubber [12]. The effect of gas residence time was then investigated with a base case designed for a residence time of 25 s. In this study the scrubber is modelled as one tall tower but it should be noted that the residence time can be achieved by having multiple lower towers connected in series. A liquid to gas ratio (L/G) of 10 was chosen for the scrubber.

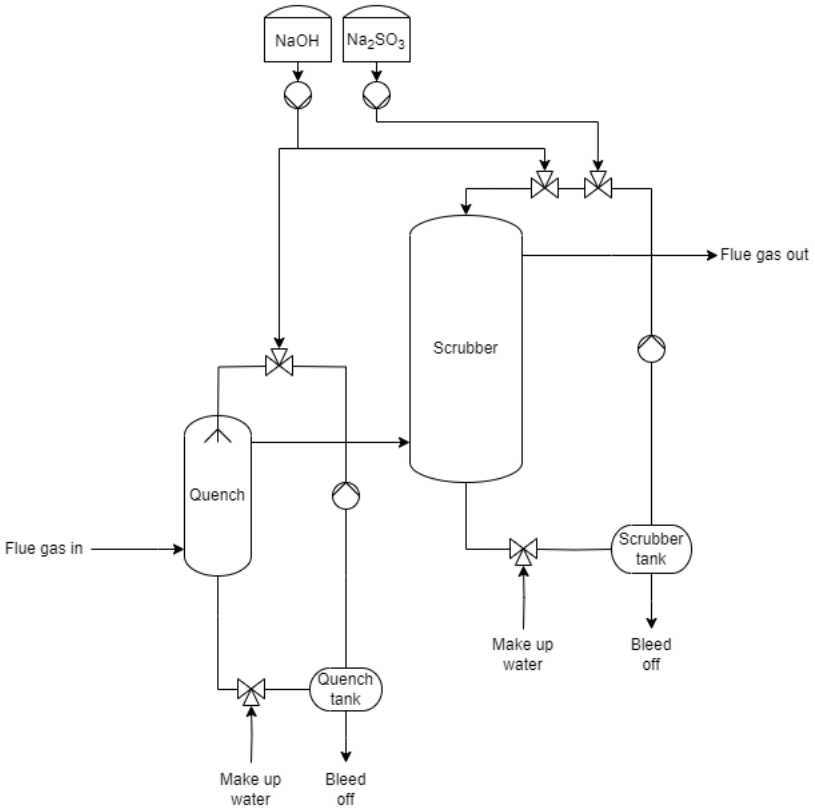


Figure 3.2: Schematic picture of the proposed flue gas cleaning system.

Both the scrubber and the quench is designed to operate at 80 % approach to flooding to maximise the efficiency which gives the diameter of these equipment. The liquid bleed off is dimensioned as to avoid solid formation in the scrubber and is therefore controlled so that the concentration of sulfate in the scrubber liquid does not exceed 25 g/l. In the scrubber the gas and liquid phase flow counter currently as in Figure 3.3 where the gas enters at the bottom of the scrubber and the liquid at the top. When the gas comes in contact with the liquid phase SO_2 and NO_2 is absorbed into the liquid where they interact with sulfite species present in the liquid phase to form sulfate, nitrite and nitrate species as well as hydroxylamine disulfonic acid (HADS).

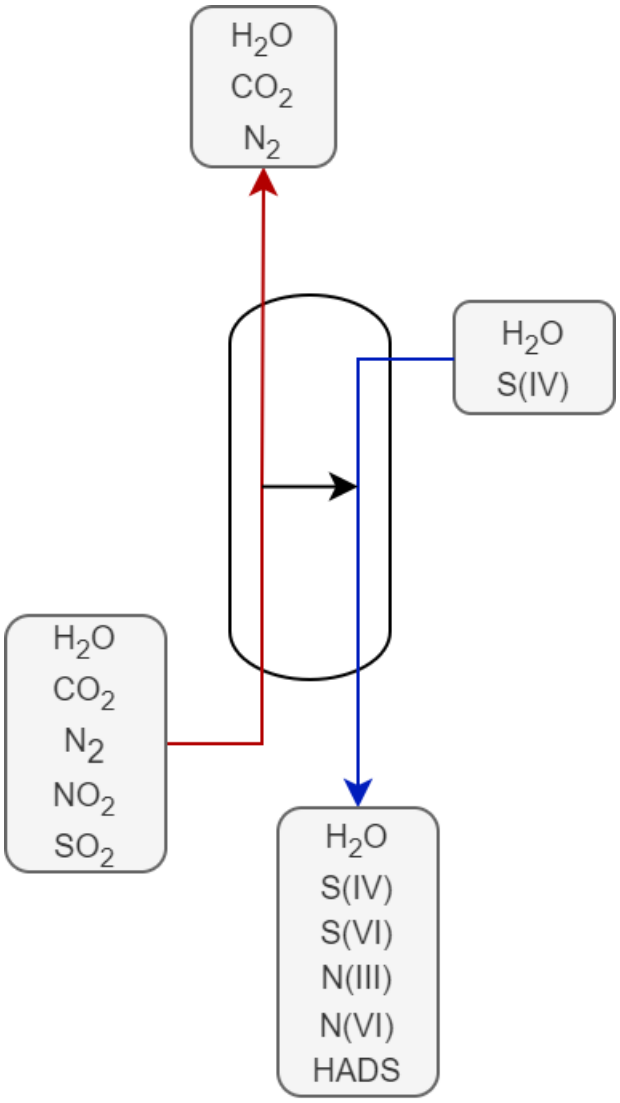


Figure 3.3: Gas and liquid flow interaction in scrubber.

To model the scrubber chemistry a reduced reaction mechanism proposed by Ajdari et al [8] is used in which the reactions in Table 3.1 is included for a pH >5.

Table 3.1: Reactions included in the reduced mechanism used in the simulations.

Reaction	Reaction ID	Phase
$2\,NO_2+H_2O\rightarrow HNO_2+NO_3^-+H^+$	2.33	Liquid
$2\,NO+O_2\rightarrow 2\,NO_2$	2.7	Gas
$HNO_2+2\,HSO_3^-\rightarrow HADS+H_2O$	2.56	Liquid
$2\,NO_2+HSO_3^-+H_2O\rightarrow 2\,HNO_2+HSO_4^-$	2.39	Liquid
$SO_2(aq)+H_2O\rightleftharpoons H^++HSO_3^-$	2.28	Liquid
$HNO_2\rightleftharpoons H^++NO_2^-$	2.34	Liquid
$HSO_3^-\rightleftharpoons H^++SO_3^{2-}$	2.29	Liquid
$H_2O\rightleftharpoons H^++OH^-$	2.58	Liquid
$CO_2(aq)+H_2O\rightleftharpoons H^++HCO_3^-$	2.57	Liquid
$HSO_4^-\rightleftharpoons H^++SO_4^{2-}$	2.32	Liquid

In Figure 3.4 a schematic overview of the interactions between the different species in the scrubber liquid according to the reaction mechanism can be seen.

