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Impact Analysis for Major Emissions from Combustion of Contaminated Wooden Fuels

- Emission mechanisms, modeling/simulation and evaluation

A Master Thesis by
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ΠΕΡΙΛΗΨΗ

Σε αυτήν την εργασία, τα ανακυκλωμένα ροκανίδια παρουσιάζονται ως ένα καύσιμο βιομάζας για συμπαραγωγή ηλεκτρισμού και θερμότητας (ΣΗΘ) με έμφαση στις κύριες εκπομπές που προέρχονται από την καύση τους. Για να διερευνηθεί τα προβλήματα των εκπομπών που προκύπτουν από τα ανακυκλωμένα ροκανίδια, ως ρυπογόνα καύσιμα βιομάζας, συγκρίνονται με τα κοινά ροκανίδια. Τα αποτελέσματα απεικονίζουν ότι, λόγω της ρυπογόνας φύσης τους, περιέχουν περισσότερα όξινα συστατικά από τα αντίστοιχα κοινά. Ως εκ τούτου, διεργασίες κατακράτησης όξινων συστατικών στον καυστήρα και στα καυσαέρια πρέπει να ληφθούν υπόψιν. Αυτά τα όξινα συστατικά που προέρχονται από τα καύσιμα, ειδικά τα S, Cl και N, παράγουν μεγάλους ρύπους κατά την διάρκεια της καύσης. Προκειμένου τα προβλήματα που προκαλούνται από τα όξινα συστατικά να αποφευχθούν, αρκετές μέθοδοι έχουν χρησιμοποιηθεί όπως πρωτογενής και δευτερογενής (SNCR) de-NO_x, χημική δοσολογία για την προστασία του συστήματος από τη διάβρωση σε υψηλή θερμοκρασία και η αλκαλική δοσολογία για την εξουδετέρωση των κύριων όξινων αερίων (π.χ. SO_x και HCl) κατά τη διάρκεια του καθαρισμού των καυσαερίων. Είναι σημαντικό να κατανοήσουμε τη μετατροπή των όξινων συστατικών σε διαφορετικές χημικές μορφές κατά την καύση και το πώς αλληλεπιδρούν με τα άλλα συστατικά του καυσίμου (π.χ. τέφρα) και χημικές ουσίες που χρησιμοποιούνται. Σε αυτή τη μελέτη, οι επιπτώσεις της ρύπανσης των ξύλων στις εκπομπές αξιολογούνται για την καύση που λαμβάνει χώρα σε μία τυπική ρευστοποιημένη κλίνης φυσαλίδων (BFB). Επιπλέον, ένα μοντέλο έχει αναπτυχθεί, με τη χρήση του Microsoft EXCEL, για την προσομοίωση της καύσης της βιομάζας, συμπεριλαμβανομένης της μετατροπής και της συγκράτησης των κύριων όξινων συστατικών που συμβαίνουν στο λέβητα και κατά τη διάρκεια του καθαρισμού των καυσαερίων. Το μοντέλο βαθμονομείται με τη χρήση δεδομένων για τη λειτουργία του λέβητα για βασικές διεργασίες

συγκράτησης όξινων συστατικών και επικυρώνεται από τα δεδομένα παρακολούθησης (δηλαδή συνθέσεις καυσαερίων και κύριες εκπομπές) που προέρχονται από τη λειτουργία του λέβητα. Επιπλέον, αρκετές περιπτώσεις ορίζονται έτσι ώστε να προσομοιώνουν τις αλλαγές στις συγκεντρώσεις του καυσίμου (S, Cl και N) και στην χημική δοσολογία (κυρίως για την δοσολογία του $\text{Ca}(\text{OH})_2$) για τον καθαρισμό των καυσαερίων. Τέλος, γίνεται ανάλυση των επιπτώσεων προσομοιώνοντας ορισμένες περιπτώσεις. Τα αποτελέσματα δείχνουν ότι:

- Η ποιότητα των καυσίμων, ειδικά του Cl, παίζει σημαντικό ρόλο στη συγκέντρωση των όξινων συστατικών στα καυσαέρια.
- Οι διαφορετικές παραλλαγές του καυσίμου καθορίζουν τις απαιτήσεις της χημικής δοσολογίας.
- Η τέφρα που παράγεται μπορεί να συντελέσει εν μέρει στην συγκράτηση των όξινων συστατικών.
- Αποτελεσματική πρωτογενής διαδικασία de- NO_x πρέπει να εφαρμοστεί για τα καύσιμα με υψηλή περιεκτικότητα σε N.

Λέξεις-κλειδιά: *waste wood, recycled wood, fuel-S, fuel-Cl, fuel-N, bubbling fluidized bed, SNCR, corrosion, deposits, ash, flue gas cleaning, flue gas quench, emissions, modeling, impact evaluation, Microsoft EXCEL*

ABSTRACT

In this work the recycled wood chips are presented as a biomass fuel for combined heat and power (CHP) production with focus on the major emissions that come from their combustion. To investigate the emission problems that arise, the recycled wood chips, being a contaminated biomass fuel, are compared with the common wood fuels. The results illustrate that, due to their contaminated nature, they contain more acidic components than the common ones; therefore retention processes in the furnace and the flue gas must be considered. These acidic components in the fuels, especially fuel-S, fuel-Cl and fuel-N, produce major pollutants during combustion. In order to prevent the problems caused by the acidic components, several processes have been used such as primary and secondary (SNCR) de-NO_x, chemical dosing for protection from high temperature corrosion and alkaline dosing to neutralize the main acidic gases (e.g. SO_x and HCl) during flue gas cleaning. It is important to understand the conversion of the acidic components to different chemical forms during combustion and how they interact with the other fuel components (e.g. ashes) and chemicals used. In this study, the impacts of the wood fuel contamination on the emissions are evaluated for combustion that takes place in a typical bubbling fluidized bed (BFB) boiler. Furthermore, a model is developed, with the use of Microsoft EXCEL, to simulate the biomass combustion, including the conversion and retention of the major acidic components that happen in the boiler and during the flue gas cleaning. The model is calibrated by using boiler operation data for key retention processes and is validated by the monitoring data (i.e. flue gas compositions and main emissions) obtained from the boiler operation. Moreover, several cases are defined so as to simulate the changes in the fuel compositions (fuel-S, fuel-Cl and fuel-N) and chemical dosing (mainly hydrated lime dosing) for

the flue gas cleaning. Additionally, impact analysis is performed by the simulations of the defined cases. The results show that:

- Fuel quality, especially fuel-Cl, plays an important role in the concentration of the acidic components in the flue gas.
- The different variations of the fuel define the demands of chemical dosing.
- The ash that is produced can result partially in the retention of the acidic components.
- Efficient primary de-NO_x process should be implemented for the fuels with high fuel-N content.

Keywords: waste wood, recycled wood, fuel-S, fuel-Cl, fuel-N, bubbling fluidized bed, SNCR, corrosion, deposits, ash, flue gas cleaning, flue gas quench, emissions, modeling, impact evaluation, Microsoft EXCEL

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CHAPTER I: Background – Objectives and Scope

1. Renewable Energy Sources.

Energy has an important role and vital factor worldwide which has made its demand to increase constantly. For that reason, diversification is the key factor to respond to such increase. Given that the deposits of non-renewable energy sources, primarily referring to the fossil fuels, are limited and significantly exploited and that the CO₂ emissions are constantly rising, the use of renewable energy sources is the only viable solution for the energy problems in a modern industrial society.

Renewable energy sources are sources that may be found in nature and that have the ability of renewing, in whole or in part by using of effective and environmentally friendly natural or artificially induced processes [14]. One kind of renewable energy is the energy that comes from biomass combustion.

1.1. Biomass: Definition, Energy values and Pollutant emissions.

Biomass is the organic matter of plant or animal origin and is one of the sources of renewable energy that is used in combustion processes or converted to systems for the production of energy (heat and electricity).[14].

Biomass energy can be an important factor in reducing greenhouse gas emissions. It can be found in nature or sometimes it occurs as a byproduct of human activities in different forms, some of which are presented below:

- Plant origin wastes that originate from agriculture, forestry and the food industry (mainly for heat production).
- Fibrous plant wastes, that are derived from pulp and paper production, for the purpose of heat generation by co-incineration.
- Wood wastes produced by the wood processing industry (mainly for heat production).
- Biomass, as a byproduct of human activities, can be encountered in: solid (briquetted biomass), liquid (biodiesel, bioethanol, biomethanol) and gaseous physical state (e.g. biogas, landfill gas).

“Biomass of plant origin is a product of photosynthesis in plant organisms. Biomass of animal origin is produced as a product – the rest is in the process of feeding of animals. Thus explained concept is very wide, but the basic concept is that the biomass is consumed and renewed continuously, in the cycle of circulation of material and energy in the nature. Man, with his activities, increases the amount of biomass that is circulating in the environment”[14]. Because of that, many countries, like Sweden, have set a goal to increase the use of bioenergy in order to meet the commitments set out in the Kyoto protocol and various other policy goals.

The standard measure of the energy content of a fuel is its heating value, sometimes called the calorific value or heat of combustion. In fact, there are two values for the heating value depending on whether the product water is accounted for in the vapor phase (Higher Heating Value - HHV) or the condensed (liquid) phase (Lower Heating Value - LHV).

Fuel moisture is a limiting factor in biomass combustion due to its effect on heating value. The combustion reaction is exothermic while the evaporation of water is strongly endothermic. Biomass fuels have higher values of moisture comparing to coal. Moreover, when there is an excess of 50 to 55% moisture wet basis in the fuel, according to the type of boiler, CO

and other undesirable products of incomplete combustion could be emitted in the atmosphere in greater quantities.

The heating value of biomass can also be correlated with ash and carbon concentration. Each 1% increase in ash translates roughly into a decrease of 0.2 MJ/kg while each 1% increase in carbon elevates the heating value by approximately 0.39MJ/kg [15], an identical result with that found by Shafizadeh[16] for the wood pyrolysis products. The heating value related to the amount of oxygen required for complete combustion is 14.022J released for each g of oxygen consumed[16]. Other compounds, such as HC in the fuel with lower degrees of oxidation, tend to raise the heating value of the biomass.

Critically related to the properties of biomass are pollutant emissions generated by combustion. Primary pollutants formed are particulate matter (PM), CO, HC, oxides of nitrogen (NO_x , principally NO and NO_2), oxides of sulfur (SO_x), HCl and sometimes heavy metals. CO and HC, including volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH), may also be emitted as products of incomplete combustion[17]. Emissions of oxides of nitrogen and sulfur and hydrochloride arise predominantly from the percentage of nitrogen, sulfur and chlorine in the fuel. It is preferred for most commercial biomass combustors to operate at temperatures low enough (such as fluidized bed combustors) in order to minimize the contribution of thermal NO_x to the total NO_x .

Finally, the nature and severity of the operational problems related to biomass depend on the choice of combustion technique. In grate-fired units deposition and corrosion problems are the major concern. In fluidized bed combustion the alkali metals in the biomass may facilitate agglomeration of the bed material, causing serious problems for using this technology for herbaceous based biofuels[18]. Currently, wood based bio-fuels is a type of biomass that can be

co-fired with other fuels like natural gas and coal. For the herbaceous biomass, the problems of deposition and corrosion that occur limit their use. The addition of biomass in these coal units may impede the utilization of fly ash for cement production.

2. Waste wood role.

Wood is a natural resource which, among others, can be used as a renewable source of energy. It can be categorized to virgin wood and waste wood. Wood wastes are mainly originated from forestry, wood industry and activities on construction and demolition sites. They are produced by a number of sectors as part of the municipal waste stream and arise in different fractions ranging from untreated, pre-consumer off-cuts to treated wood containing preservatives and via a variety of post-consumer waste [13]. As a result, these wood fuels have different composition from the virgin ones.

With the growth of industrialization and urbanization, proper treatment and recycling utilization of wastes have become important tasks of our society. While recycling and energy markets for clean, virgin wood had been growing, waste wood had been a largely overlooked resource. This is partially due to the fact that waste wood often arise as part of a mixed waste stream, with limited availability of facilities for its segregation. Considering the fact that the biomass can be contaminated with a variety of substances, waste wood is most of the times not a virgin fuel and its impurities have influences that are negative on the environmental loadings. More accurately, the combustion of waste woods is an environmental menace since, during their combustion, large amounts of air pollutants (HCl, SO_x, HF, CO, NO_x, VOCs, heavy metals, fine particulate matter) are emitted, which significantly augment the pollution of local and global environmental. The acid gases in these pollutants, such as HCl, SO_x, and HF, are the main

sources of acid rain and fog, which endanger the human life by modifying the lungs' defenses and aggravating cardiovascular or chronic lung diseases. As a result, its predominantly contaminated nature often made recycling impractical.

The energy that derives from biomass wastes and it is used for the production of heat and power in large utilities (for example boilers and incinerators) and, as mentioned before, for the co-firing with fossil fuels in big power plants has, in the past two decades, received great attention mainly because of the increasing energy prices, the advances in the waste-to-energy (WTE) technologies and the constant rise of global warming issue. The decentralized energy from the domestic waste resources not only enhances fuel diversification, but, more importantly, possesses benefits for the environment in terms of the greenhouse gas emissions and the associated global warming. [20]

According to the Eurostat News Release (168/2012 – 29 November 2012) in 2010, “*wood and wood waste contributed 5% to total gross inland energy consumption in the EU27, and it was the leading source of renewable energy, accounting for almost half of the EU27's consumption of renewable energies*”. It is also mentioned that, “*among the Member States, the highest shares of wood and wood waste in total gross inland energy consumption in 2010 were recorded in Latvia (27%), Finland (21%) and Sweden (19%), while it was 1% or less in Cyprus, Luxembourg and the United Kingdom. In the majority of Member States, wood and wood waste was the main source of renewable energy. It accounted for more than three quarters of gross inland energy consumption from renewable energies in 2010 in Estonia (96%), Lithuania (88%), Finland (85%), Poland (81%), Latvia (78%) and Hungary (77%), and less than a quarter in Cyprus (13%) and Italy (24%).*” [21]

Due to the low cost of waste wood as a biomass fuel, as shown in Table 1, it has been considered a very attractive choice of fuel for large-scale biomass combustion plants. Taken into consideration the European standards that concern the classification of waste wood, it can be ranked into seven different classes of quality, such as chemically untreated wood, bark, binder-containing and halogen-free coated wood, surface-treated wood, creosoted timber, salt-impregnated wood, and halogen plastics containing wood composite materials [22].

	Sweden		Finland	
	1999 (€/GJ)	2001 (€/GJ)	1999 (€/GJ)	2001 (€/GJ)
Pellets	5.06	5.03	8.87	NA
Logging residues	3.33 – 3.54	3.36 – 3.46	2.48	2.5
Industrial by-products	2.5 – 2.97	2.35 – 2.96	1.71	1.92
Used wood	2.41	2.04	1.17	NA

Table 1: Wood fuel prices excluding VAT in Sweden and Finland in 1999 and 2001. The Finnish prices are average prices, while the price intervals given for Sweden apply to industry (lower) and district heating (higher). (Swedish Energy Agency, 2002a, b; Hakkila, 2003; VIT Energy, 2001) [19] Pellets are the most expensive wood fuel, followed by wood chips from logging residues, industrial by-products, such as wood chips, sawdust and bark, and used wood (waste wood).

2.1. Differences between recycled wood chips and clean wood chips.

The recycled wood chips compared to the clean wood chips have different variations and as a result when used as a fuel they have different chemical composition in their produced ashes and flue gases as well. Analyzing the data of our fuel with the data from the clean wood chips (data which was obtained from the The Värmforsk Fuel Handbook, ECN Phyllis2 and BIODAT) confirms this statement. Recycled wood chips are more contaminated than the clean ones so it crucial to use the right processes in order to maintain the emissions at an acceptable level. It was noticed that the amount of S, Cl, N, heavy metals, ash production and some of the alkali components is higher. The S and Cl are found in the fuel in both organic and inorganic forms. This difference can be found also by analysing the ash composition and the emissions. This

could be the result of some preservatives, adhesives and additives on the recycled wood such as paint, impregnating agents, anti-rot agents, glue, binders and coating.

	Clean Wood Chips			Recycled Wood Chips			
		Average	Max	Min	Average	Max	Min
Moisture	% (105 °C, as received)	45	55	30	25,15	36,5	13
Ash	% (550 °C, dry basis)	2,6	4,7	1,3	4,23	10,7	1,2
Net heating value	MJ/kg (dry basis, ash free)	19,1	19,1	19,1	18,477	18,837	17,522
Carbon	% (dry basis)	51,0	54,1	42,8	48,78	50,1	46,3
Hydrogen	% (dry basis)	6,1	6,6	5,0	5,95	6,2	5,6
Oxygen	% (dry basis)	42,4	38,4	52,1	39,37	41,4	35,2
Nitrogen	% (dry basis)	0,4	0,8	0,1	1,0674	1,84	0,41
Sulphur	% (dry basis)	0,04	0,05	0,01	0,04871	0,089	0,021
Chlorine	% (dry basis)	0,02	0,04	0,01	0,12852	0,7	0,03
Aluminium	mg/kg (dry basis)	434	1133	145	1382,93	6810	381
Calcium	mg/kg (dry basis)	4654	6982	2484	4149,19	8760	2170
Iron	mg/kg (dry basis)	296	675	111	1053,13	4830	324
Potassium	mg/kg (dry basis)	1843	3000	1158	927,29	1710	575
Magnesium	mg/kg (dry basis)	580	720	323	596,08	1270	289
Manganese	mg/kg (dry basis)	254	640	44	83,55	193	60,7
Sodium	mg/kg (dry basis)	174	300	24	1121,3	3920	339
Phosphorus	mg/kg (dry basis)	461	626	178	97,98	215	47,4
Silicon	mg/kg (dry basis)	3093	4705	622	7637,58	25700	1520
Titanium	mg/kg (dry basis)	21	73	10	1112,61	2580	127

Table 2: Comparison between our recycled wood chips(fuel) and clean wood chips components.

The release of alkali metals, chlorine and sulfur to the gas-phase may lead to generation of large amounts of aerosols (sub-micron particles) along with relatively high emissions of HCl and SO₂. Because of wide fuel variations (Table 2), there will be different impacts on emission performance. However, the heating value was similar to the clean ones and the moisture content was at lower levels. Furthermore, reuse of wood waste provides great climate change benefit – reducing emissions approximately by 4.000 to 5.600 pounds of carbon dioxide equivalents (eCO₂) per ton of wood. This is mainly due to the avoidance of additional tree harvesting and continued storage of carbon in the waste wood products that are reused. [23] This carbon was originally sequestered during the growth of trees before they were harvested to manufacture wood products. As a result, we try to use recycled wood fuel as an alternative source of fuel but further methods to reduce these emissions must be considered.

Due to the differences that exist between clean wood chips and waste wood, its recent rise in large-scale biomass combustion plants and its characteristics that were mentioned before, our objective is to investigate and find the possible conversions and retention mechanisms of SO_x, HCl, ammonia (NH₃) and NO_x that happen during the combustion of contaminated wooden fuel by using industrial data, to model/simulate the conversion and retention processes with Microsoft EXCEL and to make an impact evaluation for the factors that affect the emission performance.

CHAPTER II: Literature Review

3. Description of the flow diagram.

In the following figure, the plant in which the combustion of the contaminated recycled wood chips and the flue gas cleaning is presented.

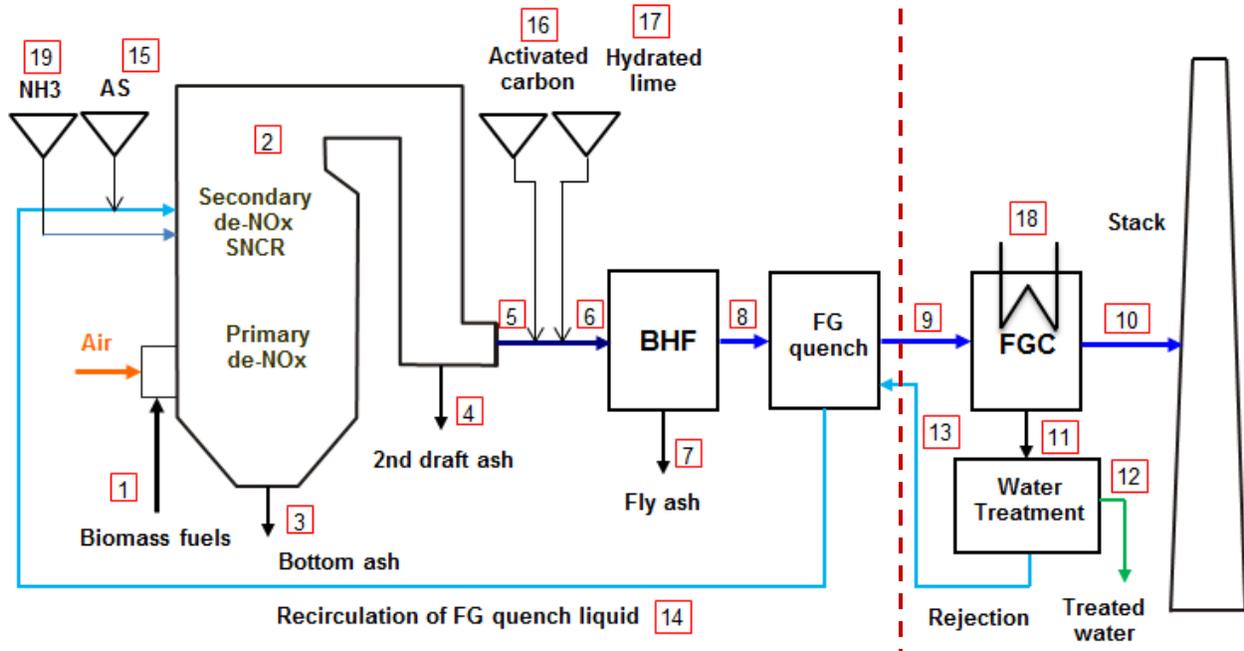


Figure 1: The flow diagram of the combustion and flue gas cleaning.

