UMEÅ UNIVERSITET

PHASING OUT PEAT AND INTRODUCING NA-RICH WASTE TO A CO-FIRED 50 MWTH CIRCULATING FLUIDIZED BED:

A theoretical sulfation potential study

Axel Bergstrand

Perstorp

Sammanfattning

Kemiindustriföretaget Perstorp AB har en 50 MWth cirkulerande fluidiserad bädd panna för att förse produktionen med processånga. Bränsleblandningen som används visar en stor variation med ett 20-tal olika bränslefraktioner som kan delas in i kategorierna returflis (RT-flis), slam, skogsbränsle, slaktrester, industrirester och torv. Från ett ekonomiskt- och miljöperspektiv bör användningen av torv minimeras eftersom den är klassad som ett fossilt bränsle. Dock har torv positiva förbränningsegenskaper vilket beror på dess innehåll av såväl svavel som kiselbaserade mineraler vilka minskar korrosions förmågan för alkali-klorider. Därför är det inte alltid möjligt att fasa ut torven utan att riskera att försämra pannans tillgänglighet. Andra aspekter förutom minskade CO_2 utsläpp som är fördelaktiga vid drift av en panna, är att minimera användningen av tillsatser som kalksten samt använda restprodukter som bränsle i största möjliga mån. Dock kan, som i fallet med torv, en minskad användning av kalksten och ett nytt restproduktbränsle ha potentiella negativa konsekvenser för pannans tillgänglighet. Om kalksten används i mindre utsträckning kan risken för klumpbildning i pannan, agglomerering, öka och ofta kan restprodukter från produktionen innehålla höga halter av problematiska grundämnen både i ett korrosions och agglomererings perspektiv.

Syftet med detta examensarbete har varit att undersöka möjligheterna att minska användningen av torv och kalksten samt möjligheten att tillföra ett nytt Na-rikt bränsle till bränsleblandningen. Detta undersöktes genom att först bestämma vad som eldades och i vilka mängder. Genom att använda data från leveransrapporter (för bränslen och additiv) och bränsleanalyser. I de fall det fanns representativ bränsleanalys användes dessa, i övrigt provtogs och beställdes nya bränsleanalyser. Med hjälp av erfaren personal som jobbar med pannan kunde olika möjliga framtida bränsleblandningar bestämmas. Dessa bränsleblandningar delades in i olika scenarion eller case som det kallas här:

> **Case 1**. Ersätta torv med skogsbränsle.
> **Case 2.** Ersätta torv med RT-flis.
> **Case 3.** Ersätta både torv och biomal (slaktrester) med RT-flis.
> **Case 4**. Introduktion av Na-rikt restbränsle.

Baserat på en tidigare kartläggning av askomvandlingen i pannan kunde det teoretiska tillgängliga SO_2 halten i rökgaserna bestämmas för varje case för tre olika kalkstenshalter. För varje case kunde sedan CO_2 utsläppen samt de ekonomiska besparingarna estimeras då torv var helt urfasad och kalkstensinnehållet halverat. Från ett SO_2 perspektiv pekar resultaten på att det skulle vara möjligt att fasa ut torven helt genom att minska kalkstenen mellan 0-50 vikt% för case 1 och 2 men inte för case 3. Att tillsätta det Na-rika bränslet kan potentiellt vara problematiskt. För att elda detta Na-rika bränslet kan det krävas en ny additiv eller ett S-rikt bränsle för att balansera tillskottet av Na och därmed minska korrosionsrisken.

Vid utfasning av samtlig torv minskar CO_2 utsläppen i case 1-3 med runt 10 000 tonCO_2/år. Eftersom utsläpp av fossil CO_2 är beskattat, uppskattas de möjliga besparingarna som betydande, 9.1 miljoner SEK/år i case 1, 10.3 miljoner SEK/år case 2 och 6.5 miljoner SEK/år i case 3 inklusive inköps- och askhanteringskostnader.

Abstract

The chemical company Perstorp AB has a 50 MWth circulating fluidized bed to supply the production plant with process steam. The fuel mixture used shows a large variation with about 20 different fuel fractions that can be divided into the categories, residue wood chips, sludge, forest fuel, animal waste, industrial residues, and peat. From an economic and environmental perspective, the use of peat should be minimized because it is classified as a fossil fuel. Peat has positive combustion characteristics due to a combination of sulfur and silica based minerals that can reduce alkali chloride related corrosion. Therefore it is not always possible phase out peat without negatively affecting the boilers availability. Besides reducing CO_2 emissions, it is desirable to reduce the use of additives such as limestone and to use cheap waste fractions as fuels when operating a boiler. Similar to peat, reduced use of limestone and the introduction of a new waste fractions can affect the boiler availability negatively. If less limestone is used the risk of agglomeration can increase and often waste products can contain ash elements problematic in both a agglomeration and corrosion perspective.

The aim of this master thesis is to investigate the possibility of reducing the usage of peat by minimizing the limestone content and to see if it would be possible to add a new Na-rich waste fraction to the fuel mixture. This was investigated by determining first what fuels that are used and in what amounts. Each fuel was either sent for new elemental analysis or existing analyses were used depending on if it was deemed to be still representative. With the help of experienced personnel working with the boiler, future possible cases for fuel mixtures could be determined:

>   **Case 1**. Replacing peat with forest fuels.
>   **Case 2.** Replacing peat with residue wood chips.
>   **Case 3.** Replacing both peat and animal waste with residue wood chips.
>   **Case 4**. Introducing Na-rich fuel.

The theoretical available SO_2 content could be determined for each case and three limestone levels. For each case the CO_2 emissions and the economic savings could be estimated when the peat were fully removed and the limestone content halved. From an SO_2 perspective, the results indicate that it could be possible to phase out peat for cases 1-2 by adjusting the limestone levels but this would not be enough for case 3. Adding the Na-rich fuel could also be problematic and more investigation has to be put into potential additives and fuels to compensate for the additional Na.

When peat is fully phased out in case 1-3 the CO2 emission would decrease by 10 000 tonCO₂/year. Due to the cost of CO_2 emissions, this could result in considerable monetary savings. From the results it is estimated that case 1 could save 9.1 million SEK/year, case 2 10.3 million SEK/year, and case 3 6.5 million SEK/year when the peat is fully removed. This does not include changes in availability and maintenance costs.

Populärvetenskaplig sammanfattning

Initiativtagare och uppdragsgivaren för examensarbetet är kemiföretaget Perstorp AB. När vissa kemikalier tillverkas behövs värme till den kemiska reaktionen och till utrustningen som används vid tillverkningen. Denna värmeenergi får företaget från en panna som är av typen cirkulerande fluidiserad bädd. En fluidiserad bädd är fylld med ett material, ofta sand, där olika bränslen eldas i. I just denna panna eldas ett flertal olika bränslen av vilket många kan vara utmanande både för själva processen och de utsläppskraven som finns. Ett av bränslena som Perstorp vill fasa ut är torv eftersom det är klassat som ett fossilt bränsle vilket innebär både en belastning på miljön och beskattning av CO_2 utsläppen. Dessvärre innehåller torv svavel vilket minskar skador i pannan i form av korrosion. Det gör att det inte är säkert att det går att minska torv användningen utan att kostnaderna för underhåll riskerar att skenar. Förutom att minska torven vill Perstorp även minska mängden kalksten som används för att det ökar kostnaderna utan att bidra med energi. Kalksten används för att reglera svavel utsläppen och det är möjligt att detta kan kompensera bortfallet av torv. Ett annat sätt att minska kostnaderna för inköp av bränsle är att elda restprodukter från produktionen. Tyvärr kan restprodukter ofta innehålla ämnen som gör dem utmanande att elda. Därför är syftet med detta arbete att undersöka om det är möjligt att elda mindre torv, kalksten samt börja elda en ny restprodukt från produktionen. Detta kunde undersökas genom att använda experimentellt framtagna samband för risk för korrosion vid olika grundämnessammansättningar på bränsleblandningen. Resultatet tyder på att det skulle kunna vara möjligt att byta ut torv mot antingen skogsbränsle eller RT-flis om kalkstens inblandningen minskar. Det kan vara värre att byta ut både slaktrester, som är ett viktigt bränsle, och torv med RT-flis utan att korrosions tendensen blir för hög. Introduktionen av ett natriumrikt restbränsle skulle kunna leda till stora korrosions problem och undersökningar måste göras kring om det finns tillsatser som skulle kunna lösa detta problem. Vidare visar resultaten att CO_2 utsläppen kan minska med cirka 10 000 $tonCO_2$/år om torven fasas ut med skogsbränsle eller RT-flis samt om både slaktrester och torv fasas ut med hjälp av RT-flis. Eftersom CO_2-utsläpp från fossila källor beskattas uppskattas de årliga besparingarna uppgå till flera miljoner kr om torv byts ut mot skogsbränsle eller RT-flis .

Preface

This 30 credits master thesis is the final part of the degree master of science in energy engineering. I would like to thank Umeå university and the TEC-lab department in particular for this informative time and for the dedication of all staff members. The master thesis is part of Perstorp AB work to reduce its environmental impact and there are plenty of people that have helped me with the master thesis. First and foremost I would like to thank Anna Strandberg and Henrik Hagman for their supervision in this project and for giving me this opportunity. Secondly, I would like to thank all that I have met during this time, Claes Stjernberg, Sofia Löwgren, Erik Malmborg, David Ekeroth, Annette Wendt, and many others too many to mention. For me to be able to do this master thesis some practical questions had to be solved and I would like to thank my parents, Ingemar and Birgitta, and my brother, Claes, for helping me make this possible. Lastly, during the time of this work the Labrador Astrid passed away and I would therefore like to dedicate this master thesis to this beloved family member.

Knoxhult June 2022

Axel Bergstrand

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1 Introduction

The initiator of this master thesis is the chemical company Perstorp AB (Perstorp), which has one of its main production sites in Perstorp Sweden. The energy production system of site Perstorp consists of several different boilers that provide process steam to several energy-intensive chemical processes. For peak and replacement steam two fuel oil fired boilers are used, together with a combined liquid waste and fuel oil firing boiler. For the steam production baseload, excess heat from formaldehyde production plants is used in combination with a 50 MWth circulating fluidized bed boiler (B6) that uses a mixture of wastes and biomass as fuels. The B6 fuel mixture is complex and consists of residue wood, forest fuel, municipal sludge, animal waste, peat together with the additives limestone, bed sand, and ammonia [1]. In recent years, the cost of emitting CO_2 into the atmosphere has increased, and the burning of peat in the boiler is the largest source of CO_2 emissions from Perstorps energy production system, causing CO2 emissions of around 10 000 tons CO_2 annually. These CO_2 emissions results in a cost of about 9 million SEK/year when the emission cost is 900 SEK/ton CO_2. Besides the obvious environmental benefits, there is therefore an additional economic incentive to reduce the usage of peat. However, the burning of peat is beneficial to the process, mainly due to the net addition of sulfur that reduces corrosion and deposit buildup in the boiler. The reduction of the corrosion and deposit buildup increases the availability and lifespan of heat exchangers and other components in the boiler [2, 3]. Additionally, a higher availability leads to a reduction in the use of expensive fossil fuel oil in the backup boilers.

1.1 Fuel selection, ash transformation, and boiler availability

Most of the fuel in the B6 fuel mix is good from a resource management and cost perspective since waste and residues should be used for energy production in favor of high-quality biomass. The use of non-virgin fuels requires a better understanding of the ash-forming elements concentrations and interactions as waste streams tend to be enriched in problematic ash-forming elements [4]. High-quality woody-type fuels generally contain high concentrations of Ca and low concentrations of Si, which is related to non-problematic ashes with high liquidus temperatures [5, 6]. Other forest fuels and residue wood can be rich in alkali, Cl, Si, and other elements related to a more challenging ash composition. Alkali metals together with high Cl levels from animal waste or other sources can increase the alkali chlorides levels that lead to severe corrosion and deposits buildup. The addition of S in the peat will compete with the Cl for the alkali and produce less problematic alkali sulfates [1, 3, 7, 8].

Ash chemistry is complex and thus increasing or lowering one fuel source could drastically change the operation safety and efficiency of the boiler. This complexity results in that firing one of these fuels alone may not be appropriate in a fluidized bed either due to ash-related issues or due to corrosion or emission control. However, the

combination of ash-forming elements from the different fuels can be used to achieve the desired process conditions and appropriate ash behavior. Using a fuel mixing strategy can reduce the need for additives and increase the range of possible biomass sources in the feedstock. This smart use of different fuels is commonly known as fuel design and has previously been shown to increase the availability of a boiler, reduce the need for additives, and potentially introduce new otherwise non-suitable feedstocks for combustion [1, 4, 9]. Zeng et al. and Nordgren et al. have both shown that the slagging propensity during combustion of wheat straw could be lowered by the addition of woody biomass [10, 11]. And Hagman et al. showed the importance of S in peat for the reduction of corrosion in a fluidized bed boiler [2]. However, while promising, the field of fuel design needs further research and literature is especially scarce when the mixing of several waste fuels is considered.

1.2 Aim and goals

This master thesis aims to reduce the environmental effects and cost of a 50 MWth circulating fluidized bed by evaluating the possibility to introduce a new Na-rich waste fuel and reduce the usage of peat and limestone additives. The goal is to evaluate substitute fuels for peat and the introduction of Na-rich fuel from a corrosion perspective. Considering the complexity of the fuel used, this will add to the body of knowledge regarding the co-firing and fuel design of waste-based fuel mixtures.

1.3 Outline of the master thesis

The master thesis starts with a background regarding combustion and fluidized beds in a historic context. This background continues with the cause of global warming and the current energy system to highlight the importance of combustion processes. A theory section follows the introduction section and introduces topics that are central to this master thesis such as combustion chemistry, ash chemistry, and thermodynamics. This is followed by the method section presenting the boiler and how the sulfation potential investigation was performed. The result and discussion section contain the findings for the current fuel mixture, sulfation potential for each case, and an estimation of the potential monetary savings and reduced CO_2 emissions. Last is the summary and conclusion section.

2 Background

The oxidation of carbon and hydrogen, combustion, has been central to human development. Besides the obvious benefits of fire like heat and light, it also allowed for cooking which led to increased nutrient availability, food choice, and a decreased time spent feeding, accelerating human development [12]. There are some indications that fire has been used as far back as 800 000 years ago and there is evidence of fires used in human housing in modern-day France dating back to 400 000 BC [1]. An open flame is inefficient in most appliances and it was in conjunction with the development of metallurgy that the first types of furnaces or kilns came to light [13]. Furnaces or kilns

are closed to the atmosphere so that a higher temperature can occur with a reduced quantity of fuel compared to an open flame. The difference between a furnace and a kiln is not well defined, but rather it is dependent on the industry in which it is used and what it has traditionally been called there. It was during the bronze age, 6000 years ago, where the first simple furnaces were used to smelt copper and commonly tin to produce bronze [1, 13]. This was then followed by the discovery of iron-ore smelting to produce even more durable tools and materials.

2.1 Development of the fluidized bed

Since then, furnaces and kilns have come a far way in terms of efficiency and demands on materials. One type of combustion technology that is popular due to its fuel flexibility and low emissions is the fluidized bed. Simply put, it is based on an inert solid material, often silica sand, that is made to behave as a fluid by forcing air through it. The bed material provides a heat buffer, helps fuel mixing, and has several other benefits when fuel is burned in it. The temperature in the bed is in the range of 750-900°C and is lower than in most other combustion conversion technologies [14].

Fluidized beds similar to what we have today, were first developed by Fritz Winkler for the gasification of lignite in 1923. At the time, gasification processes could not use small-sized fuel and this invention aimed to solve this issue [15]. The sketch of the boiler in the patent can be seen in Figure 1. After its introduction, the fluidized beds remained in the invention stage and it was not until the 60's that the technology got a renewed interest for its ability to provide low sulfur dioxide emissions, SO_x. This was accelerated by the formation of the Environmental Protection Agency in the USA that started to restrict both the SO_x and nitric oxide emissions, NOx, that fluidized beds had the lower emissions. The lower emission of these compounds compared to a more traditional grate-fired furnace is attributed to that the temperature is lower and that additives like limestone that binds S can be easily added to the bed. Until the mid-70s, the fluidized beds were of bubbling fluidized bed type where the bed material have a lower velocity than the newly developed circulating fluidized bed. A higher velocity of bed- and fuel particles mean that they travel higher in the boiler and provide a more uniform temperature throughout the boiler. Although bubbling fluidized beds are less efficient and have higher SO_x emission, it remains popular in the smaller capacity industrial segment for their fuel flexibility due to the higher residence time which allows for larger fuel particles with lower calorific value. Circulating fluidized beds are generally for higher capacity plants due to their higher efficiency [14].
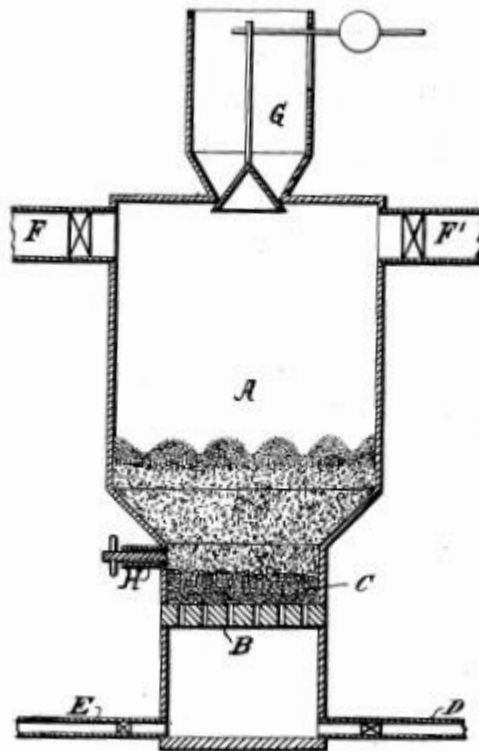
Figure 1. Winkler patent for the first fluidized bed for the gasification of lignite. Adapted from [15].

2.2 Importance of fossil fuels and combustion processes in the modern energy system

The purpose of this section is to highlight the prevalence and importance of combustion processes in the global and Swedish energy systems. First, the issues related to greenhouse emissions are discussed together with the current emission levels and CO_2 concentrations in the atmosphere. Then the global energy system is introduced, including the primary energy input, electricity generated by the source, and what fuels are used in the combustion-based power plants. This is followed by a similar section but from a Swedish perspective and the main differences between the global and Swedish energy system is discussed briefly.

