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Sulfite Oxidation in Wet Flue Gas Scrubbers

Master’s thesis in Innovative and Sustainable Chemical Engineering

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Acronyms

WTE Waste-to-energy
CCS Carbon Capture and Storage
ESP Electrostatic Precipitator
WFGD Wet Flue Gas Desulfurization
BAT Best Available Technique
VLE Vapour-Liquid Equilibrium
NRTL Non-Random Two Liquid
CSTR Continuously Stirred Tank Reactor

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Abstract

Reducing emissions of sulfur dioxide from heat and power generation is highly important in order to mitigate environmental concerns such as acidification and particulate matter concentrations in the atmosphere. Wet flue gas desulfurization (WGFD) is a key technology to achieve this.

This thesis focuses on the oxidation of sulfite (SO_3^{2-}) which is formed when sulfur dioxide is absorbed in WFGD units. The sulfite oxidises to sulfate (SO_4^{2-}). This thesis aims to model the process of wet flue gas desulfuriation and validate the results by measuring sulfite concentrations in full scale scrubber units.

The modelling was conducted using the flowsheeting software Aspen PLUS. Modelling of Renova's scrubber units at the Sävenäs waste-to-energy (WTE) plant in Gothenburg, Sweden and Fjernvarme Fyn's scrubber units at their WTE plant in Odense, Denmark was conducted. A sensitivity analysis for the model comparing different operating conditions and sulfite oxidation kinetics was carried out. Measurements of sulfite concentrations were taken at these two sites using a portable field spectrophotometer in order to validate the results from the modelling. The measurements of sulfite were found to fluctuate to a high extent between measurement occasions.

The modelling results predict sulfite concentrations in the same order of magnitude as the measurements, for example, the base case scenario of the simulations provided sulfite concentrations close to some of the measurements taken, especially for Fjernvarme Fyn's case where simulations gave a result of approximately 3700 mg/l of sulfite versus a measured 3000 mg/l.
However, the large variations in measured concentrations remained unexplained.

The spectrophotometer provided results that overestimated the concentration of sulfite by a factor of approximately 5 when compared to measurements using iodometry.

In the simulations, a rate constant for the sulfite oxidation reaction of $1.2 * 10^{-4}$ s^{-1} was used. A test using the spectrophotometer measuring the decay of sulfite over time was conducted to estimate the apparent rate constant, which yielded the result $7.21 * 10^{-5}$ s^{-1}.

Keywords: Sulfur dioxide, sulfite oxidation, scrubber, flue gas, waste incineration.

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David Norsund, Gothenburg, May 2023

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1 Introduction

1.1 Background

Emissions of sulfur dioxide are caused both by natural processes, mainly volcanic activity, as well as from anthropogenic sources. The main source is combustion of fossil fuels such as coal and oil. In Sweden, the bulk of the pollution comes from the processing industry, electricity and district heating production and heating for buildings. [1]

Since the most significant anthropogenic source of SO_2 is combustion processes, removal of sulfur dioxide (SO_2) from flue gas is essential, as it is a major pollutant, contributing to negative health and environmental effects. Sulfur dioxide pollution causes health issues such as damage to the respiratory system and cause breathing difficulties. Sulfur dioxide emissions can lead to increased concentrations of particulate matter in the air which also may lead to health concerns as well as reduced visibility. Another environmental aspect is the formation of acid rain, which may harm sensitive ecosystems by acidification. [2]

With more stringent regulations on sulfur dioxide emissions as well as the negative effects the emissions have, designing efficient flue-gas desulfurization equipment is vital. In the European Union, emissions of sulfur dioxide has dropped by 92% over the period 2004-2021 according to the European Energy Agency, largely due to more stringent legally binding emissions limits driving the usage of desulfurization technology. Reduced fossil fuels usage in large power plants is the second factor reducing emissions of sulfur. [3] Sweden has committed to the Gothenburg protocol which restricts the amount of SO_2 (among other gases) a country can emit. The protocol set targets until 2020, when the total emissions of sulfur dioxide was supposed to be reduced to 27 kt/year from 34 kt/year in 2005 in Sweden's case. In 2020 Sweden emitted 15 kt of SO_2, meaning the commitment was fulfilled. [4]

Babcock & Wilcox Vølund Environmental has designed three of the desulfurization units installed at the Renova Sävenäs waste-to-energy (WTE) plant in Gothenburg, Sweden with a capacity of approximately 200 MW as well as retrofitted one of the three desulfurization units installed at Fjernvarme Fyn WTE plant in Odense, Denmark (approx. 120 MW). The desulfurization units consist of scrubbers, also known as absorbers, a piece of equipment where the gaseous SO_2 is absorbed in a liquid phase. In the scrubber system, sulfur dioxide gas from the flue gases is absorbed in an aqueous phase with dissolved sodium hydroxide (NaOH). When this occurs, the now dissolved SO_2 can react with dissolved oxygen forming sulfite (SO_3^{2-}) and bisulfite (HSO_3^-) ions. These ions can be further oxidised to sulfate (SO_4^{2-}). The sulfite oxidation reaction is sensitive to catalysis, mainly by transition metal ions.

Predicting the rate at which sulfite is oxidized in the scrubber has multiple practical implications, slow sulfite oxidation is beneficial in order to absorb as much SO_2 as possible, as sulfite ions form a buffer system in the packed beds, reducing the pH gradients. This is important since the solubility of SO_2 in the liquid phase is pH dependent. The absorbed sulfur is used at Renova and Fjernvarme Fyn to produce gypsum ($CaSO_4$) as a byproduct and efficient oxidation of sulfite to sulfate is needed to produce gypsum of good quality, as too much sulfite will make the gypsum slurry difficult to dewater.

Renova is planning to utilise carbon capture and storage (CCS) in the future. Sulfite ions can react with nitrogen dioxide, which can prevent solvent degradation of the amines often used in CCS systems.[5]
Since high sulfite concentration is beneficial in some cases and unfavorable in others, it would be useful if the rate of oxidation can be predicted, in order to design better SO_2 scrubbing equipment.

1.2 System description

Renova operates four scrubber lines, one for each incineration boiler, of which Babcock & Wilcox has designed three. Line 2 and 3 are identical, with the same capacity to treat flue gases. Line 1 has a slightly smaller capacity.

Before the flue gas reaches the scrubber system, it is taken through an electrostatic precipitator (ESP) unit, where fine particulates and dust is removed using static electricity. It is then brought to the wet scrubber system.

The scrubber at Renova consists of three stages. First, the flue gas is brought to a quench stage where highly acidic water is sprayed into the flue gas as it passes. This serves two main purposes: to saturate the flue gas with water vapor and to cool it down to an appropriate temperature in order to not damage the equipment. The flue gas then enters the first stage of the scrubber, where acid gases, mainly hydrogen chloride is removed from the gases in a packed bed with acidic water. After this, the flue gas is brought to the SO_2 stage, which also consists of a packed bed, where an aqueous solution of NaOH is sprayed onto the packed bed to absorb the sulfur dioxide. The pH in this stage is close to 7. The liquid is gathered in a so called pump tank underneath the packed bed. The liquid level in the pump tank is held constant via a setpoint in the plant's control system. The liquid is recirculated inside the system, and 50% (by weight) NaOH-solution as well as make-up water are added to keep the pH and pump tank level constant. The second scrubber stage is the main point of consideration to this thesis, the HCl stage is neglected.

The conductivity of the scrubber liquid is measured continuously, this is an easy way to get an indirect measurement on how much sulfate and sulfite ions are present in the liquid. Conductivity is a measurement of a solution's ability to conduct electricity, measured in Siemens/meter (S/m). A higher amount of ions, i.e. charged particles leads to a higher conductivity, meaning that it is an indirect measurement of ion concentration. If the conductivity measured in the scrubber liquid reaches a setpoint in the plant control system, a bleed stream is taken from the system to purge it from ions. When the bleed stream is activated, the flow of make-up water is also activated, to keep the amount of liquid constant in the system. The bleed stream is brought to a so called condensation reactor, where additional scrubbing of the flue gas occurs. The liquid is then brought to an oxidation reactor, which aims to convert the remaining sulfite to sulfate before finally being brought to the facility's gypsum production process, where gypsum ($CaSO_4$) is produced as a by-product and sold to be used as for example construction material.

Both Renova and Fjernvarme Fyn have measured highly varying sulfite concentrations, and the reason for these variations are unclear.

1.3 Aim

The aim of this thesis is to determine the rate of oxidation of sulfur dioxide in industrial-scale absorption systems based on literature data as well as data from Renova's and Fjernvarme Fyn's desulfuriation units. The effects of operating conditions and sulfite oxidation kinetics will be quantified.

More specifically, this thesis aims to investigate the following questions:

1. Is it possible to achieve accurate simulation results for the scrubber units?
2. Can the modelling results be validated by measuring the sulfite concentration in the scrubber units?
3. Is there a noticeable catalytic effect on sulfite oxidation by metal ions present in the scrubber units?

The results will be used to better understand the process of sulfite oxidation, and to to help understand why measurements of sulfite concentrations vary to such a high extent.