A general description of our procedure is introduced by the corresponding flow diagram while more detailed information of each process will be presented below. We are more interested in the conversion and retention of the acidic components and NH_3 during the combustion of the recycled wood and as a result we are going to focus more on the behavior of S, Cl and N. This study reaches the point of flue gas (FG) quench. Each process will be explained analytically afterwards by the literature review gathered.

The combustion takes place in a Bubbling Fluidized Bed (BFB). Fluidized bed combustors are frequently used for solid fuels from waste, and are the preferred choice in larger units, because nearly homogeneous conditions of temperature can be ascertained thus enabling high burnout quality at low excess air. This makes it more suitable for fuel with low fuel ratio ($Fuel\ ratio = \frac{Fixed\ Carbon}{Volatile\ Matter}$) and low heating value. The flame's temperature is 900-1153°C. After the combustion of the fuel, the bottom ash that is produced is gathered from the bottom of the furnace by the stream 3.

In order to lower the production of CO and NO_x during incomplete combustion, the combustion air is not inserted stoichiometrically but with an excess air ratio (λ) of 1.31 (primary de-NO_x). In the primary de-NO_x is also included direct water injection, optimized fuel spray pattern and flue gas recirculation. For further reduction of the NO_x in the furnace, the secondary de-NO_x takes place. By injecting ammonia, most of the NO_x that remain are converted to N₂. The ammonia dosing consists of 24,5% v/v NH₃ and 75,5% v/v water and is injected at 850-950°C..

Furthermore, to lower the possibility of slagging, fouling and corrosion of the equipment, especially of the superheater, there is a dosing of Ammonia Sulphate (AS, (NH₄)₂SO₄) so as to react with the Cl products, which are very corrosive and have low melting and evaporation points. AS dosing follows NH₃ dosing at slightly lower temperatures. The dosing consists of 40% v/v AS and 60% v/v water and the NH₃ that is produced from the decomposition of AS can help with secondary de-NO_x (SNCR). Before the heat exchanger, there is an empty space so as to increase the residence time of the NH₃ with the NO_x during the SNCR process ($\tau > 2\text{sec}$). Any possible fouling and slagging that occurs in this empty space due to the changes in the temperature is gathered through the empty draft ash.

Fouling occurs in the colder sections of the boiler where the volatiles condensate as compounds on the colder tube surface creating a deposit layer. Also particles which are in melt phase may hit the tube, be cooled down to solid state and afterwards get stuck on the tubes. Over time the deposit layer grows in thickness and at some time the deposit can become so heavy that it may fall off the tube under its own weight. This process is called slagging [9].

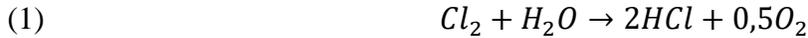
After the combustion in the furnace and the temperature drop in the heat exchanger, the flue gas passes through the flue gas cleaning. There, in the Bag House Filter (BHF), the unburned matter and other particles are removed by deflection, interception, diffusion and electrical forces. Moreover, by injecting powder of hydrated lime and activated carbon(C) in the filter cake, absorption/reaction of the gaseous impurities, such as SO₂, HCl, PCDF's, PCDD's etc., take place simultaneously with the removal of the particles. To be more precise the activated carbon and hydrated lime are injected before the BHF but because the residence time is too short, the retention reaction happens mainly on the filter cake. Because of this absorption, this technique results however in large quantities of heavily polluted rest substance (fly ash). The emissions are then recirculated back to the furnace right after the combustion at 56% while the rest of the flue gas continues to the Flue Gas Condenser (FGC).

4. The reactivity of S, Cl and NH₃ in the furnace.

4.1. Conversion of fuel-S and fuel-Cl.

Inside the furnace S and Cl are very reactive. The main reactions include the production of HCl and SO₂ from both the organic and inorganic sources of Cl and S in the fuel.

The HCl formation mainly occurs at 200-400°C from the organic Cl through this chemical reaction.



Moreover, at higher temperatures the Cl-salts such as KCl, CaCl₂, NaCl, MgCl₂, etc. are decomposed back to Cl₂ and their respective oxide, and as a result HCl is produced through the previous reaction, or they are converted to their gas phase through evaporation because their low melting and evaporation points. These salts can originate from the fuel or be created through secondary reactions with Cl(g)/HCl(g) and the char. The low melting point of the Cl-salts is one of the main reasons of slagging, fouling and corrosion incidents. Due to all of the reactions that were mentioned before, Cl⁻ almost completely is released to the flue gas and very low concentrations of it are found in the bottom ash. A summary of the Cl-products during combustion can be seen in the Figure 2 below, taken by [1].

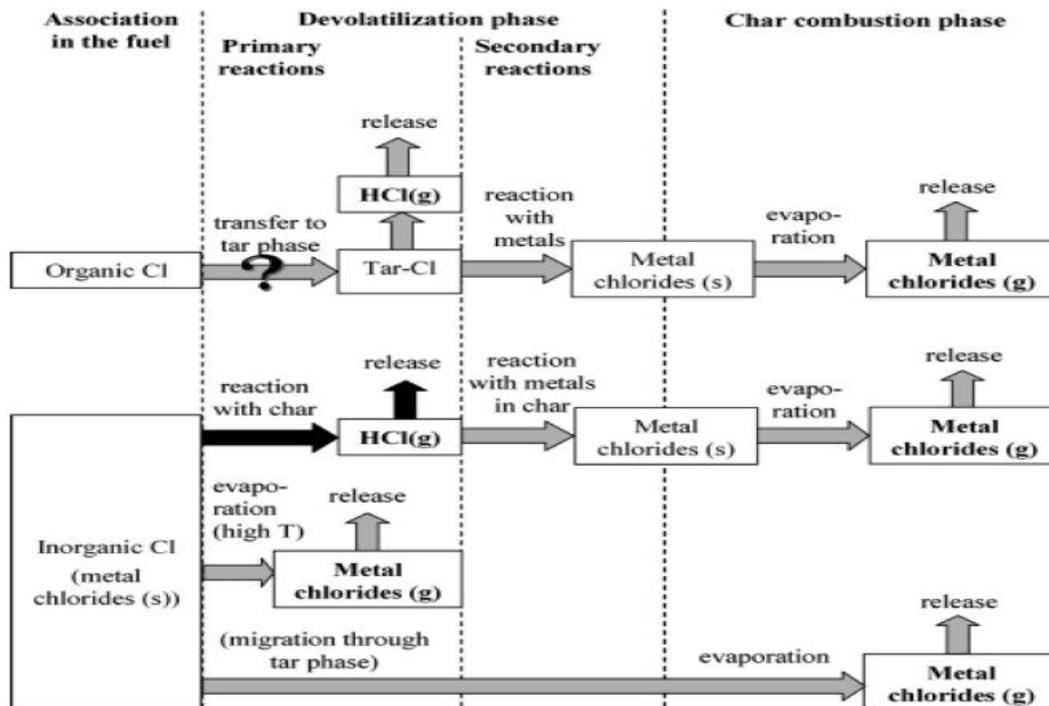


Figure 2: Possible reaction pathways and release mechanisms of Cl during devolatilization and combustion of biomass. Possible secondary reactions between Cl and metal species in the char are indicated as well. The black arrows indicate the main reaction pathway and release mechanism of Cl. [1]

The fuel-S can be oxidized to SO₂ and SO₃ according to the following reactions.



The first reaction is one of the major reactions and is produced by the decomposition of organic S at 500°C while the second one is too slow in temperatures below 900°C but it can be catalyzed by iron oxides in temperatures between 427-593°C. Comparing to Cl-salts, S-salts such as K₂SO₄, CaSO₄, Na₂SO₄, MgSO₄, etc. at temperatures higher than 500°C are mostly decomposed, back to SO₂ and their respective oxides, than evaporated, because, due to S, they have higher melting and evaporation points. However, due to the decomposition of the salts and the oxidation of organic S, a great percentage of S is released to the flue gas and low concentration of S is found in the bottom ash as well. These salts can originate from the fuel or created through secondary reactions between SO₂(g) /SO₃(g) and the char.

In the Table 3, the temperatures of the decomposition and/or oxidization, sulphation and desulphation that happen to all possible S-salts that are in the furnace during the combustion of Bulgarian coals, are shown. Similar temperatures can be assumed for the waste wood combustion. Furthermore, a summary of the S-products during wood combustion can be seen in the following figure.

Original mineral or phase	Newly-formed mineral or phase as a result of		
	Decomposition and/or oxidation (°C)	Sulphation (°C)	Desulphation (°C)
Organic matter, elemental S	SO ₂ (200-700) CaO (200-700) MgO (200-700) K ₂ O (200-700) Na ₂ O (200-700) Fe ₂ O ₃ (200-700) BaO (200-700)	CaSO ₄ (200-1000) MgSO ₄ (200-1100) K ₂ SO ₄ (200-800) Na ₂ SO ₄ (200-800) FeSO ₄ (200-700) BaSO ₄ (200-900)	CaO, SO ₂ (800-1300) MgO, SO ₂ (1100-1200) K ₂ O, SO ₂ (800-1100) Na ₂ O, SO ₂ (800-1100) Fe ₂ O ₃ , SO ₂ (700-900) BaO, SO ₂ (900-1200)
Calcite	CaO (500-900)	CaSO ₄ (500-1000)	CaO, SO ₂ (800-1300)
Dolomite	CaO (500-900) MgO (500-900)	CaSO ₄ (500-1000) MgSO ₄ (500-1100)	CaO, SO ₂ (800-1300) MgO, SO ₂ (1100-1200)
Ankerite	CaO (500-800) Fe ₂ O ₃ (500-800) MgO (500-800)	CaSO ₄ (500-1000) FeSO ₄ (500-800) MgSO ₄ (500-1100)	CaO, SO ₂ (800-1300) Fe ₂ O ₃ , SO ₂ (800-900) MgO, SO ₂ (1100-1200)
Siderite	Fe ₂ O ₃ (400-800)	FeSO ₄ (400-800)	Fe ₂ O ₃ , SO ₂ (800-900)
Pyrite, marcasite	SO ₂ (100-500) Fe ₂ O ₃ (100-500)	FeSO ₄ (100-500)	Fe ₂ O ₃ , SO ₂ (500-900)
Gypsum	CaSO ₄ (100-300)		CaO, SO ₂ (800-1300)
Anhydrite			CaO, SO ₂ (800-1300)
Jarosite	SO ₂ (300-900) K ₂ SO ₄ (300-900) Fe ₂ O ₃ (300-900)	FeSO ₄ (300-900)	K ₂ O, SO ₂ (900-1100) Fe ₂ O ₃ , SO ₂ (~900)
Hexahydrate	MgSO ₄ (100-200)		MgO, SO ₂ (1100-1200)
Barite			BaO, SO ₂ (1000-1300)

Table 3: Transformations of S-, Ca-, Mg-, K-, Na-, Fe- and Ba- bearing minerals and phases and S emissions during heating of Bulgarian coals in air. [2]

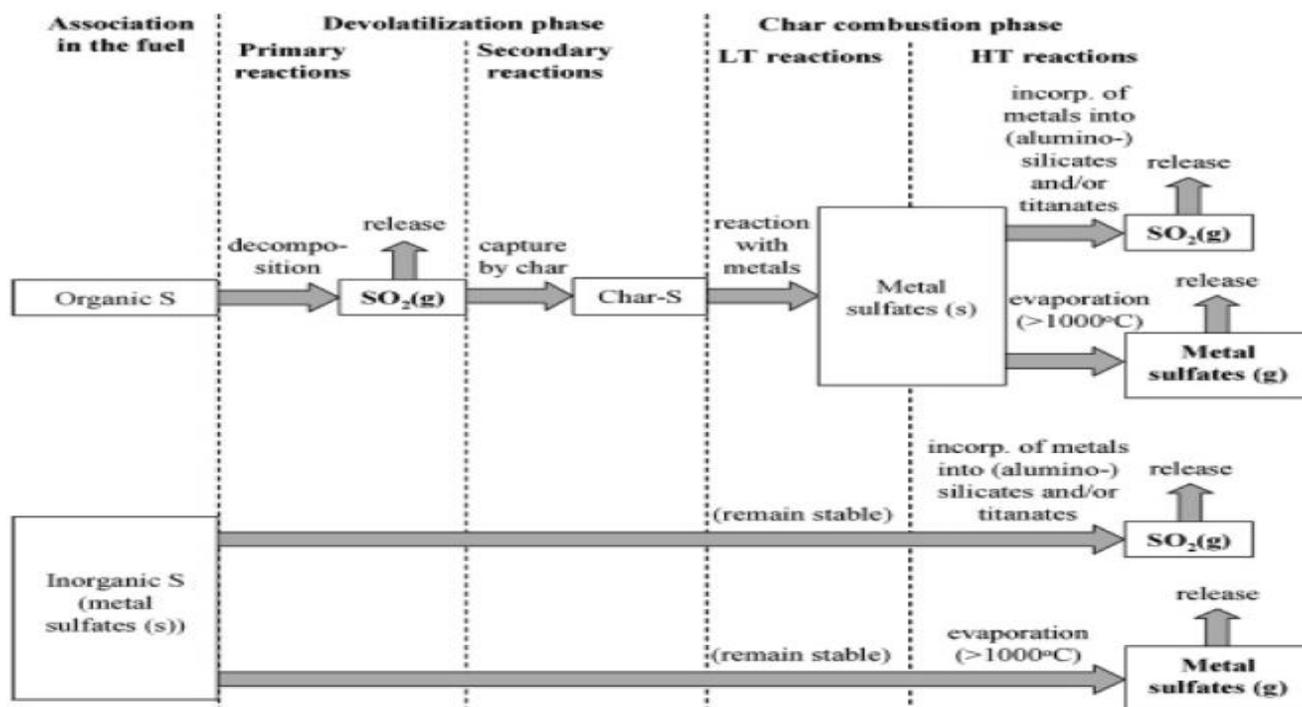


Figure 3: Possible reaction pathways and release mechanisms of S during devolatilization and combustion of biomass. Possible secondary reactions between S and metal species in the char are indicated as well. LT=between ~500 and 800-900°C while HT= higher than 800-900°C. [1]

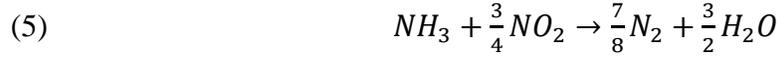
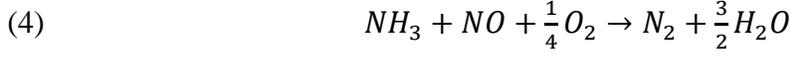
4.2. Conversion of fuel-N.

Due to the low temperatures that exist in a Bubbling Fluidized Boiler, the thermal-N and prompt-N do not have any significant impacts on NO_x formation in the furnace. However, the nitrogen that derives from the fuel is being converted mostly to N₂ and NO_x. Fuel-N exists in both the volatiles and the char residue

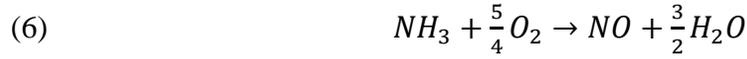
During the combustion the fuel-N is not only directly converted to N₂ and NO_x. There are some other products such as NH₃ and HCN which can afterwards react to produce NO_x (NO, NO₂ and N₂O) and N₂. Biomass fuels that are “younger” than coal; during their combustion, fuel-N is converted mostly to NH₃ instead of HCN (HCN/NH₃ = 1/9)[10], as is in the case of coals. Since NH₃ has a lower conversion rate to nitrogen oxides compared to HCN, the NO_x emissions that come from the combustion of biomass tend to be lower than those of coal, under same combustion conditions. Additionally, the nitrogen that is present in the form of HCN tends to be converted into nitrous oxide (N₂O). However, the reactions that happen with the fuel-N are quite complicated and still not completely understood.

4.3. The SNCR process.

During the SNCR (Selective Non-Catalytic Reduction) process, a small amount of NH₃ that derives from the fuel-N and the NH₃ from the ammonia dosing and ammonium sulphate (AS) dosing, react with the NO_x that are created during the combustion of the fuel and N₂ is produced. The NO_x from the oxidation of fuel-N can be more than 95% NO and less than 5% NO₂[4]. The decomposition reactions of NO_x emissions due to the presence of ammonia are shown below.



The decomposition of the NO_x from NH₃ is followed by the oxidation of NH₃ to NO_x, thereby limiting the overall de-NO_x efficiency according to the following reactions.



The reaction orders of NO_x and NH₃ at 4% volume O₂ and the empirical rate constants k_{red} and k_{ox} respectively, have been estimated from work done by Brouwer et al[3]. The NO production and decomposition reaction order was found to be 1 for both. As a result, their reaction rates at 4% volume O₂ are:

$$(8) \quad R_{NO} = -k_{red}[NO][NH_3] + k_{ox}[NH_3][O_2]$$

$$(9) \quad R_{NH_3} = -k_{red}[NO][NH_3] - k_{ox}[NH_3][O_2]$$

And the rate constants k_{red} and k_{ox} have units of $m^3/gmol-s$ and are defined as:

$$(10) \quad k_{red} = 4.24 \times 10^2 T^{5.3} e^{-E_{red}/RT}$$

$$(11) \quad k_{ox} = 3.5 \times 10^{-1} T^{7.65} e^{-E_{ox}/RT}$$

where $E_{red} = 349937.06$ J/gmol and $E_{ox} = 524487.005$ J/gmol.

As β , the NH₃/NO_x ratio, and the temperature of the reaction raises, the removal rate of the NO_x emissions raises as well. However, for NH₃/NO_x ratios above 1 and temperatures above 900°C the removal rate starts to decrease because of the oxidation of NH₃ to NO_x. Large-scale

measurements confirm the existence of maximum de-NO_x efficiency around 84% when using NH₃. [4] This statement can be shown more clearly in Diagram 1.

The NH₃ that has not reacted during the SNCR process is called ammonia slip. The ammonia slip can also be predicted and is given by the following equation[4]:

$$(12) \quad NH_{3slip} = \frac{\text{unreacted } NH_3}{C_{NH_3 \text{ initial}}}$$

where C_{NH₃} is the initial concentration of NH₃ before SNCR.

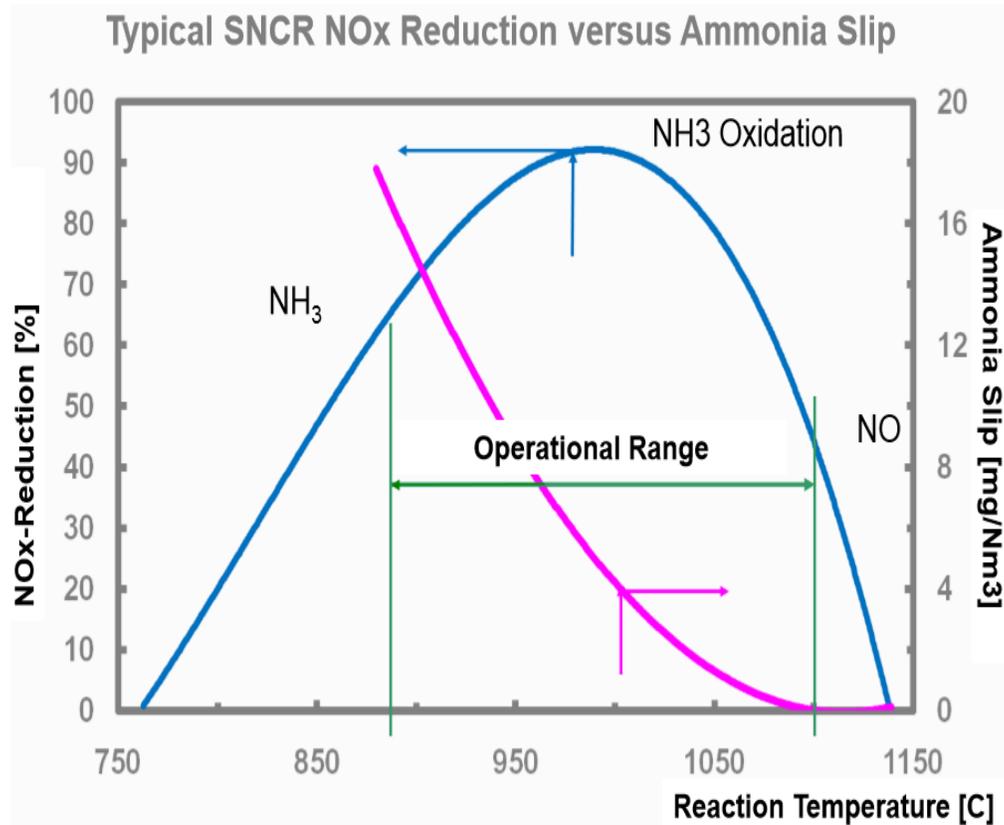


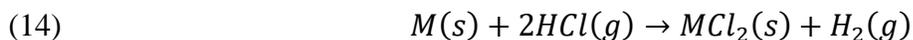
Diagram 1: Typical SNCR NOx reduction versus ammonia slip. When the temperature surpasses ~950°C the NOx concentration will be increased (blue line) while ammonia slip will be in low levels (pink line). The opposite happens when low temperatures exist during SNCR. In this diagram, it is also shown that when ammonia slip is high, NOx reduction percentage will be high as well. [24]

5. Slagging, Fouling and Corrosion in the Equipment.

5.1. Chlorine.

Biomass fuels contain high amounts of alkali metals, which can together with chlorine form combinations and matters that have very low melting point and thereby soot particles have high probability to get stuck on the boiler tubes. The main alkali and alkali earth metals Cl-salts in the furnace are KCl, CaCl₂, NaCl, MgCl₂. From them KCl and NaCl have the lowest melt and evaporation point which are 772°C / 680°C for KCl and 801°C / around 700°C for NaCl respectively[11]. These salts condense mostly at the empty draft and the heat exchanger due to the lower temperature range that there is.