2.2.1 Greenhouse gas emissions

Even today most products are directly or indirectly the result of combustion processes. An item could either be directly dependent on process heat or steam as is the case in metallurgy, limestone calcination, and more. Or indirectly by the electricity that is required during production. One drawback with burning fuels is the release of otherwise stable carbon into the atmosphere as CO_2.

An ever-increasing carbon dioxide in the atmosphere is of great concern and is monitored at many locations around the world. In the Mauna Loa observatory in Hawaii USA, the atmospheric concentration of CO_2 is measured at an elevation of 3396 meters above sea level. The yearly average of measured CO_2 levels can be seen in Figure 2, together with the estimated global emissions of CO_2 over 60 years [16, 17]. It shows a clear increase in the CO_2 concentration in the atmosphere from 1959 to 2020 by about 100 ppm or 32%. In the same time period, the emissions originating from fossil fuels and other sources increased by close to 400% in relation to the emission levels in 1959. This is of great concern and there is a clear link between the levels of greenhouse gases in the atmosphere and the temperature on earth. Without the protective layer of greenhouse gases, the temperature of earth is estimated to have an average temperature below 0^oC instead of the more comfortable 15^oC for us humans [18]. While this would be a problem, increasing CO_2 levels will as well cause serious adverse effects caused by the increasing average global temperature. Adverse effects include higher sea levels and more frequent extreme weather events [19].

To limit the effect of global warming nearly all nations have ratified the Paris agreement where the states together strive for a maximum global temperature increase of 2^oC but ideally 1.5^oC compared to pre-industrial levels [19, 20]. However, some would argue that it is optimistic that the temperature could be confined to 2^oC and that there could be severe consequences if the global mean temperature increased beyond 3^oC [19, 21].
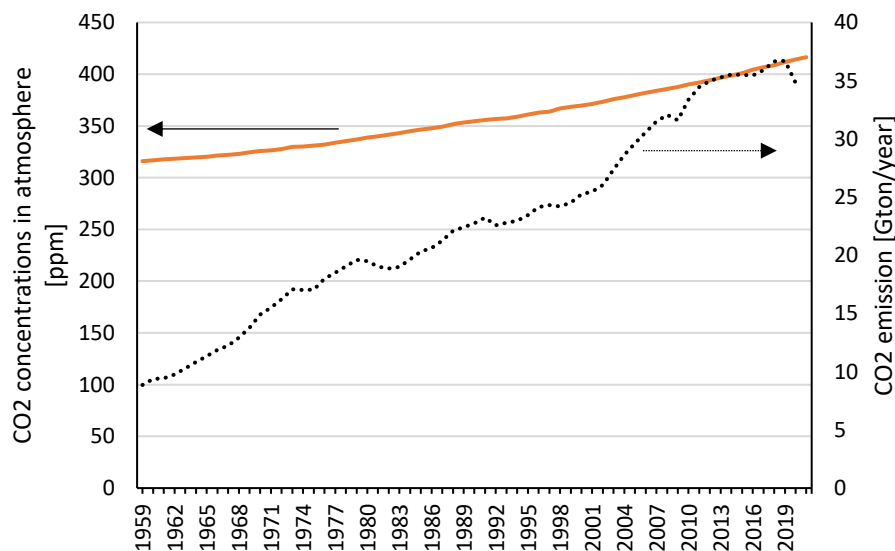

Figure 2. The annual average CO_2 concentration in the atmosphere according to the Mauna Loa observatory and the emission of CO_2 according to "Our world in data" [16, 18]. The concentration corresponds to the left axis and the right axis corresponds to the CO_2 emission.

2.2.2 Energy system globally

Despite the efforts to limit global warming and reduce the usage of fossil fuels, it is clear that the demand overall continues to increase. The international energy agency, IEA, estimates for primary energy input in the global energy system can be seen in Figure 3 [22]. The statistics in the figure indicate that oil, coal, and natural gas have increased substantially over 30 years in comparison with renewable energy sources and nuclear power. However, the trend curve for both coal and oil has flattened out in the last decade which is positive in a climate aspect. In relative terms, the increase in fossil fuel consumption is not that high while the renewable sources have increased greatly. The primary energy supply originating from wind, solar, and other sources have between 2000 and 2019 increased by more than fivefold while the coal consumption has only increased by roughly 70%. Biofuels and waste streams that are used have also seen a steady, almost linear, increase in the 30 years represented in Figure 3.
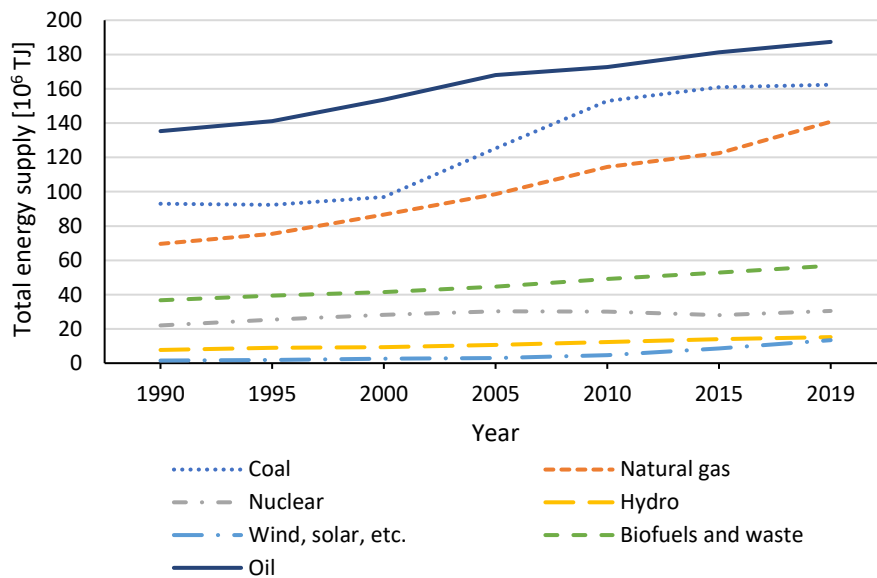

Figure 3. The main sources of primary energy globally 1990-2019 [22].

Although the primary energy input includes the fossil fuels, biofuels, and waste used in other appliances than in a combustion process, the majority is used as a fuel to burn for heat, transportation, or electricity. The electricity generated from a traditional powerplant burns fuel that generates steam which is the driving force for a turbine that generates electricity. The steam needs to be condensed after the turbine to reduce the required pumping power, and the heat can either be unused or used in for example district heating, the latter type of powerplant is then known as a combined heat and power plant [23, 24]. According to the international energy agency, electricity originating from the burning of fuels is by far the most common source. In Figure 4 the sources of electricity generation are shown from 1990 to 2019. It suggests that electricity originating from combustion processes, i.e. Coal, gas, or biofuel-based

powerplants, is by far the most common. The second most common source is hydropower followed by nuclear power. The slight decrease in nuclear power produced between 2010-2015 is the result of the nuclear accident in Fukushima Japan. But is projected to continue to grow [25]. In comparison with the primary energy input, the wind and solar input are separated. From this, we can see that solar PV starts to grow drastically in relative terms from 2015 forwards with 44000 GWh. Wind-based power started its growth spurt earlier in around 2005 and had increased by 110000 GWh in 15 years until 2019. Combined, solar PV and wind power were roughly 75% as large as the global nuclear power generated, showing that renewable energy sources will be a significant part of the energy system globally in the future.
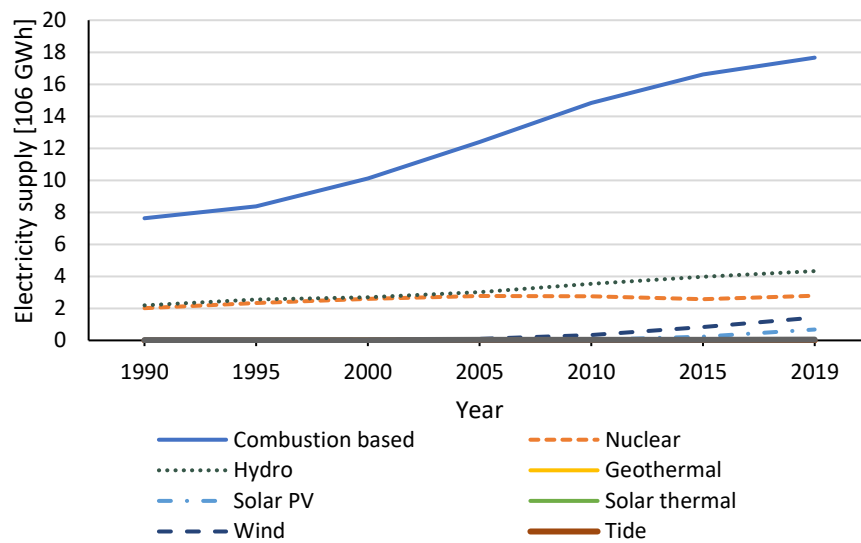

Figure 4. The sources of electricity generation globally 1990-2019 [22].

Wind, solar and other renewable energy sources have started to become a significant part of the global energy system. It is however still only a fraction of what combustion-based power plants contribute yearly to the electricity generation. It is therefore necessary that fossil fuels used are reduced in favor of biofuels and waste sources. As can be seen in Figure 5 the fuels are dominated by fossil fuels. Coal stands for 56% of the total use, natural gas 36% while oil is only 4% of the total supply. Even though oil is only a fraction compared to coal and natural gas it is still used in the same amounts as biofuels and waste combined [22]. The purpose of this comparison is to highlight the necessity of increased use of biomass to reduce net carbon emissions. Introducing new biomass as a fuel can be challenging because of the great variation in ash-forming elements especially considering biomass waste sources. Even though it can be challenging, biomass waste sources should be primarily used as it maximizes the sustainability and often the economy of the boiler [4, 11, 26].
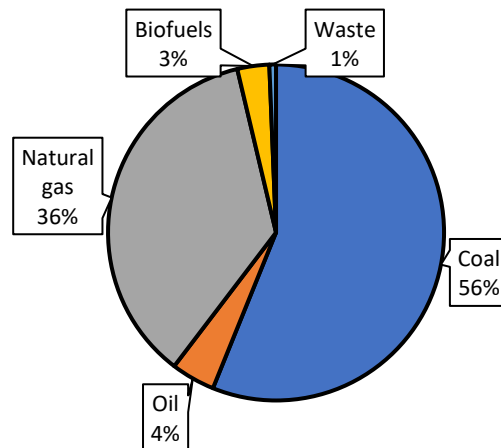
Figure 5. The global fuel sources used 2019 in combustion-based power plants [22].

2.2.3 The energy system in Sweden

Compared to the global average, the Swedish energy system differs substantially. Instead of coal, oil, and natural gas being the main energy inputs, the three main energy sources are nuclear, biofuels, and oil closely followed by hydro power as can be seen from the Swedish primary energy input over time in Figure 6. In the 80s the reliance on oil dropped sharply in favor of nuclear power. This has resulted in Sweden having the most nuclear power in its energy system of all OECD countries except for France. Sweden is also the second-largest user in OECD of biomass in relative terms, next to Finland [1]. The close to a linear decrease in oil consumption since 2000 could perhaps be explained by the similarly linear increase in biofuels. The decrease in oil used is 54 TWh while biofuels have increased to 61 TWh while the other energy sources has been relative constant to each other [27].
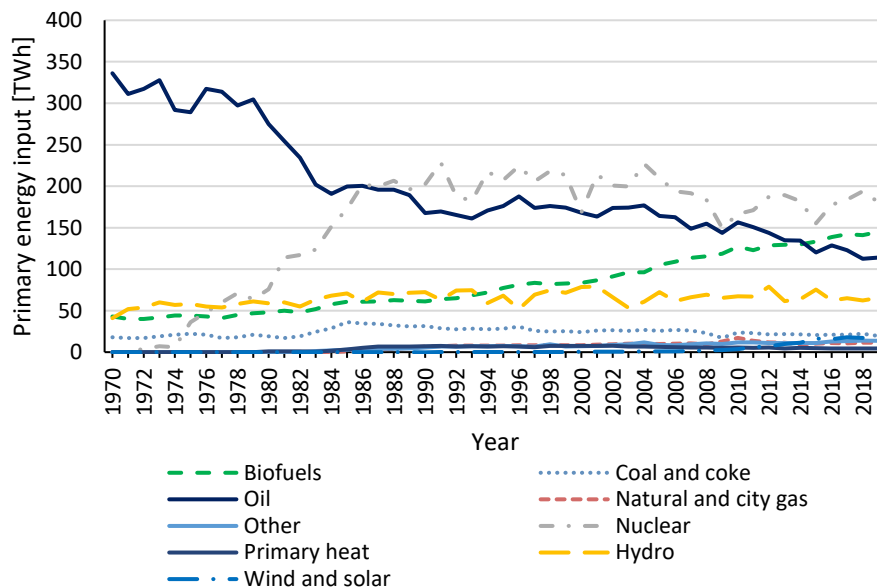

Figure 6. The main sources of primary energy in Sweden 1970-2019 [27].

Besides the Swedish affinity to nuclear power and biofuels, hydro power has been an important natural resource as it has provided cheap and emission-free electricity. The main sources of electricity generation in Sweden can be seen in Figure 7. Nuclear power and hydro power stand for roughly 40% each of the total electricity produced with combustion-based powerplants and wind power providing the majority of electricity that is remaining. If the higher amounts of nuclear and hydropower are disregarded, Sweden has comparably low amounts of combustion-based powerplants to the global average. Wind power became the third-largest electricity source between 2014-2015 and solar is closing in on providing 1 TWh of electricity in 2019 [27].
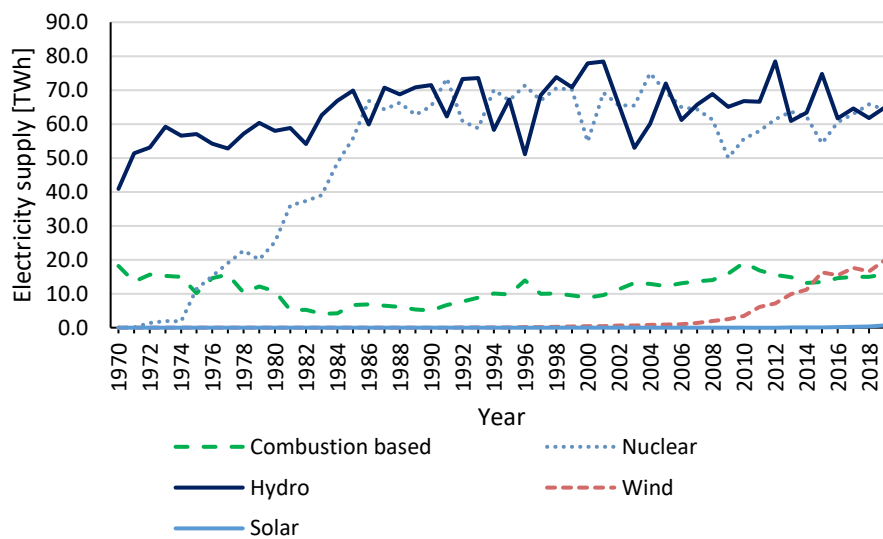
Figure 7. The electricity generated by energy source in Sweden between 1970-2019 [27].

Sweden is using combustion-based powerplants to a lesser degree than the global average and fossil fuels are used to a significantly lesser degree, see Figure 8. Together coal, oil, and natural gas make up 10% of the total fuels used compared to the global average of 92% in Figure 5. Other fuel types refer to fossil fuel-based waste like municipal waste but also some biomass such as peat that is defined somewhere between a renewable- and fossil fuel [27]. The extensive use of biofuels requires a large knowledge of the ash transformation and behavior in the power plants, especially as more complex waste sources and agricultural biomass is used which is known for increasing ash-related issues [10, 28].

Figure 8. The Swedish fuel sources used 2019 in combustion-based power plants [27].

3 Theory

The theory section aims to give the necessary theoretical background to the work done in this master thesis. First, the topic of combustion chemistry is introduced followed by ash chemistry and thermodynamics central to ash transformations.

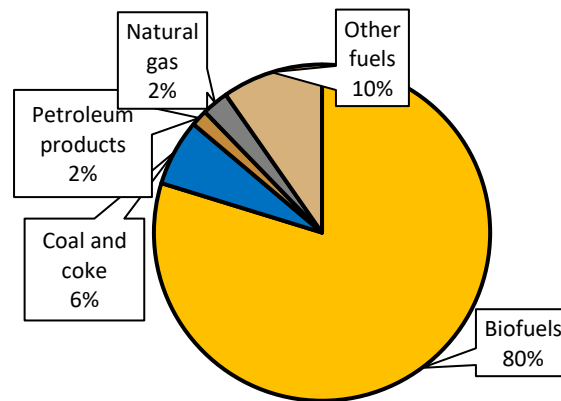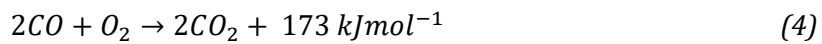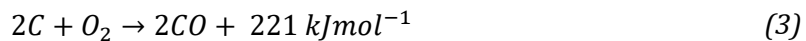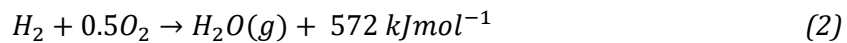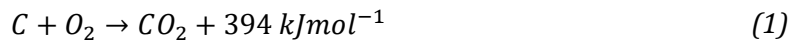## 3.1 Combustion chemistry

Combustion is the exothermic oxidation of the elements present in the fuel. Although many different elements are oxidized in biomass, it is C and H that is the main elements responsible for heat generation. Elements such as Ca and Mg are highly stable in an oxidizing environment, but the concentration is generally low and it has been suggested by Boström et al. that they already exist in an oxidized form in the fuel [29].

3.1.1 Definition of a full combustion

A full combustion is when all C and H are oxidized to CO_2 and H_2O according to the reaction formula (1) and (2). When the fuel is not fully combusted, it is not fully oxidized, and the final products will include CO that is formed according to the reaction formula (3). The oxidation of CO is included in reaction formula (4). Besides being a toxic gas that should be minimized, it decreases the heat generated by about half compared to CO_2 [13].

$$C + O_2 \rightarrow CO_2 + 394\ kJmol^{-1} \tag{1}$$

$$H_2 + 0.5O_2 \rightarrow H_2O(g) + 572\ kJmol^{-1} \tag{2}$$

$$2C + O_2 \rightarrow 2CO + 221\ kJmol^{-1} \tag{3}$$

$$2CO + O_2 \rightarrow 2CO_2 + 173\ kJmol^{-1} \tag{4}$$

These four reactions are highly simplified and there are several intermediate reactions and unstable species that form before CO_2 or H_2O has formed. For the combustion of CH_4 in pure oxygen, more than 300 reactions would occur instead of these three involving 8 stable- and 9 unstable species [13].