2 Theory

2.1 SO_2 flue gas cleaning

In order to eliminate sulfur dioxide from flue gas streams from industrial processes, wet flue gas desulfurization (WFGD) units are often used and considered to be best available technique (BAT). [6] The most common types of WFGD units use either a limestone slurry or a sodium hydroxide solution as an absorbent. Limestone slurry scrubbers are the most common with about 80% of the market share for large incineration plants. This thesis focuses on flue gas cleaning with aqueous NaOH solution as absorbent. NaOH scrubbers consist of a packed tower, where the liquid absorbent comes in contact with the flue gas. Mass transfer from the gas to the liquid occurs, reducing the amount of SO_2 in the gas stream. With such a system installed, the amount of SO_2 in the flue gas can be reduced by up to 99%. The absorbed SO_2 can be used to produce gypsum ($CaSO_4$) as a marketable by-product in the plant. An advantage with using NaOH instead of limestone which is the most common type is that no considerable amount of scaling by $CaSO_4$ occurs, since no calcium is present in the scrubber, which can be an issue with the limestone process. However, in order to produce gypsum from a NaOH scrubber (as in Renova's or Fjernvarme Fyn's case) calcium must be added later in the process.[6]

Other technologies for flue gas desulfurization exist. For example; semi-dry desulfurization which involves the direct injection of a hydrated lime slurry and water into the hot flue gas inside a spray reactor. The water evaporates due to the heat of the flue gases and the dry products containing the absorbed SO_2 are collected in a bag filter. There is also dry desulfurization, where an adsorbent is sprayed directly into the flue gas stream as a dry powder. The solid residue is removed with a bag filter. It is generally less efficient than semi-dry processes, mostly due to poor stoichiometry, leading to inefficient adsorbent utilization. [7]

2.2 Two-film theory

Mass transfer is a phenomenon that occurs when there is a gradient in concentration. Substances in the region with high concentration will spontaneously transfer to the region of low concentration. This can occur via two main mechanisms; diffusion and convection. Diffusion is a random process, that always takes place whenever there is a concentration gradient. For convection to occur, there needs to be a flow of the bulk fluid. Mass transfer is the basis on which a scrubber functions. The mass transfer occurring inside wet flue gas treatment equipment is dominated by convection and is often modelled using two-film theory, this will also serve as the basis for the mass transfer occurring in the Aspen model. The flow in the scrubber unit is counter-current, so the system will be modelled according to Figure 1 below:

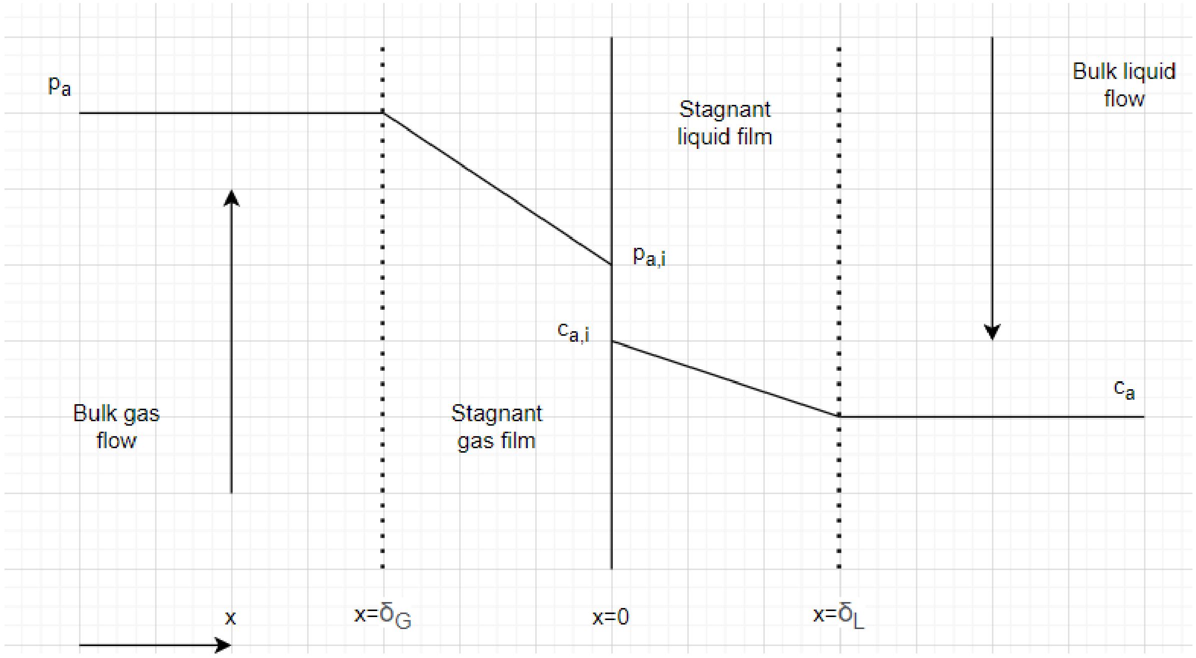

Figure 1: Explanatory sketch for the two-film theory.

There are multiple species in the gas phase that experience mass transfer to the liquid phase in this case, most importantly SO_2, CO_2 and O_2. The species have a partial pressure, p_a. This partial pressure is constant in the bulk gas phase, denoted by the straight line in Figure 1. As the species reach the stagnant film at $x = \delta_G$, the partial pressure decreases to the interface partial pressure, $p_{a,i}$. This is due to the assumption that the only location where mass transfer resistance occurs is in the stagnant boundary layer films. Over the phase boundary at x=0, phase equilibrium is assumed. This equilibrium partial pressure is calculated in the Aspen model using vapour-liquid equilibrium (VLE) parameters from the NRTL (non-random two liquid) model, which estimates activity coefficients (γ) to compensate for non-ideality and calculates the VLE partial pressure with the modified Raoult's law:

$$p_{a,i} = \gamma_a x_a P_a^{sat} \tag{1}$$

Where x_a is the mole fraction in the liquid phase and P_a^{sat} is the saturation pressure of the species.

At steady state, the mass flux of a component in the gas phase must equal the mass flux of the component in the liquid phase:

$$N_a = k_G(p_a - p_{a,i}) = -k_L(c_a - c_{a,i}) \tag{2}$$

Where k_G and k_L are overall mass-transfer coefficients in the gas and liquid phase, respectively. These coefficients are dependant on the specific fluid conditions in each phase, and are calculated through empirical correlations.[8]

In Aspen, all of the relations between the gas and liquid phase are solved iteratively for each stage in the absorbtion column, generating the final inlet and outlet concentrations and partial pressures. All of the chemical reactions that are being modelled occur in the liquid phase, so the species need to transfer over the phase interface first, then the reactions can take place, both in the liquid film and in the liquid bulk.

2.3 Chemical reactions

Several chemical reactions occur in the system, the ones being modelled are the following:

The equilibrium of carbon dioxide dissolving and dissociating in the liquid phase:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \tag{R1}$$

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)} \tag{R2}$$

The bicarbonate ($HCO^-_{3(aq)}$) ions can then be deprotonated:

$$HCO^-_{3(aq)} \rightleftharpoons H^+_{(aq)} + CO^{2-}_{3(aq)} \tag{R3}$$

At pH 7, bicarbonate is the dominating species, with very small amounts of carbonate ions present. As pH decreases, the equilibrium shifts towards physically dissolved carbon dioxide. At increased pH, carbonate ions become dominant. [9] At high pH, when the bicarbonate is converted to carbonate ions, more CO_2 is absorbed, leading to less efficient SO_2 absorption.

Most importantly for this work, the SO_2 reaction chain: first, gaseous sulfur dioxide is dissolved in the liquid phase:

$$SO_{2(g)} \rightleftharpoons SO_{2(aq)} \tag{R4}$$

The dissolved SO_2 then reacts with water:

$$SO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HSO^-_{3(aq)} \tag{R5}$$

The bisulfite ions disassociate to hydrogen ions and sulfite ions:

$$HSO^-_{3(aq)} \rightleftharpoons H^+_{(aq)} + SO^{2-}_{3(aq)} \tag{R6}$$

Finally, the sulfite ions can be oxidised by dissolved oxygen in the liquid phase:

$$2SO^{2-}_{3(aq)} + O_{2(aq)} \rightarrow 2SO^{2-}_{4(aq)} \tag{R7}$$

[10]

Most of the reactions are equilibrium controlled and the equilibrium composition of the species involved is pH dependent. For example, at low pH when the concentration of hydrogen ions is high, these reactions will be shifted to the left and vice versa due to Le Chatelier's principle.
The pH dependence on the sulfur dioxide reaction chain can be seen in Equation R8 below:

$$\begin{aligned} &SO_{2(g)} \rightleftharpoons SO_{2(aq)} + H_2O_{(l)} \rightleftharpoons HSO^{2-}_{3(aq)} + H^+_{(aq)} \rightleftharpoons SO^{2-}_{3(aq)} + 2H^+_{(aq)} \\ &low \longrightarrow pH \longrightarrow high \end{aligned} \tag{R8}$$

The equilibrium gets shifted further to the right as pH increases. At around pH 7, where Renova and Fjernvarme Fyn operates their scrubbers, the distribution between bisulfite and sulfite is about 55 mol% and 45 mol%, respectively. Due to the pH dependence in Reaction R8, at low pH the equilibrium is shifted to the left, meaning less SO_2 is sequestered due to bisulfite being the dominant species at lower pH and bisulfite oxidises more slowly than sulfite. Another factor at low pH is the solubility of SO_2, which is much lower at low pH. the combination of these factors mean that acidic SO_2 scrubbing is not feasible. [11]

The rate limiting step in the sulfur dioxide reaction chain is the oxidation of sulfite to sulfate (R7) as it is the only kinetically defined reaction, the equilibrium limited reactions reach their equilibrium quickly. The sulfite oxidation is in reality much more complex than reaction 6, it consists of several steps of free radical reactions. [12]

2.4 Kinetics of the sulfite oxidation reaction

As mentioned in Section 2.3, the sulfite oxidation reaction is a complex chain of radical reactions. [12] This chapter will not go into the details of this complex system, but deal with the kinetics of the overall reaction (R6). There exists a significant amount of research on the kinetics of this reaction. Most sources agree on the reaction being zeroth order with respect to oxygen and first order with respect to sulfite. Beilke, Lamb and Müller suggested the following rate expression for the sulfite oxidation reaction, valid for pH 3-6 at 25°C:

$$\frac{d[SO_4^{2-}]}{dt} = 1.2 \times 10^{-4}[SO_3^{2-}][H^+]^{-0.16} \qquad [moldm^{-3}s^{-1}] \tag{3}$$

Where the brackets refer to molar concentration of the species in mol/l. [10] Beilke et al has summarized several rate expressions. Other sources included in Beilke et al's summary of rate expressions do not include the dependence on H^+ concentration included in Equation 3, first order with respect to sulfite and have rate constants of $0.5 * 10^{-3}$ to $6 * 10^-3$ s^{-1} valid in different pH intervals. Some examples:

$$\frac{d[SO_4^{2-}]}{dt} = 1.7 \times 10^{-3}[SO_3^{2-}] \qquad [moldm^{-3}s^{-1}] \tag{4}$$

The rate expression in Equation 4 is valid for pH 6.8 at 25 °C, as reported by Scott and Hobbs. [13]

Winkelmann suggests the following rate expresssion:

$$\frac{d[SO_4^{2-}]}{dt} = 3.5 \times 10^{-3}[SO_3^{2-}] \qquad [moldm^{-3}s^{-1}] \tag{5}$$

Valid at pH 7 and 25 °C. [14].