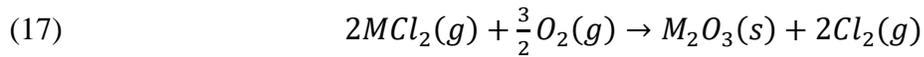
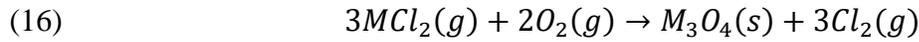
The most corrosive components are Cl₂, HCl, NaCl and KCl. Boilers operate with excess of oxygen in the furnace, creating an oxidizing environment at high temperatures (around or above 500°C) in which metal will gradually oxidize to thermodynamically stable oxides. Cl₂ and HCl diffuses through this oxide layer and reacts with the metal alloys forming metal chlorides (FeCl₂, CrCl₂, NiCl₂). Metal chlorides have high vapor pressures and continuous evaporation may take place[5,9].



where M is *Fe*, *Cr* or *Ni*.

These volatile metal chlorides may diffuse to the scale surface where due to higher oxygen concentration they are oxidized to solid metal oxides. The resulting oxides that precipitate from this gas-phase reaction form a very loose metal oxide layer that provides no

protection against further attack and as a result chlorine corrosion is often considered to have a linear corrosion rate.



Due to the previous reactions, gas Cl is released which can diffuse to the bulk gas or back to the metal surface and thus a cycle is formed which provides with a continuous transport of metals away from the metal surface (Figure 4). Gas diffusion through the scale is believed to be the rate controlling step in the corrosion process.

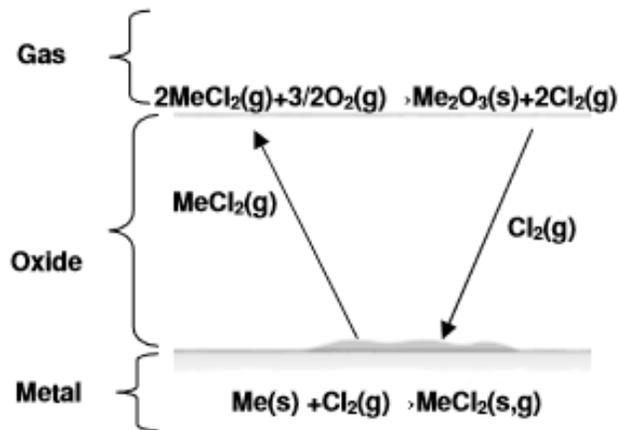
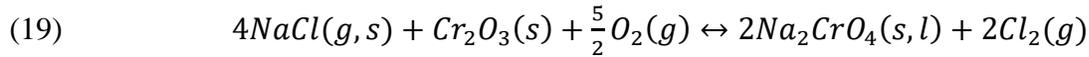
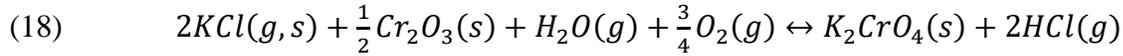


Figure 4: Schematic drawing of the chlorine cycle.[5]

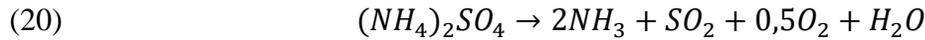
As it is mentioned before, since the temperature after the combustion is below the dew point of $KCl(g)$ and $NaCl(g)$, so the alkali chlorides condensate and accumulate on the tube surface. They are reacting with the metal oxide scale and they release chlorine that would contribute to the chlorine cycle as discussed before. However, KCl and $NaCl$, in either gas or solid form, can also react directly with the chromium oxide forming potassium chromate, K_2CrO_4 , and sodium chromate, Na_2CrO_4 , which depletes the alloy in protective chromium oxide according to the following reaction[5,9]:



The corrosion problems increase if the deposit is in melt or partly melt phase. Moreover, sulfur (in the form of SO₂/SO₃) and chlorine (in the form of Cl₂/HCl) can react with the fly ash alkaline and metal particles to create compounds that deposit in the furnace walls increasing the fouling, slagging and corrosion problem.

5.2. SO₂/SO₃ and the use of Ammonium Sulfate.

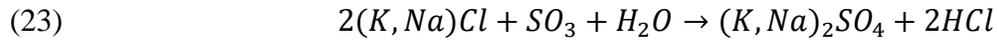
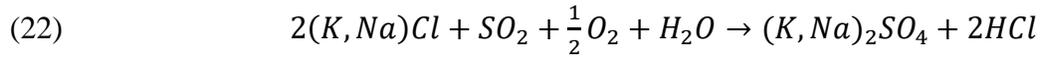
The ammonium sulfate (AS) is an ammonium-salt that when decomposed it gives ammonia and SO₂/SO₃.



The reactions are practically the same but the production of SO₃ depends to the concentration of oxygen and temperature. Ammonia can be used to help the NH₃ dosing for the SNCR process that was mentioned before while SO₂ and SO₃ can protect against the corrosion problems that occur due to chlorine.

Moreover, it was suggested that in addition to the SO₃ formation in the furnace, formation of SO₃ also takes place in the temperature range 427-593°C found in the economizer region of the boiler. This formation results from oxidization of SO₂ catalyzed by the iron oxides (Fe₂O₃) and the extent of this reaction depends on site-specific factors such as the cleanliness of the tube surfaces [6]. When the temperature is below the dew point of the SO₃, it condensates and with water it produces sulfuric acid that dissolves the protective oxide film.

The SO₂ and SO₃ content in the flue gas decrease corrosion under chloride deposits concluding that chlorides are transformed into less aggressive sulfates at high S-concentrations according to the following chemical equations.



Although a problem at even higher temperatures, alkali sulfates are considered rather stable at the temperature interval encountered in waste and biomass fired boilers and will not cause severe corrosion. Moreover, the formed alkali sulfates generally have higher melting temperatures than their chlorides. Therefore, the deposition propensity of fly ashes would be reduced by the sulphation reaction. However, HCl and SO₃ are produced through the reactions above which are corrosive as explained before. Despite the previous fact, a S/Cl ratio in the fuel above 4 was proposed as a condition to prevent severe corrosion problems[6].

6. Flue gas cleaning.

6.1. Activated Carbon (Activated C).

Activated carbon can be made from a wide range of source materials such as coal, coconut shells and wood. It is sprayed during the flue gas treatment mostly for the adsorption of trace toxic substance such as Hg, PCDDs, PCDFs and other heavy metals which derive from the combustion of the contaminated wooden fuels. The most efficient removal takes place at temperatures between 100-130°C.

However, activated carbon can absorb a small amount of the HCl, SO₃ and SO₂ emissions. Specifically, the reduction of SO₂ proceeds through the following stoichiometric reaction because it is the only reaction of the C-O-S system where the CO₂:S₂ =2:1.

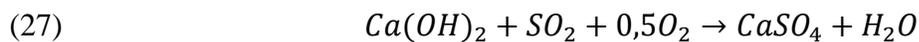
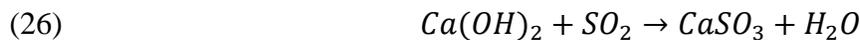
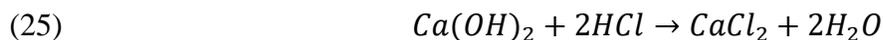


The reduction of SO₂ on activated carbons revealed that the sulfur content on the carbon increased until the reaction reached to steady-state condition. The sulfur content remained stable during this period and it was chemically bound to the carbon matrix. It can be bound as non-oxidized and oxidized sulfur. [7]

6.2. Hydrated Lime (Ca(OH)₂).

Hydrated lime plays a key role in many air pollution control applications. It is a sorbent that is used to remove the acidic components, especially SO₂, SO₃ and HCl, from the flue gas. Lime-based technology is also being evaluated for the removal of mercury.

HCl, SO₂ and SO₃ react with hydrated lime according to the following chemical equation:



The SO₂ and HCl within the flue gas react with Ca(OH)₂ and form calcium sulfite, calcium sulfate and calcium chloride. After leaving the boiler, the mixture of flue gas and solid products that was produced enters into a fabric filter where the separation of the solid compounds takes place by filtration. Because of the very short contact time available for the

sorbent and acid gases to react, most of the reactions result in the cake of the bag-house filter. This technique generates a large amount of solid particles.

These reactions with $\text{Ca}(\text{OH})_2$ are similar to each other but the reaction with the HCl is much faster and as a result, a greater amount of HCl is removed[12]. The target reaction temperature range for hydrated lime is 120-150°C.

6.3. Bag-House Filter (BHF).

After the activated carbon and the hydrated lime injection the flue gas passes through a particulate control equipment, such as a bag-house filter, to remove the fly ash, solid reaction products of the flue gas cleaning and the residual lime. As it was mentioned before, because the residence time of activated carbon and hydrated lime with the flue gas is too low, the reactions above take place mostly in the cake filter. A BHF can achieve approximately 90-99% removing efficiency of the particulate emissions at not extreme temperatures [12].

When there is ammonia slip from the SNCR process, some of it is gathered to the filter cake and makes the dust sticky, due to the formation of ammonium sulphates, which leads afterwards to an ineffective cleaning of the BHF.

7. Flue gas quench.

The flue gas quench it can be described as a wet gas cleaning for pure particulate removal with some recovery of the low temperature heat by partial condensation though its main function is to lower the temperature of the flue gas before the flue gas condensation.

When the flue gas passes through the flue gas quench, water is injected and comes in contact with it. Then, the most water soluble pollutants are transferred from the flue gas to the

injected water (water scrubbing). Suitable equipment is flue gas quenchers with a large gas/liquid contact area such as spray, tray, column or plate quenchers. [12] Absorption of the pollutants by the water is partial and, afterwards, the water is recirculated back to the furnace right before the SNCR de-NO_x reactions.

The pollutants that are mostly removed from the flue gas quench and through the water feed return back the furnace are HCl and NH₃. Both HCl and NH₃ are so soluble to water that up to 90% can be transferred to the water. Less soluble is SO₂ where up to 40% can be recirculated. Finally, small concentrations of NO_x may be absorbed by the water as well.

CHAPTER III: Methodology

8. Concept.

The concept for modeling the combustion of recycled wood and flue gas cleaning was based on the stoichiometry of the chemical reactions and the material balances in a given system. By checking the temperatures that exist in each part of the whole process, it became possible to note which reactions could be dominant based on their thermodynamic equilibriums. Then, with the help of the mass balance and by assuming that the whole process is in steady state, the flue gas composition in different points can be defined. The most important points, in the furnace and the flue gas path, are 1) after the combustion before SNCR, 2) after SNCR before the flue gas cleaning, 3) after flue gas cleaning and 4) after the recirculation in flue gas quench. In these points, the various increases and decreases in the concentrations of the acidic components and NH_3 can be monitored while the reactions which have the greatest impact on them can be defined as well. The mass balance in each point can be defined by initially knowing beforehand the composition of the fuel, the ash composition at the different points of the process and all the reactions that take place inside the furnace and during the flue gas cleaning.

Below, the main concept of the methodology is displayed through the form of a process diagram, divided into different temperature profiles, which will be explained thoroughly.

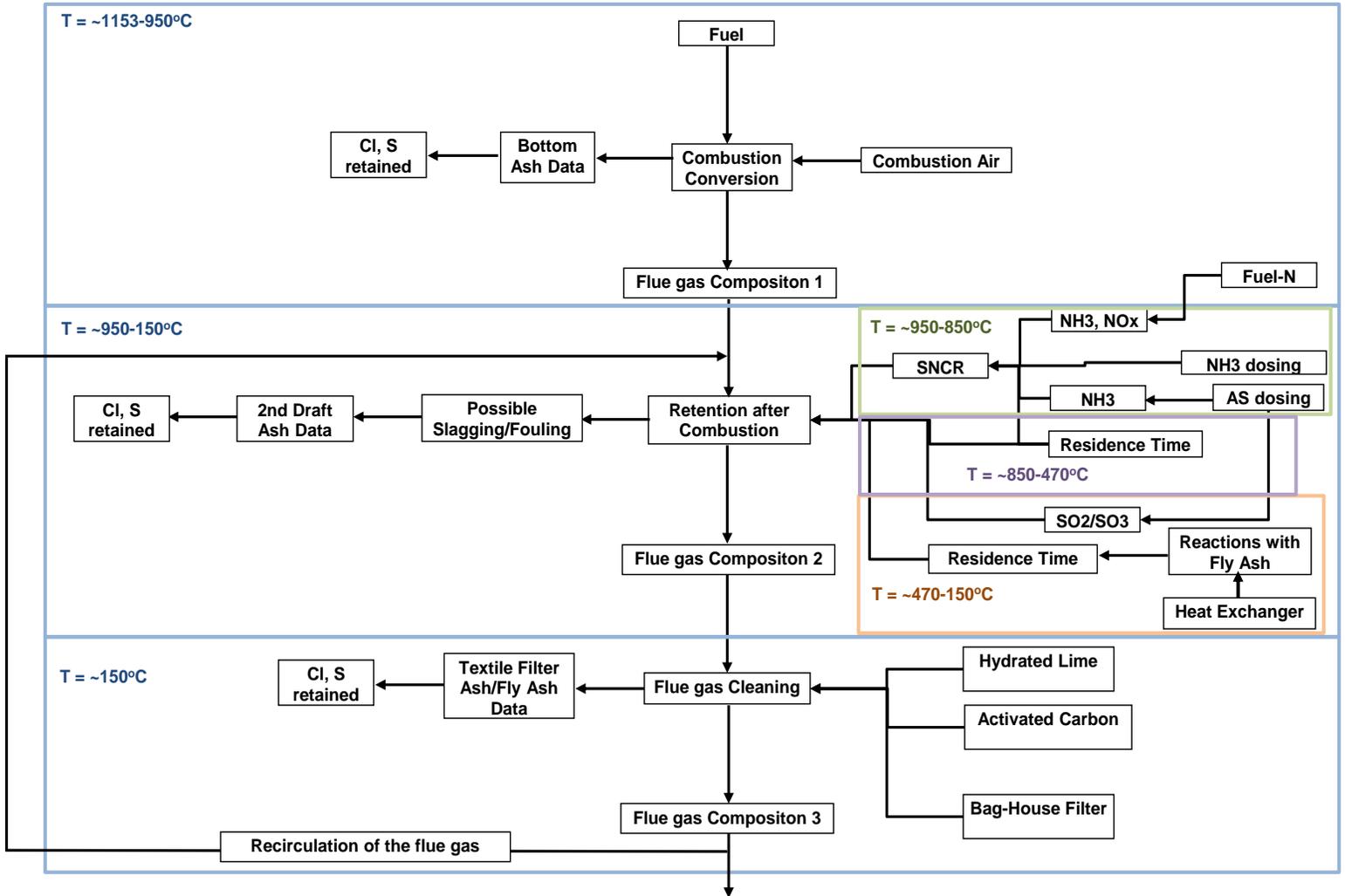
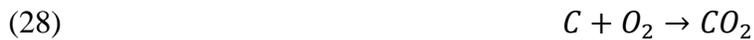


Figure 5: A process diagram of our methodology.

8.1. Estimation of combustion reactions and conversions of fuel-S, fuel-Cl and fuel-N in the furnace.

The temperature of the combustion inside the furnace ranges between 1153-959°C. To calculate the possible combustion reactions and conversions that occur, the fuel's data for high boiler load (65 MW) and the composition of the combustion air will be used. Although the fuel is not always combusted 100% it can be assumed that there is no unburned matter. By speculating that there is 100% conversion of S and Cl to SO₂ and HCl respectively, 1,5% oxidization of SO₂ to SO₃[6] and from the fuel-N that there is ~5%, ~20% and ~75% production of NH₃,

NO_x(where 95% is NO and 5% is NO₂) and N₂ respectively[8], the calculation of the flue gas composition 1 can be initiated. The combustion air is inserted with 1,31 excess air ratio and the air-N can be considered inert. So by using the (1), (2) and (3) reactions that were mentioned in the literature review, the assumptions that were made above, the main combustion reactions are as follows:



(we ignore the production of CO) and any retentions of Cl and S that occurred by the bottom ash, the *flue gas composition 1* can be determined. However, the bottom ash data includes a great amount of sand from the boiler in it so we have to remove the SiO₂ amount to find the right concentration of Cl and S that have been retained.

8.2. Conversion and Retention of S, Cl and N after the furnace.

After the combustion in the furnace, the main conversion and retention processes that take place are the SNCR reactions and the slagging and fouling of the flue gas in the empty draft and on the surface of the heat exchanger. By finding how much of the S, Cl and N has been converted and how much has been retained by the second draft ash (ash/deposits from the empty draft and the heat exchanger), the *flue gas composition 2* is defined.

8.2.1. Calculation of the SNCR process and Deposits in Empty Draft.

The SNCR takes place in top of the furnace and the empty draft at 850-950°C. To calculate how much of NH₃ has been converted from the fuel and chemical dosing the input of these reactions must be known. As was the case before, it can be hypothesized that from the fuel-

N there is ~5%, ~20% and ~75% production of NH_3 , NO_x (where 95% is NO and 5% is NO_2 [4]) and N_2 respectively [8] and that the whole reaction takes place at 900°C . From the plant data, the flow rate and composition of the AS dosing ($F=65$ l/h, 40% v/v AS, 60% v/v water) and NH_3 dosing ($F=43,73$ l/h, 24,5% v/v NH_3 , 75,5% v/v water) are known. By taking into consideration the stoichiometric reaction (20) or (21), it is possible to find how much NH_3 is attributed to the AS dosing. In order to calculate the output it is assumed that ~100% of the NO_x are composed by NO and the equations (4), (6) and (8)-(11) from the literature review can be used to find the yield. After this the flue gas continues through the empty draft where the first reactions with the fly ash occur and the first salts are being deposited at $850-470^\circ\text{C}$. The amount of S and Cl that have interacted with the ash can be found by checking the empty draft ash data.

8.2.2. Reactions with the Fly Ash and Deposits on the surface of the Heat Exchangers.

At $470-150^\circ\text{C}$ in the heat exchanger, possible slagging, fouling, corrosion and reactions with the fly ash particles can occur as well. More significance is given to the retention of the acidic components by the ash rather than to the Cl-corrosion because Cl-corrosion does not alter the mass balance of the acidic components. By using the ash data from the economizer, it is calculated how much of the total S and Cl have been retained. After the above mentioned estimations, the flue gas composition 2 is determined at 150°C .

8.3. Calculations of S, Cl and NH_3 in the Flue gas cleaning.

The temperature here, in contrast to the previous case, does not change significantly so it can be theorized that all reactions happen at 150°C . The flue gas reacts with the activated C and the hydrated lime and passes through the bag-house filter. It is considered that the bag-house

filter efficiency of particulate matter retention is almost 100%. The effects of flue gas cleaning can be estimated by using as an input the flue gas (flue gas composition 2 and mass flow), the dosing of sorbents, the absorption reactions and the fly ash. It can be found, through mass balance, how much S and Cl have reacted with the activated C and hydrated lime and have been retained by the bag-house filter and, also, the *flue gas composition 3*. Furthermore, according to the Ca mass balance, it can be roughly quantified, how much S and Cl have reacted with the hydrated lime. Afterwards by removing this from the total S and Cl retention, the same can be found for the activated carbon. By comparing the flue gas composition 3 with the data from the plant, it can be checked if there are a lot of deviations from the limits of the pollutant emissions. Finally, 56% of the flue gas is recirculated back to the furnace after combustion and the same concept is used.

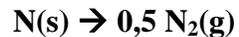
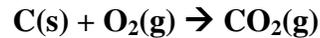
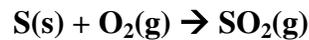
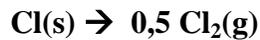
9. Model set-up.

Now that the main concept has been conceived, it must be applied in order to set up a model. The model has been created with the help of Microsoft EXCEL and, like in the concept, it was divided to 3 sub-models. The first is ‘Combustion Conversions’ in which all the combustion reactions in the furnace and the main output from it is the calculation results of the flue gas composition 1 are included; the second is ‘Retentions after Combustion’ where the SNCR reactions are involved and the flue gas composition 2 is estimated while the third one is ‘Flue Gas Cleaning – Quench’ where all the sorbent absorption and flue gas recirculation are taken into account in order to determine the final flue gas composition (flue gas composition 3) which is expected to be low in SO₂, HCl and NH₃. Through this model, an investigation of the behavior, the retention mechanisms and the distribution of the acidic components in the boiler process and

flue gas path will be conducted. Any results shown below represent the average values of fuel-S, fuel and fuel-N. The model developing will be described thoroughly in the sections below.

9.1. 'Combustion Conversions' sub-model.

Based on common boiler operation conditions, the fuel thermal input and the lower heating value of the fuel are used in order to calculate the boiler load and the fuel mass flow. To model the combustion processes it is assumed that there is 100% conversion of fuel-S and fuel-Cl during combustion into the flue gas. The major conversion reactions have been considered as shown below:



As a result, by using the wet percentage of the major components and ash from the fuel data, the stoichiometric amount of O₂ – and afterwards air – that is needed is determined. With the use of λ (excess air ratio), the actual amount of air is calculated.