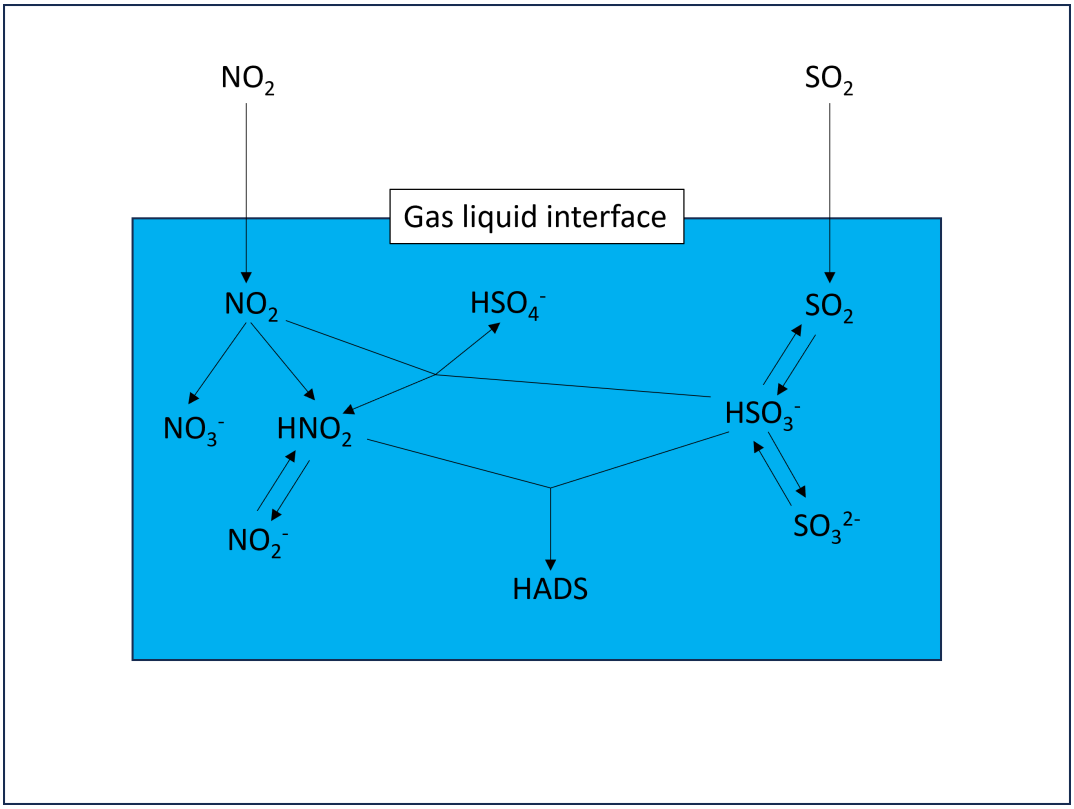


Figure 3.4: Schematic picture of the sulfur-nitrogen chemistry taking place in the liquid phase.

However, this reaction mechanism does not consider the oxidation of sulfite from radical formation which has been previously disscussed. Therefore, to get a better understanding of the actual ratio between NO_2 and $SO_3{}^{-2}$ needed in the scrubber liquid to achieve the wanted emission reduction a pseudo reaction is added to the reaction mechanism to get better agreement with the experimental results. In these

reactions O_2 dissolved in the scrubber liquid reacts with the sulfite species according to reaction 3.1 and 3.2. To model these reactions a first order reaction rate is assumed in regard to sulfite with an apparent rate constant with a magnitude ranging from 10^{-2} to 10^{-3} s^{-1} based on the work performed by Schmid et al [41].

$$2HSO_3{}^{-2} + O_2 \rightarrow 2HSO_4{}^{-2} \tag{3.1}$$

$$2SO_3{}^{-2} + O_2 \rightarrow 2SO_4{}^{-2} \tag{3.2}$$

These reactions would better explain the rate of oxidation of sulfite in a scrubber where only Na_2SO_3 is added. If however thiosulfate is added to the scrubber liquid the oxidation of Na_2SO_3 can be significantly reduced and therefore the addition of Na_2SO_3 can be expected to be lower or, given the right conditions, completely substituted by $Na_2S_2O_3$. Therefore, a total of three cases are modeled, one best case where it is assumed that thiosulfate inhibits the radical chain which is described by the original mechanism in Table 3.1, one case where reaction 3.1 and 3.2 is added to the reaction mechanism with a rate constant of k=0.001 s^{-1} representing a best case scenario when sulfite oxidation is uninhibited and a worst case scenario when reaction 3.1 and 3.2 is added with a rate constant of k=0.01 s^{-1}. In the best case it is assumed that a molar ratio of 0.5:1 between thiosulfate and sulfite is sufficient to inhibit the radical chain reaction.

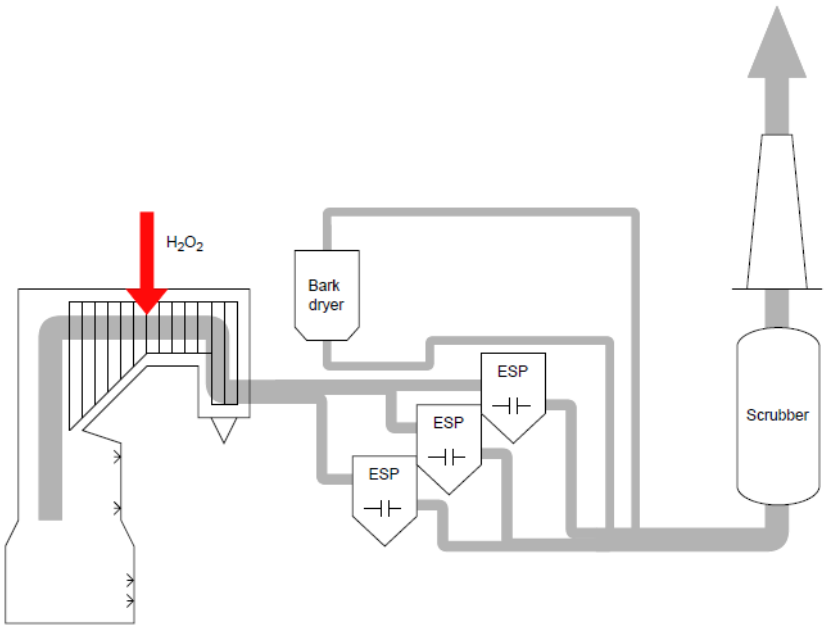
4

Results

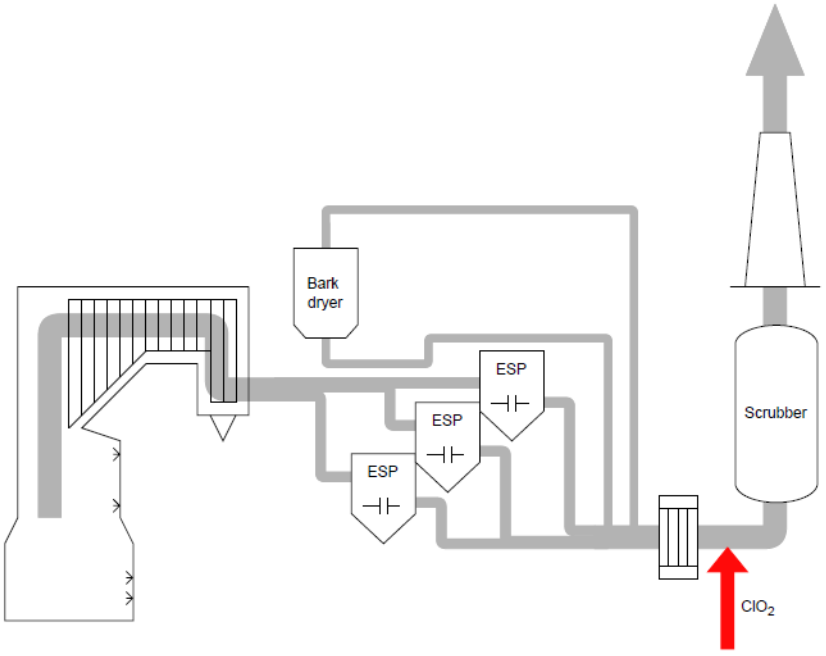
In this section results regarding the performance, resulting flows, process modifications and design of the scrubber is presented. To evaluate the impact of sulfite oxidation three cases where investigated, one where sulfite oxidation was assumed to be inhibited (k=0 s^{-1}), one where the sulfite oxidation was assumed to take place at an order of magnitude of 10^{-3} (k=0.001 s^{-1}) and one with a order of magnitude 10^{-2} (k=0.01 s^{-1}).