The reaction rate is dependent on pH, with many sources claiming a higher rate of sulfate formation with increasing pH. [10]

2.5 Catalysis and inhibition of the sulfite oxidation reaction

The sulfite oxidation reaction is very sensitive to both catalysis and inhibition. Catalysis by transition metal ions has noticeable effects, for example by manganese, iron and copper. These ions are common impurities in scrubber liquids. Ulrich, Rochelle and Prada reported enhancement factors (catalyzed rate divided by uncatalyzed rate) for a solution containing 10 mM SO_3^{2-} and 300 mM SO_4^{2-} at pH 5, 50 °C and 400 rpm agitation.

For manganese these enhancement factors of 2.5 and 5 for Mn concentrations of 5 and 10 mM, respectively. For iron, these were 3.1 and 2.4 for concentrations 0.1 and 10 mM Fe, respectively.
For copper, an enhancement factor 7.3 was reported for 10 mM Cu. For all ions investigated, there is a considerable effect on the oxidation rate. [15]

Schmid et al has studied the inhibitory effect of thiosulfate ($S_2O_3^{2-}$) and found that for a solution of 10 mM sulfite and 1 mM thiosulfate at pH 7, the oxidation rate dropped by 75 % and with a thiosulfate concentration of 2 mM, the rate dropped by 88 %. The thiosulfate inhibits the oxidation by acting as a radical scavenger in the complex radical reaction chain that sulfite is oxidized via, as mentioned in Section 2.3. The thiosulfate scavenges radicals, terminating the chain reaction. [16]
In a report by J.L. Hudson for the U.S. EPA, it was found that organic acids such as succinic and glycolic acid also can inhibit the rate of oxidation, but the reaction can still be catalyzed by manganese or iron, even in the presence of inhibitors. [11]

3 Methodology

3.1 Modelling

The modelling of the scrubber units was made using the flowsheeting software Aspen PLUS.

The model was built in several steps. An initial open-loop "once-through" model without recirculation was created. This was done in order to ensure that the final closed-loop model of the system converges. Process units were added successively to ensure convergence of each unit. The influence of varied pump tank volume, pH, sulfite oxidation rate constant and inlet SO_2 concentration were studied and different performance indicators were calculated. These include sulfite concentration in the scrubber liquid, degree of absorption, degree of oxidation and average reaction rates for the sulfite oxidation reaction. The degree of absorbtion is a measurement of how much SO_2 the scrubber has absorbed from the flue gas and is defined by the following equation:

$$Degree\,of\,absorbtion = 1 - \frac{\dot{m}_{SO_2,out}}{\dot{m}_{SO_2,in}} \tag{6}$$

Where $\dot{m}_{SO_2}$ is the mass flow of SO_2 in and out of the system.

The degree of oxidation is a measurement of how much of the sulfite has oxidised to sulfate:

$$Degree\,of\,oxidation = \frac{[SO_4^{2-}]}{[SO_3^{2-}] + [SO_4^{2-}]} \tag{7}$$

The species in brackets in equation 7 are defined as molar concentrations (mol/l).

The final flowsheet of the Aspen model is presented in Figure 2 below.

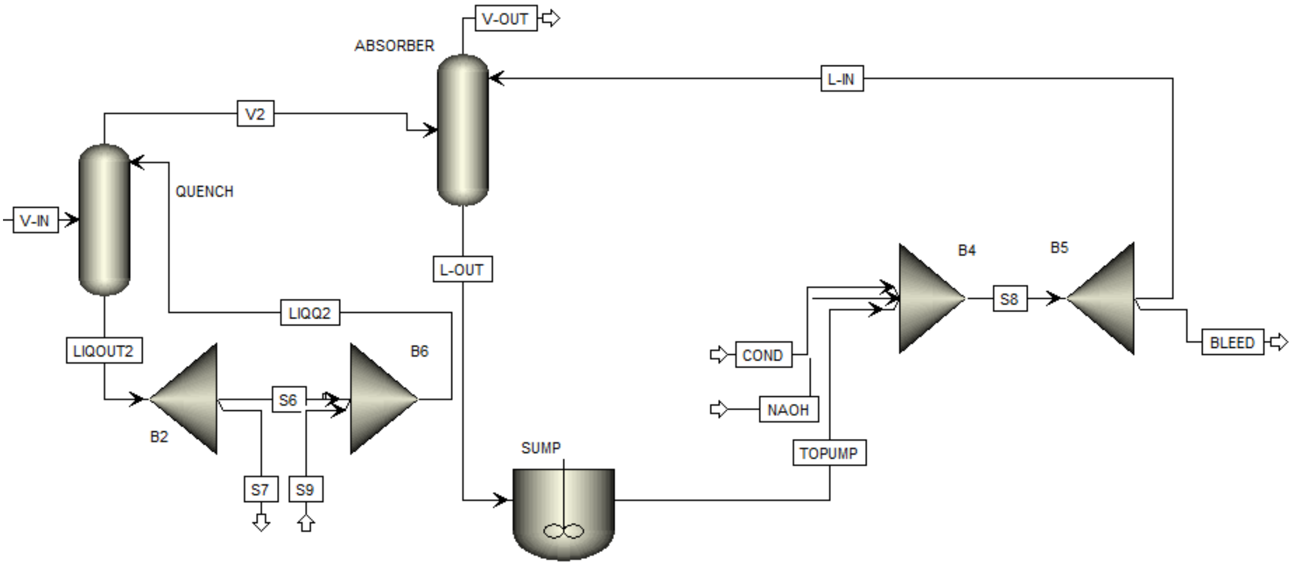

Figure 2: Flowsheet of the Aspen model used to model Renova's and Fjernvarme Fyn's scrubber units.

The electrolyte NRTL (non-random two liquid) activity model was chosen since a considerable amount of ions are present. No components were specified as "Henry Components" in Aspen, meaning that the phase equilibrium at the gas-liquid interfaces in the model are estimated with the NRTL model.

The known compositions, flows and state variables given by Babcock & Wilcox for Renova's flue gas desulfurization line no.1 were entered. The information about the inlet stream can be found in Table 1 below.

Table 1: Inlet conditions for the flue gas, stream V_IN in figure 2.

Temperature [°C]	142
Pressure [Pa]	99550
Volume flow [nm^3/h, wet gas]	86000
O_2 concentration [% vol., dry gas]	11
H_2O concentration [% vol., wet gas]	18
SO_2 concentration [$mg/nm3$, dry gas]	500
HCl concentration [$mg/nm3$, dry gas]	300
CO_2 concentration [% vol., dry gas]	10

In order to input this information into Aspen, the units were converted, all the concentrations were converted into molar flows for each component. Some assumptions were made, Table 1 refers to the stream before entering the HCl stage, and since this stage is not modeled, it was assumed that all HCl was absorbed in the HCl stage. No data on CO_2 concentration was given, so the value of 10 % in Table 1 was assumed. It was also assumed that apart from the species listed in Table 1, the remaining gas is composed of nitrogen. The values as entered in Aspen for the inlet flue gas stream (labeled V-IN in Figure 2) are presented in Table 2 below. Note that the temperature is not 142 °C as specified in Table 1, this is due it not being important in the model, instead it is set to the operating temperature for the scrubber unit (65 °C). The pressure was set to 1 bar instead of 99550 Pa as specified in Table 1, this was due to the pressure drop being small in the scrubber unit, so it was neglected in the model.

Table 2: Stream information for the feed flue gas, as entered in Aspen.

Temperature [°C]	65
Pressure [bar]	1.0
Total flow [mol/s]	1065.42
SO_2 flow [mol/s]	0.189366
O_2 flow [mol/s]	68.1391
CO_2 flow [mol/s]	87.3579
H_2O flow [mol/s]	191.845
N_2 flow [mol/s]	717.892

This data (Tables 1 and 2) is based on average values for Renova's desulfurization line no. 1. The variables fluctuate during operation, hence the averaged values were used in simulations.

3.1.1 Quench stage

The quench stage was simulated using the RADFRAC column in Aspen. The columns' sole purpose was to saturate the gas with water. H^+ ions were added to the water to make it highly acidic at a pH around zero, this was done in order to make sure that the quench step is not responsible for any absorption of sulfur dioxide, as the absorption process is pH dependent as mentioned in Section 2.3. A recycle loop where water is entered and removed were introduced to facilitate phase equilibrium based on the temperature of the flue gas. The autoprotolysis equilibrium reaction of water was added into the model for the quench. The model was set to equilibrium based, meaning no mass transfer between the phases was considered, the equilibrium composition is reached instantly and the phases are well-mixed. Finally, the number of equilibrium stages was increased until the composition and temperature of the exiting gas no longer changed. This amounted in 19 stages.

In reality, the quench stage at Renova is integrated inside the scrubber, where acidic water is sprayed into the flue gas to saturate it with water. The values entered for the quench water stream entering the quench stages (labeled S9 in Figure 2) are presented in Table 3.

Table 3: Stream information for the quench water stream.