After combustion, the flue gas and the bottom ash calculations follow. The retention of Cl and S in the bottom ash is estimated by using the mass flow of the bottom ash (obtained by the plant data on ash balance measurement in Table 3) and the bottom ash composition (measured by ash sample analysis). However, it must be taken into consideration that the bottom ash is mixed with the bed material of the combustor (sand). Therefore, it is assumed that 70% of the bottom ash is the whole amount of sand (SiO₂) that has been mixed and as a result it should be removed.

After all these, the amount of Cl and S that are retained from the bottom ash are estimated, in kg/h, and are compared with the total amount of Cl and S that have been produced.

<i>Annual Ash Data</i>	<i>%</i>
<i>Bottom Ash with Sand</i>	
<i>Bottom Ash without Sand</i>	<i>29,0</i>
<i>Empty Draft</i>	<i>9,4</i>
<i>Economizer</i>	<i>3,5</i>
<i>Fly Ash</i>	<i>58,0</i>
<i>Sum</i>	<i>100</i>

Table 3: Annual ash data for the different type of ashes. The mass flow of the bottom ash without sand is calculated by assuming that 70% of the bottom ash with sand is the actual sand that needs to be removed.

For the flue gas composition 1, via stoichiometry as well, the amount of gases that are produced from the combustion of the fuel is determined. During the combustion, it is assumed that 1,5% of SO₂ is further oxidized to SO₃. Then, by adding the real amount of air and considering that the flue gas is ideal, the actual amount of flue gas and its composition is calculated. Moreover, by using the measurement data from the plant, it is found that the fuel-N conversion during combustion is a bit different from the one that was mentioned in the description of the concept. It is assumed and validated that there is 34% production of NO_x, 1% production of NH₃ and 65% production of N₂. The concentrations of the major components in the flue gas are defined in mg/Nm³ (flue gas composition 1).

Although, as the flow diagram shows also, the primary de-NO_x process occurs before the secondary de-NO_x reactions (SNCR), it is calculated together with it in the ‘Retentions after Combustion’ sub-model.

<u>Assumptions</u>		<u>Flue gas composition 1</u>	<u>mg/Nm³ (wet)</u>	<u>mg/Nm³ (dry)</u>
		SO ₂	174,9	206,8
Oxidation of SO ₂ to SO ₃	1,50%	SO ₃	3,33	3,94
NO _x from fuel-N	34%	NO _x	729,2	861,8
Because NO _x are composed		HCl	241,3	285,2
>95% by NO we will ignore NO ₂		CO ₂	250690	296273
NH ₃ from fuel-N	1%	NH ₃	12,15	14,36

<u>Flue gas composition 1:</u>		
(%mol, %v/v)	H ₂ O	15,39
	CO ₂	12,76
	SO ₂	0,0063
	SO ₃	0,000096
	N ₂	67,53
	NO _x	0,054
	NH ₃	0,0016
	O ₂	4,25
	HCl	0,015

Table 4: Flue gas composition after the combustion of the fuel. The major acidic components are shown first, with the assumptions that were made, in mg/Nm³. Then, all components of the flue gas are shown in %mol or %v/v (because it is considered ideal gas). The calculations were made for the average values of fuel-S, fuel-Cl and fuel-N.

9.2. 'Retentions after Combustion' sub-model.

'Retentions after Combustion' refers to the secondary de-NO_x reactions (SNCR) and the retentions of SO₂ and HCl by deposits/ash in empty draft and economizer. Due to the complexity of the SNCR reactions, the de-NO_x is simulated in a general way mainly to account the relation between the NO_x reduction and NH₃ slip.

First, from the plant data, the flow rate of ammonium sulfate (AS) and NH₃ dosing and their concentrations are gathered [AS dosing (F= 65 l/h, 40% v/v AS, 60% v/v water) and NH₃ dosing (F=43,73 l/h, 24,5% v/v NH₃, 75,5% v/v water)]. Because NO_x are composed >95% by NO, the NO₂ which is <5% is ignored. Therefore, from the SNCR reactions that have been mentioned in the Literature Review, only the ones referring to the NO will be taken into

consideration (equations (4) and (6)). To calculate the concentration of NO_x in the flue gas it is assumed that because of the low temperatures which exist in the fluidized beds, only fuel-N gives NO_x and not air-N or prompt-N. On the other hand, the concentration of NH₃ in the flue gas is calculated by the properties of AS and NH₃ dosing. The amount of SO₂ that is produced by the decomposition of AS dosing is also defined and with the concentrations of S and Cl in the flue gas composition 1 the ratio S/Cl in the flue gas is determined. In these temperatures, the SO₃ that come from the decomposition of AS are quite low so it is assumed that there is no production of SO₃ from the AS.

In order to calculate the NO_x emissions after SNCR, the NO_x emissions and NH₃ slip from our data are plotted and a linear trend line with its equation is drawn.

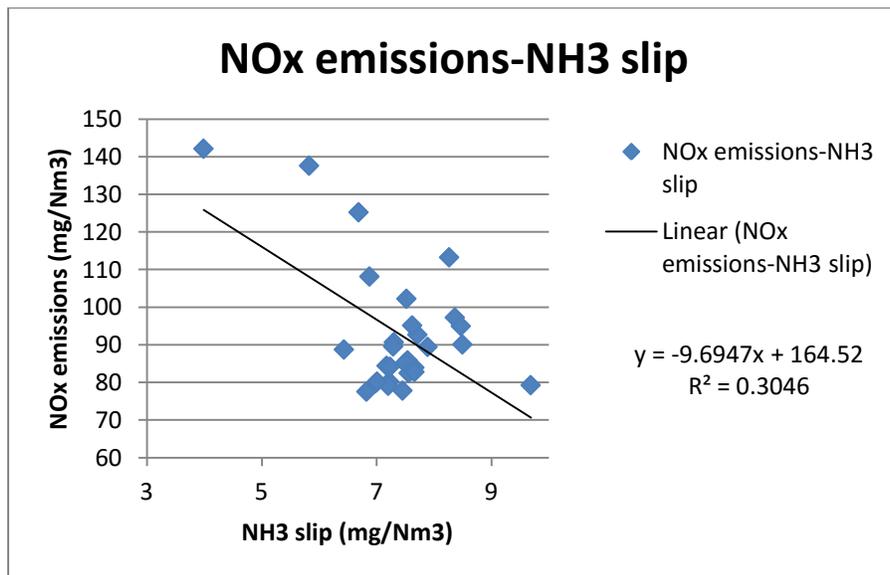


Diagram 2: NO_x emissions correlated with the NH₃ slip (based on operation and testing data for boiler load between 60 – 65 MW and this equation for the linear trend may be better for NH₃ slip range between 4 and 10 mg/Nm³).

By handling the NH₃ slip as an input, the NO_x emissions are calculated through this equation. However, in order for that equation to be valid the values of NH₃ slip must be between 4 and 10 mg/Nm³. It can be noted that, according to the diagram, as NH₃ slip rise the NO_x

emissions are reduced; something which agrees with the literature review [24]. By considering that NH₃ slip after SNCR does not significantly reacts with the acidic components in the flue gas under the operation conditions, the concentration of NH₃ after the SNCR reactions should be roughly equal to the concentration of NH₃ after the flue gas cleaning. Through the NH₃ slip as well as the SNCR reactions and by assuming that there is 92% NO_x reduction and 8% NH₃ oxidation to NO_x under these conditions [24], the amount of NO_x that reacted is determined. Using the above information, the amount of NO_x that remains after the primary de-NO_x process, the total and secondary de-NO_x efficiency and the β ratio are calculated.

After that, the retentions of S and Cl in the deposits and ashes around the empty draft and economizer are defined. The amount of Cl and S that are retained from the empty draft ash and the economizer ash are found in kg/h and they are compared with the total amount of Cl and S that are have been produced. Moreover, the mass flow of these two types of ash is extracted from the previous volumetric flow of the flue gas and a new one is measured. In the end, the flue gas composition 2 is determined. For the SO₃, it is assumed that it reacts in its totality with the flue gas' alkali and alkali earth metals (Ca, Na, K, etc.).

<u>Assumptions</u>	<u>Flue gas composition 2</u>	<u>mg/Nm³ (wet)</u>	<u>mg/Nm³ (dry)</u>
From formula (NH ₄) ₂ SO ₄ , 48% of total AS dosing is SO ₂	SO ₂	316,9	379,9
No SO ₃ remains	SO ₃	0	0
	HCl	240,1	290,7

<u>Flue gas composition 2:</u>		
(%mol, %v/v)		
	H ₂ O	15,39
	CO ₂	12,76
	SO ₂	0,011
	SO ₃	0
	N ₂	67,55
	NO _x	0,0071

NH₃	0,00095
O₂	4,25
HCl	0,015

Table 5: Flue gas composition after the SNCR and the retentions of the acidic components by the deposits/ash around the empty draft and the economizer. The major acidic components are shown first, with the assumptions that were made, in mg/Nm³. Then, all components of the flue gas are shown in %mol or %v/v (because it is considered ideal gas). The sum is not 100% probably due to the assumptions for the flue gas volumetric flow. The calculations were made for the average values of fuel-S, fuel-Cl and fuel-N.

Before the flue gas meets flue gas quencher, it undergoes a flue gas cleaning. There, it encounters some neutralization reactions and particulate removals. By handling the annual ash data (Table 3) or by removing the bottom, empty draft and economizer ash from the total ash, the percentage of fly ash that derives from the total ash and its flow rate are found. Eventually, the hydrated lime mass flow is added to the flow rate of the fly ash. Activated carbon is not taken into consideration because of its low flow rate and its low contribution to the removal of S, Cl and NH₃. Next, the dry and wet volumetric flow rates are being calculated.

Because of the neutralization reactions between hydrated lime and the acidic components, the flue gas cleaning could be simulated in a simple way. Managing the data for the hydrated lime dosing mass flow and SO₂, HCl emissions, two plots are created. One connecting hydrated lime dosing and SO₂ emissions and the other connecting hydrated lime dosing and HCl emissions. Trend lines with their respective equations are drawn for each plot.

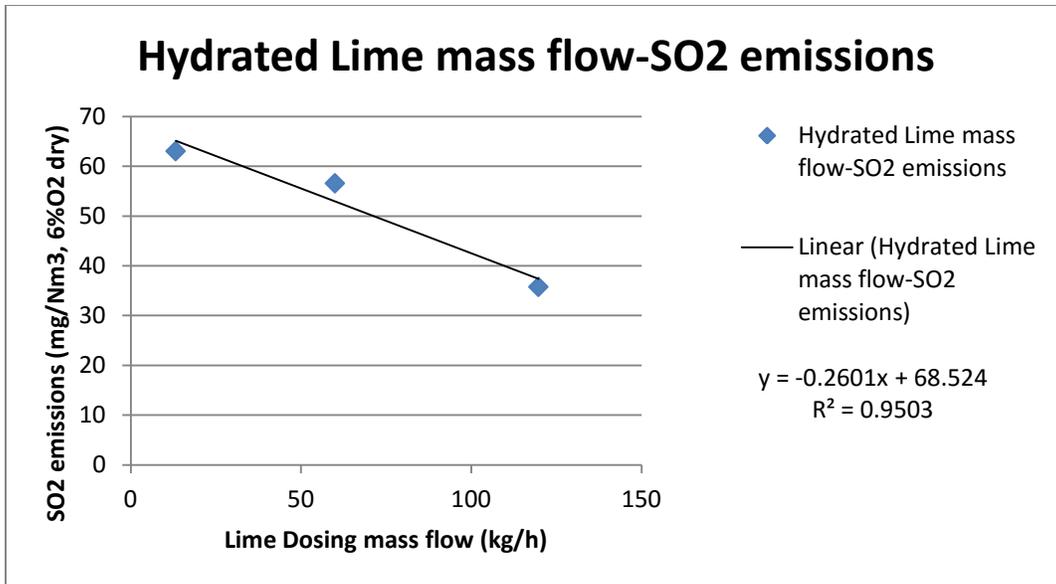


Diagram 3: HCl emissions correlated with the hydrated lime mass flow (based on operation and testing data for boiler load between 60 – 65 MW and this equation for the linear trend may be better for hydrated lime dosing range between 14 and 120 kg/h).

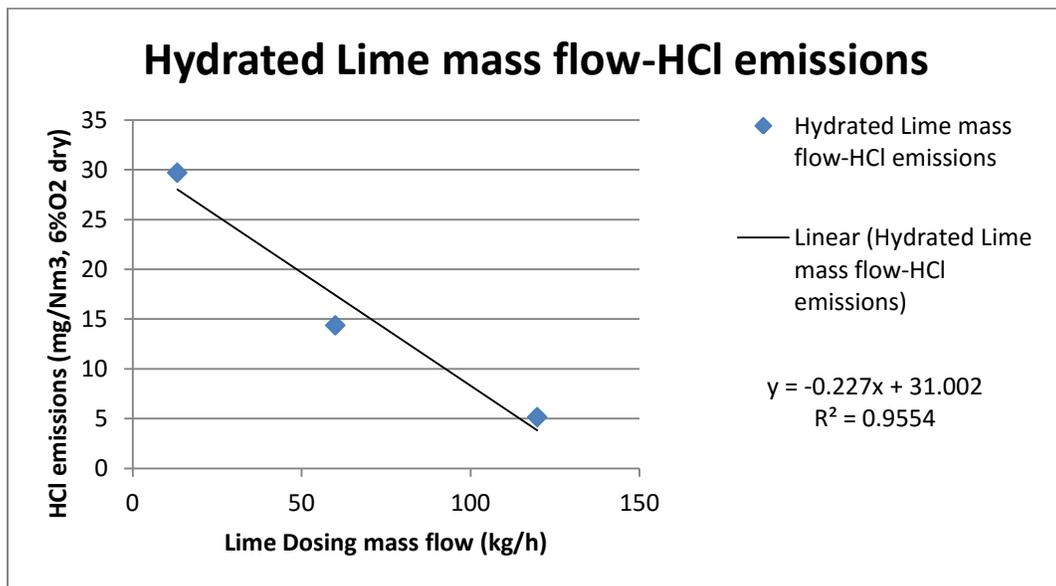


Diagram 4: SO₂ emissions correlated with the hydrated lime mass flow (based on operation and testing data for boiler load between 60 – 65 MW and this equation for the linear trend may be better for hydrated lime dosing range between 14 and 120 kg/h).

By using the hydrated lime mass flow as input the SO₂ and HCl emissions are determined through these equations. The total emissions, including NH₃ and NO_x, are calculated in mg/Nm³, 6% O₂ (dry) and in mg/Nm³ (wet) and the reduction percentage of HCl and SO₂, which is found

by comparing flue gas composition 2 with flue gas composition 3, are measured as well. It is assumed that there is 100% particulate removal from the bag-house filter.

<i>Flue gas composition 3</i>	<i>mg/Nm³, 6%O₂ (dry)</i>	<i>mg/Nm³ (wet)</i>	
SO ₂	42,52	40,21	<i>72,82% reduction of SO₂</i>
SO ₃	0	0	
NO _x	100,4	94,91	
HCl	8,30	7,85	<i>79,90% reduction of HCl</i>
NH ₃	7,59	7,18	

<i>Flue gas composition 3:</i>		
<i>(%mol, %v/v)</i>		
	H₂O	15,39
	CO₂	12,76
	SO₂	0,0014
	SO₃	0
	N₂	67,56
	NO_x	0,0071
	NH₃	0,00095
	O₂	4,25
	HCl	0,00048

Table 6: Flue gas composition after the flue gas cleaning (sorbent injection). The major acidic components and the reduction percentage of SO₂ and HCl are shown first in mg/Nm³. Then, all components of the flue gas are shown in %mol or %v/v (because it is considered ideal gas). The sum is not 100% probably due to the assumptions for the flue gas volumetric flow. The calculations were made for the average values of fuel-S, fuel-Cl and fuel-N.

With the use of a mass balance of SO₂ and HCl before and after flue gas cleaning, the amount of the acidic components that reacted can be found. Utilizing the neutralization reactions with the hydrated lime and these acidic components, the hydrated lime for 100% reaction is measured and compared with the actual amount of hydrated lime that is used. Through this comparison, the ratios Ca/Cl, Ca/S and Ca/(Cl+S), the retention of Cl and S, the theoretical demands and the removal efficiency of hydrated lime are determined.

For the flue gas recirculation in the flue gas quench, average values are assumed for the recirculation rate of the acidic components. 30%, 75% and 75% recirculation rate of the SO₂,

HCl and NH₃ emissions respectively is considered. Due to the low water solubility of the NO_x, it is not taken into consideration.

10. Model Calibration and Validation.

In order for the model to work properly, most of the inputs, the assumptions and sub-models that were used must be validated or calibrated. One way to do so, is via the plant data. To show that the reactions in the 'Combustion Conversions' sub-model are correct, the flue gas volumetric flow rate was compared with the plant data from 2014 to early 2015 for the same boiler load. Mainly, the volumetric flow rate of the flue gas is defined from the combustion of the fuel and the various increases and decreases that take place from the chemical dosing and the ash removal are quite insignificant. So, by using the average fuel composition, the average volumetric flow rate must be calculated through the model and must be similar with the one from the plant data. Another way to validate the 'Combustion Conversions' calculations is to compare some of the flue gas composition. More precisely, H₂O (%v/v) and O₂ (%v/v) are mostly defined from the combustion of the fuel and their concentrations remain quite stable throughout the whole process. The comparison of our results with the plant monitoring data is shown in Table 7.

In Table 7 the comparison of the SO₂, HCl and NO_x that were calculated through a correlation with the hydrated lime and the NH₃ slip with the ones from the plant data can also be seen. It is not expected to have significant differences because both results derive from the data. However, this poses certain limits to the model and, as a result, it cannot be easily used for a different power plant.

<i>Parameters</i>	Modeling Calculations <i>For Boiler Load = 64,12MW</i>	Plant Data <i>For Boiler Load = 60-65MW</i>
Flue Gas Flow Rate (Nm ³ /h (dry))	85873	81902
H ₂ O (%v/v)	15	19
O ₂ (%v/v)	4,2	3,3
SO ₂ emissions (mg/Nm ³ , 6%O ₂ (dry))	42	48
HCl emissions (mg/Nm ³ , 6%O ₂ (dry))	8,3	8,6
NO _x emissions (mg/Nm ³ , 6%O ₂ (dry))	100	106

Table 7: Model validation with monitoring data under boiler loads between 60-65 MW. The volumetric flue gas flow rate and the concentration of H₂O, O₂, SO₂, HCl and NO_x was found by taking the average from the plant data and it was compared with our modeling calculation. The comparison is good with small differences as was expected.

Moreover, the ash composition data that was obtained, was not sufficient enough and it was calibrated with the annual data, as it has been referred to the model set-up. The ash distribution and the different retentions of S and Cl were in accordance with the literature review.

Furthermore, another thing that was calibrated in order to get correct results was the percentage of fuel-N that converts to NO_x, NH₃ and N₂. With the plant data for the NH₃ emissions (which are consider the same with the NH₃ slip) and for the NO_x emissions, the percentage of fuel-N that converts to NO_x, NH₃ and N₂ was found by using the SNCR reactions backwards.

In the end, so as to validate the whole simulation, a S and Cl mass balance was calculated. In order for the model to be correct, the difference between the input and the output of the two mass balances when compared with the input, must be close to zero. For S, the input is the fuel-S and the AS dosing while the output is the different ash retentions of S, the SO₂ emissions and the SO₃ consumption that occurs in the 'Retentions after Combustion' sub-model. For Cl, the input is the fuel-Cl while the output is the different ash retentions of Cl and the HCl emissions. The mass balances are presented below.

Mass balances:

S (mg/h)

$$\text{Fuel}_S + \text{AS}_S = \text{Bottom Ash}_S + \text{Empty Draft}_S + \text{Economizer}_S + \text{Fly Ash}_S + \text{Emissions}_S + \text{SO}_3 \text{ Consumption}$$

$$17071065.12 = 16924302.63$$

$$\text{Difference} = 146762.4845$$

$$\text{Compare to Total Input} = 0.86\%$$

Cl (mg/h)

$$\text{Fuel}_{Cl} = \text{Bottom Ash}_{Cl} + \text{Empty Draft}_{Cl} + \text{Economizer}_{Cl} + \text{Fly Ash}_{Cl} + \text{Emissions}_{Cl}$$

$$24638450.31 = 24398081.1$$

$$\text{Difference} = 240369.2132$$

$$\text{Compare to Total Input} = 0.97\%$$

CHAPTER IV: Impact Evaluation

11. Purpose.

The necessity for conducting an impact evaluation is to know how pollutants formation and flue gas cleaning will be affected by important factors. The impact evaluation is performed by the simulations using the model that has been set-up and described in the methodology section. The changes in pollutant formation and effects of flue gas cleaning are corresponding to the variations of input parameters in the simulations. Moreover, impact evaluation can predict the problems that can arise when the inputs are altered within logical limits. As a result, different precautions can be used in order to resolve these problems when they emerge.

In the impact evaluation, the main input parameters are fuel compositions focusing on fuel-S, fuel-Cl and fuel-N and chemical dosing for protection of high temperature corrosion and flue gas cleaning. The outputs at interest are the SO_x, NO_x and HCl concentration in the flue gas, the efficiency of the different retentions in each part of the process and the possibility of corrosion in the furnace; while the fuel quality, the chemical dosing and the recirculation rate of the flue gas are also considered as main inputs. By using the model and simulation results, the corresponding impacts are demonstrated and evaluated in the following sections.