4.1 Process modifications

To effectively oxidise NO to NO_2 using H_2O_2 or ClO_2 certain temperatures are required. In Figure 4.1a the position in the recovery boiler where the optimum temperature span is achieved is indicated with a red arrow. As can be seen this is in the convective section of the recovery boiler due to temperatures between 400-650 °C being required for efficient oxidation. For ClO_2 it can be seen in Figure 4.1b that the required optimum temperature span can not be achieved with the current achievable temperatures of the flue gas. To be able to apply NO oxidation with ClO_2 the temperature out of the ESP and the bark dryer needs to be further decreased. It is here proposed that this could be done by installation of a flue gas condensation system which decreases the temperature of the flue gas to below 180 °C.



(a) Proposed injection point of H_2O_2 and placement of scrubber in flue gas path.

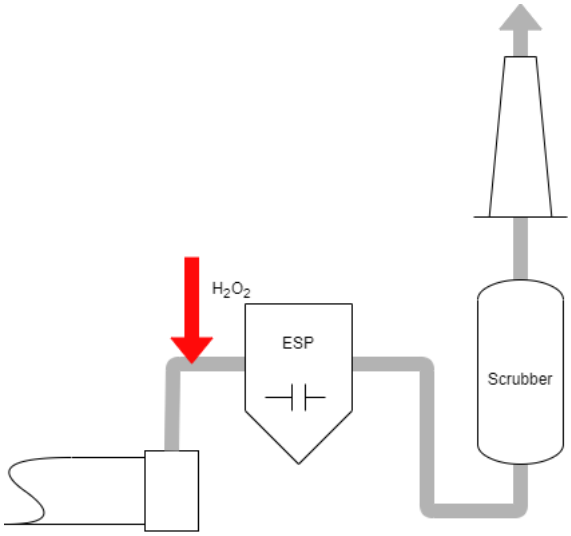


(b) Proposed injection point of ClO_2, placement of heat exchangers and scrubber in flue gas path.

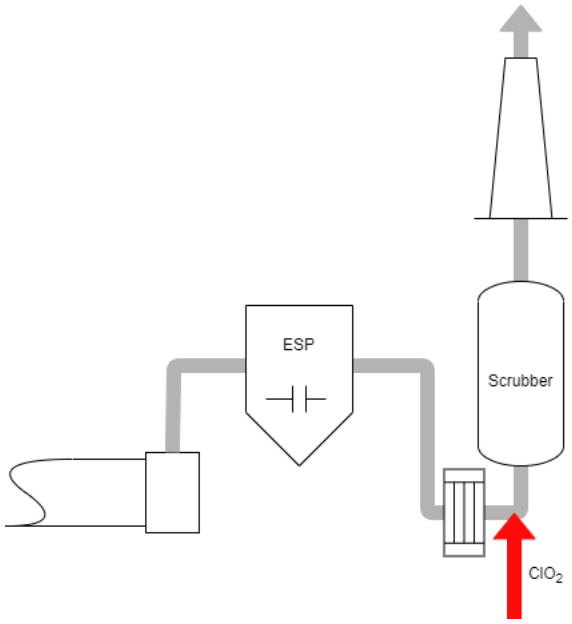
Figure 4.1: Proposed modifications to the flue gas path depending on oxidising agent being used in the recovery boiler.

In Figure 4.2 the injection point of the oxidising agents can be seen for the lime kilns. From figure 4.2a it can be seen that to achieve the desired temperatures for H_2O_2 should be injected before the flue gas enters the ESP. Similarly to the recovery boiler to apply ClO_2 oxidation to the lime kilns, flue gas condensation will be necessary as

can be seen in Figure 4.2b.



(a) Proposed injection point of H_2O_2 and placement of scrubber in flue gas path.



(b) Proposed injection point of ClO_2, placement of heat exchangers and scrubber in flue gas path.

Figure 4.2: Proposed modifications to the flue gas path depending on oxidising agent being used in the lime kilns.

4.2 The effect of pH

Due to the dissociative reactions present in the liquid chemistry of the scrubber, pH will have a significant impact on the scrubber performance. In Figure 4.3 the composition of the liquid at the bottom outlet of the scrubber can be seen for the

case where sulfite oxidation is assumed to be inhibited. The results were achieved by adding Na_2SO_3 until 90% of the NO_2 entering the scrubber was absorbed without any addition of NaOH to the scrubber liquid and controlling the liquid bleed to limit the concentration of sulfate to 25 g/l for the first pH value in the pH range. Then to obtain the other concentrations for the rest of the pH range, NaOH was added to control the pH and the makeup water controlled to maintain a L/G ratio of 10. In Table 4.1 the resulting flows in and out of the scrubber as well as operating parameters can be seen for the first pH in the investigated pH range for when sulfite oxidation is inhibited.

Table 4.1: Resulting flows in and out of the scrubber and operating parameters for the first pH in the pH range in Figure 4.3.

Parameter	k=0 s^{-1}
NO_2 removed (kg/h)	112
pH	7
L/G	10
S(IV)/NO_2	1.1
Makeup water (m^3/h)	2.7
Na_2SO_3 (m^3/h)	1.6
Liquid bleed (m^3/h)	4.7
NaOH (m^3/h)	0

From the figure it can be seen that increasing the pH from 7 to 8 results in a slight increase in concentration of nitrite. This can be explained by the reduced formation of HADS which also can be seen in the graph which is due to the equilibrium of reaction 2.29 being shifted towards SO_3^- at higher pH values. As the formation of HADS decrease the amount of sulfite available to hydrolyse NO_2 increases through reaction 2.39 which explains the correlation between increased nitrite concentration and increase in sulfate concentration. It can also be seen that the amount of CO_2 absorbed increases exponentially with increasing pH by observing the increasing amounts of carbonates present in the liquid. Also it can be seen that the concentrations of nitrate and sulfite is relatively low compared to the other species. The low concentration of nitrate indicates that the amount of NO_2 absorbed through reaction 2.33 is low compared to absorption through reaction 2.39 which also explains the low concentrations of suflite.