3.1.2 Higher and lower heating value

From the reaction formula of the oxidation of H_2, water vapor is the final product. The energy that is generated from this reaction includes the heat that is collected from the condensation of said vapor. Not all appliances can fully condense the vapor in the

resulting flue gas and thereby not harvesting the latent heat of moisture. Therefore, two heating values are included for the fuels. One includes the water condensing, higher heating value (HHV), and one where it is not included, lower heating value (LHV) [30].

3.1.3 Determining the air-to-fuel ratio for stochiometric combustion

When working with fuel mixtures it is often necessary to take the entire atmosphere in the boiler into consideration. This includes temperature, pressure, and oxidizing medium. When a full combustion is being simulated, oxygen is required to be added into the atmosphere so that all C and H are oxidized to CO_2 and H_2O. This requires some calculations to ensure that enough oxygen is added to the process.

From the fuel analysis, the number of different elements is included. When determining the stochiometric required oxygen the first assumption is that the element is oxidized to its most stable form. For C and H, it is straightforward but for certain metals that can be found in a variety of different oxide forms, this is more of an assumption. Depending on the fuel analysis the amount of oxygen required to oxidize the most common metals including Si and, S is not included in the oxygen content and needs to be added. The relative amounts of oxygen gas that are required to be added can be determined from the oxidation reactions stochiometric coefficients. The number of moles of oxygen gas and mono atomic oxygen that are required to be added to fully oxidize the organic and ash-forming elements can be seen in Table 1. For example, to oxidize 1 mole of C we require 1 mole of O_2 and 2 moles of O. For 1 mole of Mg, we require ½ mole O_2 and 1 mole O.

Table 1. The number of moles O_2 and O required to fully oxidize 1 mole of the following elements.

Oxidized form	O2/element [mol/mol]	O/element [mol/mol]
CO_2	1	2
H_2O	1/4	1/2
NO	1/2	1
Na_2O	1/4	1/2
MgO	1/2	1
Al_3O_2	1/3	2/3
SiO_2	1	2
P_2O_5	5/4	5/2
SO_3	3/2	3
K_2O	1/4	1/2
MnO	1/2	1
Fe_2O_3	3/4	3/2

There are several ways to quantify how much oxidizer that is required to be added. One way is the air-to-fuel ratio in equation (5) where the mass, moles, or volume air that is required to be added in relation to the fuel added.

$$AIR_{stoichiometric} = \frac{n_{O2} + n_{N_2}}{n_{fuel}}. \tag{5}$$

Where n_{O2}, n_{N_2} and n_{fuel} is the stoichiometric mass, moles, or volume of O_2, N_2, and the fuel [31]. Often, to ensure full combustion, an excess amount of oxidizer is added to the process. If the amount of stochiometric required oxidizer is known, then the needed oxidizer can be determined with the desirable fraction of excess air from

$$\lambda = \frac{n_{oxidizer,actual}}{n_{oxidizer,stoichiometric}} = \frac{AFR}{AFR_{stoichiometric}}. \tag{6}$$

This is the air-to-fuel equivalence ratio and can be determined by either the mass or mole fraction of the actual amounts of oxidizer, $n_{oxidizer,actual}$, to the stoichiometric required amounts of oxidizer, $n_{oxidizer,stoichiometric}$. As well as the fraction between the actual air-to-fuel ratio, AFR, and the stochiometric, $AFR_{stoichiometric}$ [32].

3.2 Ash chemistry

In biomass and most other fuels, elements other than C and H exist that will affect the process without adding much to the heat generation. These are called ash-forming elements and despite of their name they do not only form ash but also gaseous species and deposits. The main ash-forming elements in biomass are Si, Ca, Mg, K, Na, P, S, Cl, Al, Fe, and Mn but can include a few more or less elements depending on the author and fuel [29]. Some elements may have an important role in the plants biological function while others originate from contaminants of sand- or clay minerals. Other elements can exist as several different compounds in the biomass and can therefore be both inherent in the plant or due to contaminants. Depending on the origins or function of the compounds the elements exist in, it has been suggested by Doshi et al. to classify them into three different categories according to Table 2 [33]. Often biomass is concerned with plant-based biomass, and it is therefore possible that other compounds would also be found if animal waste was included, which it might be. Ash forming elements in biomass might also be of non-biological origin, it can be the result of mineral contaminants as it grows or during harvest e.g. phytolite, quarts, kaolinite in Table 2. The minerals that originate from an external source can be more stable than those inherent in the plant and they are less reactive leading to a lesser impact [29].

Table 2. Ash-forming element compounds found in biomass according to Doshi et al. [33].

Element	Ionic salts	Organically bound inorganics	Minerals
Na	Sodium nitrate Sodium chloride		
K	Potassium nitrate Potassium chloride		
Ca	Calcium nitrate Calcium chloride Calcium phosphate	Calcium pectate	Calcium oxalate Calcite
Mg	Magnesium nitrate Magnesium chloride Magnesium phosphate	Chlorophyll Magnesium pectate	
Si	Amorphous silica		Phytolite Quartz
S	Sulfur tetraoxide-2ion	Sulfolipids	
N		Protein Sulfolipids	
P	Phosphate-3ion	Nucleic acids	Phytates Phytic acid
Cl	Chloride ion		
Al			Kaolinite
Mn		Organic structures of proteins and carbohydrates	
Fe		Chelates Organic sulfates	Phytoferritin Iron oxide

As fuel is heated and its structure breaks down, the ash-forming elements will start to undergo phase transitions and/or rearrange to create new compounds. This is a series of complex interactions as the number of variables such as process conditions,

number, and concentration of elements will all have an impact on the final chemical reactions. These reactions are a scientific field of their own and are known as ash transformations.

To simplify the complex reaction paths the reactions can be divided into primary-, secondary- and even tertiary ash transformations. Primary phase transitions are the first most stable form, mainly oxides, that an element thermodynamically is expected to be in. These primary compounds serve as the reactants in the secondary ash transformations while the tertiary ash transformations include a negatively charged molecular ion besides hydroxide among the reactants [34]. The reactions involved could be prioritized differently depending on the reactants strengths as Lewis bases and acids. The Lewis base/acid concept together with the primary- and secondary ash transformations will be briefly introduced in the following paragraphs.

3.2.1 Lewis acids and bases

Contrary to the mainstream interpretation of acidity and bases as the propensity to donate and accept a proton, a Lewis base and acid is defined as the propensity to donate and accept an electron pair. When a Lewis base and a Lewis acid react, an electron pair is donated from the base to the acid and a coordinate covalent bond is formed between the two reactants. All molecules without a full outer electron orbital can act as a Lewis acid [35]. All metals cations will therefore act as acid while some in their oxidated states will act as a base.

3.2.2 Primary ash transformations

The elements Si, P, S, and Cl will initially form compounds that act as Lewis acids for the most part, meaning that they can accept an electron pair from a Lewis base. The metals Ca, Mg, K, Al, and Fe form compounds that tend to act as a Lewis base [34]. This concept with acids and bases helps to give an estimate between which elements a reaction will be prioritized, the strongest base will donate an electron pair with the strongest acid, and so forth. To help utilize this acid-base concept the primary ash transformations can be thermodynamically expected to form the compounds in Table 3 and the compounds can be divided into either acid- or a base group. The compounds reactivity as an acid or a base decrease from the top of the table downwards but can change depending on process conditions like the temperature in some circumstances [29].

Table 3. The classification of ash-forming elements in terms of their first initial stable form into Lewis bases and acids. The compounds reactivity as acids or bases decreases from the top down. Adapted from Boström et al. [29].

Basic compounds	Acidic compounds
KOH(l,g) (K_2O)	P_2O_5(g)
NaOH(l,g) (Na_2O)	SO_2(g)/SO_3(g)
CaO(s)	SiO_2(s)
MgO(s)	HCl(g) (Cl_2)
H_2O(g)	CO_2(g)
	H_2O(g)

3.2.3 Secondary ash transformations

The primary compounds are what are expected to form based on their thermodynamic stability. More details can be seen in Boström et al. discussing the ash transformation when combusting biomass [29]. From this schematic approach we can see that during the secondary ash transformation, alkali-phosphates are prioritized to form. This is because this combination has the largest difference in the basicity and acidity of the primary ash-forming compounds. If there would be a surplus alkali in relation to phosphate, alkali-sulfates would be the compound that starts to form next. This continues so that the compound with the highest acidity is matched with the compound with the highest basicity. There is also a possibility for several different basic compounds to together form more complex phosphates, sulfates, silicates etcetera. This is a simplified and thermodynamic approach. In practice, there are reaction kinetics, ash fractionating, and a few other considerations that must be made [29].

3.2.4 Alkali chlorides, corrosion, and sulfation

Although K and Na are different elements they behave similarly and can therefore often be discussed together under the alkali umbrella term. During combustion, alkali is evaporated in the char burnout stage and only a small part is evaporated during the devolatilization stage of the combustion process for a fuel particle [36]. Both K and Na are transported in the gas phase as chlorides for the most part and the ash transformation of alkali is of major interest for boiler operators as it is linked to agglomeration, deposits build-up, and corrosion. Alkali chlorides are in particular heavily linked to corrosion and are therefore the subject of major research [2, 3, 7, 36-38]. The corrosion is especially severe on the super heaters as the heat transferring surfaces are often cooler than the melting point of the alkali salts which promotes the formation of sticky layers that build chloride-rich deposits.

On the alloy materials in the boilers, an oxide layer constitutes the first protective layer against the corrosive flue gas atmosphere. The alloys used are commonly a mixture of, Fe, Ni, and Cr with an oxide layer that can be protective but also non-protective depending on the oxide properties. A protective oxide layer has been suggested to be protective if its molar volume is larger but not more than double then its pure metal form. If the oxide layer decreases as the metals oxidize the oxide layer is suggested to be porous which allows for mass transport into and out through the protective layer. Similarly, if the volume expansion is too great, stresses will reduce the ability of the layer to minimize the diffusion inward and outward from the material [1, 39]. Other authors have defined that a protective oxide layer should:
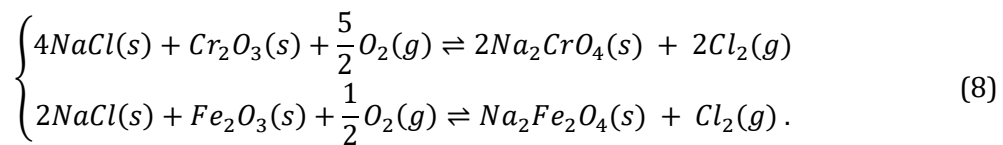
a) Exhibit good adhesion to the un-oxidized material
b) High liquidus temperature
c) High-temperature plasticity
d) Slow growth rate
e) Low difference in thermal expansion between the un-oxidized material and oxide layer
f) Low diffusion coefficient and electrical conductivity for metallic ions and oxygen [37].

The ability of the oxide film to protect and limit the diffusion and transport of material to the un-oxidized material has an impact on the corrosion rates. There are many different types of corrosion products and mechanisms but in terms of alkali salts and Fe-Ni-Cr alloy, it has been suggested that active oxidation and alkali chromate formation is two of the main corrosion mechanisms. Alkali chromate formation is the interaction between the Cr-oxide and KCl according to reaction (7),

$$Cr_2O_3(s) + 4KCl(s) + 2H_2O(g) + \frac{3}{2}O_2(g) \leftrightarrow 2K_2CrO_4(s) + 4HCl(g). \qquad (7)$$
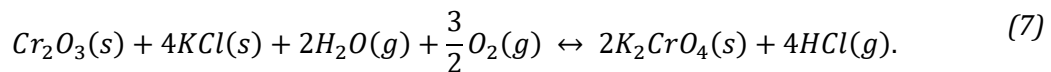
This can cause severe mass loss of the protective oxide as the Cr oxide is depleted and the rapid buildup of the Fe oxide protective layer [37].

Active oxidation is another suggested corrosion mechanism that is based on that the partial pressure is low enough locally between the oxide scale and bulk material so that metallic chlorides form. The competitiveness of chlorides and oxides for Fe can be seen in the predominance diagram in Figure 9 to illustrate active oxidation. As the alkali salts are deposited on a surface either directly due to condensation or due to the impact of aerosols, the alkali salt can react according to equation (8) [37].

$$\begin{cases} 4NaCl(s) + Cr_2O_3(s) + \frac{5}{2}O_2(g) \rightleftharpoons 2Na_2CrO_4(s) + 2Cl_2(g) \\ 2NaCl(s) + Fe_2O_3(s) + \frac{1}{2}O_2(g) \rightleftharpoons Na_2Fe_2O_4(s) + Cl_2(g) . \end{cases} \qquad (8)$$

As the alkali form, new solid compounds with the Cr and Fe gaseous Cl_2 are formed in the process. Some of the Cl_2 can travel through defects in the

protective oxide layer to the bulk material. Although contested, it has been theorized that the oxygen partial pressure can be locally low enough so that gaseous Fe form as is represented in the reaction formula (9) below,
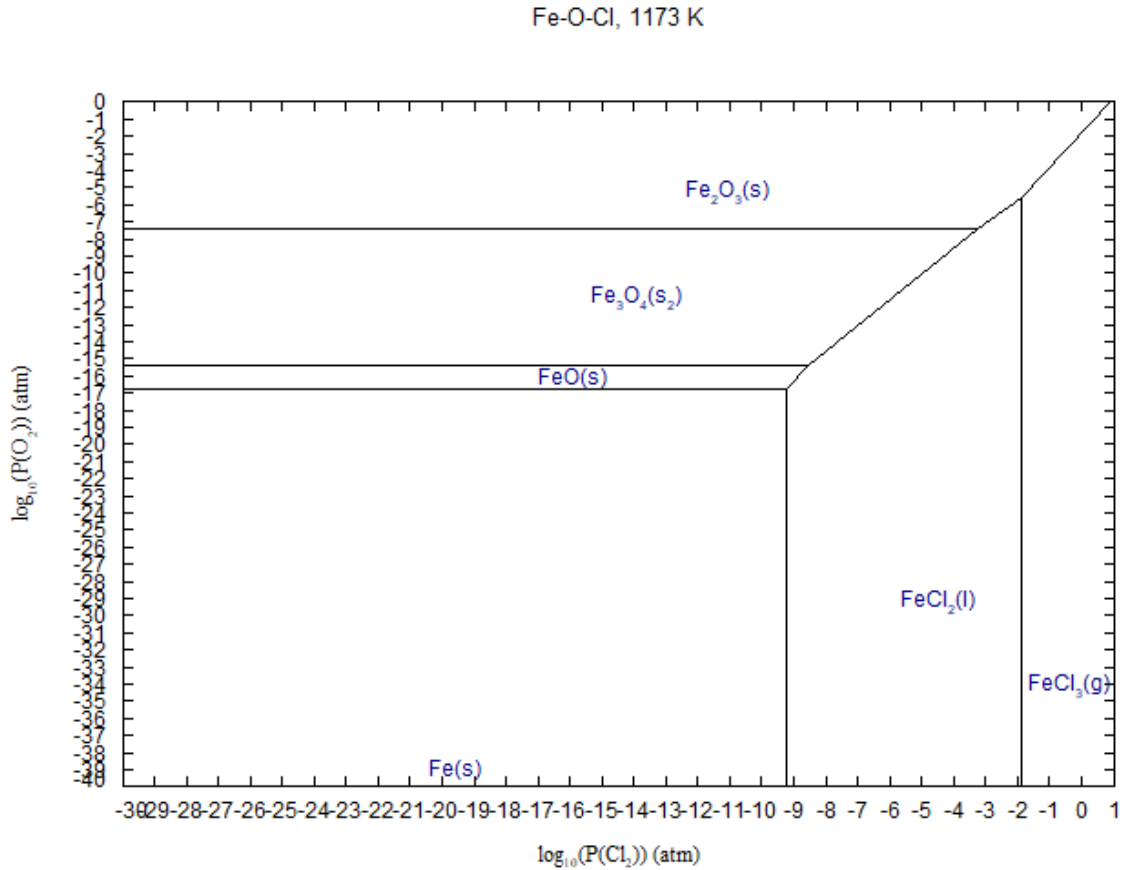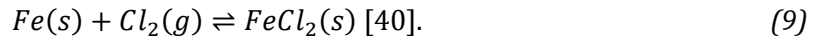

Fe-O-Cl, 1173 K

Figure 9. Predominance diagram at 1173K for the FE-O-Cl system. The horizontal axis is the Cl_2 partial pressure, and the vertical axis represents the partial pressure of O_2.

$$Fe(s) + Cl_2(g) \rightleftharpoons FeCl_2(s) \text{ [40]}. \tag{9}$$

This can be seen on the right side of the predominance diagram where the Cl_2 partial pressure is high. As the volatilized Fe species travel through the defects of the oxide scale, the number of O_2 molecules increases, and its partial pressure increase. When the O_2 partial pressure is sufficient Fe oxide becomes stable which is equivalent to moving up and/or right in the predominance diagram. The oxidation of $FeCl_2$ can be seen in reaction formula (10) [40],

$$\begin{cases} 3FeCl_2(g) + 2O_2(g) \rightleftharpoons Fe_3O_4(s) + 3Cl_2(g) \\ 2FeCl_2(g) + \dfrac{3}{2}O_2(g) \rightleftharpoons Fe_2O_3(s) + 2Cl_2(g). \end{cases} \tag{10}$$
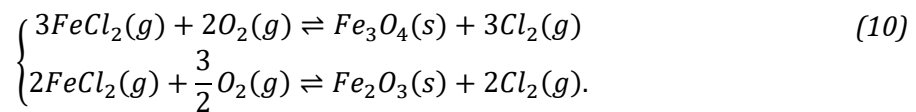
The transport of un-oxidized Fe to the oxide scale can cause rapid deposit build-up and corrosion rates. This mechanism is relatively disputed since the assumption of a low O_2 partial pressure at the bulk material surface is unintuitive since the O_2 molecule is smaller than Cl_2 and should therefore have an easier transport through the defects in the oxide scale. Therefore other corrosion mechanisms such as electrochemical have also been suggested [37].