12. Impacts of fuel quality.

The fuel, recycled wood, does not have a standard composition but it varies with their resources in certain range. Depending on the present contamination level, the fuel quality has different impacts on the whole boiler process. As a result, the various impacts of the fuel quality must be defined based on critical components from emission control point of view. The most

concerned fuel components that mostly concerns us are the fuel-S, fuel-Cl, fuel-N and fuel-ash. Fuel-S and fuel-Cl affects the concentration of SO₂ and HCl in the flue gas respectively, the ratio S/Cl (the total amount of S/the amount of fuel-Cl) which affect Cl-corrosion in the furnace and the ratio Ca/(S+Cl) which indicates the efficiency of flue gas cleaning using hydrated lime. In recycled wood fuels, the percentage of S in the fuel is often less than the percentage of Cl, therefore it is expected that fuel-Cl will have more impacts compared to fuel-S. Fuel-N influences the consideration of de-NO_x measures with relatively large impacts on the SNCR process for existing boiler while fuel-ash affects the retentions of S and Cl in the furnace and flue gas path.

In order to show the impacts of the fuel quality better, three different cases were studied. In the first case, the average values of fuel-S, fuel-Cl and fuel-N (0.0487%, 0.1285% and 1.067%) were used, while in the second and the third case the maximum values (0.089%, 0.7% and 1.84%) and the minimum values (0.021%, 0.03% and 0.41%) were used respectively. It is important to show the flue gas composition after combustion (flue gas composition 1) and before flue gas cleaning (flue gas composition 2) in order to evaluate the conversion and retention mechanisms of the acidic components that take place in the furnace so that the right amount of hydrated lime can be used. The main results that the model generated for each case are presented in Table 8.

Fuel data	Units	Case 1	Case 2	Case 3
Fuel input	kg/s	5.325	5.325	5.325
	MW	70	70	70
Boiler load	MW	64.12	64.12	64.12
Fuel properties				
Lower Heating Value	MJ/kg (wt)	13.15	13.145	13.145
C	wt% (wet)	36.53	36.00	36.53
O		31.00	31.00	31.00

H		4.80	4.80	4.80
<i>S</i>		<i>0.05</i>	<i>0.09</i>	<i>0.02</i>
<i>Cl</i>		<i>0.13</i>	<i>0.70</i>	<i>0.03</i>
<i>N</i>		<i>1.07</i>	<i>1.84</i>	<i>0.41</i>
H ₂ O		23.35	23.35	23.35
Ash		3.12	3.12	3.12
Total	wt% (wet)	100.05	100.90	99.26
Flue gas composition 1				
Flue gas flow rate	Nm ³ (wet)/h	101509	101711	101377
	Nm ³ (dry)/h	85891	86128	85754
H ₂ O	mol%	15.385	15.321	15.411
CO ₂		12.762	12.737	12.779
SO ₂		0.006	0.011	0.003
SO ₃		0.000	0.000	0.000
N ₂		67.527	67.494	67.533
NO _x		0.054	0.094	0.021
NH ₃		0.002	0.003	0.001
O ₂		4.247	4.257	4.249
HCl		0.015	0.083	0.004
<i>Sum</i>			100	100
SO ₂	mg/Nm ³ (wet)	175	323	73
NO _x		729	1255	280
HCl		241	1338	52
NH ₃		12	21	5
Flue gas composition 2				
Flue gas flow rate	Nm ³ (wet)/h	101509	101711	101377
	Nm ³ (dry)/h	85891	86128	85754
H ₂ O	mol%	15.386	15.322	15.412
CO ₂		12.762	12.737	12.779
SO ₂		0.011	0.016	0.008
SO ₃		0.000	0.000	0.000
N ₂		67.548	67.515	67.553
NO _x		0.007	0.007	0.007
NH ₃		0.001	0.001	0.001
O ₂		4.247	4.257	4.249
HCl		0.015	0.082	0.003
<i>Sum</i>			100	100
SO ₂	mg/Nm ³ (wet)	317	464	215
NO _x		95	95	95
HCl		240	1337	51
NH ₃		7	7	7

Table 8: Results presentation for each case. In the second case the amount of HCl in the flue gas is practically the dominant pollutant.

12.1. Fuel-S.

By increasing the percentage of S in the fuel there will be an increase in SO₂ concentration in the flue gas, However, due to the retentions that take place, the amount of this increase is not 1:1 proportional. Additionally, the formation of SO₂ in the boiler is not only from the biomass combustion but also due to the decomposing ammonium sulphate (AS, using for high temperature corrosion protection). In Diagram 5, the SO₂ concentration increase, at the flue gas before the flue gas cleaning process, can be shown for AS dosing fixed at 65 l/h which is an average value.

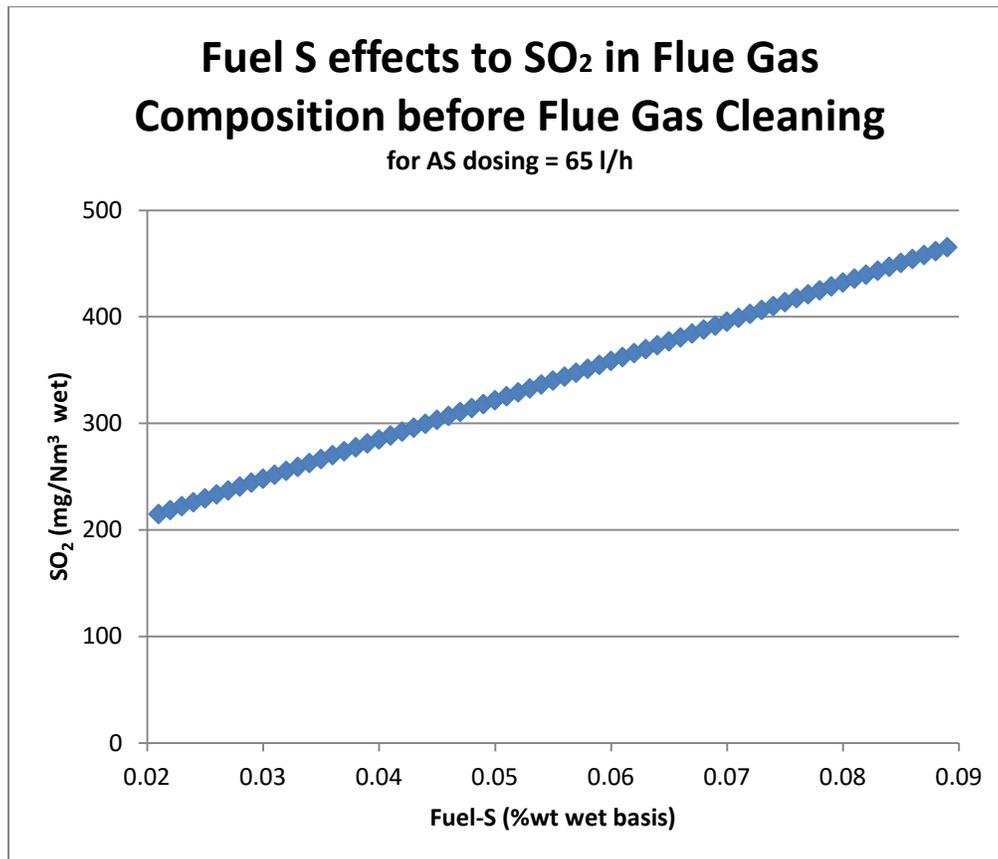


Diagram 5: Impacts of fuel-S to the concentration of SO₂ in the flue gas before the flue gas cleaning process for AS dosing at 65 l/h and high boiler load (65MW). The increase of SO₂ is proportional with the increase of fuel-S reaching a maximum of ~480 mg/Nm³ of SO₂.

Furthermore, as it was mentioned, the fuel-S is not the only source of SO₂ emissions, but rather when AS is decomposed, some amounts of SO₂ are produced as well. In Diagram 6, the discrepancies of the ratio [SO₂ produced from fuel-S/total SO₂ (fuel-S+AS-s)] according to the percentage of fuel-S are shown for AS dosing at its average value. When the ratio is above 0.5 it means that fuel-S produce more SO₂ than AS whereas when it is below 0.5 it means the AS decomposing provides more SO₂ than fuel combustion. The red lines shows when the ratio is equal to 0.5 which indicates that same amount of SO₂ is produced by fuel-S and AS.

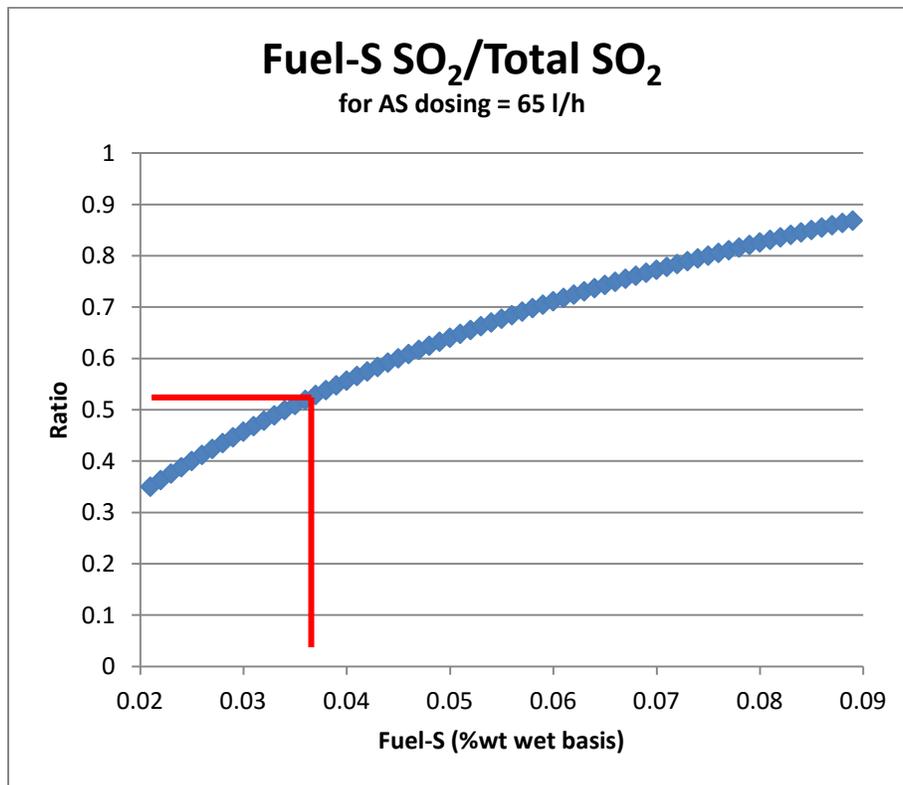


Diagram 6: Comparison of the SO₂ that are produced from the fuel-S with the total SO₂ that is produced for AS dosing at 65 l/h and high boiler load (65MW). Because only fuel-S and AS produce SO₂, when the ratio is above 0,5 it means that fuel-S produce more SO₂ than AS while when it is below 0,5 it means the opposite. For ~0.035% weight wet basis fuel-S the ratio is 0,5 which means that they produce the same amount.

The point where the same amount of SO₂ is produced from fuel-S and AS dosing is at 0.035% weight percentage of fuel-S. This means that on case 3, where the value of fuel-S was considered 0.02%, AS dosing produces more SO₂. This can also be found by comparing the

concentration of SO₂ in flue gas composition 2 with the one in flue gas composition 3 where the SO₂ from AS dosing is included.

Sulfur also helps against the corrosion that happens due to Cl. When Cl concentration is higher compared to S, the likelihood for severe corrosion and more substantial amounts of deposits is high. In Diagram 7, fuel-S is correlated with the S/Cl ratio and compared with the fuel-Cl from the three cases for AS fixed at 65 l/h.

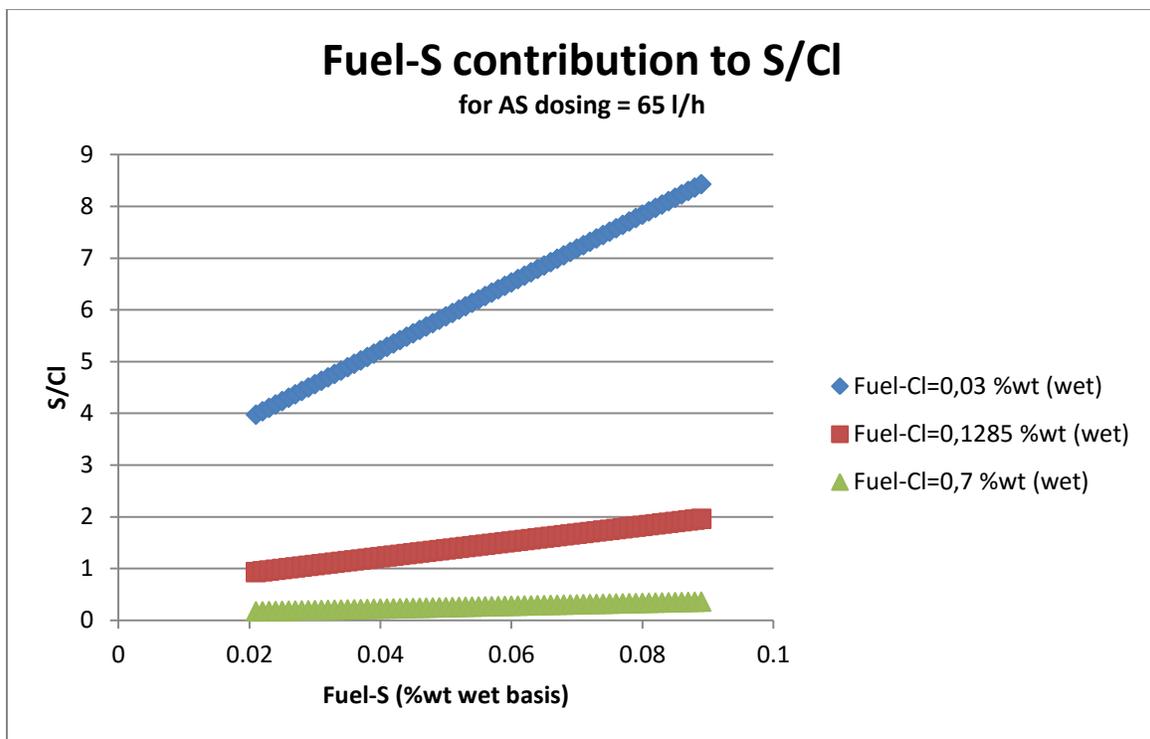


Diagram 7: Fuel-S contribution to the S/Cl ratio for AS dosing at 65 l/h, different values of fuel-Cl and high boiler load (65MW). The results are quite different. For the highest percentage of fuel-Cl, the ratio stays below 1 in all of fuel-S values while for the lowest fuel-Cl percentage, the S/Cl varies from 4 to 8,5. For the average value of fuel-Cl, the ratio S/Cl is between 1 to 2.

It becomes apparent that when fuel-Cl is at 0.7% (like is case 2), fuel-S cannot influence the S/Cl ratio almost at all. As the fuel-Cl acquires lower values, the S/Cl ratio is easily influenced when the fuel-S changes.

Finally, in order to see the fuel-S impacts on the flue gas cleaning efficiency, it is compared with the removal efficiency of hydrated lime (because activated C was not taken into consideration due to its low flow rate and low SO₂ and HCl removal efficiency). In Diagram 8, fuel-S is compared with the theoretical demands of hydrated lime, actual hydrated lime dosing and the flue gas cleaning efficiency (removal efficiency of acidic gas components) under fixed-Cl and hydrated lime dosing. In Diagram 9, the changes of Ca/(S+Cl) ratio are correlated to the variation of fuel-S. This is another way to measure the utilization efficiency of the hydrated lime. The theoretical demands are calculated by dividing the amount of lime that is needed for the stoichiometric reaction of Ca(OH)₂ with SO₂ and HCl, with the hydrated lime that is actually used. On the other hand, the flue gas cleaning efficiency is measured by dividing the difference in the concentration of the acidic components before and after flue gas cleaning with the concentration of the acidic components before flue gas cleaning. The ratio Ca/(S+Cl) measures the amount of hydrated lime that is used flue gas cleaning in comparison with the theoretical demands to neutralize the SO₂ and HCl in the flue gas. In practice, a ratio (Ca/(S+Cl)) of 1.2 is normally required for flue gas cleaning in order to achieve an effective removal of the acidic components.

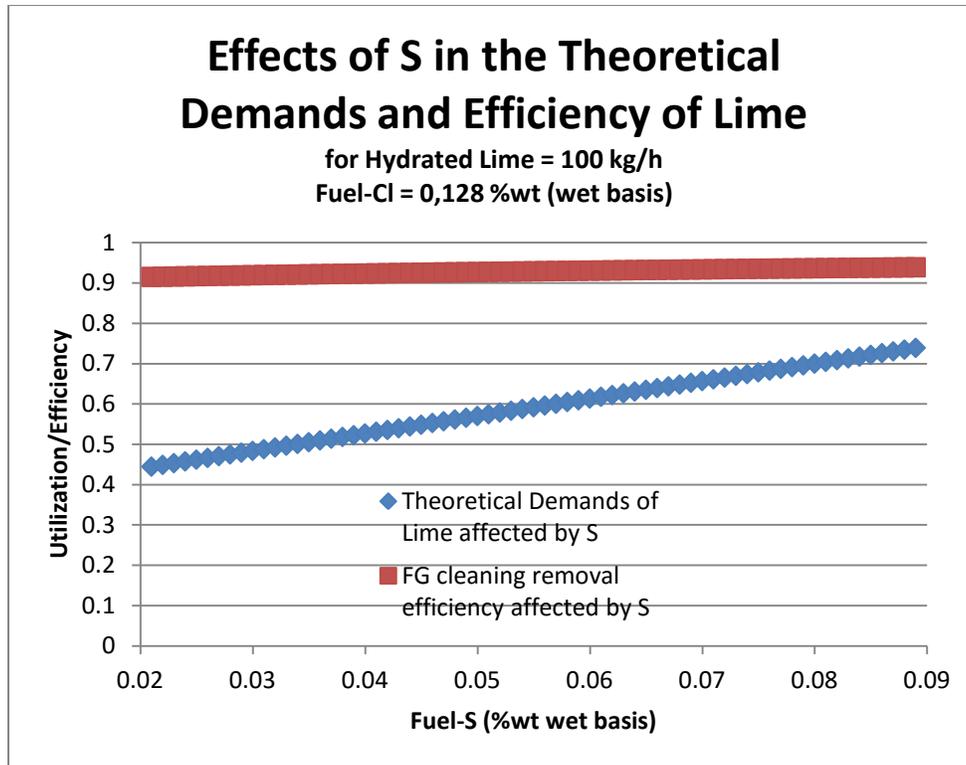


Diagram 8: Effects of S in the theoretical demands and efficiency of hydrated lime for hydrated lime flow at 100 kg/h and fuel-Cl at 0,128% wt (wet basis), which are the values from case 1, and high boiler load (65MW). The removal efficiency stays almost stable at 0,9 while the theoretical demands vary from 0,45 to 0,75.

As the fuel-S rises, the theoretical demands escalate to 0,7 while the flue gas removal efficiency remains almost stable at 0,9. This means that for all the values of fuel-S and the average value of fuel-Cl (case 1), the mass flow rate of hydrated lime (100 kg/h) is acceptable for the sufficient removal of the acidic components from the flue gas. This can also be validated in Diagram 9.

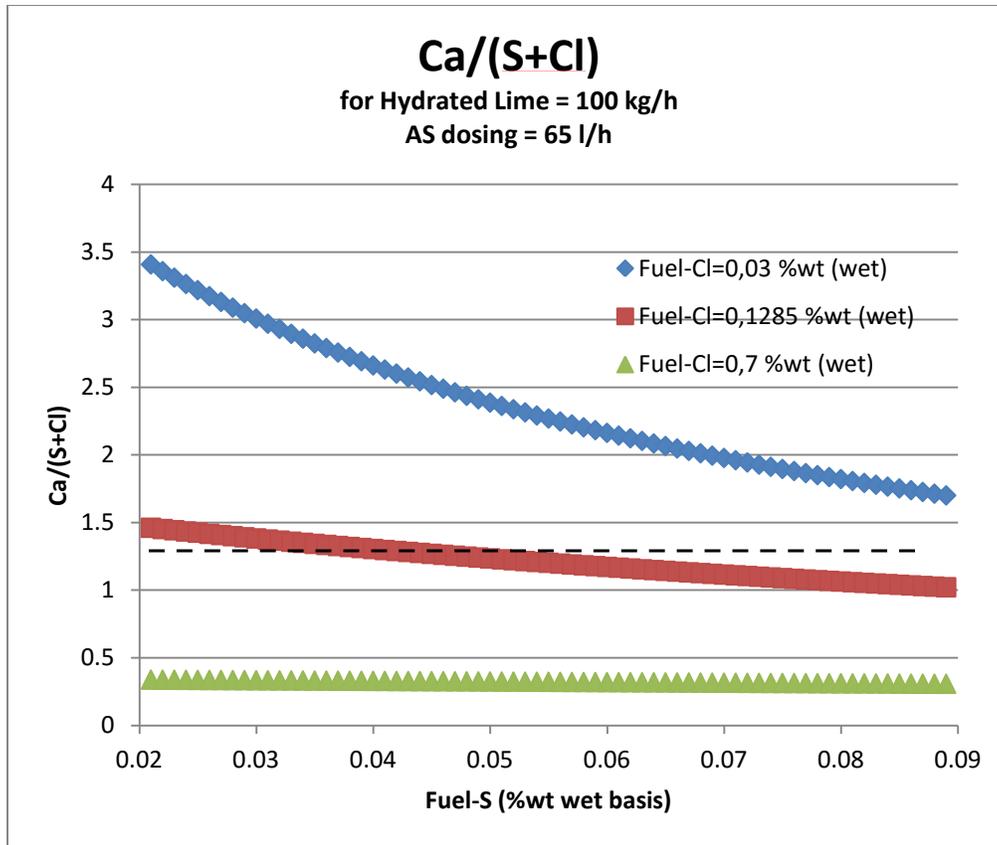


Diagram 9: Contribution of fuel-S to the Ca/(S+Cl) ratio for AS dosing at 65 l/h, hydrated lime flow at 100 kg/h, different values of fuel-Cl and high boiler load (65MW). For the highest percentage of fuel-Cl, the ratio stays below 1 in all of fuel-S values while for the lowest fuel-Cl percentage, the Ca/(S+Cl) varies from 3,5 to 1,75. For the average value of fuel-Cl, the ratio Ca/(S+Cl) is between 1,5 to 1. The black line shows the optimum value of Ca/(S+Cl) ratio which is 1,2.