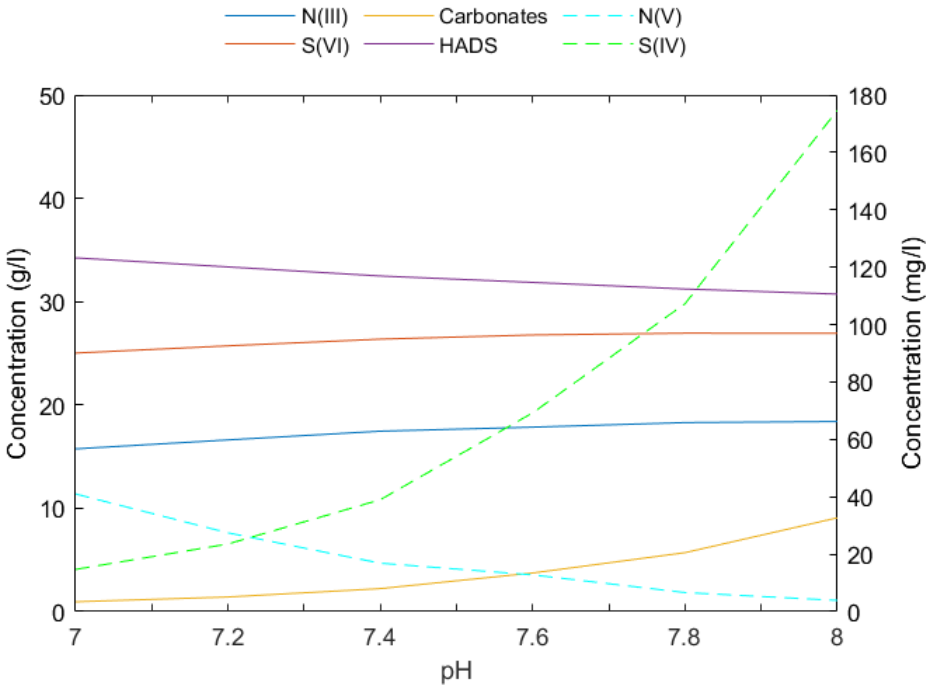


Figure 4.3: Bottom liquid composition and percentage of inlet NO_2 absorbed as function of pH. Concentration of the solid lines are read from the left axis and dashed lines from the right axis.

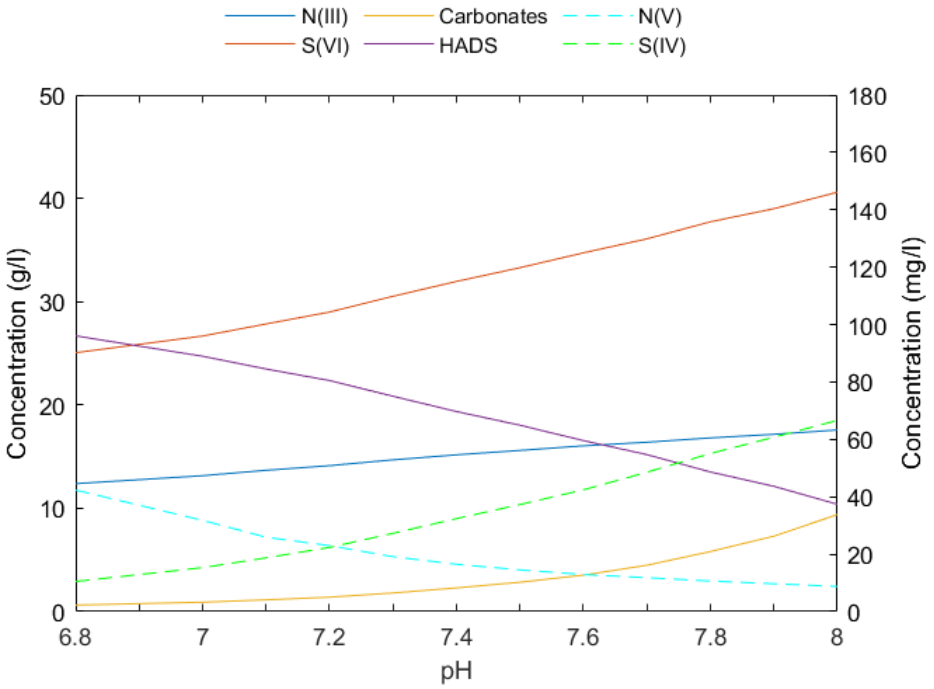
In Figure 4.4 the change in scrubber liquid composition when including the pseudo reactions 3.1 and 3.2 to account for sulfite oxidation is included in the reaction mechanisms can be seen. The results were obtained in the same way as for the case where sulfite oxidation by O_2 was assumed to be inhibited. In Table 4.2 the resulting flows in and out of the scrubber as well as operating parameters can be seen for the first pH in the investigated pH ranges for when sulfite oxidation is added to the reaction mechanism.

Table 4.2: Resulting flows in and out of the scrubber and operating parameters for each if the investigated oxidation rates for the first pH in the pH ranges in Figure 4.3.

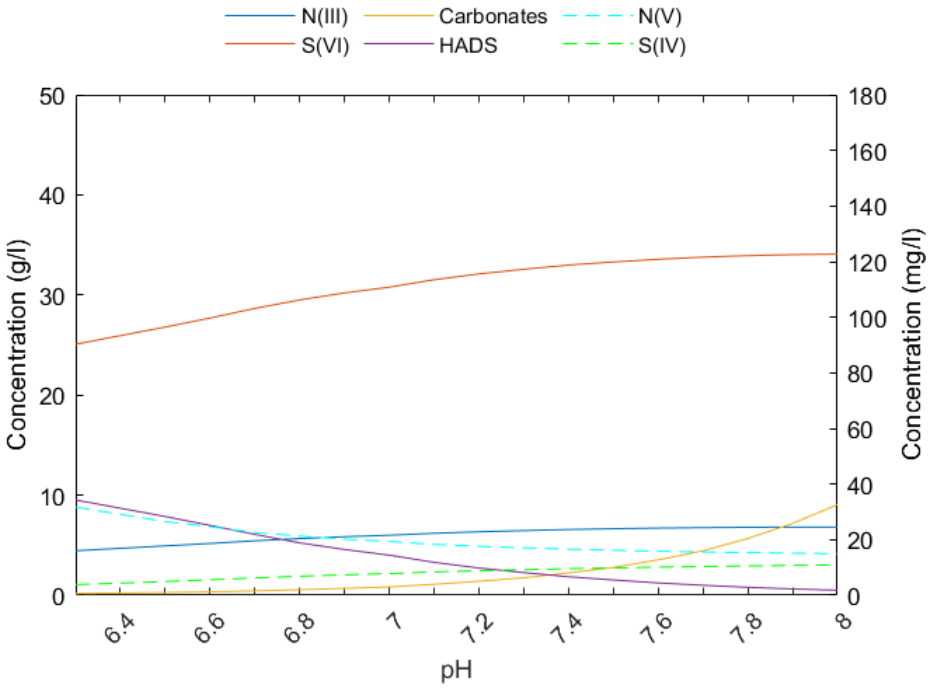
Parameter	k=0.001 s^{-1}	k=0.01 s^{-1}
NO_2 removed (kg/h)	112	112
pH	6.8	6.3
L/G	10	10
S(IV)/NO2	1.3	2.5
Makeup water (m^3/h)	3.9	13.2
Na_2SO_3 (m^3/h)	1.8	3.4
Liquid bleed (m^3/h)	5.9	16.6
NaOH (m^3/h)	0	0