3.3 Thermodynamics

These sections aim to present the theory that leads up to the concept of Gibbs free energy that is used to predict the spontaneity and equilibrium of a chemical reaction. Thermochemical equilibrium utilizes the minimization of Gibbs free energy to determine the phases and compounds present at a certain pressure and temperature.

3.3.1 Internal energy and enthalpy

For a perfectly insolated system energy cannot be created nor destroyed. The total energy content, or internal energy denoted U, can be described as the sum of its individual molecules translational, vibrational, rotational kinetic energy, and potential energy from intermolecular attractive forces

$$U = E_{Translational} + E_{Vibrational} + E_{Intermolecular} \text{ [41].}$$

It is not useful to define the current internal energy content and for the most part, it is the difference between two states that are of interest. The first law of thermodynamics, also known as the conservation of energy, can help to describe the difference in internal energy, ΔU. It stated that

"If heat is recognized as a form of energy, then the total energy of a system plus its surroundings is conserved" [42].

For a system that is closed i.e., no mass can enter or exit its system boundaries. The sum of the system and its surroundings constitutes the universe and because only heat and work can traverse the system boundaries, the change in internal energy in equation (11) must be the sum of heat and work transfer [43].

$$\Delta U = q + w. \tag{11}$$

Heat transfer, q, is the energy transfer that originates as a response to a temperature difference, and work, w, is energy transfer that is not due to a temperature difference. If the work other than volume work is disregarded, then the difference in ΔU is described with

$$\Delta U = q - \Delta(PV).$$

Where P is the pressure and V is the volume. The difference in energy content due to heat transfer at constant pressure is often of interest. Therefore, enthalpy is defined as

$$\Delta H = \Delta U + \Delta(PV) = q - P\Delta V + P\Delta V = q. \qquad (8)$$

From equation (8) the volume work performed cancels out during constant pressure and the enthalpy change equals the heat transfer. Another implication of this is that for solids and liquids that are incompressible, the volume change is often negligible. And the change in internal energy equals the change in enthalpy [44].

3.3.2 Entropy

Similar to internal energy and enthalpy, entropy is a state function, and it was defined in conjunction with the second law of thermodynamics to determine a process tendency to happen spontaneously. There are numerous examples of processes that would occur in theory without violating the first law of thermodynamics but would not occur in practice. One example of this is a cooler object transferring heat to a warmer object. The concept of entropy was therefore required together with the second law [42].

Entropy can be described in several ways, as the disorder, trend toward uniformity, or as the amount of heat that is not available to produce work. The entropy change of a system, ΔS, is defined in the field of thermodynamics as

$$\Delta S = \frac{q_{rev}}{T}.$$

Where q_{rev} is the reversible heat transfer and T is the temperature of the system. From the definition above we can see that for an isolated system the entropy must be zero or increase which is the main point of the second law of thermodynamics [42].

For a closed system there is heat transfer over the system boundaries and according to the second law of thermodynamics, the entropy in the system i.e. the universe must increase. Giving the commonly seen condition for a spontaneous process

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0 \ [45]. \qquad (12)$$

3.3.3 Gibbs free energy

Even though the entropy can tell if a process is spontaneous or not it can be hard to determine some of the surroundings parameters. Gibbs free energy is only described with the parameters of the system and at constant pressure and temperature the change in Gibbs free energy can be described as follows

$$\Delta G = \Delta H - T\Delta S = -T\Delta S_{univ} \qquad (13)$$

The change in Gibbs free energy is, ΔG, at constant pressure and temperature, T. This can be seen as the driving force for a process considering both the release of heat and entropy change of the system. The change in Gibbs free energy has the opposite sign of the entropy change in the universe and as discussed prior with equation (12) a negative ΔG will yield a spontaneous process and a process with positive change will not happen spontaneously. From inspection of the relation for the change of Gibbs free energy above, one can see that if ΔH and ΔS have the same sign, it yields a process that is spontaneous depending on the temperature. If both terms have different signs the process is either spontaneous or non-spontaneous independent of the temperature according to Table 4.

Table 4. Implications of the sign of ΔH and ΔS on the spontaneous nature of a process.

	$\Delta H > 0$	$\Delta H < 0$
$\Delta S > 0$	Spontaneous depending on temperature	Spontaneous independent of temperature
$\Delta S < 0$	Non-spontaneous independent of temperature	Spontaneous depending on temperature

For a chemical process with reactants and products, the change in Gibbs free energy is dependent on the distribution between the reactants and products. It can be determined with equation (14) below,

$$\Delta G = \Delta G^o + RTlnQ. \qquad (14)$$

The reaction quotient is Q, gas constant R, and change in standard Gibbs energy ΔG^o. The ΔG can be seen as the driving force dependent on the reaction quotient. When ΔG is positive the reaction quotient is large, and the reaction is shifted towards more reactants causing the reaction to continue. And in the same way, if the reaction is small, ΔG will be negative and the reaction is pushed towards the products. At $\Delta G=0$ the reaction is at equilibrium, and the reaction quotient is then the equilibrium constant K, giving

$$\Delta G^o = -RTlnK \; [46]. \qquad (15)$$

3.3.4 Ellingham diagram

The concept of Gibbs free energy has led to some tools that are commonly used in academia and industry. Ellingham diagrams are one of these tools that can be used to determine the stability of a species in a specified temperature and or atmosphere by itself or compared to other species. An Ellingham diagram of the formation of oxides can be seen in Figure 10. Each oxide reaction is a function of the oxide partial pressure

or temperature depending on the axis used in the graph. The right axis corresponds to the oxygen partial pressure and the left axis is the change in standard Gibbs free energy. For an oxide, the line corresponds to where there is a thermochemical equilibrium, $\Delta G = 0$, above the line corresponds to a non-spontaneous reaction, $\Delta G > 0$, and under the line corresponds to a spontaneous reaction, $\Delta G < 0$.

If two lines are compared the lower line is more stable since it has a lower standard Gibbs free energy and if we are in the area between the two lines, the bottom oxide reaction will compete for the oxygen and reduce the oxide reaction above. The line can be determined from equation (13) and equation (15) where the entropy terms correspond to the slope of the line and enthalpy to the intersection with the y-axis according to equation (13),

$$\Delta G = 0 \rightarrow \Delta G_o = \Delta H_o - T\Delta S_o = -RTln(K). \qquad (16)$$

The change in entropy and enthalpy is approximated as being independent of the temperature giving the straight-line equation. However, this is not a good supposition if the species in the reaction undergoes a phase transition as its entropy contribution and enthalpy will change greatly. This can be seen by the sudden change in the slope of the line as the temperature increases [47].

It is the entropy term that governs the slope of the lines in the Ellingham diagram. If we look at the oxidation of C to 2CO we can see that the reaction goes from having 1 unit of gas, O_2, to 2 units, 2CO. Independent on if the entropy is defined as a measure of disorder or as the heat that is unavailable to produce work, more gas yields a higher entropy in comparison to condensed phases. This reaction will therefore have a negative slope. If we instead look at a line with a positive slope such as the oxidation of Mg. We can see that there are 1 unit, O_2, in the reactant but only solids in the products. The entropy is then reduced by the reaction implying a positive slope. To further explain this, the Mg in the reaction starts to boil at 1100°C. As the Mg is volatilized the relative amounts of gas increase to 3 units including both Mg(g) and O_2. This extra addition of gas can be seen by the steeper slope that occurs after the boiling point.

The change in entropy and enthalpy is approximated as being independent of temperature giving the straight-line equation. However, as was argued in the prior section, this is not a good supposition if the species in the reaction undergo a phase transition as its entropy contribution and heat capacity that governs the enthalpy can change greatly [47].
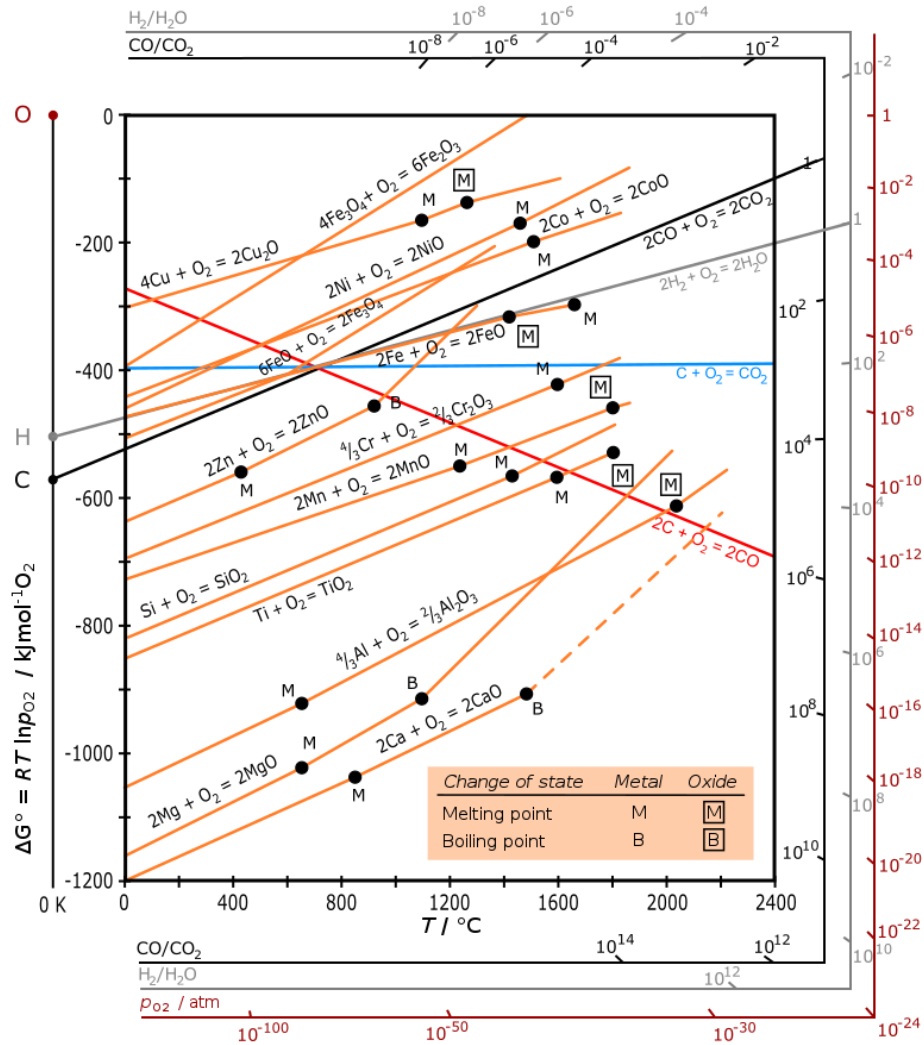
Figure 10. Ellingham diagram for several oxides. The left axis is the standard free Gibbs energy, axis to the right correspond to the partial pressure oxygen and fraction of CO/CO2 and H2/H2O. Adapted from [48].

4 Method

The method section begins with an introduction of the Perstorp B6 boiler both in terms of how it works and the different parts. This is followed by how the fuel mixtures were calculated and the data gathered. The last section presents how the alkali salt-related corrosion tendencies were estimated by determining the theoretical available SO_2 in the flue gas.

4.1 Perstorp 50 MWth circulating fluidized bed

The B6 boiler subject to this master thesis is a 50 MWth, Megawatt thermal, large circulating fluidized bed and can be seen in Figure 11. The boiler together with its heat transferring surfaces can be divided into sections according to its purpose. First is the

furnace where the fuel is mixed with the oxygen and bed material. To separate the solids entrained in the gases the furnace is followed by a particle collection system. The remaining gases continue to the vertical flue-gas draft containing the main heat transfer devices outside the furnace.

4.1.1 Fuel feeding system

Forest fuel and peat are mixed on a stockpile and fed to the boilers using stokers. On the same stockpile residue wood is stored but separated from the forest fuel and peat by a wall because it is a waste fuel and extra control is required. Before these fuels are added to the boiler the fuel is separated according to its size and scanned with a metal detector. Limestone is then added to this fuel stream to control the SO_2 levels in the flue gas. Animal waste, sludge, and industrial waste are added separately to the boiler.

4.1.2 The furnace

In the B6 circulating boiler, the furnace is 18.5 m high with an 18.5 m^2 large base. If the fuel particles have a mean velocity of 4.9 m/s the fuel particles are entrained in the furnace for 3.8 s. From the bottom of the furnace and between the air inlets, the tubes are lined with refractory to protect from high temperatures. There are two air nozzles, one primary at the bottom and one secondary 2.5 m above the first air inlet. The primary inlet fluidizes the bed material and together with the secondary air inlet, the atmosphere becomes oxidizing throughout the freeboard. In the bottom part of the furnace, fuel is added together with certain additives and the recycled solids from the loop seals are also re-inserted in this part. The furnace wall is made of tubes that circulate water both to cool the furnace and to evaporate the water. The water continues to a steam dome that separates the steam from the liquid water. Steam continues to the superheaters in the vertical flue-gas shaft while the liquid water is recirculated into the tube wall.

After the furnace, the flue gas, fuel particles, and some bed material enter two cyclones that have the purpose to separate the solids from the flue gas by centrifugal forces. In the cyclone entrance NOx reducing additives are added in the form of ammonia, NH_3. In the cyclones exits, vortex finders, particles smaller than 120 μm can exit while the larger particles enter the loop seals that separate heavier ash and re-circulate bed material and other lighter materials. The vortex finders are not cooled or lined with a refractory as the rest of the cyclone.

4.1.3 Vertical flue-gas shaft

After the majority of coarser particles are separated from the flue gas, the flue gas enters the second main heat transfer area. The heat exchanger that requires the highest temperatures i.e the superheaters is located at the beginning of the shaft. There is a total of three superheaters, the ternary-, secondary-, and the primary superheater that superheats the steam from the steam drum. They are followed by the upper vaporizer and the lower vaporizer. Four economizers are installed where the first four economizers aim is to saturate the feedwater before entering the furnace tubes. Economizer 0 is currently not operational. All the superheaters, vaporizers, and

the first four economizers are coupled with a soot-blowing system. After the vertical flue-gas draft the flue gas Is cleaned with a baghouse filter to reduce particle emissions.
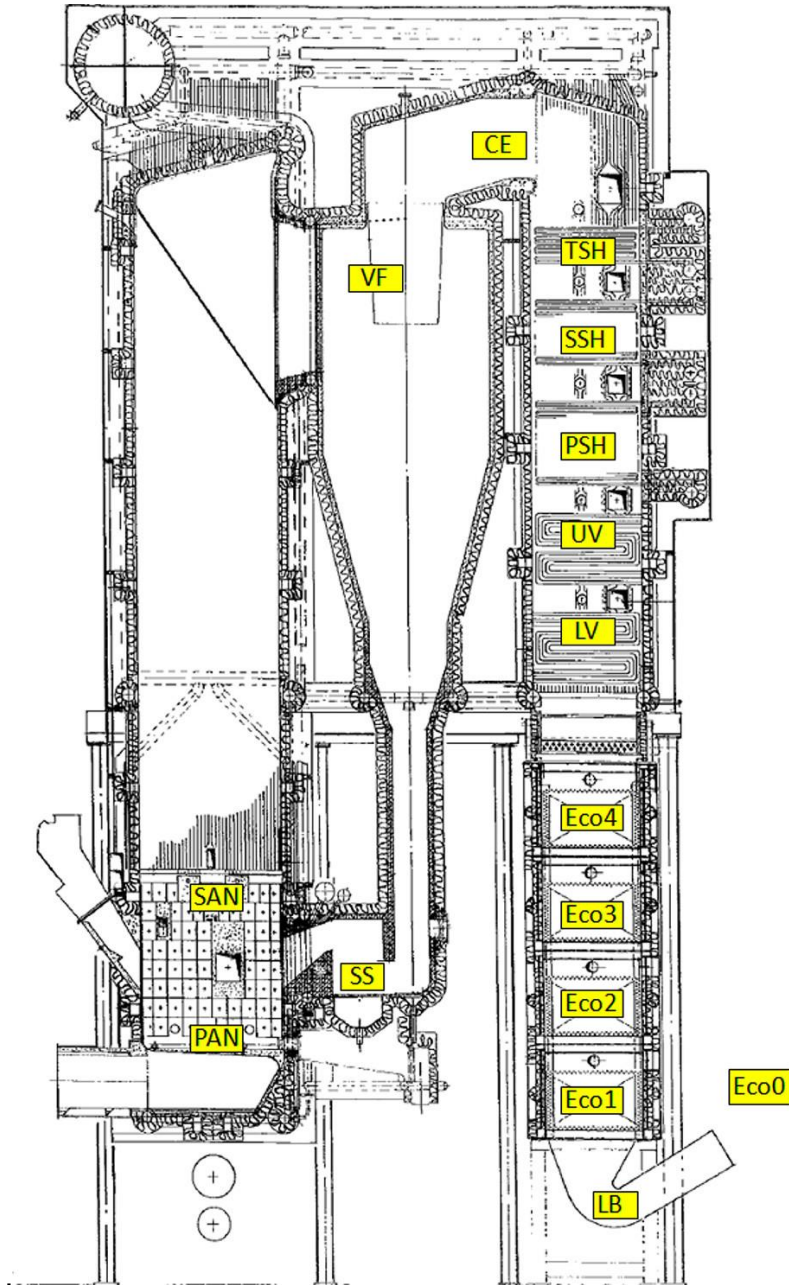

Figure 11. A sketch of Perstorp 50 MWth circulating fluidized bed and the name of each component. To the right is the furnace including the primary air nostril (PAN) and secondary air nostril (SAN). The particle separation system in the middle includes the vortex finders (VF) and loop seals (SS) and the exits for the cyclones (CE). In the right part of the figure is the vertical flue-gas draft containing primary-, secondary- and ternary superheaters (PSH, SSH, and TSH). These components are followed by upper vaporize (UV), lower vaporizer (LV), economizers (ECO 0-4), and lastly lower bend (LB). Adapted from Henrik Hagman. [1]. ©Metso Power.