Like the S/Cl, when the fuel-Cl is at its maximum (case 2), the fuel-S does not influences almost at all the Ca/(S+Cl) ratio while for its minimum value it changes drastically. Moreover, for the highest value of fuel-Cl the ratio is below 1 which means that more hydrated lime is required. For the lowest value of fuel-Cl (case 3), though, the ratio is between 3,5 to 1,75 which means that a lot of hydrated lime is not needed. However, for the average value of fuel-Cl (case 1), the Ca/(S+Cl) ratio varies from 1,5 to 1 which confirms the results from Diagram 8.

12.2. Fuel-Cl.

Fuel-Cl can affect the S/Cl ratio for corrosion protection, the HCl emissions and the flue gas cleaning using hydrated lime. It should be noticed that the range of fuel-Cl in recycled wood chips is from 0.03% to 0.7%, which is considerable larger than the range of fuel-S. Therefore, bigger impacts of fuel-Cl are expected in the combustion of the recycled wood.

Unlike fuel-S, fuel-Cl is the only input of Cl in the whole process. The formation of HCl in the combustion of the recycled wood, depends only on the percentage of Cl in the fuel. Although, it is assumed that there is 100% conversion of fuel-Cl to HCl, the rise in HCl emissions as fuel-Cl increases is not exactly 1:1 proportional due to the different retentions reactions that take place in the whole process (mostly from the interaction with ash). In Diagram 10, this rise of HCl in the flue gas, before the flue gas cleaning process, can be observed for different values of fuel-Cl.

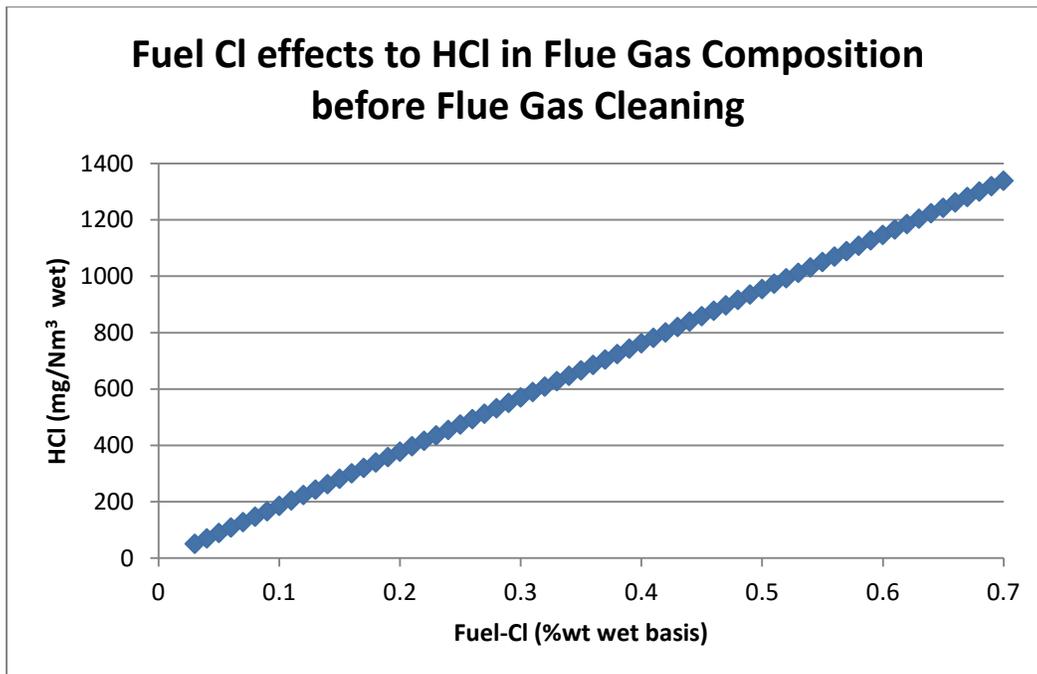


Diagram 10: Impacts of fuel-Cl to the concentration of HCl in the flue gas before the flue gas cleaning process for high boiler load (65MW). The increase of HCl is proportional with the increase of fuel-Cl reaching a maximum of ~1400 mg/Nm³ of HCl. The range of fuel-Cl is from 0.03% till 0.7% which is higher than the range of fuel-S.

As it has been mentioned before, Cl is very corrosive to the metal surface of heat exchangers, for example the super heat exchangers over the furnace. To protect the high temperature corrosion, the ratio of fuel-S to fuel-Cl should be kept in certain value by dosing ammonium sulphate if the fuel-Cl is too high. Diagram 11 shows the impacts of fuel-Cl on the S/Cl ratio and fuel-Cl, under the conditions of three levels of fuel-S and fixed AS dosing.

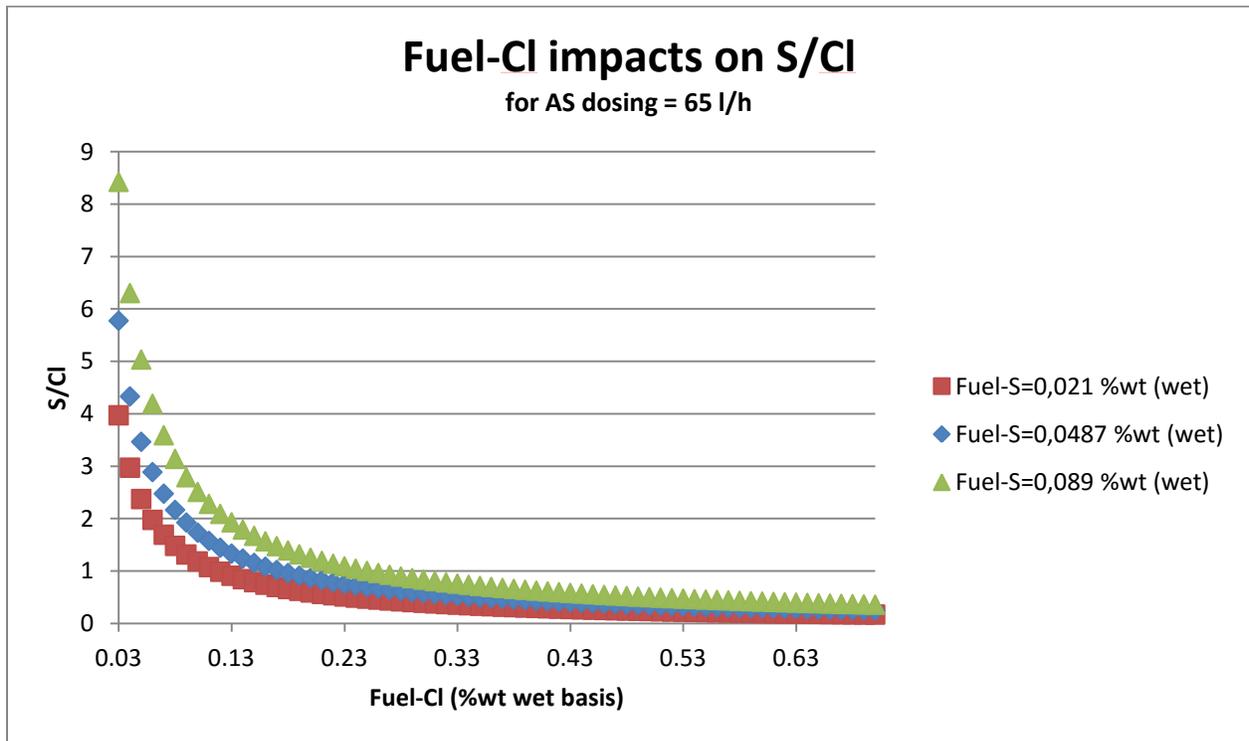


Diagram 11: Fuel-Cl impacts to the S/Cl ratio for the lowest, average and highest values of fuel-S and for high boiler load (65MW). For all the values of fuel-S, after one point, fuel-Cl lowers the S/Cl ratio below 1. For lower values of fuel-Cl, the fuel-S impacts are easier to observe.

This diagram shows that fuel-Cl has significant influence over the S/Cl ratio. When the fuel-Cl is at its maximum value (case 2) the ratio is below one, while for the its minimum value (case 3) the ratio remains is greatly above one.

Finally, for the fuel-Cl impacts on the flue gas cleaning efficiency, similar diagrams as impacts from fuel-S, are plotted in Diagram 12 and Diagram 13. Diagram 12 shows the impacts

of fuel-Cl on lime utilization under fixed hydrated lime dosing rate (100 kg/h). The theoretical demands of hydrated lime for various fuel-Cl contents are also shown in Diagram 12. Diagram 13 shows how the Ca/(S+Cl) ratio is affected by the variation of fuel-Cl under fixed hydrated lime dosing rate.

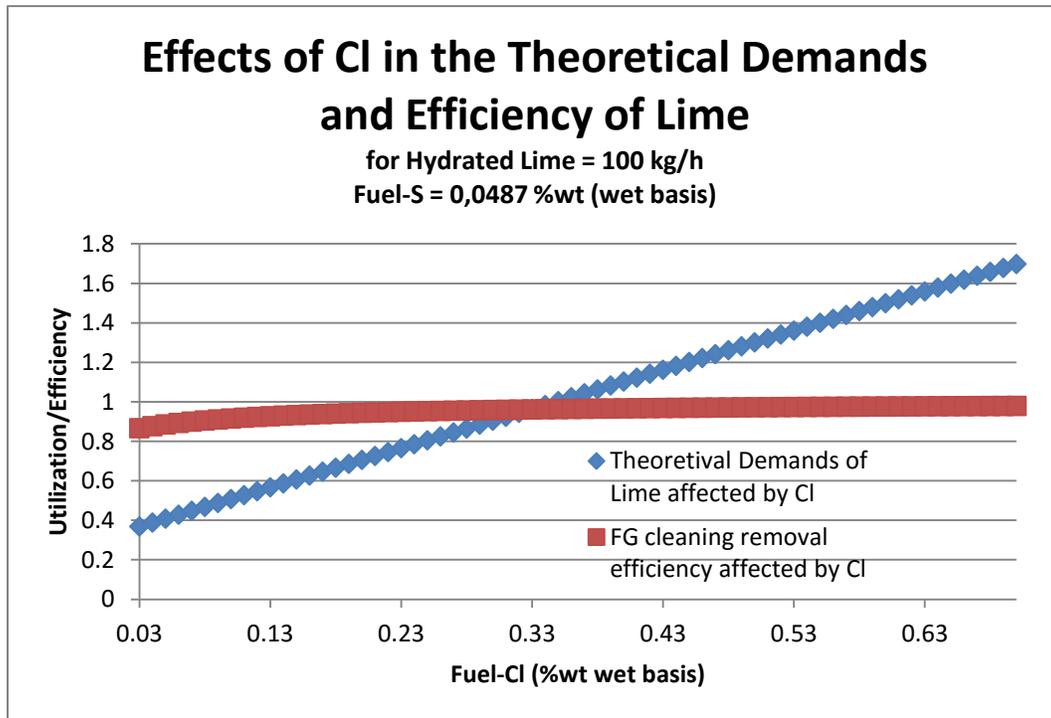


Diagram 12: Effects of Cl in the theoretical demands and efficiency of hydrated lime for hydrated lime flow at 100 kg/h and fuel-S at 0,0487%wt (wet basis), which are the average values and high boiler load (65MW). The removal efficiency rises from 0,8 to 1. After 0.33% of fuel-Cl, the theoretical demands take values above 1. This is not reasonable and it means that more hydrated lime is needed for a sufficient removal of the acidic components.

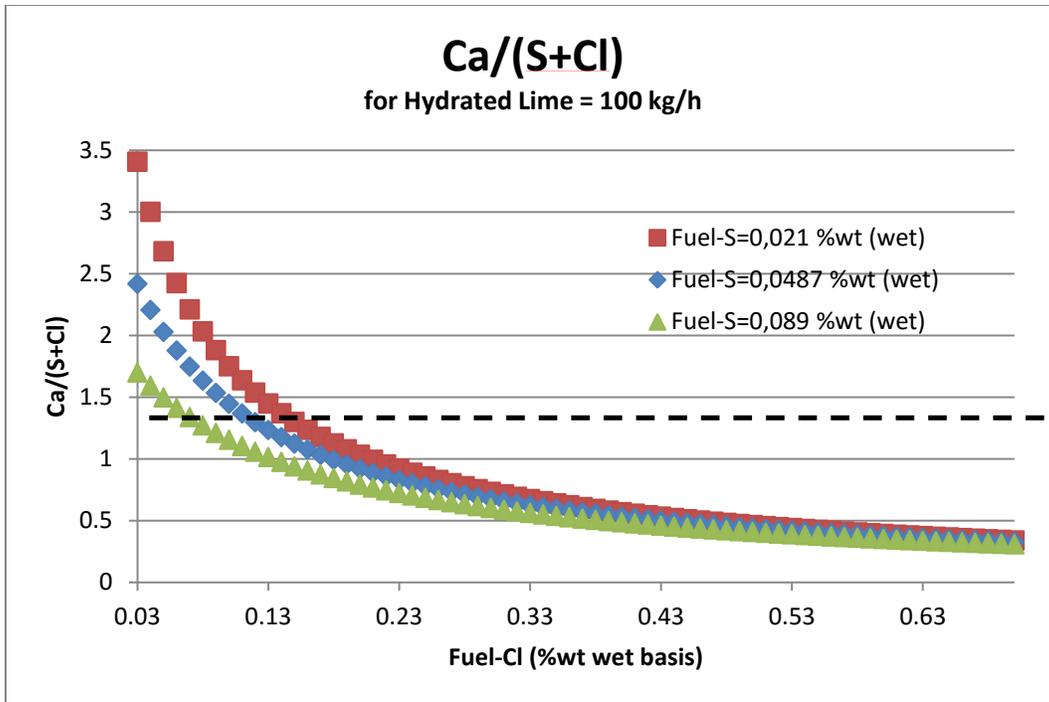


Diagram 13: Contribution of fuel-Cl to the Ca/(S+Cl) ratio for hydrated lime flow at 100 kg/h, which is the average value, and high boiler load (65MW). For all the values of fuel-S, after one point, fuel-Cl lowers the Ca/(S+Cl) ratio below 1. For lower values of fuel-Cl, the fuel-S impacts are more dominant. The black line shows the optimum value of Ca/(S+Cl) ratio which is 1,2.

In Diagram 12, the utilization of hydrated lime increases with rising in fuel-Cl under fixed lime dosing rate. However, after a certain value of fuel-Cl the theoretical demands of hydrated lime are above 1 which is something not reasonable. This can only mean that in case 2, more hydrated lime is needed for a sufficient removal. In Diagram 13, it is shown that the Ca/(S+Cl) ratio is close to 1,2 when the fuel-Cl is in its average value (case 1: fuel-Cl=0,13 and fuel-S=0,05) and larger than 3 when fuel-Cl is at its minimum value (case 3: fuel-Cl=0,03 and fuel-S=0,02). For the maximum value of fuel-Cl (case 2: fuel-Cl=0,7 and fuel-S=0,09), the ratio goes below 0,5 which indicates the hydrated dosing level of 100 kg/h is far more not enough to react with the amount of acidic gases.

12.3. Fuel-N.

The percentage of N in the fuel affects NO_x formation in combustion and corresponding NO_x reduction measures such as primary and secondary de-NO_x processes. In this study the secondary de-NO_x-SNCR reactions, NO_x emissions and NH₃ slip have been evaluated for combustion of recycled wood with a simplified primary de-NO_x assumption. Because NO_x emissions and NH₃ slip are mostly connected with the secondary and primary de-NO_x, they are mainly affected by fuel-N and boiler operation conditions. We assume a normal boiler operation condition and fuel-N dependence of NO_x formation after the primary de-NO_x and then consider the secondary de-NO_x to be the final NO_x emission control process..

In Diagram 14, the impacts of fuel-N with the total and secondary de-NO_x efficiency are shown for the average values of NH₃ dosing, AS dosing and NH₃ slip.

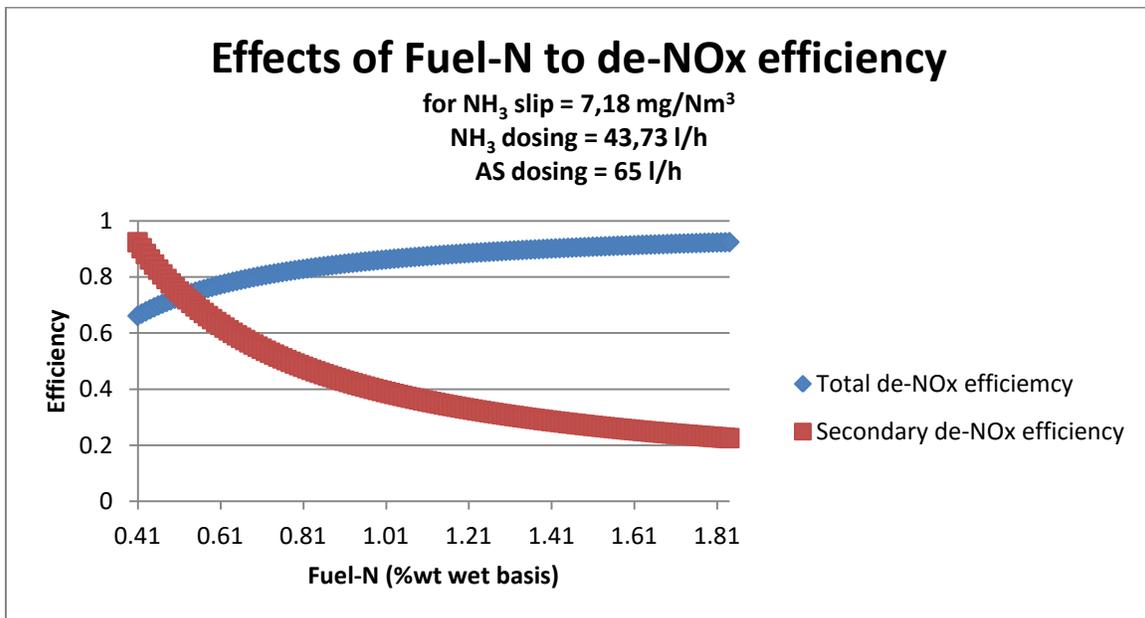


Diagram 14: Effects of fuel-N to total and secondary de-NO_x efficiency for NH₃ dosing, AS dosing and NH₃ slip at their average values. For low fuel-N, the secondary de-NO_x efficiency is higher than the total de-NO_x efficiency, something which is not reasonable. This means that there is either too much NH₃ or too less NO_x.

As fuel-N rises, the formation of NO_x increases in the biomass combustion. This requires an increase in the total de- NO_x efficiency if a certain level of NO_x emission is to be maintained. At the same time, if the NH_3 slip should also be controlled in an accepted level, the efficiency of secondary de- NO_x , i.e. SNCR will be decreased although the absolute NO_x reduction is increased in the SNCR process. As shown in Diagram 14, the total de- NO_x increases with fuel-N rising if the NO_x emission should be kept in an acceptable level. The amount of NO_x after the primary de- NO_x should normally be increased with fuel-N as well. Therefore more NO_x should be reduced by the secondary de- NO_x , SNCR. However, the de- NO_x efficiency by the SNCR could be decreased in comparison with combustion of low fuel-N biomass if an increase of NH_3 slip is not allowed. The simulation results imply that control of NO_x emissions must effectively combine the primary de- NO_x with the secondary de- NO_x measures especially for the combustion of biomass that contains higher fuel-N.

12.4. Fuel-ash.

The ash that the fuel produces after its combustion, is divided to bottom ash, empty draft ash, economizer ash and fly ash. These kinds of ashes play a significant role in the retention of the acidic components, especially S and Cl. The highest retention of acidic components in the boiler occurs in the fly ash and is associated with the hydrated lime in the flue gas cleaning. The other types of ash retention are going to be examined as well. The overall ash retention of acidic gas components highly depends on fuel ash contents and ash properties. For certain type of biomass, e.g. recycled wood, the ash contents in the fuel are important to account for the ash retention capability. In this section, the ash retention of sulphur and chlorine by bottom, empty draft and economizer ashes is evaluated based on the variations of fuel-ash contents as shown in

Diagram 15. The retention behavior of fly ash will be addressed together with the flue gas cleaning using hydrated lime.