One difference that can be seen comparing to Figure 4.3 is that the concentration

of all species except sulfate and carbonates are lower than in the case when sulfite oxidation is inhibitied. This is due to faster build up of sulfate due to reactions 3.1 and 3.2 which decreases the amount of scrubber liquid that can be recirculated before reaching a sulfate concentration of 25 g/l and therefore more makeup water needs to be added which decreases the concentration of the other species. Another trend that can be observed in Figure 4.4 is that at higher reaction rates of sulfite the lowest achievable pH in the scrubber liquid decreases. This can be explained by the increased amounts of water added to the scrubber liquid and decreased HADS due to there being another reaction in the reaction mechanism which competes for HSO_3^-. As there is less HSO_3^- present in the liquid less HNO_2 reacts with HSO_3^- to form HADS which increases the amount of HNO_2 that can dissociate to H^+ and NO_2^- through reaction 2.34 which contributes to decreased pH. This also indicates that if the sulfite oxidation rate were to be higher than assumed here the lowest achievable pH could decrease even further. From Figure 4.4 it can also be seen that the sulfate concentration increases more drastically than in the inhibited case which is due to the addition of reactions 3.1 and 3.2 which allows for sulfate formation from SO_3^{2-}. Comparing Figure 4.4a and Figure 4.4b it can be seen that in Figure 4.4b the nitrite concentration is continuously increasing in the investigated pH range while in Figure 4.4b the nitrite concentration reaches a maximum at around pH $\approx$ 7.5. This is due to the the equilibrium of reaction 2.29 being shifted towards SO_3^- at higher pH values and the oxidation rate being high enough that HSO_3^- becomes limited and the consumption of SO_3^- being high enough that HSO_3^- is not reformed at a sufficient rate to allow for increased nitrite formation. For all the cases investigated it can also be seen that the concentration profile for the carbonates is the same for all cases which is due to CO_2 absorption only depending on the amount of water present in the scrubber which does not change between the cases.



(a) Bottom liquid composition as function of pH with an assumed sulfite oxidation rate of k=0.001. Concentration of the solid lines are read from the left axis and dashed lines from the right axis.



(b) Bottom liquid composition as function of pH with an assumed sulfite oxidation rate of k=0.01. Concentration of the solid lines are read from the left axis and dashed lines from the right axis.

Figure 4.4: Bottom liquid composition when the pseudo reactions are added to the reaction mechanisms with two sulfite oxidation rates investigated.

The percentage of inlet NO_2 absorbed was also investigated and the results can be seen in Figure 4.5. From the figure it can be seen that the highest absorption correlates well with the pH corresponding to the highest concentration of nitrite seen in the previous figures. The exponential increase in absorption with increasing pH can be explained by the decreased formation of HADS seen in Figure 4.3 and 4.4. This indicates that the absorption is heavily dependent on the availability of sulfite and the hydrolysis of NO_2 which is dependent on the sulfite oxidation rate. An increased absorption percentage can also be interpreted as decreased addition of Na_2SO_3 to achieve a certain degree of absorption. Therefore, to minimise the consumption of Na_2SO_3 to obtain an absorption percentage of 90% in the case of k=0.01 the scrubber should be operated with a pH around 7.5 while in the other cases a pH around 8 would yield the lowest consumption of Na_2SO_3 according to the model.

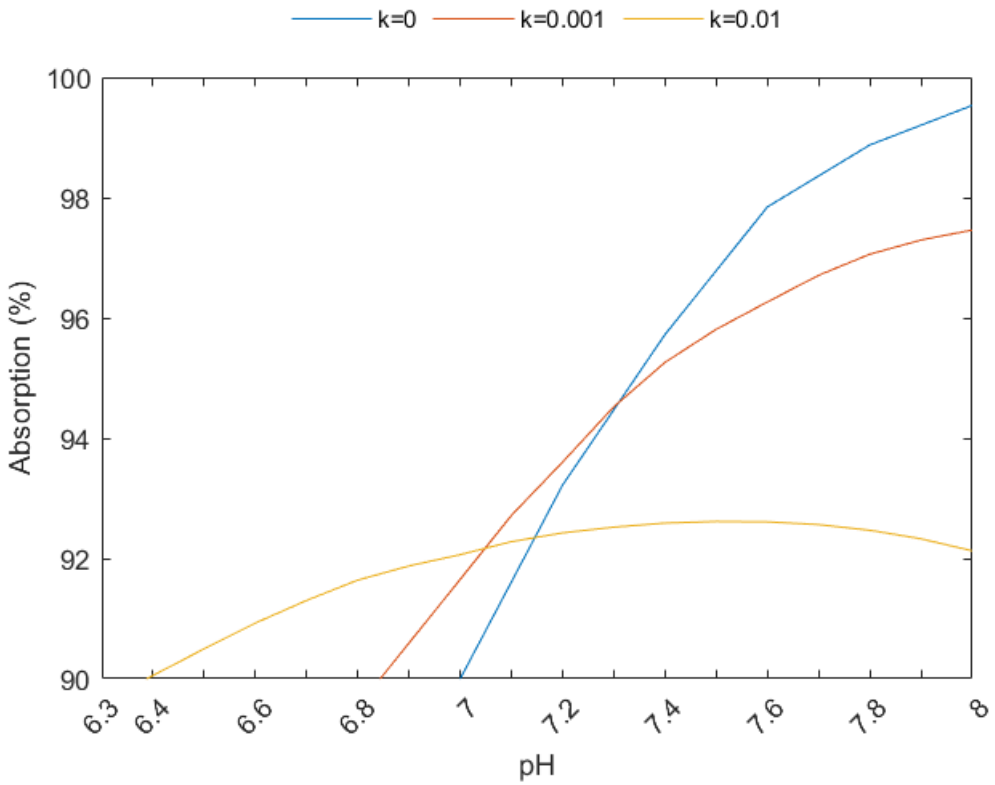


Figure 4.5: Percentage of inlet NO_2 absorbed for the different investigated oxidation rates as function of pH.

To maintain the pH at a certain value, NaOH was added to the scrubber liquid. In Figure 4.6 the amount of NaOH needed to maintain a specific pH can be seen for the three sulfite oxidation rates investigated. From the figure it can be seen that at higher oxidation rates the higher the consumption of NaOH. This is as previously discussed due to decreased HADS formation increasing the prescence of HNO_2 in the scrubber liquid and decreased recirculation of the scrubber liquid which increases the amount of makeup water added causing an increase in bulk mass that need to

be alkalised. The exponential increase in NaOH dosing to maintain a higher pH correlates with the increasing carbonate concentrations seen in Figure 4.3 and Figure 4.4. Therefore, there is a trade of between decreasing Na_2SO_3 consumption and NaOH consumption due to the increased absorption of CO_2 at higher pH.