Temperature [°C]	63
Pressure [bar]	1.0
Total flow [m^3/h]	1.0
H^+ mole fraction	0.0005
Cl^- mole fraction	0.0005
Water mole fraction	0.9999

It was important to get the vapor phase saturated with water in order to prevent water from the scrubbing liquid in the absorber downstream from evaporating and entering the exiting flue gas from the absorption column.

3.1.2 Absorber

The absorber was modeled in a similar fashion to the quench stages using the RADFRAC column. In reality, the scrubber consists of two stages where HCl is removed in the first stage. This was not considered in the model, the HCl was assumed to be completely absorbed when entering stage two. The reactions mentioned in Section 2.3 were entered into the RADFRAC model. The kinetics of the sulfite oxidation reaction where based on Beilke et al [10] with the rate expression:

$$\frac{d[SO_4^{2-}]}{dt} = 1.2 \times 10^{-4}[SO_3^{2-}] \qquad [moldm^{-3}s^{-1}] \tag{8}$$

Note that the dependence on $[H^+]^{-0.16}$ from Equation 3 is not present. It was initially included, but later removed due to uncertainties in if Aspen can handle a rate expression with dependencies on species that are not taking part in the actual reaction. As mentioned in Section 2.4, there are rate expressions similar to the one used here which do not include the $[H^+]$ dependence, with rate constants in a similar order of magnitude.

The remaining reactions are equilibrium reactions and their equilibrium constants were taken from Aspen's tabulated values, meaning their default setting were used.

The absorber was simulated as a rate-based model with mass and heat transfer as well as simultaneous chemical reactions. The flow model used inside the absorber was set to mixed, meaning that both the gas and liquid streams are well mixed. For the film resistance, film reactions were chosen for both the liquid and gas phase. When film reactions is chosen, Aspen includes film resistance to mass and heat transfer as well as chemical reactions occurring inside the film (for the gas phase this does not matter as no reactions take place here, but transport resistance is still considered).

The specifications of the absorber internals were chosen to be as similar as possible to the actual scrubber installed at Renova. The specifications are presented in Table 4.

Table 4: Scrubber internals specifications in the Aspen model.

Packed height (m)	3.0
Packed bed diameter (m)	4.5
Packing material	2-inch plastic Pall-rings
Void fraction	0.94
Packing specific surface area (m^2/m^3)	110

The number of stages was altered until the outlet concentrations stabilized, this amounted in 30 stages.

The pump tank is modeled using the RCSTR model in Aspen, which simulates reactions according to a simple CSTR (continuously stirred tank reactor) model, where the components are assumed to be perfectly mixed.
In reality, the pump tank is integrated inside the scrubber, but it was simulated as a separate unit in Aspen. The volume of the pump tank was set to 5.0345 m^3, which is the volume of the internal pump tank at Renova when operated at 50% level, which is typical operating conditions. The heat duty was set to zero to make the reactor isothermal. The same chemical reactions as in the scrubber were inserted in the pump tank. The effluent from the pump tank is brought to a mixer where makeup-water, called condensate is added, as well as sodium hydroxide. The mixture is brought to a splitter were the bleed stream is extracted and the rest recycled.

The mixer and splitter labeled B4 and B5 in Figure 2 which model the addition of condensate and sodium hydroxide as well as the removal of the bleed stream were used to keep the sulfate concentration, recirculation stream and pH of the system constant between simulation runs. This was done to get the results to more accurately represent the system at Renova. The recirculation was attempted to be held constant at 470 m^3/h, the pH around 7 and the concentration of sulfate in the scrubber liquid around 40 g/l. The flow of NaOH and the split fraction in the splitter were altered during runs to get as close as possible to the desired flows, pH and scrubber liquid sulfate concentration in order to get comparable results from the simulations.
The NaOH added is a 50% (by weight) solution, which is roughly equivalent to a molar concentration of 19.1 mol/l. In reality, the bleed stream is not a continuous flow, but taken intermittently when the conductivity of the scrubber liquid is high enough, as mentioned in section 1.2. The condensate flow was pure water, and the flow was altered between runs in order to get the desired recycle flow, pH and sulfate concentration. In reality, the condensate flow is also an intermittent flow, used as make-up water to refill the absorber loop as the bleed stream is activated.

3.1.3 Base case scenario

Table 5 below includes the values for the simulation that were used as a base case. The pump tank volume was set to 5.0345 m^3 which represents 50% of the total volume (10.069 m^3), as this represents typical operating conditions for the scrubber units at Renova.

Table 5: Base case operating conditions used in the Aspen simulations.

Pump tank volume [m^3]	5.0345
Rate constant [$mols^{-1}l^{-1}$]	0.00012
Inlet flue gas SO_2 concentration [mg/nm^3]	508.02
pH	7

3.2 Modelling of the Fjernvarme Fyn scrubber

The scrubber at Fjernvarme Fyn was modelled using the same Aspen model presented in Section 3.1 but with some modifications. The inlet flow of flue gas (labeled V_IN in Figure 2) had a different composition and flow, values are presented in Table 6.

Table 6: Inlet conditions for the feed flue gas at Fjernvarme Fyn.

Temperature [°C]	58.4
Pressure [Pa]	96825
Volume flow [nm^3/h, wet gas]	113547
O_2 concentration [% vol., dry gas]	6.9
H_2O concentration [% vol., wet gas]	19.1
CO_2 concentration [% vol., dry gas]	11.9
SO_2 concentration [mg/nm^3, dry gas]	623

In order to input the information in Aspen, the compositions were converted to molar flows, these are presented in Table 7. It was assumed that apart from the species listed in Table 6, the remaining flue gas consists of nitrogen.

Table 7: Inlet component flows for the model of Fjernvarme Fyn's scrubber.

Total flow [mol/s]	1401.62
SO_2 flow [mol/s]	0.248
O_2 flow [mol/s]	77.94
CO_2 flow [mol/s]	135.45
H_2O flow [mol/s]	267.72
N_2 flow [mol/s]	924.56

Modifications were also made to the specifications of the scrubber system, presented in Table 8.

Table 8: Scrubber specifications for the Aspen model of Fjernvarme Fyn's scrubber.*(No data was available for these parameters, the same values as in Renova's case were used)

Pump tank volume [m^3]	16
Recirculation flow [m^3/h]	480
Scrubber pH	6.5
Scrubber liquid SO_4^{2-} concentration [g/l]	40.9
Scrubber packed height [m]	4.2
Scrubber packed diameter [m]	4.5
Packing material*	2-inch plastic Pall rings
Packing specific surface area [m^2/m^3]	83
Packing void fraction*	0.94

Only the base case with the parameters presented in Tables 6 and 8 was simulated. The method was the same as in previous simulations of Renova's scrubber units: the bleed, make-up water and NaOH flows were varied until the desired recirculation flow, pH and scrubber liquid sulfate concentration were achieved (values in Table 8).

3.3 Measurements at Renova and Fjernvarme Fyn

In order to validate the modelling results, measurements of sulfite concentration were taken at Renova and Fjernvarme Fyn.

At Renova, measurements were taken on desulfurization lines 1, 2 and 3.
Measurements were also taken at Fjernvarme Fyn on their desulfurization lines 11, 12 and 13. Fjernvarme Fyn conducted their own measurements using iodometry (a wet titration method) in their own laboratory at the same time.

The measurements were taken using a portable spectrophotometer (Merck Spectroquant Nova 60). The apparatus measures the absorbance of light in a sample collected in a cuvette (Merck Supelco Spectroquant Sulfite Test Cell). To measure sulfite in the scrubber liquid, a sample is extracted from the scrubber and diluted with distilled water. To the cuvette, 1 μg of a substance known as Ellman's reagent is added, the cuvette is capped and shaken vigorously until the reagent is dissolved. 3 ml of the diluted sample is added to the cuvette which is the left to react for two minutes. The sample forms a yellow coloured complex with the reagent, changing the solution's absorbance so it then can be analyzed using the spectrophotometer. The detection limits for the sulfite test is 1.0-20.0 mg/l at temperatures between 10 and 30 °C. In Table 9, the interference limits for various substances for the test cells is presented, gathered from the documentation included with the test cells.

Table 9: Interference concentrations for various substances for the sulfite test cells in mg/l or %.

Ag^{+}	1 mg/l	Cu^{2+}	100 mg/l	NO_2^{-}	500 mg/l	EDTA	1000 mg/l
Al^{3+}	10 mg/l	F^{-}	1000 mg/l	Pb^{2+}	100 mg/l	Hydrazine	100 mg/l
Ca^{2+}	100 mg/l	Fe^{3+}	25 mg/l	PO_4^{3-}	1000 mg/l	Surfactants	500 mg/l
Cd^{2+}	100 mg/l	Hg^{2+}	0.1 mg/l	S^{2-}	0.1 mg/l	Na-acetate	20 %
CN^{-}	10 mg/l	Mg^{2+}	500 mg/l	SiO_3^{2-}	1000 mg/l	NaCl	20 %
$CO3^{2-}$	1000 mg/l	Mn^{2+}	100 mg/l	$S_2O_3^{2-}$	1 mg/l	$NaNO_3$	20 %
Cr^{3+}	10 mg/l	NH_4^{+}	1000 mg/l	Zn^{2+}	100 mg/l	Na_2SO_4	20 %
$Cr_2O_7^{2-}$	10 mg/l	Ni^{2+}	100 mg/l				

In order to validate the results from modelling altered pump tank volume, Renova was asked to lower the pump tank level in two of the scrubber units. It was lowered to 25% from 46-49% in scrubber 2 and 23% from 50-53% in scrubber 3. Measurements of sulfite concentrations using the spectrophotometer were taken approximately 24 hours after the level change, and then again approximately 48 hours after the change.

At the same time as the tests with lowered pump tank level, a sample with high sulfite concentration was extracted to test how quickly the sulfite decayed to sulfate, to investigate the kinetics. Approximately 100 ml of scrubber liquid was extracted. The sample was put in a water bath with water extracted from the scrubber, in order to keep the temperature of the sample closer to the actual temperature inside the scrubber. Sulfite measurements were taken intermittently approximately every 10 minutes, in the same way as mentioned above.