4.1.4 Flue gas cleaning system

After the vertical flue-gas draft the particles in the flue gas are separated with a fabric filter to reduce emissions according to Figure 12. The flue gas filter is composed of a series of filter hoses with a large total surface area. As the filter fills up the pressure drop increases and at a certain point the hoses are required to be cleaned by the addition of air from the opposite direction of the flue gas. This filter cake is collected and stored with the fly ash. To ensure a slightly lower pressure in the boiler the fabric filter is followed by a flue gas fan. After the flue gas fan, the flow is separated into two streams where one is circulated into the boiler and the other stream continues to a wet gas scrubber. In the scrubber, chemicals are added to reduce the emissions of NH_3, SO_2, and HCl.
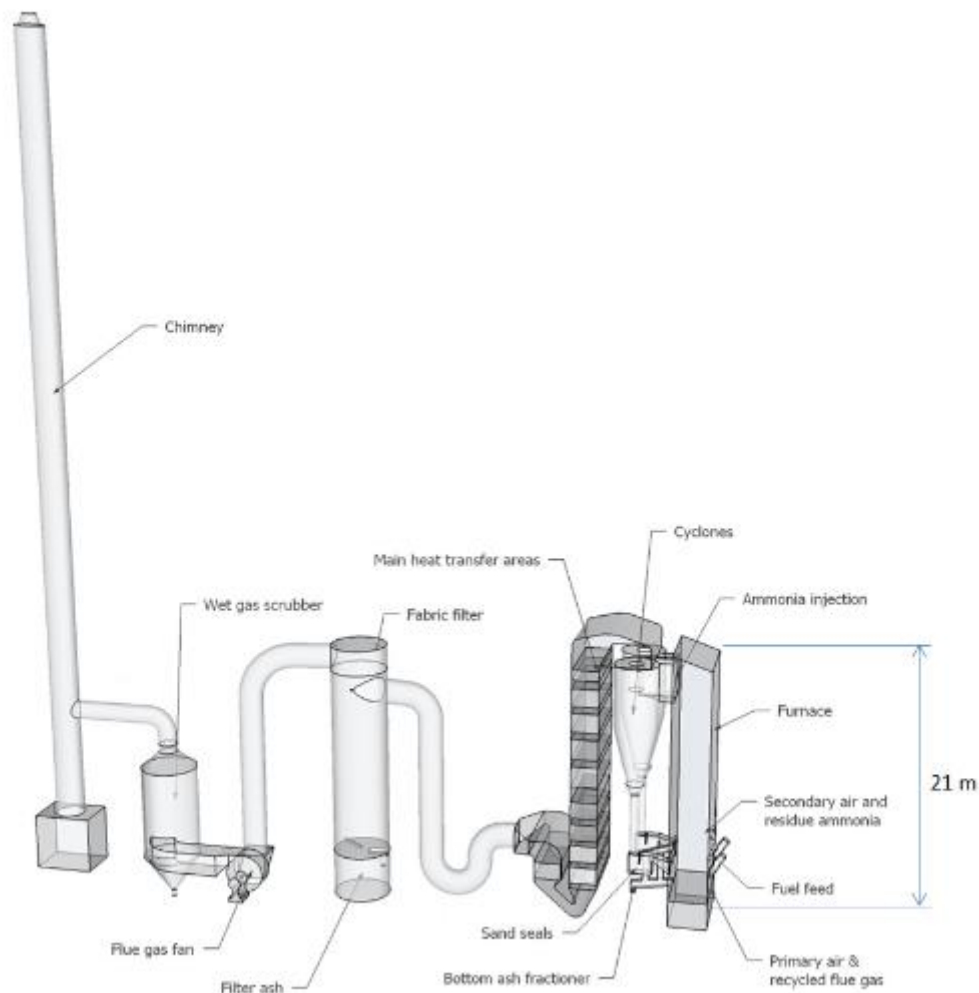

Figure 12. Features and components of the Perstorp B6 50 MWth circulating fluidized bed. Adapted from Henrik Hagman [1].

4.2 Data gathering and sampling

To enable the evaluation of possible peat reduction and introduction of a Na-rich fuel, a baseline had to be made from 2021 data. The baseline consisted of determining what

fuels were used, in what amounts, what fuel analyses that are available, and if they are still representative of the fuel. This was done by interviewing experienced staff working with the boiler operations and by using work done prior by Henrik Hagman concerning corrosion on the B6 boiler [1]. The fuels identified in this work can be seen in Table 9 in Appendix A, where they are sorted into different categories depending on their origins. A total of 21 different fuels and additives were identified and categorized into residue wood, sludge, peat, forest fuels, additives, and industrial waste. The mass as received for each category used in 2021, can be seen in Table 5 below.

Table 5. As received mass of each fuel category 2021 [As received tons].

Residue wood chips	Sludge	Peat	Forest fuels	Animal waste	Additives	Industrial waste
28000	2800	9300	34600	27400	1020	1850

Besides being a prerequisite for the fuel mixture evaluation, the mass of each fuel served as an indication of how important a certain fuel was. A large number of fuels made getting new fuel analysis on all fuels impractical and unnecessary. If a fuel had a low total contribution to the ash content and did not have any obvious reasons to change over time, older fuel analyses from 2009-2016 are used or the fuel is estimated to have the same composition as a similar fuel. For more important fuels in the residue wood chips, peat, forest fuels, and animal waste category newer analysis were available or samples were sent for new analyses. A total of 6 different fuels in the prior mentioned categories were sent for new analysis. Animal waste that is important is analyzed yearly and additional tests were in this case superfluous. The new samples were sent to an accredited laboratory and analyses were made in regards to the energy content, moisture-, ash content, and elementary analysis for the following elements: Al, As, Ca, Cd, Cl, Cr, Cu, Fe, K, Mg, Mo, Na, P, Pb, S, Si, Ti, V, Zn, C, O, H, and N.

4.3 Fuel mixture composition

From the identified fuels, mass fractions, and analyses for the year 2021, the aim was to determine the mean composition for the entire fuel mixture. First each fuel fraction contribution to the ash- and water content was determined by multiplying the yearly mass used with their respective fuel analyses. The ash, moist and elemental content were summed up into their respective fuel category yielding the result in Table 9 in Appendix A. For each fuel category, the concentrations of the main ash-forming elements can be seen in Figure 13.
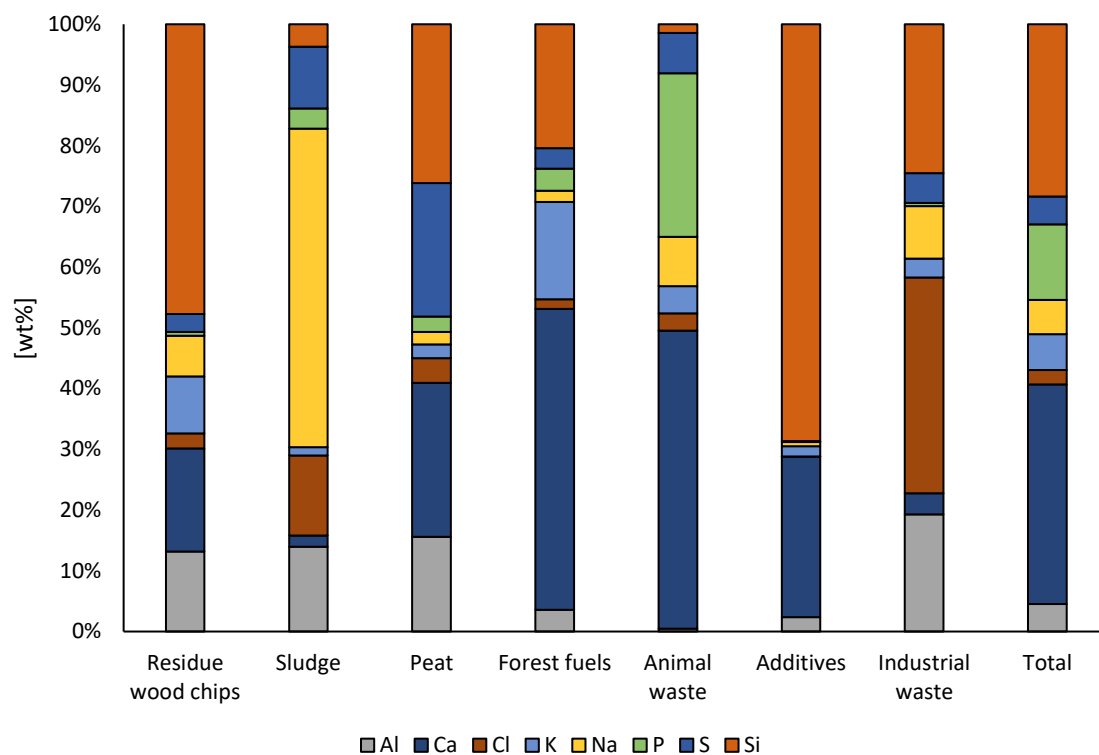
Figure 13. The relative concentration of the main ash-forming elements in each fuel category and in total 2021.

For each parameter, the yearly accumulated mass was divided by the total amount of fuel to determine the relative fuel composition for the entire fuel mixture seen in Table 6.

Table 6. The mean fuel mixture composition as recieved for the year 2021 in Perstorp B6 boiler.

	Mean fuel mixture composition	Unit
Ash	3.4	wt%
H20	46.4	wt%
C	27.7	wt%
H	33440.7	mg/kg
N	1.0	wt%
O	19.6	wt%
Al	768.4	mg/kg
As	1.9	mg/kg
Ba	53.3	mg/kg
Ca	6112.4	mg/kg
Cl	403.7	mg/kg
Cr	12.1	mg/kg
Cu	6.6	mg/kg
Fe	613.5	mg/kg
K	993.6	mg/kg
Mg	364.1	mg/kg
Na	957.1	mg/kg
P	2097.0	mg/kg
S	783.2	mg/kg
Si	4792.5	mg/kg
Ti	133.1	mg/kg
Zn	79.1	mg/kg

4.4 Determining new possible fuel mixtures

After the baseline had been made, possible replacement fuels to replace the energy content of the peat had to be established. First, it was determined if it would be possible to increase the supply of the replacement fuel to cover the reduced energy content of the peat. Then it was considered if any other fuels then peat trended to disappear in the future and if the replacement fuels could cover this energy loss as well. Lastly, because of EU regulations, no more than 75% of the flue gas can originate from waste fuels and must full fill the following constraint,

$$\frac{V_{residue\ wood+} + V_{sludge} + V_{animal\ waste} + V_{Industrial\ waste}}{V_{total}} < 0.75.$$

Where V is the flue gas volume for each fuel fraction at an excess O_2 of 11%.

By interviewing experienced staff working on the B6 boiler the main possible routes for a future fuel mixture were divided into the following Cases:

Case 1. Replacing peat with forest fuels.
Case 2. Replacing peat with residue wood chips.
Case 3. Replacing both peat and animal waste with residue wood chips.
Case 4. Introducing Na-rich waste fuel to the current fuel mixture.

Forestry fuels are in general considered more attractive to use as a fuel than residue wood chips hence Case 1. However, residue wood is cheaper and was therefore included in Case 2. In Case 3, the longer trend of a lower animal waste supply was considered and because it is defined as a waste fuel, residue wood could be used as a replacement while not exceeding the 75% waste fuel constraint.

For determining the elemental composition for the different cases, the baseline composition was used. The peat was phased out in 10 wt% steps to see how the composition changed. Because of the different heating values, this had to be taken into account when adding a replacement fuel. First, the mean lower heating value was determined for the different categories. Then the amounts of replacement fuels that would replace the energy content of the peat could be determined. The composition that would result from the reduction of peat in each of the cases can be seen in Table 10. Similarly, the animal waste is removed from the baseline all at once and then the peat is replaced in 10 wt% steps with residue wood chips as in case 2. Lastly, for case 4 the new waste fuel, NAC, was added in to the fuel mixture in 10 wt% steps until all of the 12660 tons of NAC were included. In this case no other fuel were reduced when the NAC were added.

4.5 Fuel mixture corrosion tendency

Although many aspects need to be considered when choosing a fuel mixture, this work primarily focuses on the corrosion-related issues caused by alkali salts. The corrosion tendencies of a fuel mixture could be estimated using indexes that have been shown to estimate the corrosion tendencies by theoretically calculating the concentration of available SO_2 in the flue gas according to equation (17) below,

$$S_{availible} = S - 0.96Ca - 0.5K - 0.5Na + 1.6P + 0.4Si \leq S. \qquad (17)$$

The input for each element should be in terms of mole fraction after oxidation and including excess air. The parameters moisture and excess O_2 that were used in the calculations are the mean measured values in the flue gas in 2021. Because Ca will affect the available S the effects of reducing limestone levels to 50 wt% and 0 wt% were calculated as well.

When adding the Na-rich NAC to the baseline in case 4, the sulfur required to compensate for the negative effects of Na on the sulfation potential was determined. This was done by multiplying the S with a factor ranging from 1-6 in 0.5 increments.

5 Results and discussion

The result and discussion section start with a presentation of the current fuel mixture 2021. After the baseline, the theoretical sulfation potential results are presented for each case and for three different levels of limestone content. From the baseline and sulfation potential results, the potential monetary and CO_2 savings are estimated for three fuel mixtures.

5.1 Current fuel mixture

The current fuel mixture or baseline is complex due to the large number of fuels that differ significantly from each other in terms of elemental composition or other characteristics like water content. This is illustrated in Figure 14 where the different fuel categories' contribution to the ash-, energy content, and the total mass as received is presented. From an energy perspective, the two largest fuels are residue wood followed by forest fuels. Animal waste is the third-largest fuel source followed by peat. Forest fuels are the second-largest source of input mass and energy content but are only the fourth largest source of ash, indicating a high-quality fuel category. Additives high ash contribution is due to limestone and bed sand that has a very high ash content and no heating value. The main conclusion in this figure is that peat is a relatively small part of the current fuel mixture in terms of its energy content and even more in terms of the ash content. A small contribution to the ash content can indicate that the peats effect on the ash chemistry is small and thus, increases the possibility of a reduced peat usage without large changes or risks to the boiler.
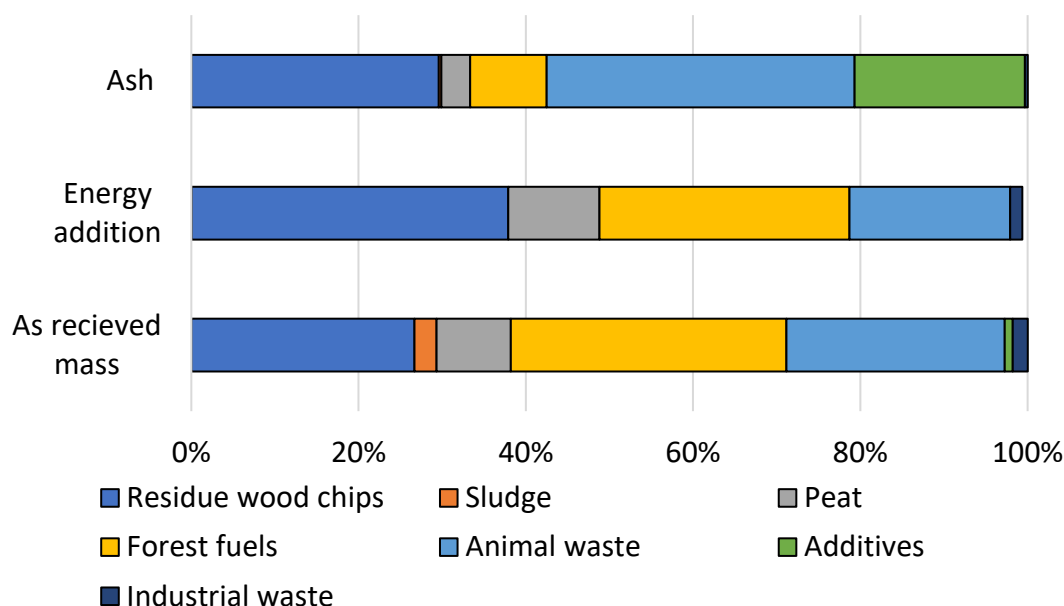
Figure 14. Contribution of each fuel category to the water-, ash-, energy content, and to the total mass as received.

Respective fuel categories contribution to the main ash-forming elements can be seen in Figure 15. The bed material is the largest source of Si followed by residue wood and

the reactivity of silica sand has been shown previously to be rather low and may not react with other elements fully [1]. It is therefore likely that the effects of silica in this boiler could be overstated if the bed sand is included in the calculations. However, the sulfation potential relation in equation 15 is developed for this boiler and may account for this lack of reactivity. Another reason to keep the bed sand in the calculations is that it circulates in the boiler and wears down over time perhaps increasing its reactivity.

When it comes to the element S, peat is not the main source but rather animal waste. Animal waste is also the largest source of Cl that may offset the positive effects of the additional S on the alkali chloride corrosion. The contribution of each fuel category to the main ash-forming elements, similarly to the previous figure, indicates that peat affects the boilers ash chemistry in a small manner and could be possible to remove without any large negative effects.

The alkali originates from several different fuels, Fe from mainly wood residue and peat, and Al from mainly residue wood chips. The largest element in the ash is Ca. Animal waste is the dominating source of Ca followed by additives and limestone in particular. This is because the bone that is one of the sources of animal waste. Similar to the bed sand the Ca originating from bone may not be as reactive as other sources of Ca and the impact on the ash chemistry may therefore be lower than in theory. But as is the case with Si this may be built into the factors for the sulfation potential relation.

In terms of the economy of the boiler operations, the figure suggests that the additives are a large part of the ash content while not adding to the heating value. Therefore, it would be beneficial if bed sand and limestone could be used to a lesser extent in a future fuel mixture.
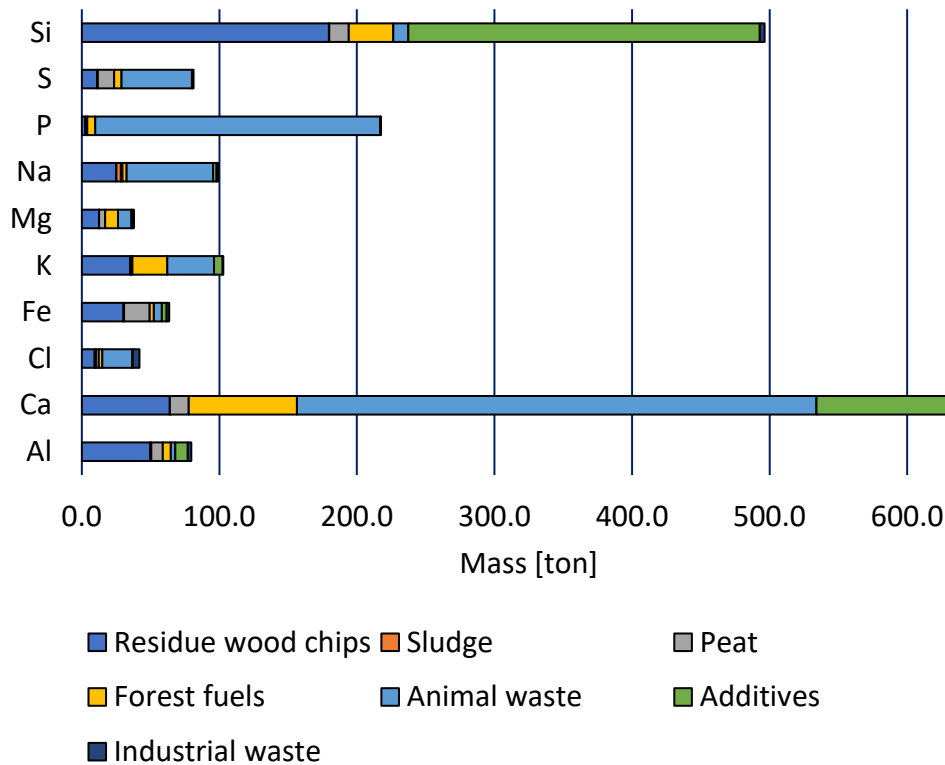
Figure 15. Respective fuel categories contribution to the mass of the main ash-forming elements.