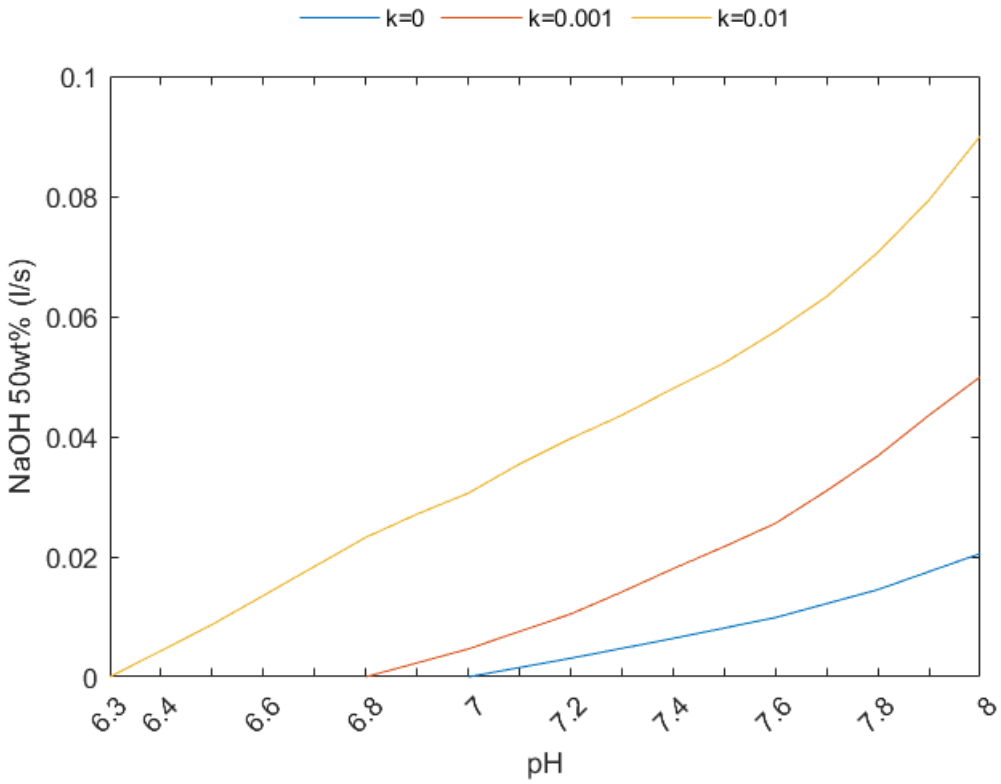


Figure 4.6: Amount of NaOH added to the scrubber liquid added to maintain a specific pH for different rates of sulfite oxidation.

4.3 The effect of residence time

Residence time is an another parameter that will affect the process performance as it determines how high the concentration of sulfite needs to be to achieve a certain degree of absorption. In Figure 4.7 it can be seen how the absorption of NO_2 varies with the height of the scrubber when the highest sulfite oxidation rate is assumed. The only parameters that are changed to obtain the results is the height of the scrubber and the amount of NaOH to maintain the pH at the optimum of 7.5. Only one case is shown since increasing or decreasing the residence time will have the same effect regardless of oxidation rate. Na_2SO_3 was added to the liquid to be able to obtain 90% absorption of NO_2 at a height of 32 m. In Table 4.3 resulting flows in and out of the scrubber as well as operating parameters can be seen at a scrubber height of 32 m.

Table 4.3: Resulting flows in and out of the scrubber and operating parameters at a scrubber height of 32 m.

Parameter	k=0 s^{-1}
NO_2 removed (kg/h)	112
H (m)	32
pH	7.5
L/G	10
S(IV)/NO2	1.6
Makeup water (m^3/h)	2.7
Liquid bleed (m^3/h)	4.7
NaOH (m^3/h)	0.2

From Figure 4.7 it can be seen that the increase in absorption per added meter of height will decrease with increasing height due to diminishing partial pressure of NO_2 in the flue gas and diminishing concentration of sulfite in the liquid. It can be seen that increasing the height above 32 m with the given dosing of Na_2SO_3 will not gain any significant benefit in terms of decreasing the consumption of Na_2SO_3 to achieve 90% absorption. Decreasing the height below 32 m will start to have a significant impact on the absorption below 20 m. A decrease in height below 20 m could therefore be seen to have a significant impact on the consumption of Na_2SO_3 to achieve 90% absorption of NO_2.

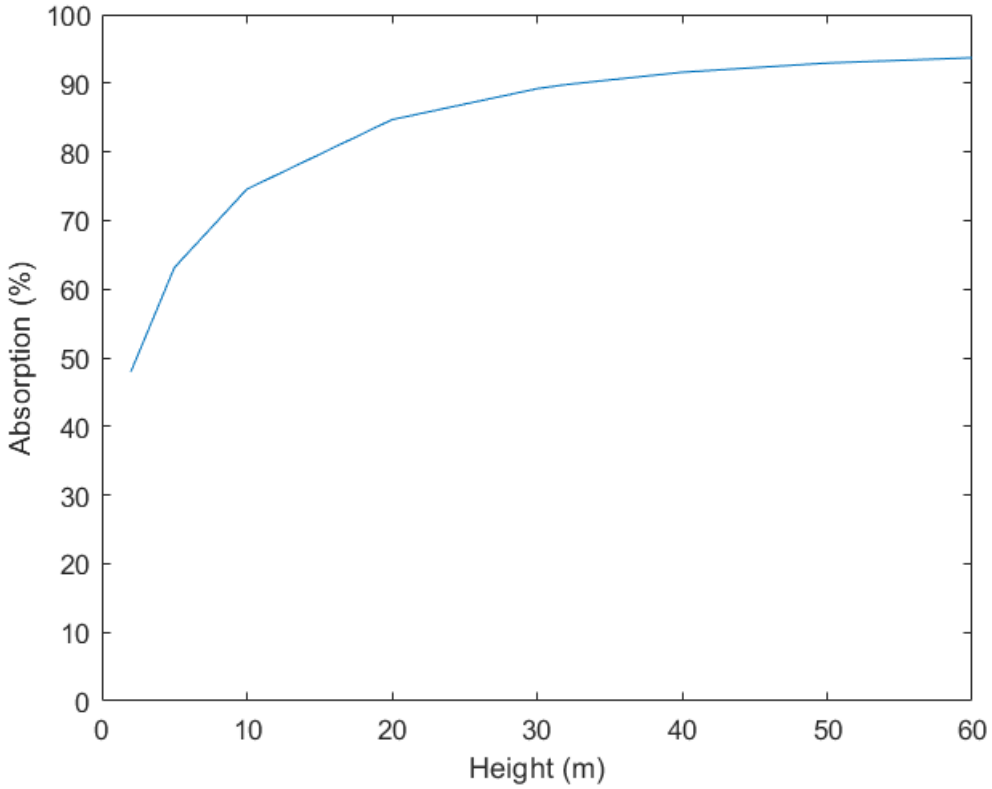


Figure 4.7: How the NO_2 absorption varies with height for the highest assumed sulfite oxidation when applying the scrubber to the recovery boiler.

4.4 Design and resulting flows

Based on the investigation on the effect on pH and residence time a final design was decided upon. In Table 4.4 the final design for the scrubber can be seen. For the recovery boiler the height was chosen to be 32 m and to achieve a 80% approach to flooding a diameter of 17 m was needed. The height of the lime kiln scrubber to achieve the same residence time as in the recovery boiler was determined to be 29 m with a diameter of 6 m to reach 80% approach to flooding. Also seen in Table 4.4 is the resulting consumption of oxidising agent, ClO_2 or H_2O_2, for complete NO to NO_2 oxidation depending on which oxidising agent is being used and in which combustion unit the scrubber is applied to. Please note that only one of the oxidising agents are used to perform the oxidation step of the scrubber process and therefore the consumption of ClO_2 and H_2O_2 should be looked at individually. In the table the resulting consumption of process chemicals and flows out of the scrubber depending on what rate of sulfite oxidation is assumed can also be seen.

Table 4.4: Resulting performance parameters for the scrubber design.