At some occasions, a sample was extracted and sent to Eurofins (a laboratory testing service provider) for a metal concentration analysis.

4 Results

4.1 Modelling results

4.1.1 Effect of pump tank volume

Presented in Figure 3 is the effect of varying the pump tank volume, for the rate constant $k = 0.00012$, and 508.02 mg/nm^3 SO_2 in the feed flue gas, these values were kept as a base case scenario in the simulations where they were not the parameters being explicitly varied, see Table 5. The bleed, make-up water and NaOH flows were varied to keep the sulfate concentration in the scrubber liquid constant at 40 g/l, pH 7 and recirculation flow at 470 m^3/h. The normal case in terms of the sump tank volume is 50%, as this represents typical operating conditions at Renova. The liquid hold-up inside the absorber was calculated, for comparison with the pump tank volume. It was calculated using Aspen to be approximately 2.82 m^3.

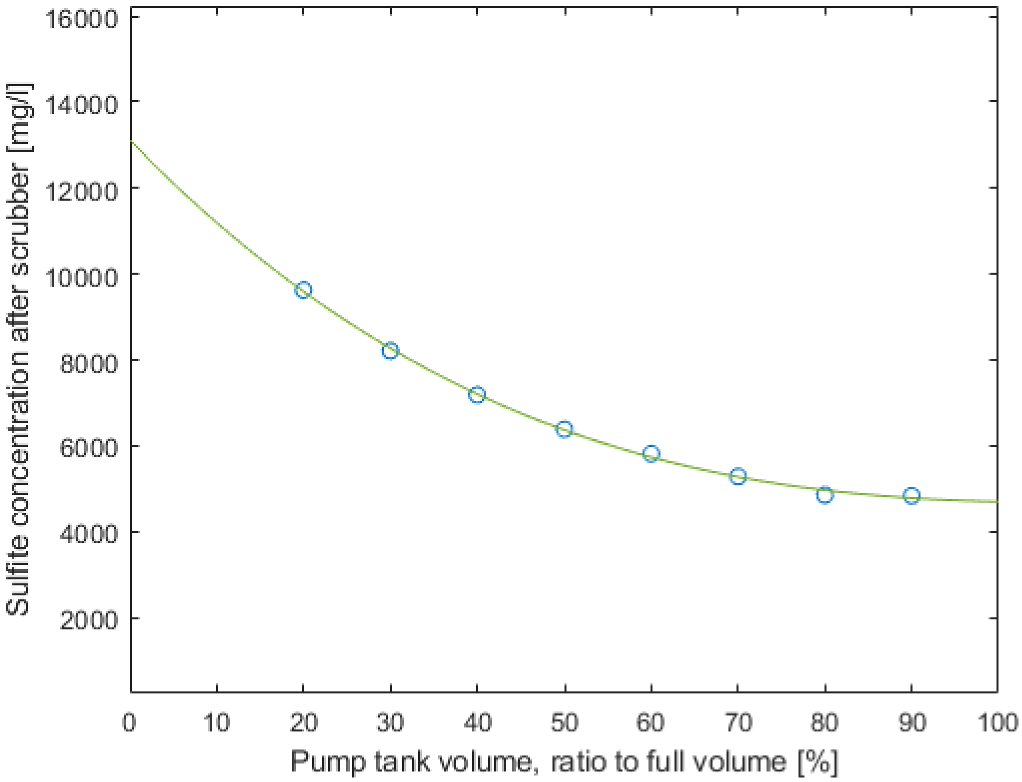

Figure 3: The effect of varying the pump tank volume on sulfite concentration after the scrubber along with a fitted trend line.

The effect of pump tank volume to the degree of oxidation, before and after the pump tank and the average reaction rate for the formation of sulfate in the absorber and pump tank is presented in Table 10.

Table 10: The effect of pump tank volume on degree of oxidation, pre and post pump tank, as well as the average reaction rate in the pump tank and absorber. (*base case scenario)

Pump tank volume [%]	20	30	40	50*	60	70	80	90
Degree of oxidation, pre pump tank [%]	77.45	80.07	82.20	83.80	84.87	86.12	87.11	87.13
Degree of oxidation, post pump tank [%]	77.52	80.18	82.32	83.95	85.13	86.28	87.28	87.92
Average reaction rate, absorber [mol/s]	0.0787	0.0678	0.0592	0.0529	0.0476	0.0434	0.0403	0.0262
Average reaction rate, pump tank [mol/s]	0.0581	0.0744	0.0867	0.0963	0.1053	0.1117	0.1171	0.1314

4.1.2 Effect of oxidation rate

Presented in Table 11 is the effect of varying the rate constant of the sulfite oxidation reaction on the sulfite concentration in the scrubber liquid. The pump tank volume was kept at 50% and the feed flue gas SO_2 concentration was kept at 508.02 mg/nm^3. The sulfate concentration was attempted to be held constant as close to 40 g/l as possible, the pH around 7 and the recirculation flow at 470 m^3/h.

Table 11: The effect of varied rate constant for the sulfite oxidation reaction on sulfite concentration in the effluent scrubber liquid.(*base case scenario)

Rate constant, k [s^{-1}]	Sulfite concentration [mg/l]
0.000012	35074.34
0.00012*	6384.30
0.0012	762.25
0.012	74.98
0.12	4.77

In Table 12, the effect of varying the rate constant on the degree of oxidation is presented:

Table 12: Effect of different rate constants on the degree of oxidation as defined by equation 7, calculated before and after the pump tank. (*base case scenario)

Rate constant	Degree of oxidation pre sump tank [%]	Degree of oxidation post sump tank [%]
0.12	99.87	99.98
0.012	99.60	99.78
0.0012	97.57	97.76
0.00012*	83.80	83.95
0.000012	48.49	48.53

4.1.3 Effect of pH

The pH was altered in the system by changing the amount of NaOH added. The inlet SO_2 concentration was kept at 508.02 mg/nm^3, 50% pump tank volume and the rate constant at $k = 0.00012\ s^{-1}$. In Figure 4 below, the sulfite concentration after the scrubber is plotted versus the pH after the scrubber. The sulfate concentration was held close to 40 g/l and the recirculation flow at 470 m^3/h.

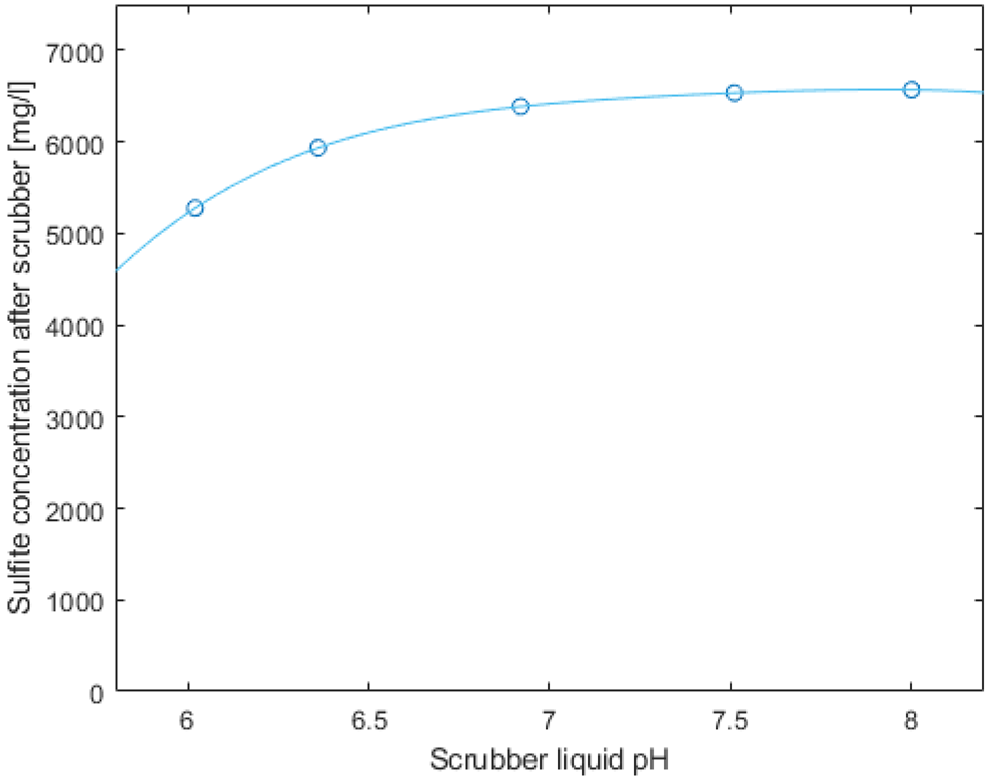

Figure 4: The effect of pH on sulfite concentration in the scrubber liquid with a fitted trend line.

The effect of lowered pH on the degree of absorption is presented in Table 13.

pH	Degree of absorption [%]
6.02	90.85
6.36	95.54
7.0	96.81
7.51	96.91
8.0	96.91

Table 13: Effect of pH on the degree of absorption.

4.1.4 Effect of inlet sulfur dioxide concentration

The inlet flue gas SO_2 concentration was varied while keeping the pH and recirculation flow constant at 7 and 470 m^3/h, respectively. The pump tank volume was kept at 50% and the SO_4^{2-} concentration in the liquid phase at 40 g/l. The values used for the inlet SO_2 concentration can be seen in Table 14.