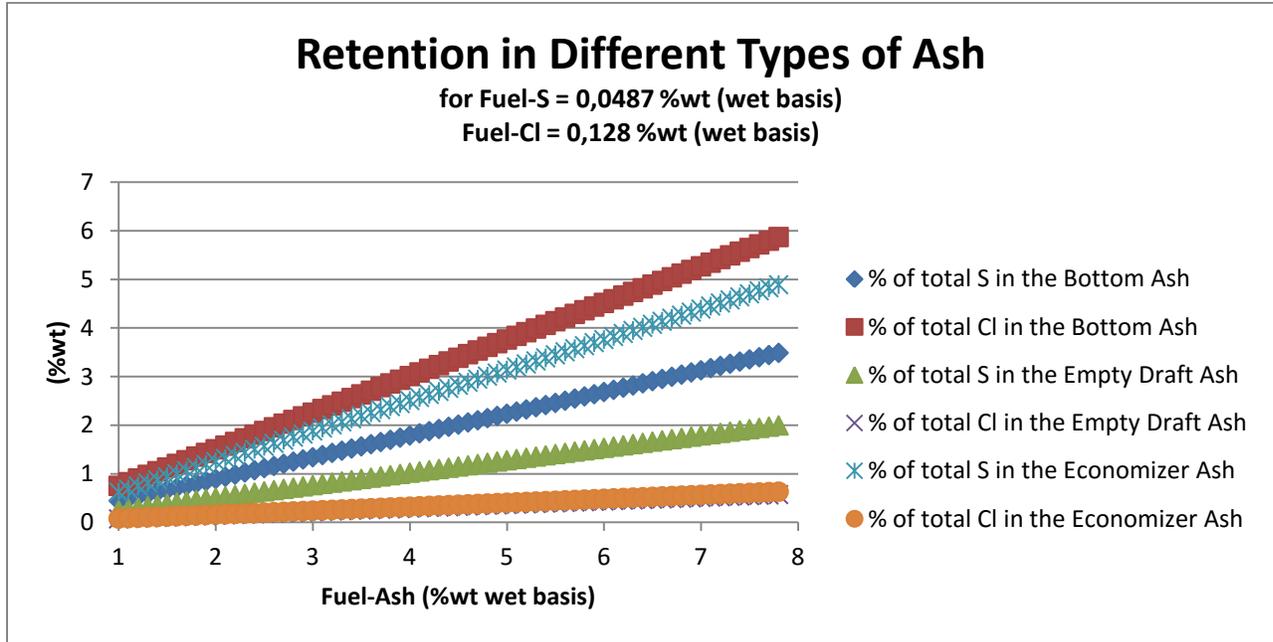


Diagram 15: Impacts of fuel-ash to the retention of S and Cl in the different types of ashes, for the average values of fuel-S and fuel-Cl. The highest retention of Cl occurs in the bottom ash and the lowest in the empty draft ash. The highest retention of S occurs in the economizer ash while the lowest in the empty draft ash as well.

It seems that: (1) the retention of Cl by bottom ash is relatively higher in comparison with empty draft and economizer ashes, (2) more S retention has been achieved by the economizer ash, and (3) only less than 7% of S and Cl has been captured by the bottom, empty draft and economizer ashes. The majority retention of S and Cl (> 90%) is carried out by the interactions with the fly ashes and hydrated lime.

13. Impacts of chemical dosing.

The phrase 'chemical dosing' refers to the ammonium sulfate (AS) dosing, ammonia (NH₃) dosing and hydrated lime (Ca(OH)₂) injection. The purposes of the chemical dosing are the protection of high temperature corrosion (AS), the NO_x reduction (NH₃) and the acidic gas

components retention ($\text{Ca}(\text{OH})_2$). The chemical dosing should properly be performed during boiler operation, otherwise, their excessive use may have side effects. AS dosing contributes to SO_2 and NH_3 into flue gas. Although SO_2 could replace Cl to protect high temperature corrosion, it also contributes to SO_2 emission. The NH_3 decomposed from the AS could be used as reagent in SNCR. However it could become NH_3 slip if it is not effectively reacted with NO_x . In case studies, AS dosing varies from 18 l/h to 94 l/h with an average value of 65 l/h, NH_3 dosing takes values from 25 l/h to 115 l/h with 43.73 l/h being its average value while hydrated lime injection is from 50 kg/h to 120 kg/h with an average value of 100 kg/h. The ranges of chemical dosing are chosen based on a yearly plant operation data (from September 2014 to May 2015) with a consideration of the needs for impact evaluation. Full boiler load (65 MW) is used for all of the evaluation.

13.1. Ammonium Sulfate (AS) Dosing.

The primary use of the AS is to reduce severe corrosion on the surface of super heat exchangers caused by Cl. Depending on the conditions of temperature and O_2 level, decomposition of AS produce SO_2 and NH_3 during the AS dosing. The SO_2 and NH_3 produced from AS increase their concentrations in the flue gas. Diagram 16 shows the contribution of AS dosing to flue gas SO_2 in comparison to the SO_2 generated from fuel-S. As shown in Diagram 17, the SO_2 concentration is almost leanly increased with the AS dosing rates. Diagram 18 and 19 show the contribution of AS dosing to the total NH_3 and the impact on flue gas NH_3 concentration before SNCR.

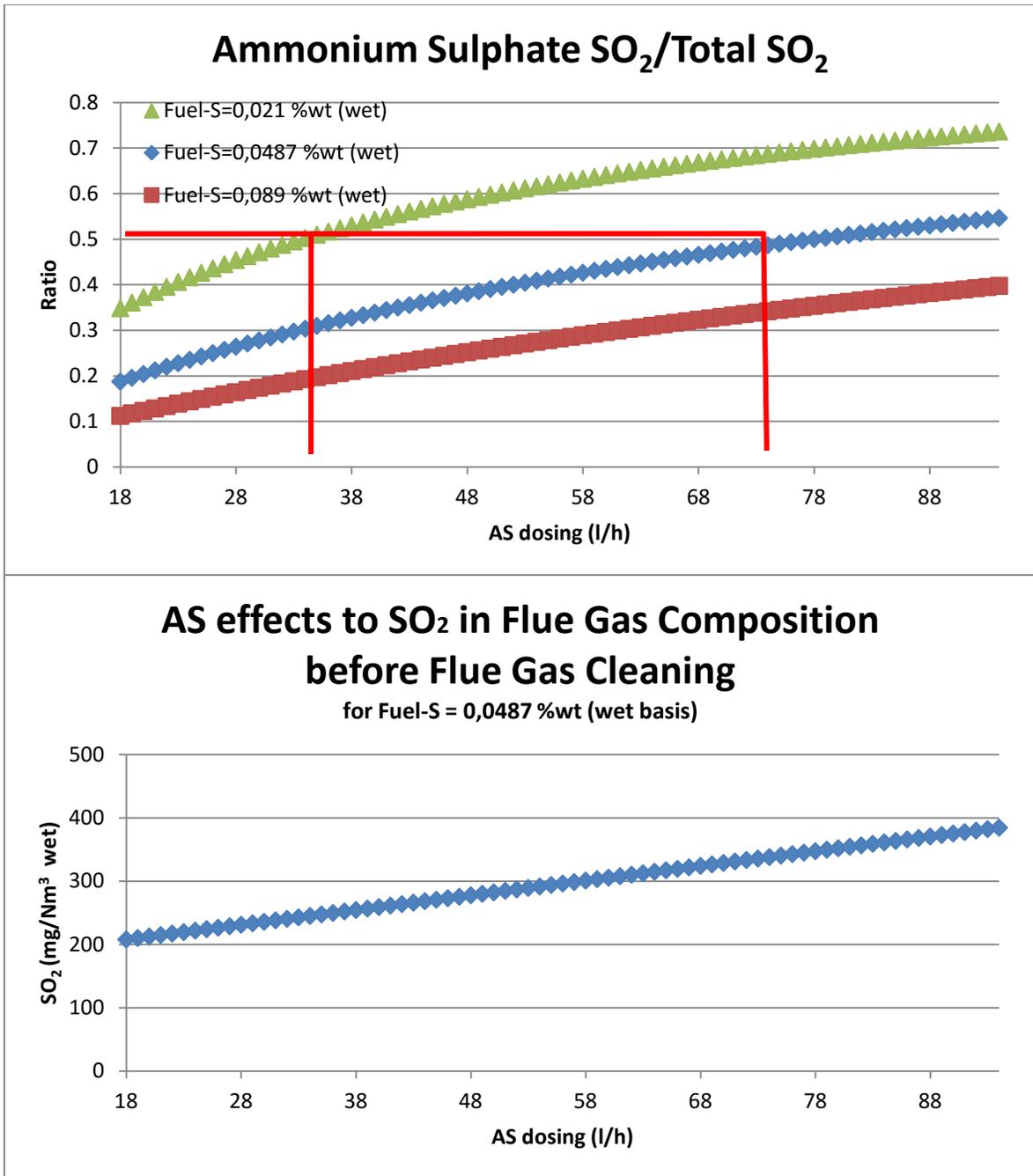


Diagram 16 (top) and 17 (bottom): Contribution of AS dosing to the SO₂ concentration. In the first diagram it is compared with total amount of SO₂ for the lowest, average and highest value of fuel-S while in the second, the changes in the concentration of SO₂ in the flue gas before flue gas cleaning, because of AS dosing, for the average value of fuel-S is shown. Both diagrams are for high boiler load (65MW). The red lines in diagram 16 show that for the lowest and average amount of fuel-S, AS can surpass the amount of SO₂ that is produced from it. The range of SO₂ that is produced from AS is ~200-400 mg/Nm³.

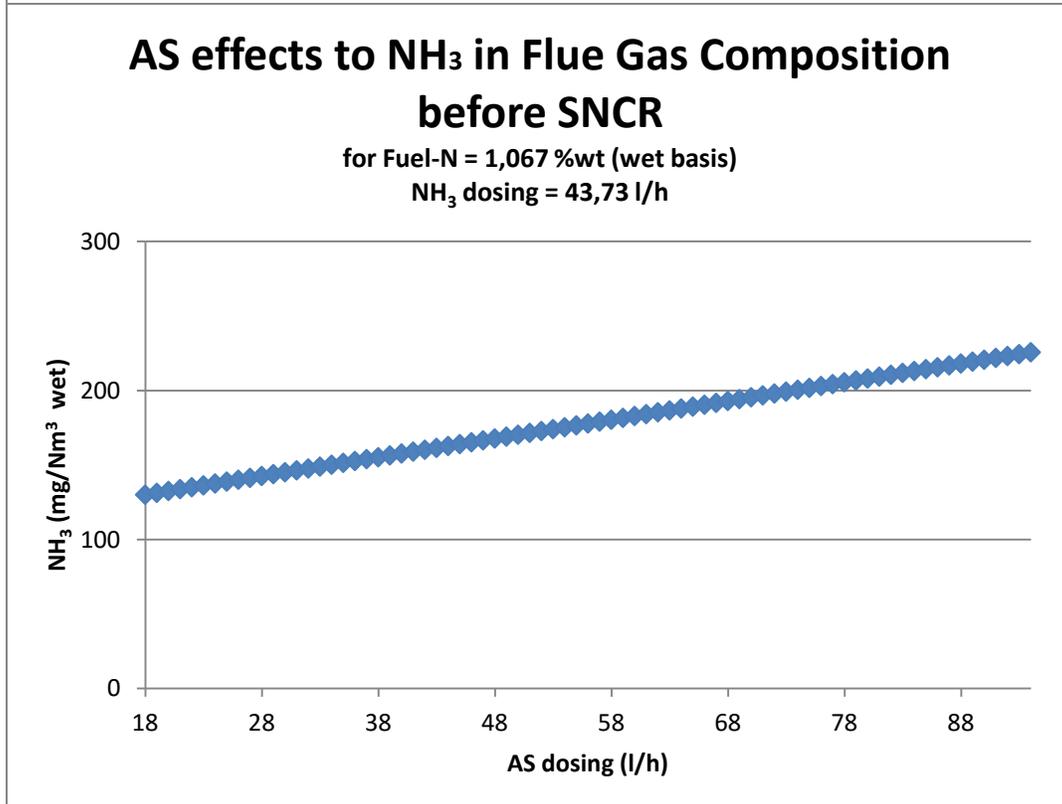
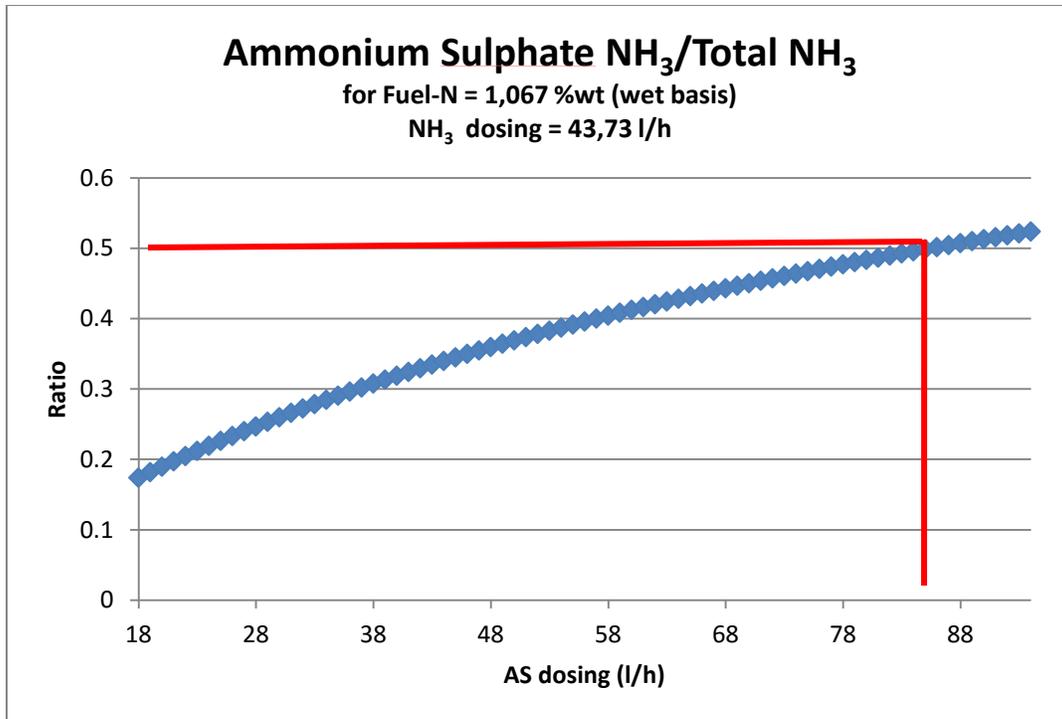


Diagram 18 (top) and 19 (bottom): Contribution of AS dosing to the NH_3 concentration. In the first diagram it is compared with total amount of NH_3 while in the second, the changes in the concentration of NH_3 in the flue gas before SNCR, because of AS dosing, shown. Both diagrams are for the average value of fuel-N and NH_3 dosing and for high boiler load (65MW). The red lines in diagram 18 show that for the average amount of fuel-N and NH_3 dosing, AS can surpass the amount of NH_3 , that is produced from them, when it is injected in high volumetric rates (above 85 l/h). The range of NH_3 that is produced from AS is $\sim 120\text{-}220 \text{ mg/Nm}^3$.

From the diagrams above, it is confirmed that AS decomposition could contribute significantly to the concentrations of SO_2 and NH_3 in flue gas when AS dosing is up to 80 l/h. For average fuel-S, AS may provide more SO_2 in flue gas than that converted from the fuel as the AS dosing rate is larger than 80 l/h. Therefore, the negative impacts of AS dosing should be carefully handled when high AS dosing is required for high fuel-Cl combustion. As shown in Diagram 18, AS decomposition could provide more than half of NH_3 that is required for SNCR when AS dosing rate is larger than 80 l/h for average fuel-N content. This means that the demand of NH_3 for SNCR must consider the contribution of NH_3 from AS decomposition when a high AS dosing is required. Otherwise, high NH_3 slip may occur when high dosing rates are required for both NH_3 and AS injections.

The primary role of AS dosing is to protect heat exchangers from the Cl-corrosion by providing enough SO_x to replace Cl. The ratio of S to Cl (S/Cl) is a important parameter to determine the effect of AS dosing. In Diagram 20, the impacts of AS dosing to the S/Cl ratio are shown for the average value of fuel-S with variation of fuel-Cl contents.

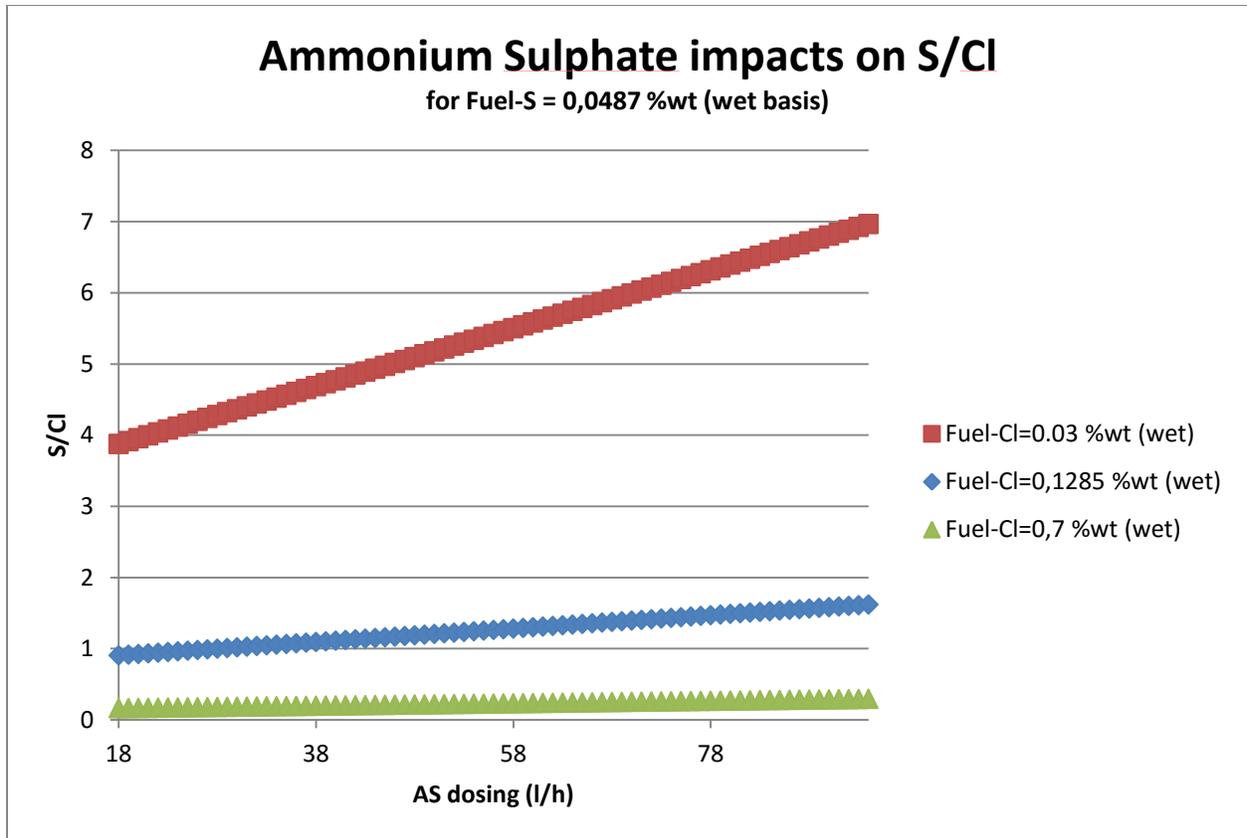


Diagram 20: AS dosing impacts to the S/Cl ratio for the lowest, average and highest values of fuel-Cl, for average value of fuel-S and for high boiler load (65MW). The results are quite different. For the highest percentage of fuel-Cl, the ratio stays close to 0 in all of fuel-S values while for the lowest fuel-Cl percentage, the S/Cl varies from ~ 4 to 7. For the average value of fuel-Cl, the ratio S/Cl is between 0,8 to 1,7.

When fuel-Cl is at 0.7%, AS dosing cannot influence the S/Cl ratio almost at all due to the extremely high fuel-Cl. AS dosing has more visible impacts on the S/Cl ratio when the fuel has relatively lower fuel-Cl as shown in the diagram.

Furthermore, AS dosing can produce SO₂ in the flue gas. Significant increase of SO₂ in flue gas could be expected when AS dosing rate is in a high level. This in turn can influence the flue gas cleaning for acidic gas removal. To evaluate this influence, the AS dosing is correlated with the Ca/(S+Cl) ratio in Diagram 21, which shows the impacts of AS dosing on the Ca/(S+Cl) ratio for average fuel-S (0,05 wt%) and fixed hydrated lime dosing (100 kg/h) but with variation of fuel-Cl.