Parameter	SP4+SP6			MU1+MU2		
Liquid flow (m^3/h)	10033			1093		
L/G (kg liquid/kg gas)	10			10		
Height (m)	32			29		
Diameter (m)	17			6		
ClO_2* (kg/h)	93			18		
H_2O_2* (kg/h)	243			49		
NO_2 removed (kg/h)	112			22		
SO_2 removed (kg/h)	0			0.4		
Oxidation rate (s^{-1})	k=0	k=0.001	k=0.01	k=0	k=0.001	k=0.01
NaOH (l/s)	0.03	0.03	0.05	0.005	0.007	0.001
S(IV)/NO_2	0.8	0.9	1.6	0.8	0.8	1.5
$Na_2S_2O_3$ (kg/h)	169	0	0	34	0	0
Makeup water (m^3/h)	3.2	4.5	14	0.6	0.8	2.3
Liquid bleed (m^3/h)	4.6	5.9	17	0.9	1.1	2.8
Carbonates (g/L)	2.7	2.7	2.7	4.2	4.2	4.2
HADS (g/L)	15	8.4	1.0	18	12	2.1
N(III) (g/L)	21	17	6.5	19	17	7.5
N(V) (mg/L)	39	37	25	43	44	28
S(IV) (mg/L)	17	14	5.8	20	15	8.7
S(VI) (g/L)	25	25	25	25	25	25

*Note that ClO_2 and H_2O_2 are not used simultaneously in the scrubber process.

From the results in Table 4.4 it can be seen that the consumption of H_2O_2 to achieve 90% absorption of NO_2 from the recovery boiler would increase the site consumption with around 9% while for the lime kilns the consumption would increase with around 2%. With the assumption regarding ClO_2 consumption the site consumption could be expected to increase with around 4% for the recovery boiler and around 2% for the lime kilns. In the final design the operating pH of the scrubbers was chosen to be 7.5 as this would be the optimum pH to minimise Na_2SO_3 consumption if the higher rate of sulfite oxidation were to take place. From Table 4.4 it can be seen that the consumption of NaOH is significantly affected by the sulfite oxidation rate with the highest consumption corresponding to the highest oxidation rate and the lowest when oxidation is inhibited. This indicates that the consumption of NaOH depending on if sulfite oxidation can be inhibited or not can increase in the order of magnitude between 3% to 5% compared to the consumption today during normal operation if the scrubber is applied to the recovery boiler. To apply the scrubber to the lime kilns would result in a increase in NaOH consumption in a order of magnitude between 0.5% and 1%. Similarly to the NaOH consumption, the sulfite oxidation rate will impact the makeup water consumption and increase the site consumption in the order of magnitude in between 0.1% and 0.6% for the recovery boiler and in between 0.02% and 0.1% for the lime kilns. The amount thiosulfate needed to inhibit the sulfite oxidation in the scrubber dedicated to the recovery boiler would amount in a 10% increase of white liquor sent to the white liquor oxidation plant. This is given

that the white liquor is partially oxidised so that the majority of the oxidised sodium sulfide remain as sodium thiosulfate and is not further oxidised to sodium sulfate and that the concentration of sulfide in the white liquor is 50 g/l. For the lime kilns the amount of white liquor sent to the white liquor oxidation facilities would increase with about 2%. In Table 4.5 the increase of process chemical consumption depending on which combustion unit the scrubber is being applied to is summarised.

Table 4.5: Summary of the increase in process chemical consumption when comparing to normal operating conditions depending on which combustion unit the scrubber technology is applied to.

Process chemical	Increase from recovery boiler (%)	Increase from lime kilns (%)
H_2O_2	9	2
ClO_2	4	1
NaOH	3-5	0.5-1
Water	0.1-0.6	0.02-0.1
Oxidised white liquor	10	2

Based on the concentrations and liquid bleed from the scrubber in Table 4.4 it can be seen that the amount of nitrite that is removed with the scrubber effluent is in the magnitude of 2.4 tonnes/day independent of the rate of sulfite oxidation for the recovery boiler. This is since nitrite corresponds to the amount of NO_2 that is hydrolysed which is similar for all cases since the same amount of NO_2 is absorbed. The amount nitrate removed with the scrubber effluent would amount to around 4 to 10 kg/day depending on the rate of sulfite oxidation and the amount of sulfite would amount to around 2 kg/day independent of of the sulfite oxidation rate. Sulfate removed with the scrubber effluent is heavily dependent on the oxidation rate and varies between 3 tonnes/day when sulfite oxidation is assumed to be inhibited and 10 tonnes/day at the highest rate of sulfite oxidation. Similarly, the amount of carbonates removed will vary between 0.3 to 1 tonnes/day depending on the sulfite oxidation rate. The amount of HADS removed with the effluent will decrease with increasing sulfite oxidation and would amount to around 1.6 tonnes/day when oxidation is inhibited and 0.6 tonnes/day at the highest rate of oxidation. For the lime kilns the amount of each specie that has to be handled is between 85 to 65% less than for the recovery boiler. In Table 4.6 the amount of each substance in the scrubber liquid released to the wastewater treatment system depending on which combustion unit the scrubber is being applied to is summarised.

Table 4.6: Summary of the amount of each substance released from the scrubber to the wastewater treatment system depending on which combustion unit the scrubber is being applied to.

Substance	Recovery boiler (tonnes/day)	Lime kilns (tonnes/day)
N(III)	2.4	0.5
N(IV)	0.004-0.01	0.001-0.002
S(IV)	0.002	0.0005
S(VI)	3-10	0.6-2
Carbonates	0.3-1	0.1-0.3
HADS	0.6-1.6	0.14-0.4

5

Discussion

With the current process conditions for the lime kilns and recovery boiler it is not possible to achieve the relation between SO_2 and NO_2 in the flue gas that is need to reach a 90% absorption of NO_2. This results in almost all sulfite having to be provided through the addition on Na_2SO_3 which negatively affects the economic performance of the scrubber. Therefore, the scrubber would benefit from increasing the SO_2 out from the combustion units. This could for example be achieved by increasing the sulfidity of the white liquor which could change the relationship between sodium and sulfur in the upper part of the furnace to allow SO_2 to be present in the flue gas.

There are also other benefits than in the context of improving the scrubber performance that can be obtained by increasing white liquor sulfidity. For example by increasing the sulfidity of the white liquor a higher delignification rate can be achieved as well as production of pulp with improved mechanical properties. Increasing the sulfidity of the white liquor could also decrease the load of the causticization plant as less NaOH would be needed for cooking [42].

Another benefit that could stem from increased amount of sulfur in the upper part of the boiler is decreased chloride content in the dust due to increased alkalisulfation through reaction 2.6 as a consequence of higher availability of SO_2. This would decrease the chloride build up when recirculating dust to the process allowing for a higher recovery of sulfur from the dust collectors. The chloride would then be removed from the flue gas by the quench before the flue gas enters the scrubber and would therefore not be able to exit into the surrounding.

One potential problem with operating with increased sulfur to sodium ratio could be the formation of bisulfate as seen in Figure 2.5. This could lead to fouling and corrosion in the convective section of the boiler. At the same time the amounts of sticky alkali chlorides might be possible to reduce due to increased sulfation. Also cooking at high sulfidity is often associated with corrosion problems in process equipment like the digesters.

Other ways to increase the SO_2 in the exiting flue gas from the recovery boiler could be by decreasing the temperature in the lower part of the boiler. This would also result in decreased amounts of sodium vapours in the upper part of the boiler meaning that more sulfur can exit the boiler in the form SO_2. To decrease the temperature of the lower furnace the moisture content of the black liquor could be increased. This would decrease the load of the evaporators in the evaporation step of the chemical recovery cycle while increasing the SO_2 escaping the boiler and

decreasing the amount of NO_x formed due to decreased temperatures within the furnace. The drawbacks on the other hand would be reduced high grade steam production and as discussed previously increased fouling in the convective section.