Table 14: The values used when varying the inlet flue gas SO2 concentration. (*Base case scenario)

Run no.	1	2	3	4	5
Inlet concentration $[mg/nm^3]$	110.01	244.15	508.02*	761.97	1015.96

The resulting SO_3^{2-} concentration in the scrubber liquid is presented in Figure 5 below:

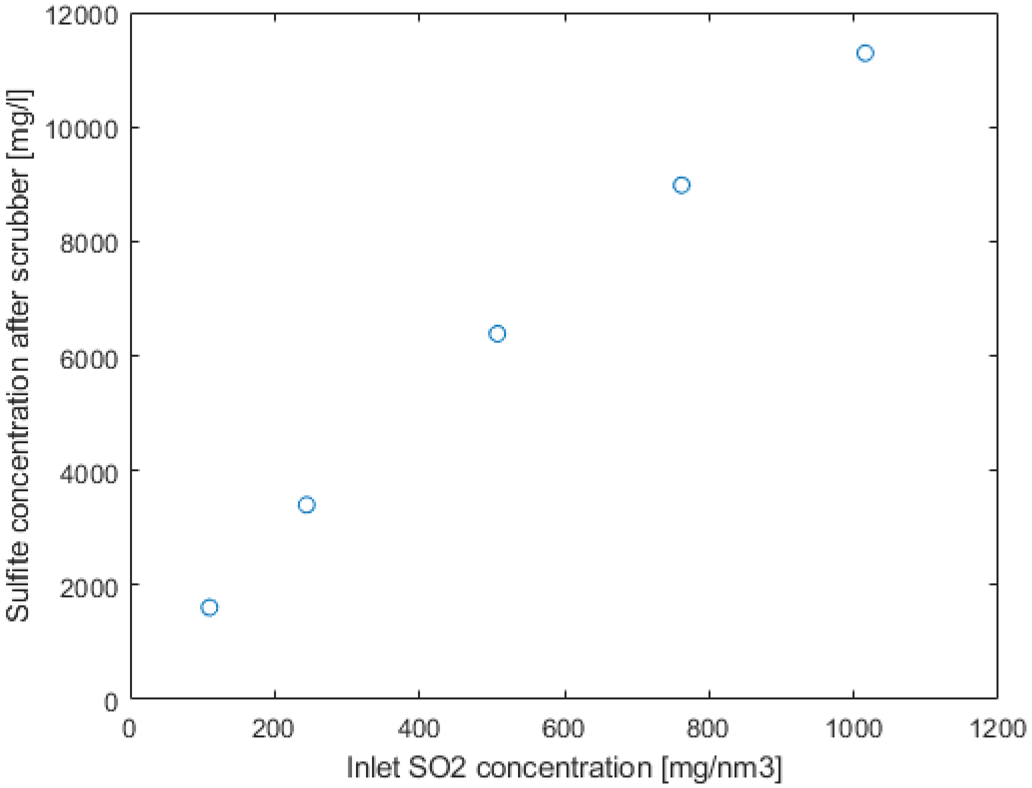

Figure 5: The effect of inlet flue gas SO_2 concentration on sulfite concentration in the scrubber liquid.

4.2 Modelling of Fjernvarme Fyn's scrubber line 13

The sulfite concentration in the scrubber liquid was calculated to 3705.26 mg/l using the model and corresponds to a degree of oxidation of 91.71 % when the sulfate concentration is held at approximately 40.9 g/l, the pH at 6.5 and the recirculation flow at 480 m^3/h. The degree of absorption was calculated to 99.35 %. The average rate of sulfate formation was 0.0409 mol/s and 1.178 mol/s inside the scrubber and in the pump tank, respectively. The liquid holdup inside the scrubber is 3.58 m^3 with the scrubber specifications in Table 8.

4.3 Measurement results from Renova

The results from sulfite measurements taken at Renova WTE plant in Gothenburg are presented. Desulfurization lines 1,2 and 3 were sampled for sulfite on four occasions with normal operating conditions and two occasions with lowered pump tank level.

4.3.1 First sample occasion

The first test took place on 21/2 2023. In Table 15, test results from measuring the sulfite concentrations in Renova's desulfurization lines 1 and 2 are presented along with data on conductivity, pH and temperature in the respective scrubber. Note that line 3 was not tested at this occasion, due to it not being in operation.

Table 15: Measurement results from the first sample occasion on Renova lines 1 and 2. For the concentrations of sulfite, note that the degree of sample dilution is written in parentheses.

	Line 1	Line 2
Temperature [°C]	64	64
Conductivity [mS/cm]	69.5	74.4
pH	6.94	7.16
SO_3^{2-} concentration [mg/l]	1.6, 1, 1.2 (1:2)	1300, 1280, 1280 (1:200)

The sample from line 1 was sent to Eurofins for metal analysis. Selected results from the analysis are presented in Table 16.

Table 16: Selected results from the metal concentration analysis conducted by Eurofins for the sample from line 1. The analysis was conducted on 12/5 2023.

Species	Concentration
Iron	0.073 mg/l
Manganese	0.063 mg/l
Copper	0.69 mg/l

4.3.2 Second sample occasion

The second test took place on 14/3 2023. In Table 17 below, test results from the second occasion are presented, along with operating conditions for each respective scrubber unit.

Table 17: Results from the second sample occasion at Renova, degree of sample dilution for sulfite in parentheses.

	Line 1	Line 2	Line 3
Temperature [°C]	64	64	63
Conductivity [mS/cm]	69.71	73.36	105.09
pH	7.01	7.16	7.17
SO_3^{2-} concentration [mg/l]	5 (1:50)	10 (1:100)	4000 (1:50)

The sample from line 3 was sent to Eurofins for a metal concentration analysis. Selected results from the analysis are presented in Table 18.

Table 18: Selected results from the analysis conducted by Eurofins for the sample from line 3. The analysis was conducted on 12/5 2023.

Species	Concentration
Iron	0.2 mg/l
Manganese	0.028 mg/l
Copper	0.61 mg/l

4.3.3 Third test occasion

The third test took place on 23/3 2023. In table 19, the results from the samples are presented, along with operational data for each scrubber unit.

Table 19: Results from the third sample occasion at Renova, degree of sample dilution for sulfite in parentheses.

	Line 1	Line 2	Line 3
Temperature [°C]	63	62	52
Conductivity [mS/cm]	63.7	73.4	101.6
pH	7.04	7.4	7.16
SO_3^{2-} concentration [mg/l]	0.7, 0.8, 0.7 (1:2)	0.9 (1:1)	5 (1:50)

4.3.4 Fourth test occasion

The fourth test took place on 30/3 2023. In Table 20, results from the fourth occasion is presented.

For line 1, the sulfite concentration exceeded the detection limit, so it is likely higher than the reported 20000 mg/l. The same is true for line 2, but it was close enough to the detection limit for the spectrophotometer to extrapolate to 21000 mg/l.

Table 20: Measurement results from the fourth test at Renova, degree of sample dilution in parentheses.

	Line 1	Line 2	Line 3
Temperature [C]	62.7	63	55.3
Conductivity [mS/cm]	68.3	74.3	100.5
pH	7.26	7.75	7.22
SO_3^{2-} concentration [mg/l]	20000 (1:1000)	21000 (1:1000)	0.2 (1:2)

4.3.5 Lowered pump tank level measurements

Tests with lowered sump tank level were conducted at Renova on 25/4 and 26/4 2023. Results from the tests are presented in Tables 21 and 22.

Table 21: Results from the first test with lowered pump tank level.

	Line 2	Line 3
Temperature [°C]	63	54
Conductivity [mS/cm]	74.5	101.8
pH	6.94	7.19
SO_3^{2-} concentration [mg/l]	0.2 (1:2)	1080, 1085, 1080 (1:50)

Table 22: Results from the second test with lowered pump tank level.

	Line 2	Line 3
Temperature [°C]	64	54
Conductivity [mS/cm]	78.4	107.9
pH	7.55	7.14
SO_3^{2-} concentration [mg/l]	20500 (1:1000)	10 (1:50)

4.3.6 Kinetics test

The sample from line 3 from 25/4 mentioned in section 4.3.5 was tested to determine the rate of degradation of sulfite. The results are presented in Figure 6.

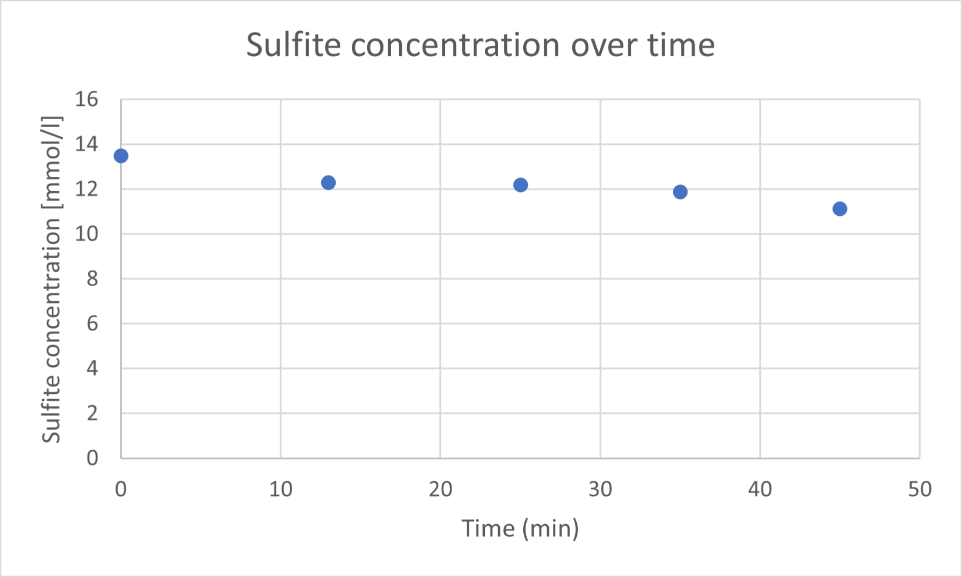

Figure 6: Sulfite concentration in the sample versus time.

The average apparent rate of sulfite oxidation was calculated to approximately -0.00088 mmol/(l*s) and the average rate constant was calculated to approximately $7.21 * 10^{-5}$ s^{-1} using Equation 8.
In order to compare the rate to the simulated reaction rates, the measured rate can be divided by the volume of the sample taken (approx. 100 ml) to yield a rate in mol/s. This gives the result -0.0088 mmol/s.