From the baseline composition and assuming full combustion with the yearly mean of 3.56% excess O_2 the theoretical available SO_2 in the flue gas could be determined to be 134.9 ppm$_v$. The mean measured SO_2 concentration in the flue gas 2021 reached 94.6 ppm$_v$. Considering the number of possible sources of error ranging from the measured SO_2 to the fuel analysis, the estimation is consistent with the measured values and can be useful for boiler operators.

5.2 Peat, limestone, and Na-rich fuels impact on available SO_2

From equation (17) the sulfation potential, or theoretical available SO_2, can be calculated. This can be interpreted as how much S in the fuel mixture will be available as SO_2 in the flue gas after the ash interactions in the boiler. Therefore it is also constrained by the actual S content in the flue gas. According to the relation, reduced limestone additives can be beneficial to a certain degree as long as the sulfation potential in the equation is lower or equal to the S concentration. This section aims to investigate the impact of phased-out peat on the sulfation potential for each case when the limestone additive is reduced. Because Cl is the root cause of the alkali chlorides the concentration of Cl is also included in this chapter as peat is phased out from the fuel mixture.

5.2.1 Case 1: Replacing peat with forest fuels

Forest fuels are considered a high-quality fuel with a low ash and Cl concentration. In general, the Ca to Si ratio is high and will lower the agglomeration risk in the boiler [6]. In Figure 16 the theoretical available SO_2 in the flue gas is presented as peat is removed in 10 wt% steps in the fuel mixture. At the same time, forest fuel is added in to keep the energy content constant. Additionally, the effects of reduced limestone additives are shown with three lines representing 100 wt%, 50 wt%, and 0 wt% limestones. These calculations suggest that replacing peat with forest fuel will reduce the levels of SO_2 in the boiler. The theoretical calculated SO_2 decrease by about 38% when the peat is fully phased out. However, the reduction of limestone seems to be able to almost offset the effects of the reduced peat. If the limestone additives are halved or fully removed the theoretical available SO_2 can increase by 57% when peat is fully phased out. Thus, there is a possible positive effect on the SO_2 concentration if limestone is reduced to somewhere between 0-50 wt%. When limestone is reduced beyond 50 wt% we can no longer see any benefits on the SO_2 levels because the S content in the fuel mixture limits the possible SO_2 concentration.
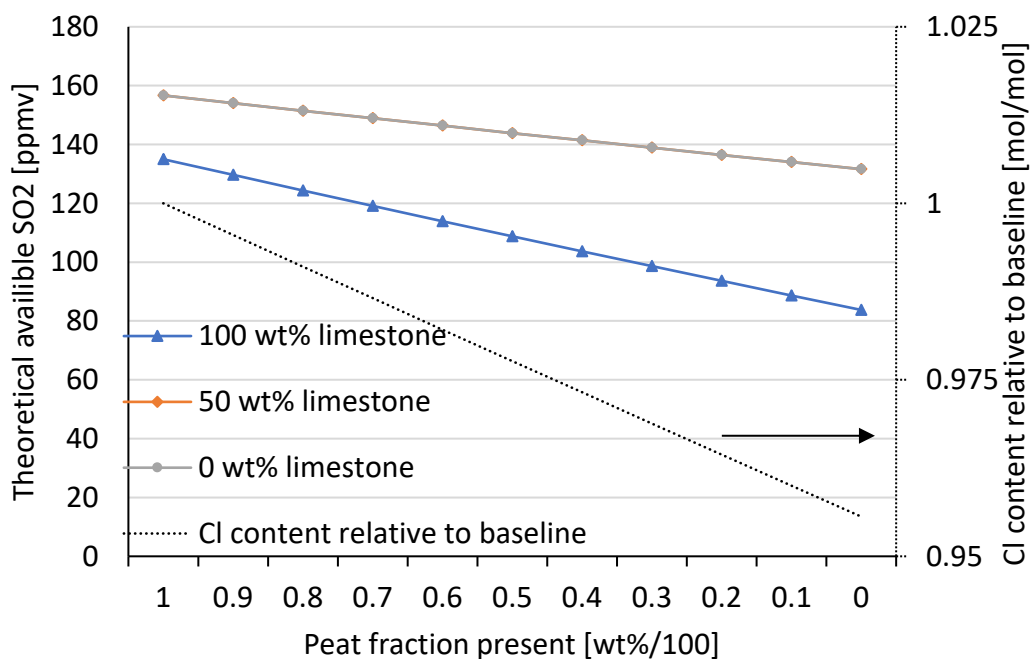

Figure 16. Sulfation potential when replacing peat with forest fuels for three different limestone additives levels. The right secondary axis shows the theoretical Cl concentration in the flue gas relative to the baseline.

Figure 16 also contains the theoretical Cl concentration in the flue gas. This is the dotted line that corresponds to the right axis. It indicates that the Cl concentration will decrease by about 4.5% when forest fuels substitute the peat. Because Cl is one of the root causes behind alkali salt corrosion, this further suggests that it would perhaps be possible to phase out peat in favor of forest fuels from a corrosion perspective.

The theoretical available SO_2 calculations take the complex ash-forming elements relations into consideration. Figure 17 shows each term in the sulfation potential when fully replacing peat with forest fuels in the fuel mixture both with and without limestone. The S, P, and Si content is decreasing when the forest fuels are added, resulting in a lower sulfation potential. There is a lower Ca concentration in the fuel mixture as well but not enough to make up for the other elements. If the limestone is removed from the fuel mixture, the sulfation potential will increase by about 150 ppm and therefore be limited by the S content.
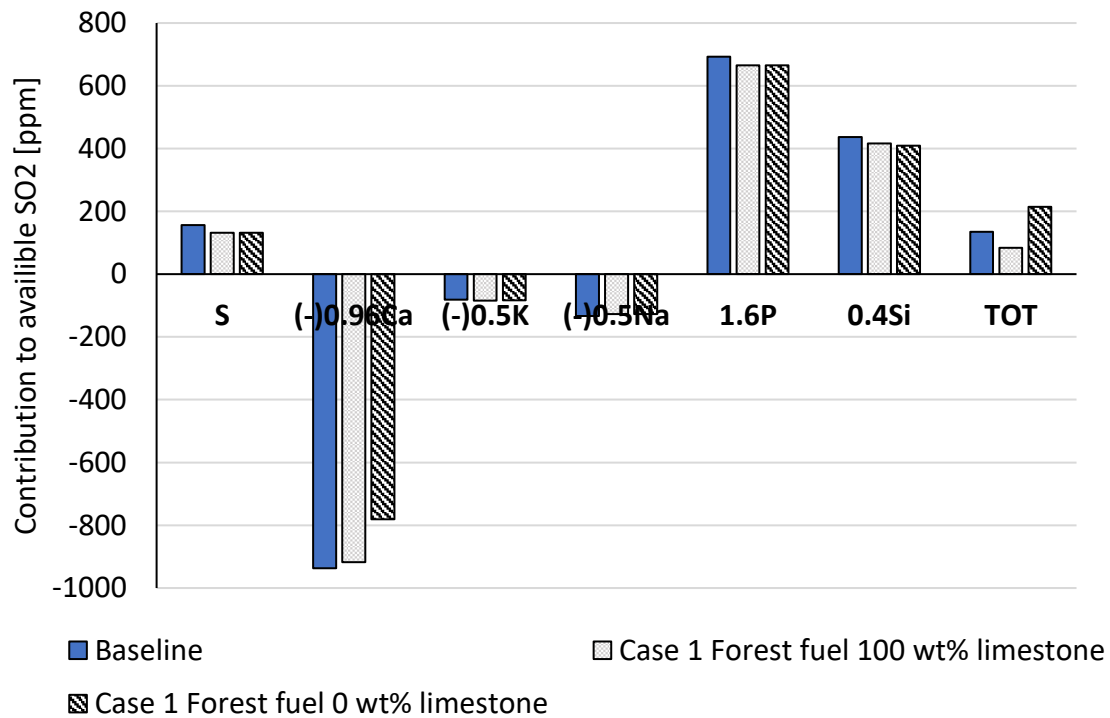

Figure 17. The terms in the sulfation potential relation when replacing peat with forest fuels.

5.2.2 Case 2: Replacing peat with residue wood chips

Similarly, to case 1, case 2 indicates that with decreased peat content the available SO_2 will decrease but to a smaller extent. Figure 18 illustrates the theoretical available SO_2 in the flue gas as peat is decreased in 10 wt% steps and substituted with residue wood chips in order to keep the energy content constant. At baseline levels of limestone, the SO_2 will only decrease by roughly 4% meaning that residue wood could be a good candidate to replace peat. Additionally, the SO_2 concentration could be higher than the baseline if the limestone additives are reduced by 0-50 wt%. Above 50 wt% this effect could no longer be seen similarly to case 1. If the limestone is decreased by 50 wt% or more, the results suggest that the sulfation potential could increase by roughly 6% in comparison to the baseline even though peat is fully removed.
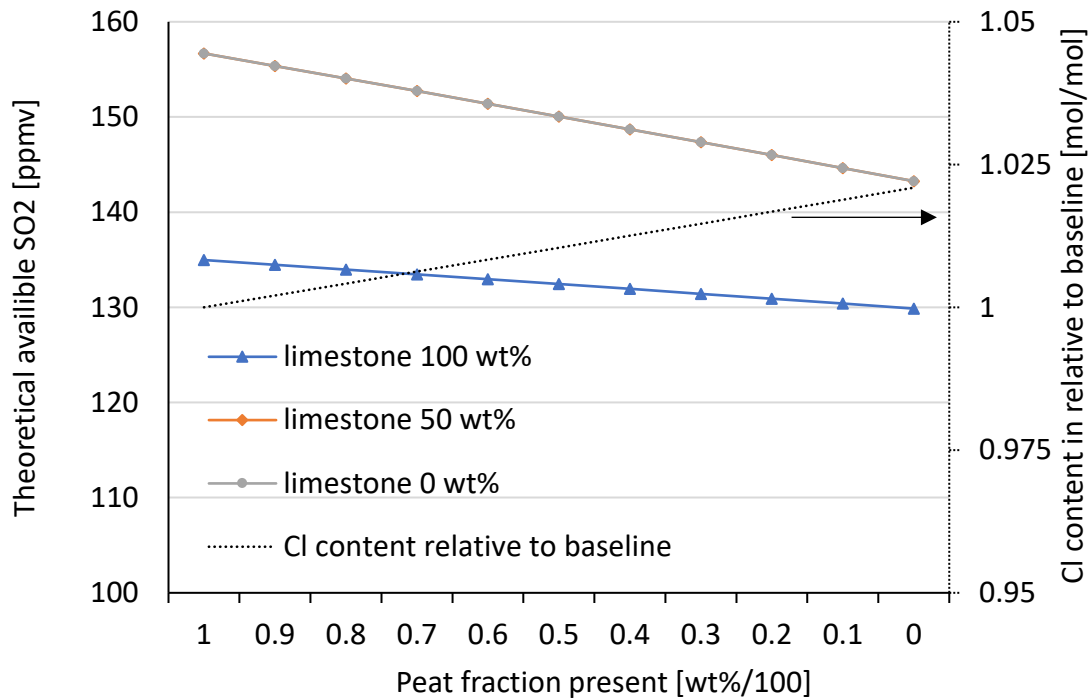
Figure 18. Sulfation potential when replacing peat with residue wood chips. The right secondary axis shows the theoretical Cl concentration in the flue gas relative to the baseline.

Besides the sulfation potential, it is also necessary to take the Cl content into account to assess the alkali corrosion tendencies. These results suggest that the Cl concentration will increase by 2.1% when residue wood replaces peat in the fuel mixture. If compared to Case 1 the Cl concentrations would be roughly 6.8% higher when residue wood chips are used instead of forest fuels. This means that although the residue wood chips seem to yield a higher SO_2 concentration in the flue gas, a higher Cl content makes forest fuels to be similarly attractive as a replacement fuel. In practice, the peat may be replaced by a combination of forest fuels and residue wood chips due to supply and other more practical reasons. These results indicate that it may be possible to do a mixture of case 1 and case 2 without experiencing excessive alkali chloride corrosion.

Figure 19 shows the contribution of each element in equation (17) to the sulfation potential when peat is fully replaced with residue wood both with and without limestone. The main cause behind residue wood yielding a higher sulfation potential than forest fuels is that it contains slightly higher contents of S and Si. The S content is especially important as it tends to limit the SO_2 as the limestone additives are reduced. Besides the positive effects of S, Si will positively affect the sulfation potential. Depending on the compound in which the Si originates from, it can be more or less reactive and may therefore affect the results [1].
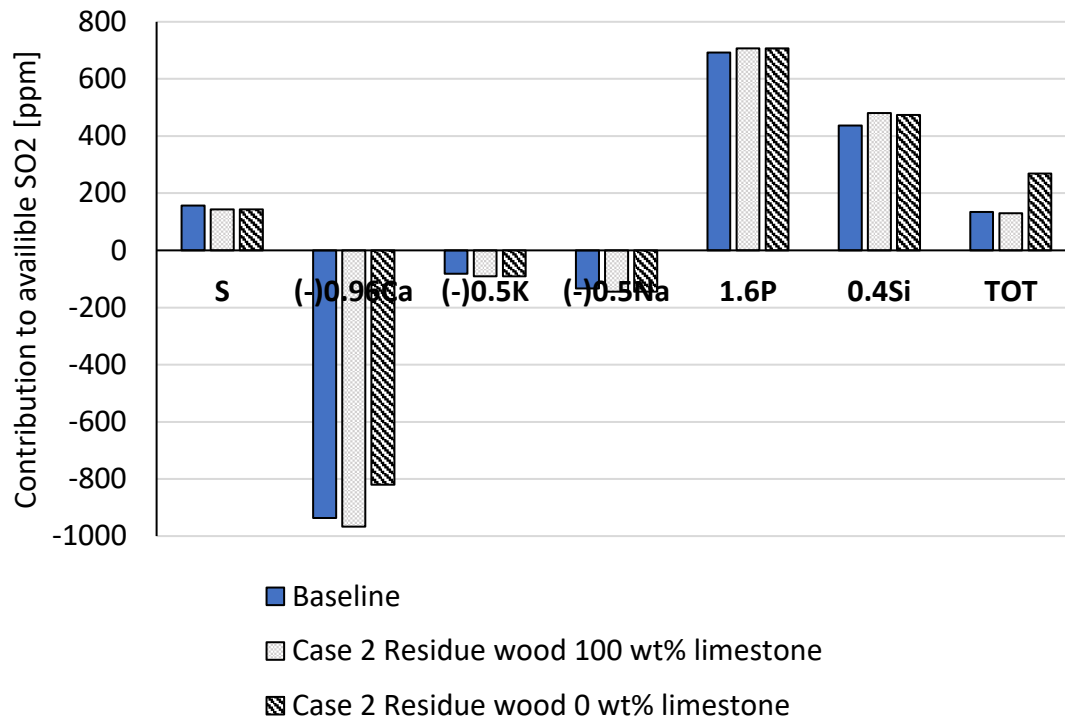
Figure 19. The terms in the sulfation potential equation when replacing peat with residue wood chips.

5.2.3 Case 3: Replacing animal waste and peat with residue wood chips

In comparison with case 1 and case 2, replacing both animal waste and peat with residue wood chips has a greater negative impact on the theoretical available SO_2. This is expected as animal waste is the largest source of S and P in the baseline. Figure 20 illustrates the Cl concentration and theoretical available SO_2 in the flue gas as the animal waste is fully excluded and peat is phased out in 10 wt% steps with wood residues as a substitute. If the baseline is compared to when animal waste is removed but the peat is still in the fuel mixture, the SO_2 content will decrease by 50% from 134 ppm_v to 67 ppm_v. The decline in SO_2 is however modest as the peat is replaced with forest residues as was indicated in case 2.