The scrubber effluent should if possible not be treated in the current wastewater treatment facility without in some way removing the sulfate from the effluent. This is due to a suspected presence of a sulfur consuming specie named Thiotrix which is a filamentous microorganisms which can hinder the sediment from settling which affects the efficiency of the wastewater treatment plant.

To remove sulfate from the effluent one might consider chemical precipitation using lime and separation of sulfate from the rest of the effluent using sedimentation. Another option which avoids the scrubber effluent entering the wastewater treatment plant is incineration of the liquid. This could be seen as both a way recycling sulfur back to the recovery process while also treating the effluent if recycled to the recovery boiler. To be able to recover the sulfate in the scrubber effluent as sulfide one should aim to bring in the scrubber effluent as far down in the boiler as possible to make sure that the sulfate ends up in the smelt. One way to achieve this would be to bring back the effluent by mixing it with the weak black liquor before the black liquor evaporation step. This would probably cause the lowest amount of heat losses in the process due to the high efficiency of the evaporators. However, this could amount in release of NO during the evaporation step due to the volatility of nitrite. This NO would then most likely end up with the non condensable gases which are then incinerated at the secondary air register in the recovery boiler which most likely would increase the NO_x emissions from the recovery boiler. However, if it is possible to bring in the nitrite at the bottom of the recovery boiler it is a good possibility that the nitrite is reduced to N_2 [43]. Injecting the effluent higher up in the boiler is another alternative which has been shown to have a positive impact on the NO_x formation when performing scrubber effluent injections at a waste to energy plant [13]. Using this solution the sulfate in the effluent would most likely end up in the dust which then is captured by the ESP and can be put back into the process. This would however result in a energy loss due to the injection water into to the furnace, this loss could be to some degree recovered as lower grade heat through the installation of a flue gas condensation system which would be required if ClO_2 is used as oxidising agent.

Another aspect to take in consideration when deciding if it is possible to treat the scrubber effluent in the wastewater treatment plant is if bleaching is carried out using chloride dioxide in which case the plant needs to be able to handle chlorate. As previously discussed this would be achieved by removing the aeration from the ANOX basin to force the microorganism to reduce chlorate to retrieve oxygen. However, this could also result in denitrification which mean that the microorganisms instead of reducing chlorate would reduce nitrogen compounds, such as nitrate and nitrite, decreasing the efficiency of the chlorate removal. Also, when denitrification takes place nitrogen gas i released which could potentially inhibit the sludge from settling. Otherwise addition of nitrogen to the wastewater treatment system can be seen as beneficial since it is a macro nutrient which is essential for the microorganisms.

When comparing the consumption of process chemicals in the scrubber it can be seen

that the scrubber would have a somewhat significant impact on the consumption ofH_2O_2 at the site, however the consumption can be expected to be lower. If ClO_2 where to be used at the site the impact can be seen to be much less significant impact. Similarly, the impact on water consumption can be seen to be low while the increase of chemicals such as NaOH and white liquor can be seen to be more significant. To decrease the amount of NaOH used in the scrubber process it is possible to operate at a lower pH which would reduce the amount CO_2 absorbed, however this would increase the amount of Na_2SO_3 added to the scrubber to achieve the same percentage of absorbed NO_2. Based on the results, sulfite oxidation will have a negative impact on the consumption of process chemicals especially on the consumption on sulfite to which the main cost of the scrubber operation is assigned and NaOH. Therefore it is important to be able to limit the sulfite oxidation. However, to limit the sulfite oxidation using chemicals present at the site, would cause a relatively large increase of oxidised white liquor production.

With the designed scrubber 90% of the total nitrogen emissions from the recovery boiler can be removed. This will have a significant impact on the effect of recovery boilers being included within the NO_x fee and crediting is decreased to 60% from 100%. With the current emissions from the recovery boiler the changes to the NO_x fee would result in a net cost of around 30 kr/kg_{NO_x} which would amount to a yearly cost around 30 million SEK. However, if the proposed scrubber is installed and the proposed changes to the NO_x fee goes through the site would be able to gain around 150 kr/kg_{NO_x} from the crediting system which would amount to around 15 million SEK yearly. To be able to avoid additional costs due to the changed NO_x fee the site would not have to reduce their emissions as far to 90% but around 60%. But depending on how fast others manage to reduce their emissions reducing only 60% might soon come to be associated with a cost. By looking at achieving a lower decrease in emissions this implies that the scrubber chemical consumption would be reduced or that a smaller size of the equipment is sufficient.

6

Conclusion

In this study a scrubber for simultaneous absorption of SO_x and NO_x was designed to achieve 90% removal of NO_x from the lime kilns and the recovery boiler. The resulting dimensions for the scrubber dedicated to the recovery boiler was 32 m in height and 17 m in diameter and for the lime kilns the height was 29 m with a diameter of 6 m.

Based on the mapping of NO_x and SO_x emissions from the combustion units it was concluded that during the current conditions the amount of SO_2 present in the flue gas would not be sufficient to achieve the wanted degree of NO_x removal. This indicates that close to all sulfite required for the absorption process would have to be retrieved from addition of Na_2SO_3 which put a high emphasis of limiting the oxidation of sulfite to minimise the cost of operation.

To be able to efficiently oxidise NO to NO_2 using H_2O_2, the oxidising agent would be required to be injected in the convection section in the recovery boiler and for the lime kilns before the ESP. When using ClO_2 to achieve the required temperature, the flue gas would have to be further cooled and therefore the installation of a flue gas condensation unit would be required.

The results show that the scrubber will have a low impact on the consumption of process chemicals such as ClO_2, if it were to be used, and water while the consumption of NaOH, H_2O_2 and oxidised white liquor is of higher significance. To decrease the consumption NaOH similarly to the amount of sulfite needed to operate the scrubber sulfite oxidation needs to be limited. Other ways to decrease the consumption of NaOH would be decreasing the operating pH of the scrubber to absorb less CO_2, however this would increase the amount of sulfite needed to be added to the scrubber. Limiting sulfite oxidation would also decrease the consumption of water.

Due to the amount of sulfate present in the scrubber effluent and the suspected presence of Thiotrix in the wastewater treatment the effluent should not be treated in the wastewater treatment system. Therefore, other alternatives which either includes removal of sulfate before the water treatment step or other ways of treating the effluent should be considered.

Site specifically further studies should focus on how the oxidation of NO should be carried out using H_2O_2. These studies should focus on if it is possible to inject H_2O_2 at the identified points in the lime kilns and recovery boiler and how the equipment in the present process would be affected. Similarly further research should also focus on how the scrubber effluent should be treated whether it is more beneficial

to remove the sulfate prior to the wastewater treatment using for example chemical precipitation or if it is possible to recycle the effluent into the process through for example incineration. Also, future work should focus on the economics of the scrubber and designing a scrubber that minimises the cost taking in consideration both capital and operational cost.

Technology specifically further studies should focus on the sulfite oxidation to be able to better predict the speed of oxidation and how to inhibit the oxidation. Specifically, the understanding of the radical reactions should be further increased and how these can be inhibited. This would allow for better predictions regarding the scrubber performance and how to optimise the process.

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