4.4 Measurement results from Fjernvarme Fyn

Presented in Table 23 are the results from measurements taken at Fjernvarme Fyn in Odense, Denmark on 11/5 2023.

Table 23: Results from measurements at Fjernvarme Fyn, degree of sample dilution in parentheses. Note that some data on conductivity, temperature and pH is missing.

	Line 11	Line 12	Line 13
Temperature [C]	Missing	60.3	Missing
Conductivity [mS/cm]	Missing	106	Missing
pH	Missing	6.5	Missing
SO_3^{2-} concentration [mg/l]	600 (1:100)	16000 (1:1000)	670 (1:100)

Fjernvarme Fyn conducted tests for line 12 at the same time in their own laboratory, their results are presented in Table 24 below:

Table 24: Measurement results on sulfate and sulfite as well as metal concentrations taken by Fjernvarme Fyn's laboratory for Line 12 on 11/5 and 12/5 2023.

Species	Unit	Result 11/5	Result 12/5
Sulfite	mg/l	2960	2480
Chloride	mg/l	2702	3152
Iron	$\mu g/l$	10.8	10.8
Manganese	$\mu g/l$	2.9	2.7
Arsenic	$\mu g/l$	<12	<12
Cadmium	$\mu g/l$	<4.8	<4.8
Chromium	$\mu g/l$	<5.6	5.6
Copper	$\mu g/l$	<9.6	<9.6
Nickel	$\mu g/l$	<5.6	<5.6
Lead	$\mu g/l$	10.6	10.9
Zinc	$\mu g/l$	93	98

Fjernvarme Fyn also tested Line 13 for sulfite on 11/5 2023 and produced the result 140 mg/l.

All sample from Fjernvarme Fyn were sent to Eurofins for metal analysis. Selected results from the analysis are presented in Tables 25, 26 and 27.

Table 25: Selected results from the analysis conducted by Eurofins for the sample from line 11. The analysis was conducted on 12/5 2023.

Species	Concentration
Iron	0.027 mg/l
Manganese	0.0058 mg/l
Copper	0.0088 mg/l

Table 26: Selected results from the analysis conducted by Eurofins for the sample from line 12. The analysis was conducted on 12/5 2023.

Species	Concentration
Iron	0.022 mg/l
Manganese	0.0058 mg/l
Copper	0.0025 mg/l

Table 27: Selected results from the analysis conducted by Eurofins for the sample from line 13. The analysis was conducted on 12/5 2023.

Species	Concentration
Iron	1.2 mg/l
Manganese	0.12 mg/l
Copper	0.019 mg/l

4.5 Effect of metal ion concentration

In Figures 7, 8 and 9, the results from the metal analyses made by Eurofins in terms of manganese, copper and iron are plotted versus the sulfite concentration.

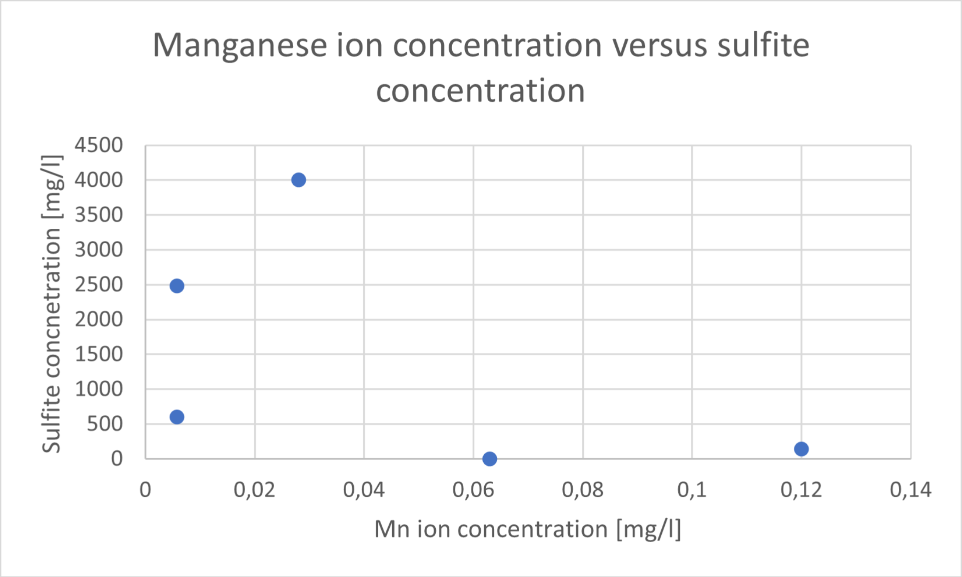

Figure 7: Manganese ion concentration plotted against sulfite concentration.

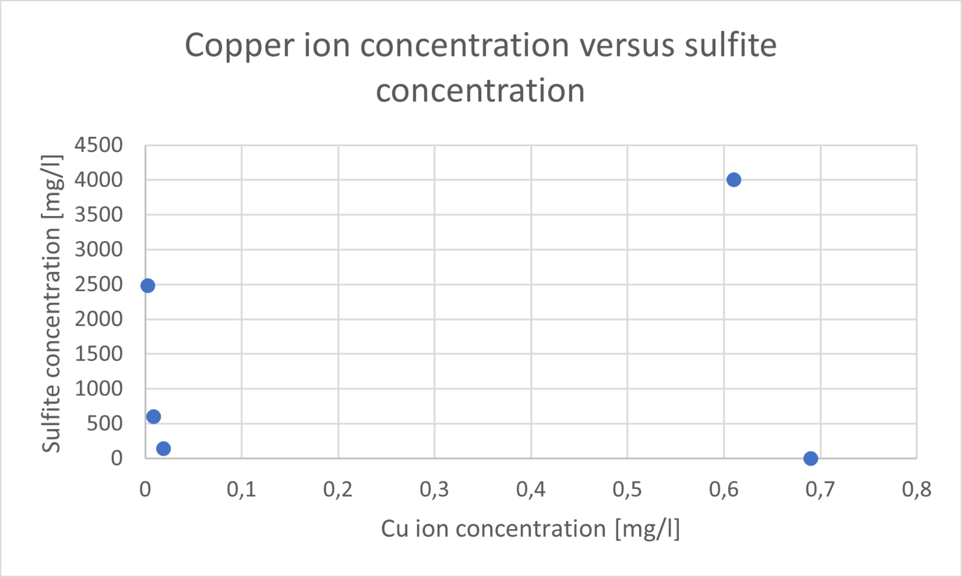

Figure 8: Copper ion concentration plotted against sulfite concentration.

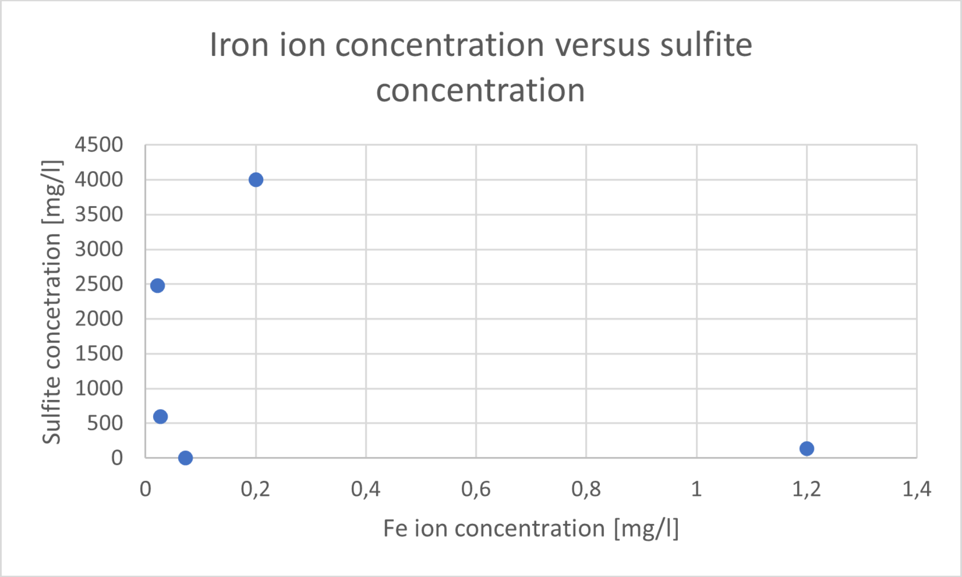

Figure 9: Iron ion concentration plotted against sulfite concentration.

5 Discussion

The results from varying the pump tank volume in the model generated expected results. The simulations were only run in the span 90-20% pump tank volume since a lower or higher level would be unfeasible in reality as a too high level leads to risk of overflow and spillage into the HCl stage below and a too low level risks damaging the circulation pumps.
As the level is decreased the amount of sulfite in the liquid increased, since the residence time in the pump tank decreases, and thus less sulfite reacts to sulfate. As seen in Table 10 the average rate of sulfate formation is initially higher in the pump tank than the absorber, until around 20% pump tank volume. This is due to the pump tank volume decreasing below the liquid holdup volume in the absorber at 20%, leading to a lower volume of reacting liquid in the pump tank compared to the absorber.

The results from varied rate constant in the sulfite oxidation reaction also showed expected results. A lower rate constant leads to higher sulfite concentration. The rate was increased with a factor 10 for each run, and the sulfite concentration became an order of magnitude lower each time, as can be seen in Table 11.

The model predicts lower sulfite concentrations at lower pH as seen in Figure 4. This is due to the fact that the solubility of SO_2 is lower at low pH, so less SO_2 is dissolved meaning lower sulfite concentration, this can also be seen in Table 13; as pH decreases, the degree of absorption also decreases. Some kinetics models of the sulfite oxidation reaction include a pH dependence in the rate expression, such as Beilke et al.'s model mentioned in Section 2.4. This was initially included in the Aspen model, but later removed due to uncertainties in how Aspen handles kinetic dependencies on species not taking part in the actual reaction. As mentioned in Section 2.4, there are other rate expressions that do not include the pH dependence. So the only way pH has an influence is in the solubility of sulfur dioxide.