Even though it is expected to be a sharp decline in S we can still see a positive effect on the SO_2 levels as the limestone is reduced in the range of 0-50 wt%. Removing limestone further to 100 wt% would no longer have a positive effect similarly to cases 1 and 2. When peat is fully phased out, the maximum increase in SO_2 due to limestone reduction is suggested to be 20 ppm_v corresponding to a roughly 19% increase. This is however not enough to offset the lost positive contribution of animal waste and peat on the sulfation potential.
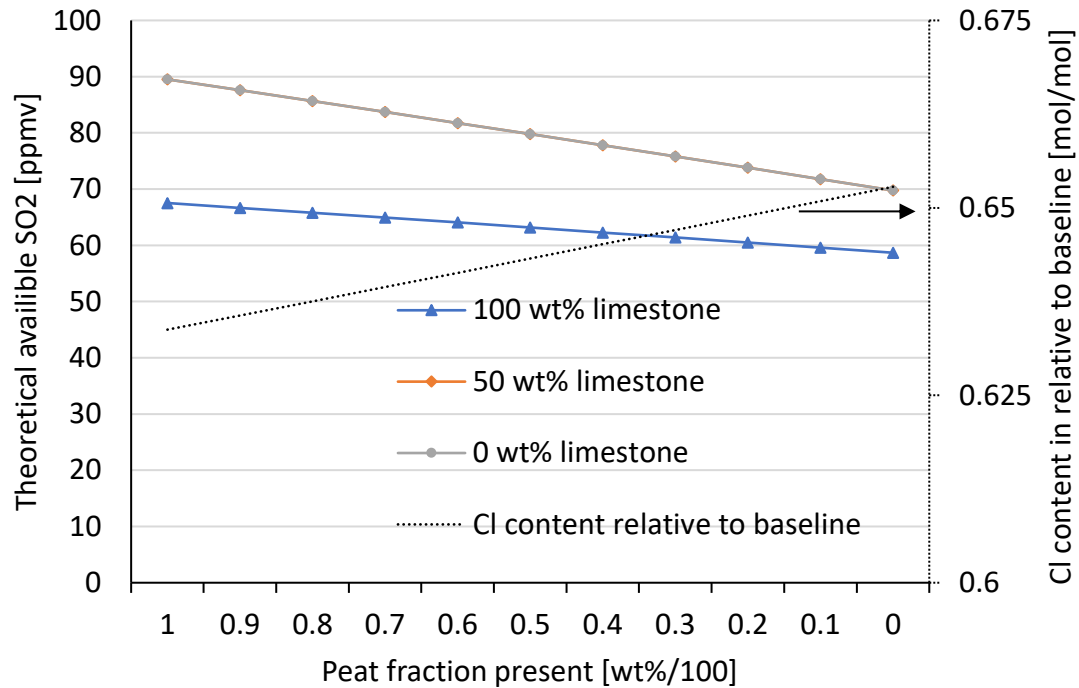
Figure 20. Sulfation potential when animal waste is fully removed and peat phased out at 10 wt% steps while replacing both with residue wood chips. The right secondary axis shows the theoretical Cl concentration in the flue gas relative to the baseline.

Removing animal waste could substantially reduce the available SO_2 in the flue gas. This could be compensated to a great extent by the reduced Cl in the fuel mixture that can be seen in Figure 20. Animal waste is the largest source of Cl in the fuel mixture and when it is removed the Cl concentration is calculated to decline by 36%. As discussed in the prior section, this will reduce the alkali chloride concentration and therefore should reduce the need for SO_2. What levels of SO_2 that is required as a function of the Cl concentration need further investigations.

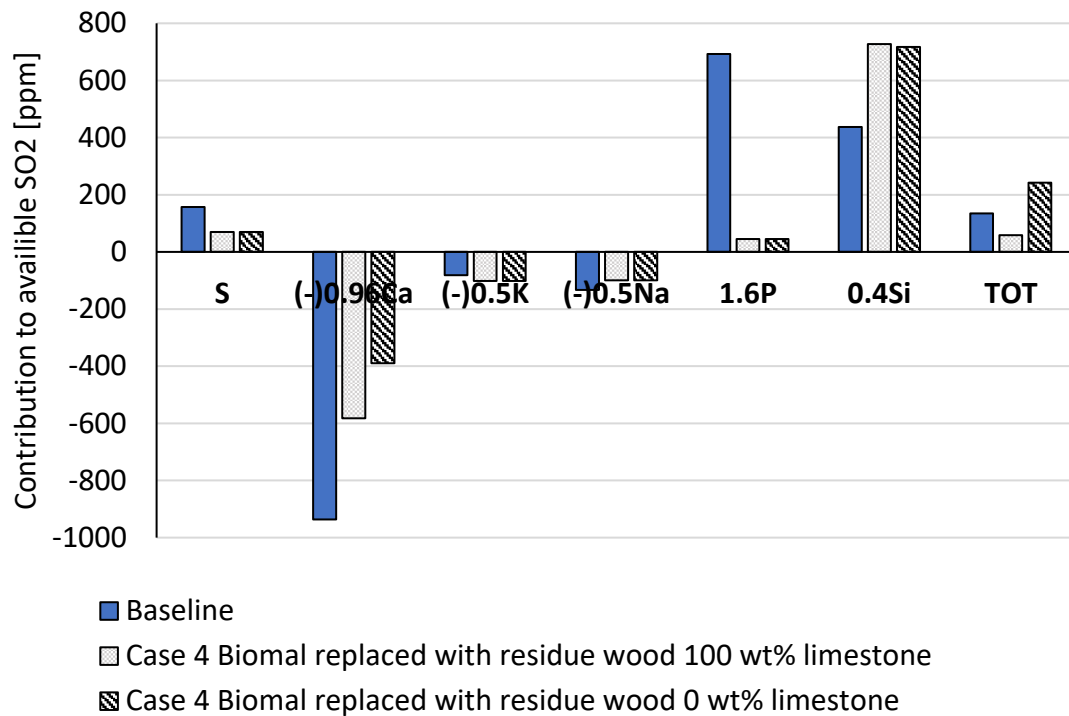When looking at the sulfation potential terms from equation (17) in

Figure 21. It is clear that the removal of animal waste has a drastic effect on the S, Ca, Si, and P contribution to the sulfation potential. The increase in Si and decrease in Ca will to a large extent offset the lack of P in the fuel mixture but will then be limited by the low S content. This may differ in practice depending on the origins of Ca and P similar to what has been previously discussed for Si. If the animal waste is high in bone matter it is possible that Ca and P is less reactive than what is presented here.
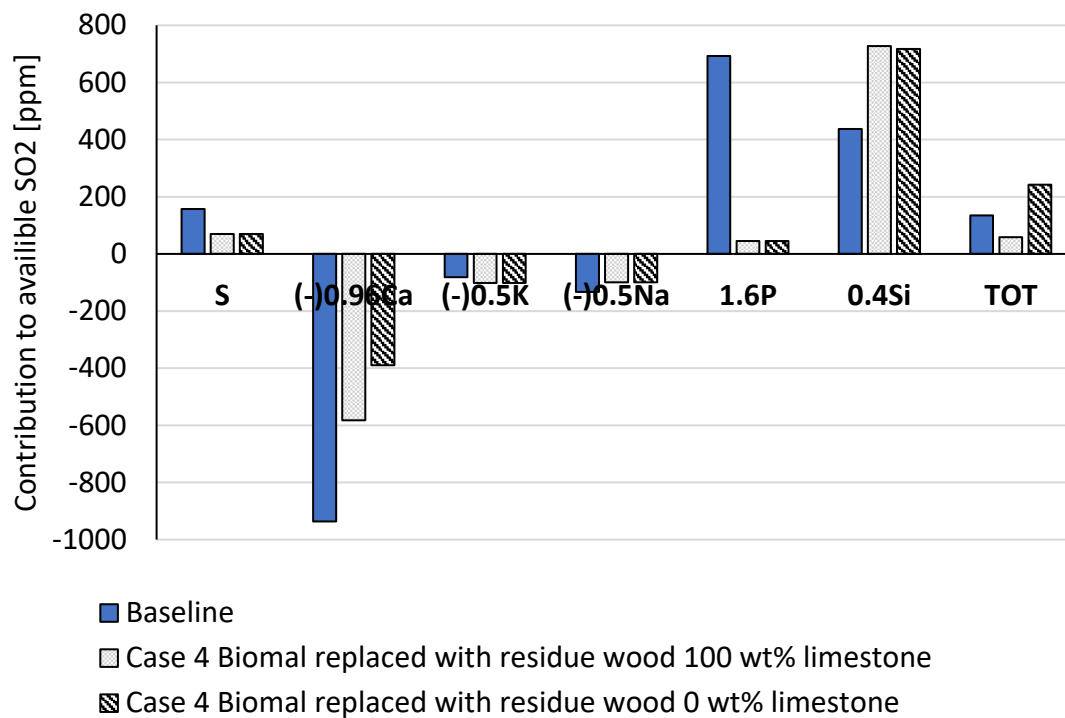
Figure 21. The terms in the sulfation potential equation when replacing both animal waste and peat with residue wood chips.

5.2.4 Case 4: Introducing Na-rich NAC fuel

Last of the possible new fuel mixtures is the addition of Na-rich fuel to the baseline thus   keeping   the   peat   in   the   fuel   mixture.   In
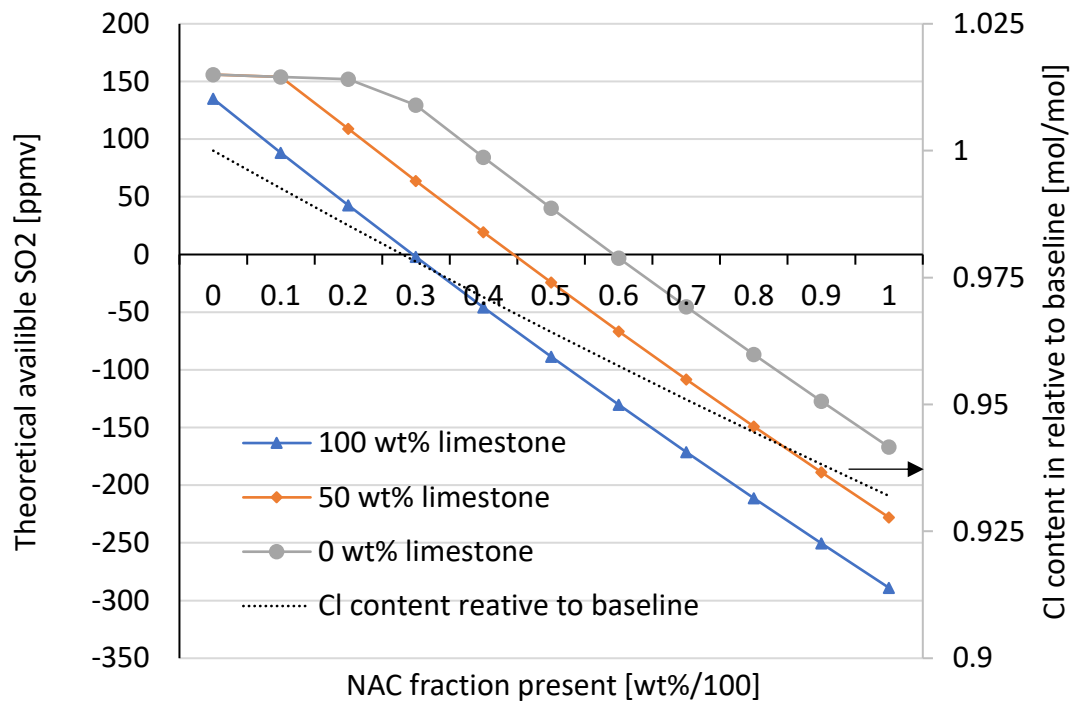
Figure 22 the effects on the sulfation potential when adding Na-rich fuel in 10 wt% steps to the current fuel mixture are illustrated, together with three levels of limestone, 100 wt%, 50 wt%, and 0 wt%. It suggests that adding this fuel will have large negative effects on the sulfation potential and the use of additives or beneficial fuels should be considered. When more than 60% of the total Na-rich fuel is added there will be no available SO_2 in the flue gas regardless of the limestone additives levels.

Contrary to the other cases for a future fuel mixture, it is not the S content that limits the available SO_2 but rather the ash chemistry effects. As a result, it is always beneficial to decrease the limestone content in the fuel mixture with the exception when only a small fraction of the NAC fuel is added up to 10 wt%. Similar to case 1, the Cl concentration in the flue gas is lowered by about 7% when the NAC is fully added. These beneficial effects are however not enough to offset the lowered SO_2 concentration overall.
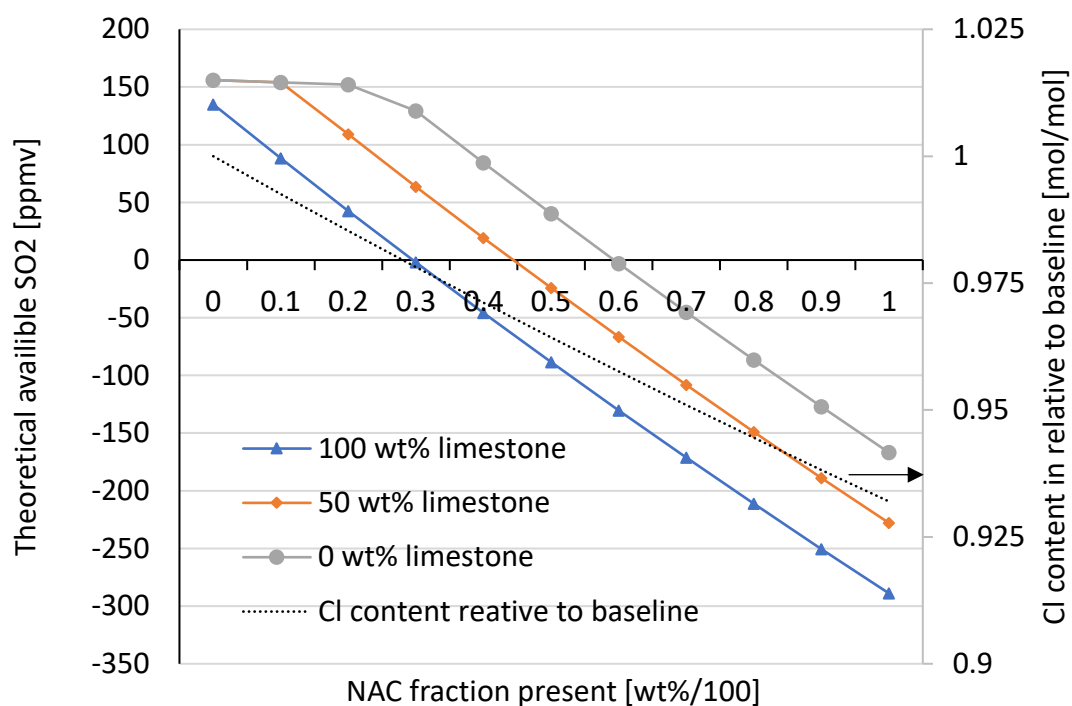
Figure 22. Sulfation potential when adding Na-rich fuel in 10 wt% increments for three limestone levels 100, 50, and 0 wt%.

The effect of the additional Na is especially clear when examining the sulfation potential in
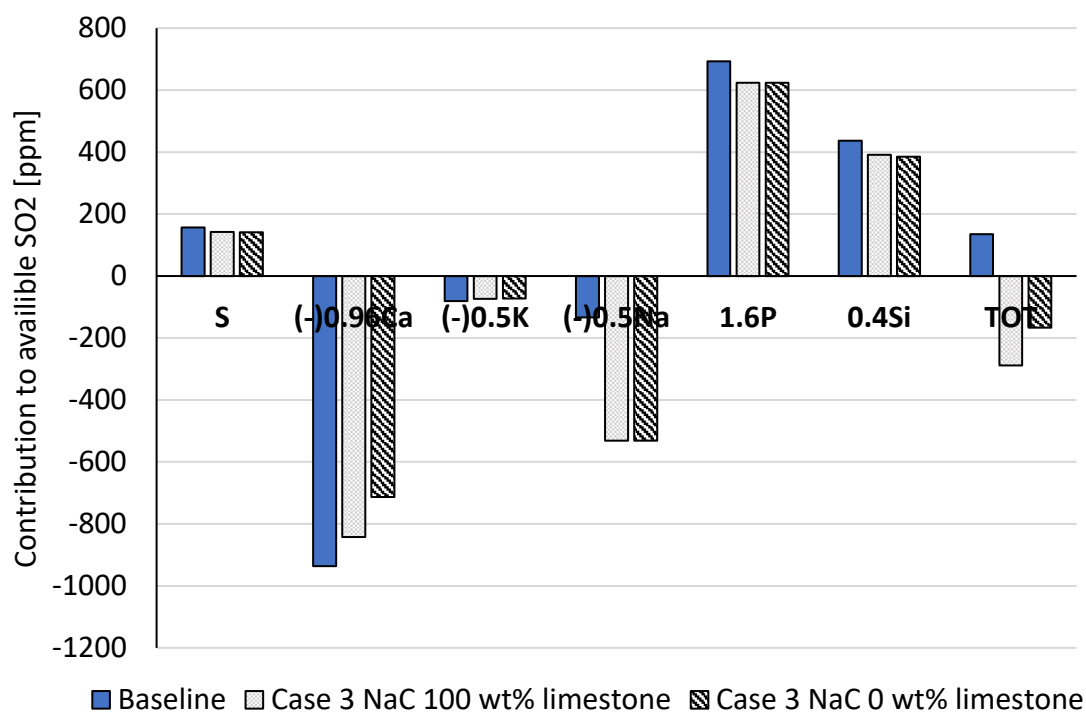
Figure 23. From the baseline, the additional Na negative effect has increased by a factor of about 3.9. In the figure Ca, P, and Si decrease as the new fuel is added, likely due to low contents in the fuel and a dilution effect from the large influx of Na. A potential effect that has not been considered in this master thesis thus far, is that it is possible that the alkali can saturate the Cl at a certain point making additional alkali less problematic from a corrosion perspective. Adding the amounts of Na that is the case for NAC could saturate the Cl in some way. This is however only speculations and further investigation must be conducted.
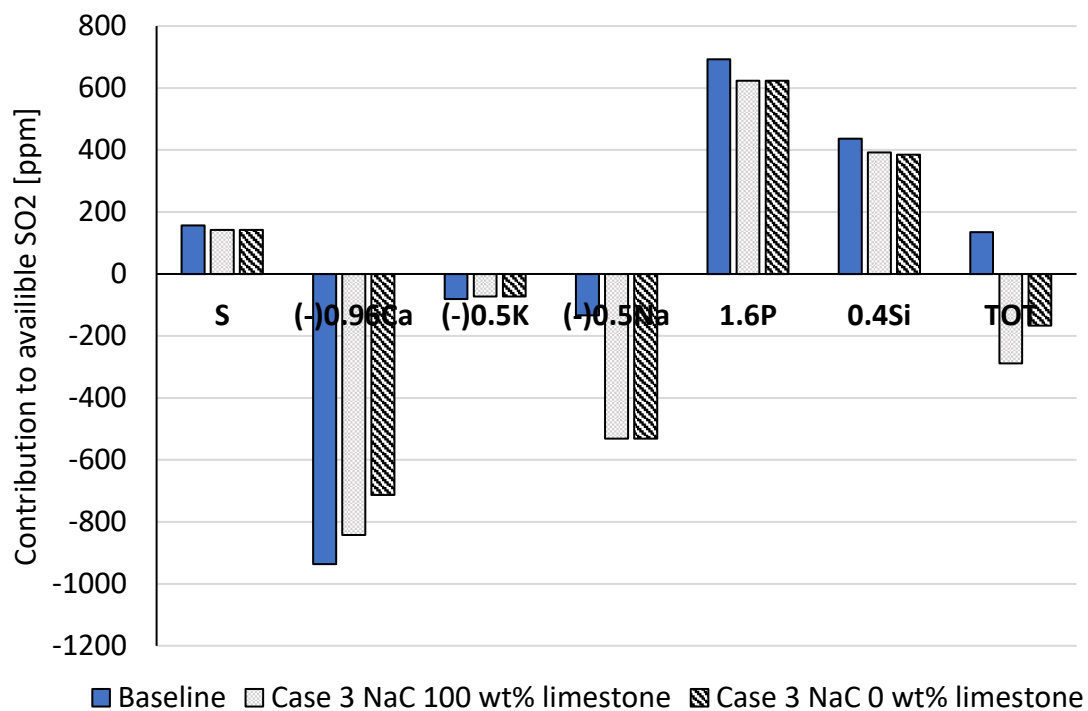
Figure 23. The terms in the sulfation potential equation when adding Na-rich fuel to the current fuel mixture.