The expected trend was observed when the amount of SO_2 in the inlet stream was increased or decreased. An increase in inlet SO_2 concentration leads to a higher amount of sulfite present in the liquid and vice versa. It follows an approximately linear trend as can be seen in Figure 5.

Modelling was carried out for the case of Fjernvarme Fyn's plant as well, which has measured high sulfite concentrations with dewatering issues in their gypsum production as a likely consequence, but the sulfite concentration in their scrubber varies from time to time making the variations difficult to capture in the model. The model predicts a sulfite concentration of 3705.26 mg/l, which is close to the value measured by Fjernvarme Fyn on line 12 (2960 mg/l), but values below and above this have been measured in the plant at other occasions.
The average reaction rates differ highly between the absorber and the sump tank, with a significantly higher rate in the sump tank. Following the same reasoning as for the model of Renova's scrubber unit, the liquid holdup inside the absorber is only 3.58 m^3 while the pump tank has a volume of 16 m^3. This means that the scrubber liquid has a much longer residence time inside the pump tank and thus the sulfite is allowed to oxidize for a longer period of time.

Further improvements to the model could have been made, for example, one could have tried specifying Henry components and using Henry's law to estimate the phase equilibrium inside the scrubber instead of using the NRTL activity coefficients and the modified Raoult's law. This might have yielded different results since the Henry coefficients are empirically derived from experiments. Another improvement could have been to choose a different flow model inside the scrubber unit, the model used a well-mixed flow, which might not be a completely true assumption. Perhaps plug flow could have been more appropriate, at least for the gas phase. This was tried, but it led to convergence issues and was left out due to time constraints. Finally, the rate expression used is valid for 25°C, and not extrapolated to 63°C as is the scrubber units' operating temperature. This could also affect the results.

One could also investigate the full radical reaction chain for sulfite oxidation mentioned in Section 2.4 and model it, since rate expressions for these reaction steps exist. It could perhaps produce different results than using the overall reaction.

The measurements taken at Renova differ greatly at different occasions. From one occasion to the next, the sulfite concentration can shift from several grams per liter to just a few milligrams per liter in the same scrubber line, as can be seen in Tables 15, 17, 19 and 20.
One hypothesis was that the amount of sulfite in the scrubber liquid could be controlled by lowering the pump tank level, since the modelling results support this. When Renova lowered their levels on line 2 and 3, it was noted that the concentration could still vary greatly as can be seen in Tables 21 and 22. For example, 24 hours after the level was lowered, line 2 had 0.2 mg/l of sulfite. Another 24 hours later, line 2 had a staggering 20500 mg/l of sulfite. The reverse of that result was seen with line 3. After 24 hours with lowered level, line 3 was measured at approximately 1080 mg/l. 48 hours after the level change, only 10 mg/l was measured.

Another uncertainty is the use of the portable spectrophotometer to measure sulfite and sulfate in scrubber liquids. As can be seen in Tables 23 and 24, the measurements taken using the spectrophotometer differ greatly with respect to sulfite concentrations when compared to measurements taken using iodometry. This might be due to interference when using the spectrophotometer by other species present in the liquid. The measurements taken by Fjernvarme Fyn's own laboratory reports a sulfite concentration of 2960 mg/l as can be seen in Table 24, compared to the concentration of 16 000 mg/l measured with the spectrophotometer seen in Table 23. This places some doubt in to which extent the measurement results from the spectrophotometer can be trusted. At least, the measurements from the spectrophotometer are reproducible and seem to be able to show whether the concentration is high or low.

The high concentration of sulfite measured on line 12 at Fjernvarme Fyn could possibly be partially explained by low concentration of transition metal ions, as mentioned in Section 2.5, relatively low amount of metal ions such as manganese, iron and copper could catalyse the oxidation of sulfite. However, the concentrations of metal ions reported by Fjernvarme Fyn in Table 24 are considerably lower than the concentrations studied in the paper cited in Section 2.5, meaning there might not be enough catalytic effects to get lower sulfite concentrations. For example, the paper by Rochelle et al. cited in Section 2.5 studies metal ion concentrations of 0.1-10 mM, but the scrubber liquid at Fjernvarme Fyn had only 0.00019 mM of iron and 0.000053 mM of manganese as measured by Fjernvarme Fyn. The measurement of metal concentrations from line 13 could possibly support the claim that higher metal concentration yields lower sulfite concentration, but at the same time, line 11 also has low sulfite concentration, but considerably lower metal concentrations. Another observation is that the concentrations of metals differ between Fjernvarme Fyn's own measurements and the measurements conducted by Eurofins.

The same argument might help explain why line 1 at Renova has had very low sulfite concentrations relatively consistently. The electrostatic precipitator (ESP) upstream from the scrubber unit on line 1 is reportedly less efficient than on the other lines. This could possibly lead to more metal particles being dissolved in the scrubber liquid, leading to catalysis and thus lower sulfite concentrations. However, more data on metal concentrations from line 1, with comparisons from the other lines are needed to fully support this claim.

When metal ion concentrations were plotted against sulfite concentation in Figures 7, 8 and 9, only weak evidence of catalysis can be seen. Only a slight tendency towards low sulfite concentration at high metal concentration is observed. More research on this topic is required to investigate catalysis on sulfite oxidation with comparatively low metal ion concentrations. As mentioned before, studies on this topic have investigated solutions with higher metal concentrations than the ones found in this thesis.

When the kinetics were tested in a sample as mentioned in Section 4.3.6, an average reaction rate for the formation of sulfate was reported as 0.0088 mmol/s. This is an order of magnitude lower compared to the base case simulation, for which average reaction rates can be found in Table 10. It is difficult to determine whether this result is representative of the sulfite oxidation inside the scrubber. Firstly, as mentioned, the method of measuring sulfite concentration using a spectrophotometer might not give accurate measurements. Secondly, nothing is known about the metal concentration in this specific sample, more testing of this kind is required to determine whether metal found in scrubbers concentrations have an impact on the rate at which sulfite oxidises. The average rate constant was found to be approximately $7.21 * 10^{-5}$ s^{-1} compared to $1.2 * 10^{-4}$ s^{-1} used in the simulations. The calculated rate constant is thus relatively close to the theoretical (approx. 40% lower), but more testing of this kind could be useful to quantify the oxidation rate in these kinds of systems.

6 Conclusions

Full scale scrubber units installed at Renova and Fjernvarme Fyn have been modelled. Validation of the modelling results has been conducted by measuring sulfite concentrations at the two plants. Metal ion analysis has been conducted by Eurofins in order to investigate the catalytic effects.

The model is able to predict sulfite concentrations in the same order of magnitude as measured at Renova and Fjernvarme Fyn. For example, the simulation of Fjernvarme Fyn's scrubber unit produced a sulfite concentration of approximately 3700 mg/l and Fjernvarme Fyn measured a concentration of approximately 3000 mg/l. However, the large variations in concentrations measured at Renova and Fjernvarme Fyn remain largely unexplained by the model.
It proved difficult to predict for which operating conditions the sulfite concentration in the scrubber liquid would be high or low, due to the large variation in measurement results. The operating conditions inside the real scrubber units are fluctuating on an hourly basis, the amount of SO2 in the flue gas depends on what kind of waste is being incinerated at that time, and this influences for example how much sodium hydroxide is added, how much the bleed stream is activated and how much make-up water is added. At the same time, different amounts of metal ions might be present in the liquid, which might catalyse the oxidation of sulfite to different extents. All these uncertainties are difficult to capture in the modelling.

Some trends can be observed from the results, showing what might be expected for some operating conditions, but the combination of effects leading to specific concentrations of sulfite is difficult to capture. For example, the simulation results suggest that most of the oxidation of sulfite takes place inside the pump tank, leading to the conclusion that a lower pump tank volume should yield higher sulfite concentrations. This was not observed in measurements, as the sulfite concentration was not consistently higher as predicted by the model, meaning that some other factor or combination of factors is having an effect on the sulfite oxidation.

The measurements of sulfite with the spectrophotometer were reproducible and could at least provide an indication on if the concentration was high or low. In the samples from Fjernvarme Fyn, where a comparison with iodometry exists, the spectrophotometer overestimates the sulfite concentration approximately by a factor 5. However, low concentration measurements from the spectrophotometer correspond to low concentrations measured with iodometry and the same is true for measurements with high concentration. The measurement with the spectrophotometer gave the result of approximately 16000 mg/l compared to approx. 3000 mg/l using iodometry. Comparing this to a sample with low concentration: 640 mg/l with the spectrophotometer versus 140 mg/l with iodometry.
Better measurement techniques for sulfite are needed, since results using the spectrophotometer differed from other measurement methods. From the results this seems to be needed especially for samples containing high amounts of sulfite.

More research on the kinetics as well as the potential for catalysis of the sulfite oxidation reaction is needed, as data in this study was scattered, but there was a tendency for low

sulfite concentrations at high metal concentrations and the other way around.
The previous research cited has investigated sulfite solutions with much higher concentrations of potentially catalyzing species than was found in the scrubber liquids investigated in this thesis. The studies cited investigate one species of potentially catalyzing species at a time, but do not investigate the combination of species found in scrubber liquids.

When the rate constant was calculated from the measurement results in Section 4.3.6, the calculated value was close to the theoretical value used in simulations. More testing of this kind would be useful to more accurately evaluate sulfite oxidation in these kinds of systems.

Varying concentrations transition metal ions in the scrubber liquid catalyzing the oxidation of sulfite might help partially explain the scattered measurements, but only limited and weak evidence was found for this.
More research is needed on measurement methods for sulfite as well as the effect of catalysis on sulfite oxidation, to fully explain why concentrations of sulfite fluctuate as greatly as they seem to do.

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