It has been suggested in the two previous figures that the reduction of limestone will not alone offset the effects of Na on the sulfation potential. Therefore, the amount of additional S that is required to increase the available SO_2 in the flue gas is determined for this case. Figure 24 illustrates the effect of increasing the S mass content by a factor ranging between 1-6 with 0.5 increments. These results indicate that to create an interval containing the baseline sulfation potential. The S content needs to be increased by a factor of 4-4.5 for 100 wt% limestone, 3.5-4 for 50 wt% limestone, and lastly 3-3.5 when adding 0 wt% limestone.

Figure 24. The effects of increased S when the Na-rich fuel is fully-added to the current fuel mixture.

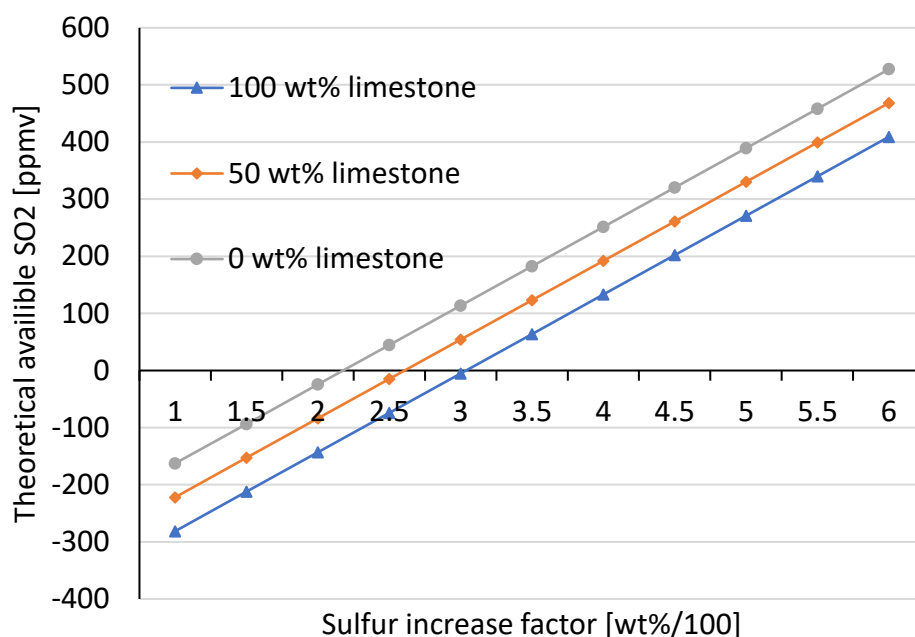From the intervals, the lower- and upper limit that S is required to increase with can be estimated. The lower limit, according to these calculations, is that the S content would have to increase by a factor of 3 on a mass basis while in the upper limit, the S content needs to increase by a factor of 4.5. Based on the S content in the fuel mixture including the Na-rich fuel the required mass of S can be determined and seen in Table 7.

Table 7. The amount of S that could be required to get equal sulfation potential to the baseline and the amount of peat and ammonium sulfate that correspond to this S content.

	Sulfur factor increase	Required S [ton]	Additional S [ton]	Required peat [ton]	Required ammonium sulfate $(NH_4)_2SO_4$ [ton]
Upper limit	4.5	368.4	286.5	224116.0	1183.1
Lower limit	3.0	245.6	163.7	128066.3	676.0

To compensate for the extra Na in the fuel, an additional 286.5 tons of S would be needed in the worst-case scenario and 163.7 tons in the best-case scenario. Peat is considered to be a fuel high in S and still, it would be required to add roughly 128000-224000 tons of peat to add the additional S required. Considering that the current fuel mixture has a mass of about 100000 tons it would not be possible to use peat as an S source to offset the influx of Na from the new waste fuel. Additionally, this estimation does not take into account that adding S purely will be more potent than adding it as

peat because the S will be diluted by the other elements. Further, the peat used in 2021 will have higher Ca than Si causing the sulfation potential to be lower. When this is taken into account peat would in theory be needed to be added in even higher amounts than that in Table 7. As discussed prior there could however be a saturation effect of Na on Cl and in practice therefore the amount of peat required could differ substantially.

Another possible source of S that has been shown to be effective, is to add ammonium sulfate, $(NH_4)_2SO_4$, instead of ammonia as an additive [7]. According to these best and worst cases, this would require an addition of 670-1180 tons of $(NH_4)_2SO_4$. Because this is added instead of ammonia its purpose is, besides adding S to the fuel mixture, to reduce the NOx emissions. Therefore an excessive amount cannot be added without causing NH_3 to "slip" through the boiler and become a source of emission. To assess the risk of this the required amounts of $(NH_4)_2SO_4$ and the resulting NH_3 can be compared to the current levels of NH_3. If $(NH_4)_2SO_4$ is added about 25.7% of its mass will end up as NH_3. This results in that between 173.7-304.0 tons of NH_3 will be added in the best to worst-case scenario. When this is added it is diluted so that 25 wt% is NH_3 which would be equivalent to 694.8-1216 tons of diluted NH_3 being added. The current amount of diluted NH_3 that is used is 205 tons and is substantially less than the calculated required amounts. Depending on how sensitive the boiler is to "slip" the use of this additive could cause the boiler to exceed emission requirements.

5.3 CO_2 emission and cost of possible new fuel mixtures

The primary purpose of this master thesis is to reduce the environmental impact of the boiler when burning fossil peat. Besides the environmental impact, the emission is part of the EU emissions trading system which results in an increased monetary cost of releasing greenhouse gases.

From the results in the prior section three perhaps possible future fuel mixtures could be determined. Table 8 present the possible reduced CO2 emissions for each fuel mixture together with estimated monetary savings. In case 1 and case 2 it seemed to be possible to phase out peat if the limestone additives are reduced by half. In case 3 the results were more negative in a sulfation potential aspect, but considering the low Cl content the table also contains a fuel mixture when all peat and animal waste is replaced with residue wood and the limestone content is reduced by 50 wt%. Because case 4 indicates that larger investments in additives have to be made for it to be possible to combust the Na-rich waste fuel, a financial estimation would contain too high uncertainty and was therefore not included.

The findings included in the table suggest that case 1 has a similar ash content to case 3. This is likely due to forest fuels low ash content and that animal waste is not included which is a high ash content fuel. The highest ash content is 3.58% and this is when peat is replaced with residue wood. The variation in specific energy that can be seen is mainly due to a difference in moisture content thus leading to case 3 having the driest fuel mixture followed by case 2 and then case 1.

Perhaps the most important conclusion is that in all cases the phasing out of peat will result in a substantial decrease in net CO_2 emissions in the range of 10000 $tonCO_2$/year. Residue wood chips are a mixture of wood and fossil-based products. In these calculations, it is estimated that 2 wt% of the residue wood chips are fossil fuels based and will have net CO_2 emissions. Therefore, substituting peat with forest fuels as in case 1 will have about 500 tons lower CO_2 emissions than in case 2 and 1000 tons lower CO_2 emissions than in case 3. It is necessary to have in mind that even though residue wood chips contain fossil-based products they may be hard to recycle in other ways than for energy. Because of this, the waste incineration could be beneficial for the environment and society as a whole even though the net CO_2 emission increase slightly.

In Table 8 the cost of the identified fuel mixtures relative to the baseline is included. When the cases are compared these calculations suggest that the ash cost will be lower for case 1 and case 3 than for case 2. This is caused by mainly the ash content but also the specific energy as was discussed prior. In both case 1 and case 3 the purchasing cost of the fuels will increase. Animal waste is a fuel with a low purchasing cost of 30 SEK/MWh, leading to that the fuel cost will increase by roughly 3 million SEK/year when replaced by residue wood. When replacing only the peat with residue wood on the other hand this will lead to a cheaper fuel mixture by about 1 million SEK/year. These purchasing costs will however be subject to variation over time and these results can change. At the time of writing the war in Ukraine and following sanctions on Russia may add further volatility to the fuel prices. Lastly, the total cost of additives in comparison with the baseline is the same for the three cases as the limestone content is halved. This is however only an assumption it is possible that more or less limestone can be added or removed depending on how the fuel mixtures will affect the sulfation potential and agglomeration risk.

When estimating the cost of a certain fuel mixture it is clear that when the cost of releasing 1 ton/CO_2 is 900 SEK peat is an expensive fuel. The price of peat when considering the CO_2 tax is 460 SEK/MWh and if comparing it to forest fuels, 168 SEK/MWh, or residue wood chips, 107 SEK/MWh, it is clear that it will increase the cost of the fuel mixture substantially. This is indeed the case as the total price of CO_2 emission from the peat is close to 10 million SEK/year. In comparison to ash handling cost, fuel purchasing cost, and additives cost the CO_2 emission will dominate the total cost of the fuel mixture, leading to that case 1-3 would result in a large cost reduction compared to the baseline. The cheapest fuel mixture is case 2 with a possible savings of 10.3 million SEK/year compared to baseline. The second cheapest fuel mixture is case 1 with a possible savings of around 9.1 million SEK/year. Case 3 is the most expensive of the three but will still lead to a large savings of about 6.5 million SEK/year.

Table 8. Plausible future fuel mixtures and their respective ash content, specific energy, net CO$_2$ emission savings and cost in comparison to the baseline.

	Case 1 Replacing peat with forest fuels	Case 2 Replacing peat with residue wood chips	Case 3 Replacing animal waste and peat with wood residue
Limestone content [wt%]	50	50	50
Peat content [wt%]	0	0	0
Ash content [wt%]	3.26	3.58	3.25
Energy density [MJ/ton]	9243	9651	11061
CO2 emission savings to baseline [ton/year]	10900	10400	9500
Ash cost difference to baseline [SEK/year]	-99000	155000	-918000
Fuel cost difference to baseline [SEK/year]	869000	-1029000	3082000
Additive purchasing cost difference to baseline [SEK/year]	-83000	-83000	-83000
CO2 emission cost difference to baseline @ 900 kr/tonCO2 [SEK/year]	-9817000	-9363000	-8562000
Accumulated cost difference from baseline [SEK/year]	-9131000	-10319000	-6481000
Annual possible savings [Million SEK/year]	9.1	10.3	6.5

5.4 Future work

Following this master thesis, there are numerous interesting questions to be investigated further and the result from this work needs to be corroborated by practical tests in particular. The effects on SO_2, corrosion rate, and agglomeration over time need to be measured as peat is phased out to ensure that the availability of the boiler is not affected negatively.

The use of new additives or fuels with high S content or other traits could be investigated further. Examples of this would be the introduction of ammonium sulfate as a source of S if the current fuel mixture would be insufficient in S. It would be interesting to look at other additives or fuels as well such as gypsum, $CaSO_4 \cdot 1.5H_2O$, and iron sulfide, $FeS(S)$, that has been shown previously to be effective.

It was clear that in some cases the sulfation potential decreased at the same time as the Cl content. The required SO_2 concentration as a function of the Cl concentration would be good to study further as there is no clear definition of when the SO_2 concentration is too low.

For the introduction of the Na-rich waste fuel, it would be interesting to see if there is a saturation point at which additional Na does no longer contribute to alkali chloride corrosion. This is especially interesting as the theoretical results point towards that the Na-rich waste fuel would not be possible to add to the current fuel mixture.

6 Summary and conclusions

Peat has over the years become a less used fuel in Perstorp B6 boiler. In the year 2021, 9293 tons of peat were burned which is equivalent to 11% of the energy content and 3.4% of the ash content of the fuel mixture. This indicates that while still a considerable energy source, its impact on the ash chemistry in the boiler could be limited because of its low ash contribution. Further, peat is not the main source of S but rather animal waste that is also the main source of Cl. The indicated low impact of peat on the ash- and S content suggest that peat could be phased out without any larger investments in additives or special fuels.

From the baseline composition and assuming full combustion with the yearly mean of 3.56% excess O_2 the theoretical available SO_2 in the flue gas could be determined to be 134.9 ppm_v. The mean measured SO_2 concentration in the flue gas 2021 reached 94.6 ppm_v. This indicate that the model used is valid and can be a useful tool for boiler operators to theoretical evaluate the corrosion tendency of a fuel mixture.

In cases 1 and 2 when substituting peat with forest fuels and residue wood chips, the theoretical available SO_2 concentration in the flue gas could be at the same levels or higher if the limestone content decreased in the range of 0-50 wt%. If the limestone was decreased further no positive effects on the SO_2 levels could be seen due to all S being theoretically found as SO_2. Forest fuels are not as good of a substitute for peat as residue wood. When comparing the SO_2 concentrations there was a 38% theoretical SO_2 decrease for forest fuels and only 4% in the case of residue wood. This is mainly due to the higher S and Si contents in residue wood. However, if the Cl content is taken into consideration the roughly 7% lower Cl content in relation to the baseline fuel mixture, makes forest fuels similarly good as residue wood. In practice, it could be possible to use a mixture of the two fuel categories to replace peat. Similarly, in case 3 the loss of both peat and animal waste would decrease the theoretical SO_2 in the flue gas by 50% and the reduction of limestone could not compensate for this decline. The Cl content would decrease by about 35% perhaps compensating for the theoretical loss of SO_2.

When adding the Na-rich waste fuel to the current fuel mixture the theoretical available SO_2 became 0 when more than 60 wt% of the fuel was added. This suggests that additives are required to offset the large influx of Na. It was determined that the S content needed to increase by 3-4.5 times for the SO_2 levels to be similar to the baseline. This is equivalent to an additional 164-287 tons of S. According to the calculations it would not be possible to use peat as the source of S because it would require excessive amounts even more than the total fuel mixture combined on a mass basis. If the additive ammonium sulfate is used as the S source this would result in 676-1183 tons of ammonium sulfate. Because this additive supplies both S and NH_3 for NO_x emissions this amount of additive would result in 695-1183 tons of NH_3 with

a 25 wt% concentration. This is substantially higher than the 205 tons of NH_3 used today and could result in excessive slip. More investigation into different additives and fuels to compensate for the additional Na is required before this is used as a fuel.

In terms of fossil fuel-based CO_2 emissions, cases 1-3 will result in substantial reductions of around 10 000 tons CO_2 when all peat is replaced. The forest fuels have slightly lower emissions because it is assumed that 2 wt% of the residue wood is fossil fuel-based waste. This reduced emissions at the cost of 900 SEK/tonCO_2 can lead to significant monetary savings. In case 1 it is estimated that 9.1 million SEK/year can be saved, in case 2 10.3 million SEK/year and in case 3, 6.5 million SEK/year. This assumes, based on the results, that the rate of corrosion and availability is not affected negatively and would not add additional maintenance costs. In case 4 no cost estimations were conducted because of the uncertainties regarding what and if investments and additives were required.

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Appendix A   Fuel mixture 2021

Table 9. Identified fuel fractions used 2021 in Perstorp B6 boiler together with their respective fuel category.

Residue wood chips	Sludge	Peat	Forest fuels	Animal waste	Additives	Industrial waste
Jolax AB	Sewagesludge	Axhult milled peat	Axhult mixture (50/50 peat/sawdust) sawdust fraction	Biomal	Limestone	Production waste
Timsfors	clean water sludge	Axhult mixture (50/50 peat/sawdust) peat fraction	Gustavsborg säteri AB GROT		Ammonia	Na rich fuel
		Neova milled peat	Stora ENSO GROT		Bedmaterial	
		Neova shaped peat	Södra GROT			
		Södra milled peat	Södra barch			
			Södra sawdust			
			Timsfors GROT			
			Timsfors barch			
			Timsfors sawdust			

Table 10. Accumulated mass of ash, water and each respective element using the year 2021 fuel mixture.

[ton]	Residue wood chips	Sludge	Peat	Forest fuels	Animal waste	Additives	Industrial waste	Total
ash	1031.0	10.5	119.7	319.1	1282.1	709.1	11.6	3483.1
H20	5997.8	2759.2	3446.9	16692.8	17989.4	20.6	1194.3	48101.0
Al	49.6	0.9	8.4	5.7	3.5	8.9	2.6	79.6
As	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.2
Ba	2.8	0.0	0.2	0.8	0.9	0.8	0.0	5.5
C	10701.4	6.5	3220.3	9186.9	5020.6	97.2	496.6	28729.6
Ca	63.9	0.1	13.7	78.5	377.9	98.4	0.5	633.0
Cl	9.4	0.8	2.2	2.5	22.0	0.1	4.8	41.8
Cr	0.6	0.0	0.0	0.0	0.0	0.0	0.6	1.3
Cu	0.4	0.0	0.0	0.1	0.1	0.0	0.0	0.7
Fe	30.3	0.5	18.4	3.2	5.8	3.5	1.9	63.5
H	1269.9	0.8	325.8	1077.1	736.7	10.9	41.8	3463.1
K	35.3	0.1	1.2	25.4	34.2	6.3	0.4	102.9
Mg	12.6	0.0	4.3	9.5	9.6	1.5	0.2	37.7
N	248.2	1.1	62.7	74.7	618.0	41.9	0.6	1047.2
Na	25.2	3.2	1.1	3.0	62.8	2.6	1.2	99.1
O	8727.2	4.5	2095.9	7247.9	1695.8	467.6	98.0	20336.8
P	2.4	0.2	1.4	5.7	207.2	0.2	0.1	217.2
S	11.1	0.6	11.9	5.3	51.2	0.3	0.7	81.1
Si	179.8	0.2	14.2	32.4	10.8	255.6	3.3	496.3
Ti	11.3	0.0	0.4	0.9	0.9	0.2	0.0	13.8
Zn	6.3	0.0	0.1	0.8	0.6	0.3	0.1	8.2