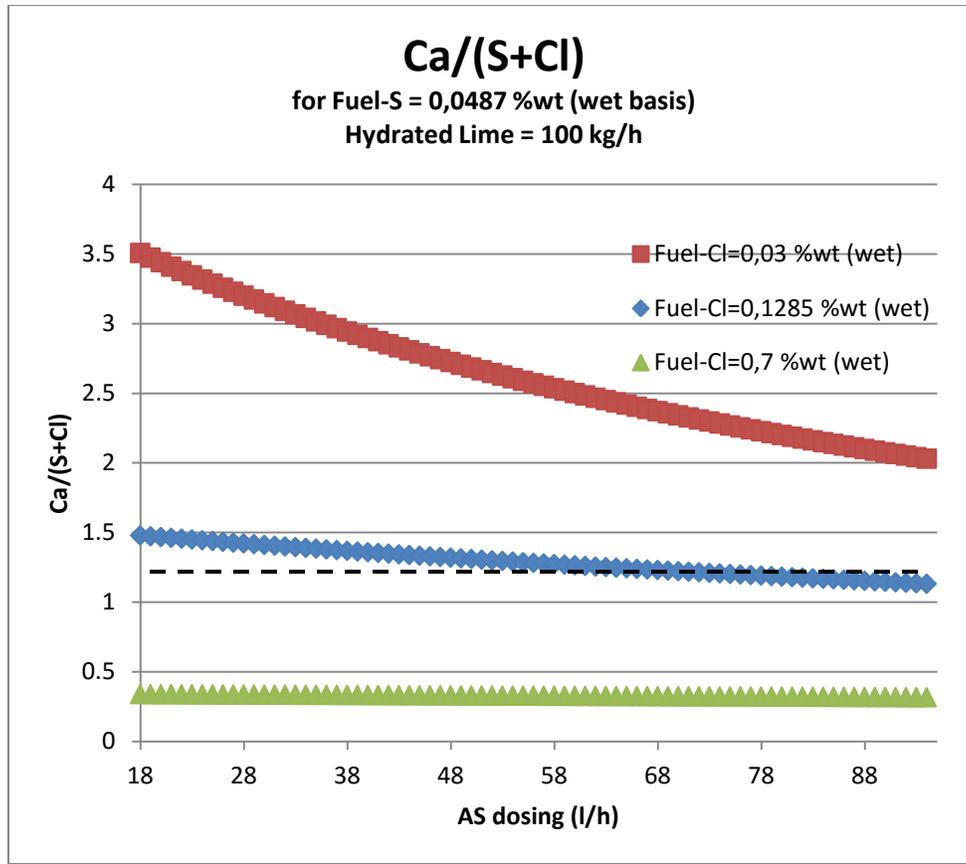


Diagram 21: Contribution of AS dosing to the $Ca/(S+Cl)$ ratio for fuel-S at 0.0487%wt and hydrated lime flow at 100 kg/h, which are the average values, and high boiler load (65MW). For the highest percentage of fuel-Cl, the ratio stays below 1 in all of AS values while for the lowest fuel-Cl percentage, the $Ca/(S+Cl)$ varies from 3,5 to 2. For the average value of fuel-Cl, the ratio $Ca/(S+Cl)$ is between 1,5 to 1. The black line shows the optimum value of $Ca/(S+Cl)$ ratio which is 1,2.

The results are quite similar with the results from the comparison of fuel-S with the $Ca/(S+Cl)$ ratio. When the fuel-Cl gets to its highest peak, the impacts of AS dosing to this ratio are barely noticeable. On the other hand, the more the fuel-Cl gets closer to its lowest value, the more impacts AS dosing has to the $Ca/(S+Cl)$ ratio.

13.2. Ammonia (NH₃) Dosing.

The NH₃ dosing primary use is to provide NH₃ in order to reduce the NO_x emissions through the secondary de-NO_x process (SNCR). However, AS and a really small percentage of fuel-N produces NH₃ too. In Diagram 22, the contribution of NH₃ dosing to the total amount of NH₃ is presented for AS dosing and fuel-N at their average values.

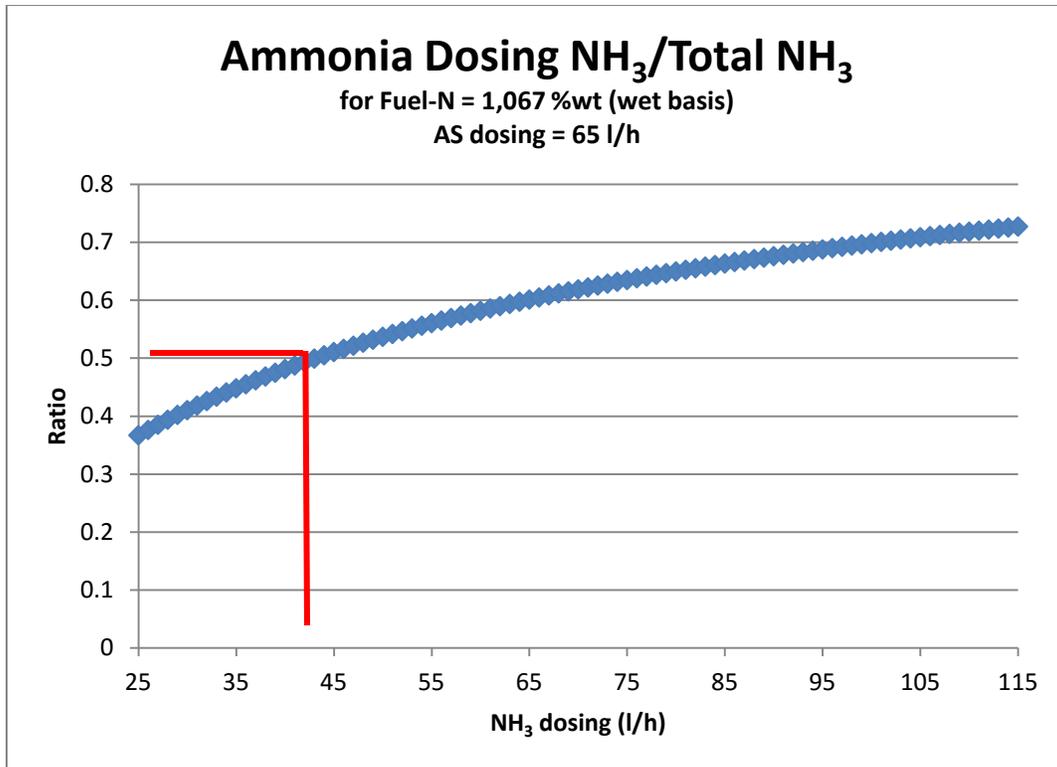


Diagram 22: Comparison of the NH_3 that derives from NH_3 dosing with the total NH_3 that is produced for AS dosing at 65 l/h and fuel-N at 1.067%, which are their average values, and high boiler load (65MW). When the ratio is above 0,5 it means that NH_3 dosing produce more NH_3 than AS while when it is below 0,5 it means the opposite. For 40 l/h of NH_3 dosing the ratio is 0,5 which means that they produce the same amount.

It seems that NH_3 dosing at >40 l/h produces more NH_3 from AS dosing. This means that even if NH_3 dosing has lower volumetric flow rate than AS dosing it may produce more NH_3 something that can be observed also is Diagram 18. In Diagram 23, the concentration of NH_3 before SNCR shows a linear dependence of NH_3 dosing under a constant AS dosing (65 l/h) condition. If Diagram 23 is compared with the same diagram of AS dosing (Diagram 19), this previous statement can be easily confirmed.

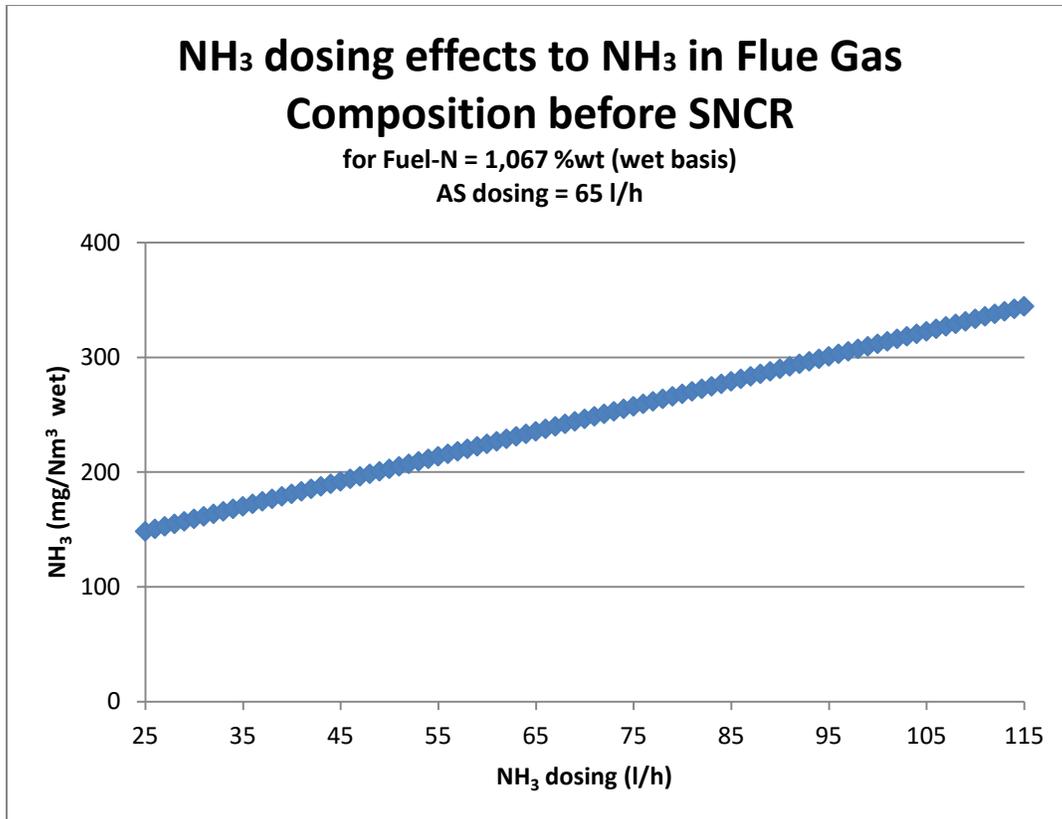


Diagram 23: Impacts of NH₃ dosing to the concentration of NH₃ in the flue gas before SCNR reactions for high boiler load (65MW) and for the average values of AS dosing and fuel-N. The increase of NH₃ is proportional with the increase of the flow of NH₃ dosing reaching a maximum of ~350 mg/Nm³ of NH₃. The range of NH₃ dosing is from 25 till 115 l/h which is higher than the range of AS dosing.

13.3. Hydrated Lime (Ca(OH)₂) Injection.

Hydrated lime injection plays a significant role to the retention of the acidic components.. The best way to observe these impacts is to compare hydrated lime with the Ca/(S+Cl) ratio, which is an important parameter to determine the general performance of acidic gas removal and the effect of hydrated lime utilization. In Diagram 24, a connection of hydrated lime mass flow with the Ca/(S+Cl) ratio, for the average values of fuel-S and AS and the highest, average and lowest value of fuel-Cl, is presented. Like the previous Ca/(S+Cl) ratio diagrams, fuel-Cl is dominant to this ratio when it has its highest value. As the fuel-Cl takes lower values, the impacts of hydrated lime to the Ca/(S+Cl) ratio are more noticeable. For the lowest value of fuel-Cl, the Ca/(S+Cl) ratio takes really high values. This means that for an efficient removal of the

acidic components, hydrated lime must be injected in different amounts according to the percentage of Cl in the recycled wood fuels. The dotted line refers to the 1,2 value which is acceptable. [26]

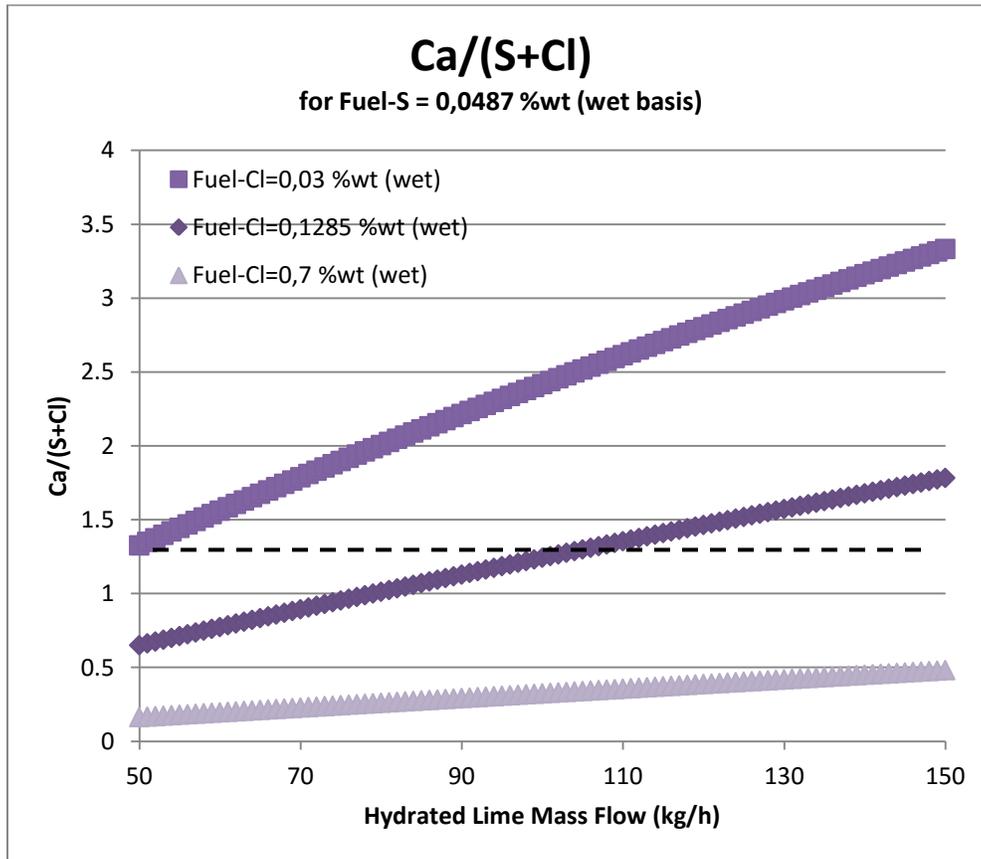


Diagram 24: Contribution of hydrated lime to the $Ca/(S+Cl)$ ratio for fuel-S at 0.0487%wt and AS dosing at 65 l/h, which are the average values, and high boiler load (65MW). For the highest percentage of fuel-Cl, the ratio stays below 1 in all of hydrated lime values while for the lowest fuel-Cl percentage, the $Ca/(S+Cl)$ varies from ~1,5 to 3,5. For the average value of fuel-Cl, the ratio $Ca/(S+Cl)$ is between 0,75 to 1,75. The black line shows the optimum value of $Ca/(S+Cl)$ ratio

14. Impacts of flue gas recirculation from the flue gas quench.

For the flue gas recirculation, the increases in the pollutants concentration must be taken into consideration. Because for the flue gas quench is used water, a high percentage of HCl and NH₃ contained in the flue gas will be captured by the quench water and then recirculated back to boiler due to their high solubility in water. Less soluble SO₂ could be captured with lower percentage in the quench process in comparison to HCl and NH₃. On the contrary, NO_x(mainly

NO) is not very water-soluble. Therefore its capture rate is not taken into consideration in the calculations. Diagram 25 shows how the quench water recirculation can affect the flue gas composition in comparison to that without the quench water recirculation. In Diagram 25 the percentage difference means the concentration increase (%) for given recirculated components (e.g. HCl, SO₂ and NH₃). As shown in the diagram, a range of capture rate for given component has been assumed based on the experience of wet scrubbing process. The impacts of the quench water recirculation on the increase of flue gas concentrations are shown within the capture range..

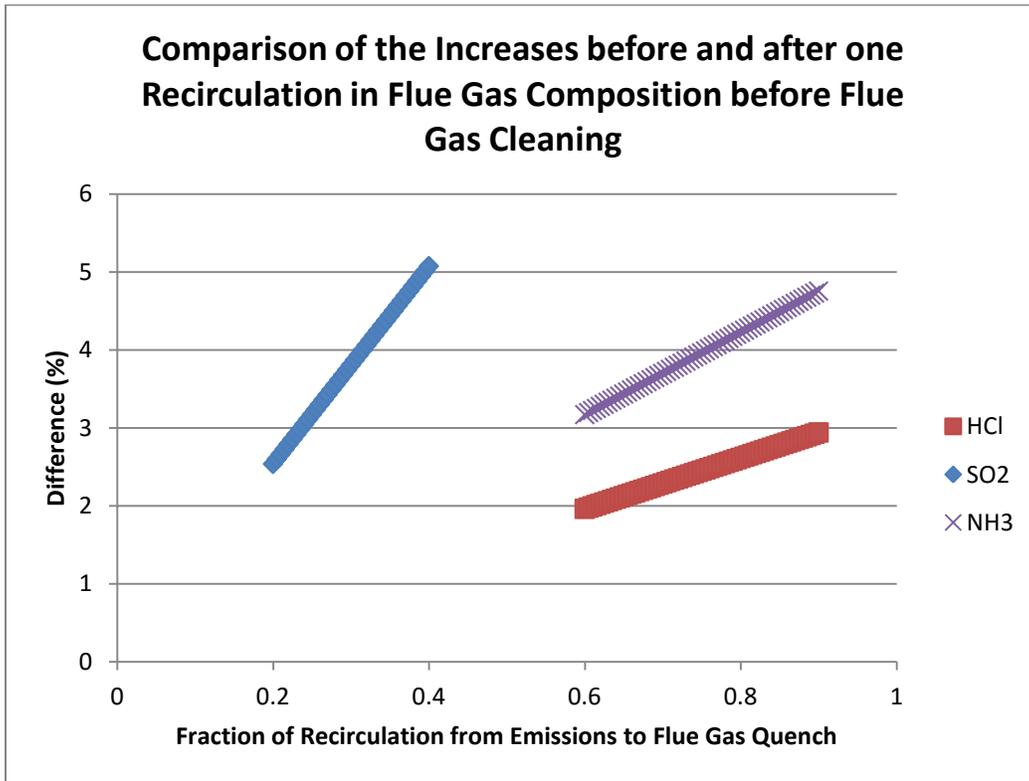


Diagram 25: Presentation of the percentage of increase that the pollutants (HCl, SO₂ and NH₃) have before flue gas cleaning after one recirculation. Although HCl and NH₃ have higher fraction of their amount recirculated back to the furnace, SO₂ has the highest increase and it is ~5%. This diagram has been drawn by using average values.

Although HCl and NH₃ have higher fraction of capture rates, the impact of SO₂ recirculation is larger than the recirculation of HCl and NH₃. This is because the SO₂

concentration in flue gas is much higher than HCl and NH₃. The results indicate that the increase in flue gas concentration due to the quench water recirculation could generally be less than 5% for SO₂ and NH₃ and less than 3% for HCl. The impacts on flue gas cleaning (i.e. demand of hydrated lime dosing) should be low due to the limited increase in the flue gas concentrations. This can further be confirmed through Diagram 26, where the changes to the Ca/(S+Cl) due to the flue gas recirculation are observed. The ratio stays close to 1.2 for both SO₂ and HCl with limited variation due to the quench water recirculation. To make these diagrams, average values for all the other inputs has been used (i.e. Case 1).

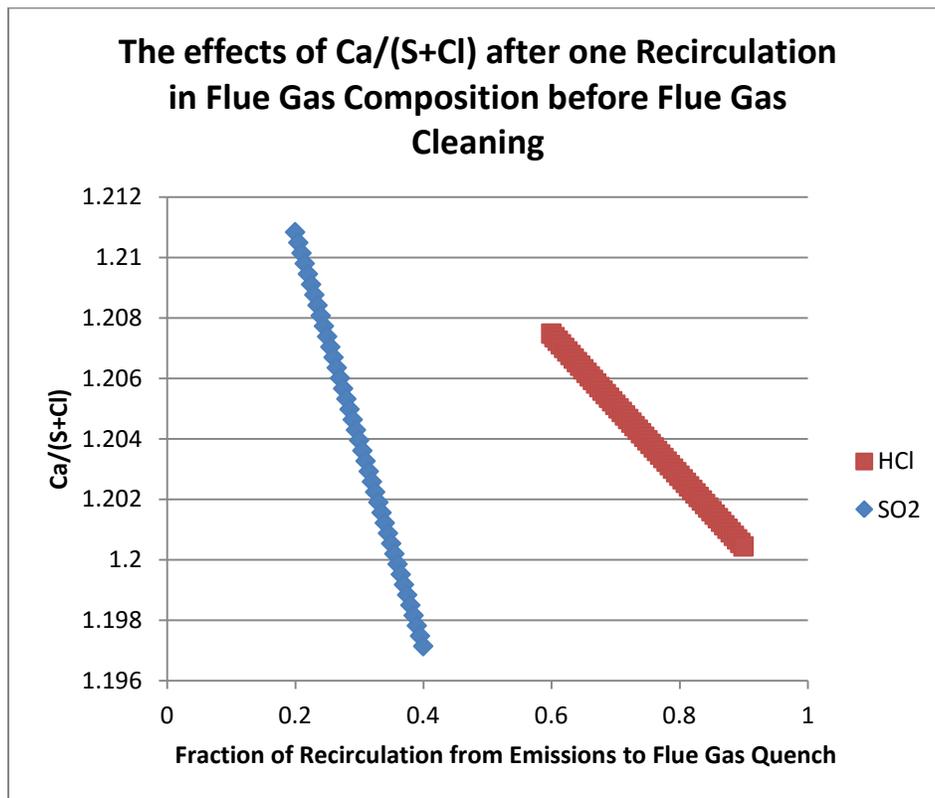


Diagram 26: Impacts of the SO₂ and HCl to the Ca/(S+Cl) after one recirculation. The effects to this ratio are not very significant as all the results are close to 1,2. This diagram has been drawn by using average values.

15. Sensitivity analysis.

For better understanding of the impacts of fuel quality and the impacts of chemical dosing, a sensitivity analysis is has been made. This sensitivity analysis will show how much, the concentration of the acidic components in the flue gas and the $Ca/(S+Cl)$ ratio, are influenced by small changes in the fuel quality and chemical dosing. The work has been carried out using the "Sensitivity Analysis Knoll" Add-In for Microsoft EXCEL [25].

The concentration of SO_2 in the flue gas before flue gas cleaning, is influenced by the percentage of S in the fuel and by AS dosing. In Diagram 27, the comparison between the different influences is shown. These influences are evaluated for AS dosing and fuel-S at their average values while their values are decreased and increased up to 20% of their initial value.

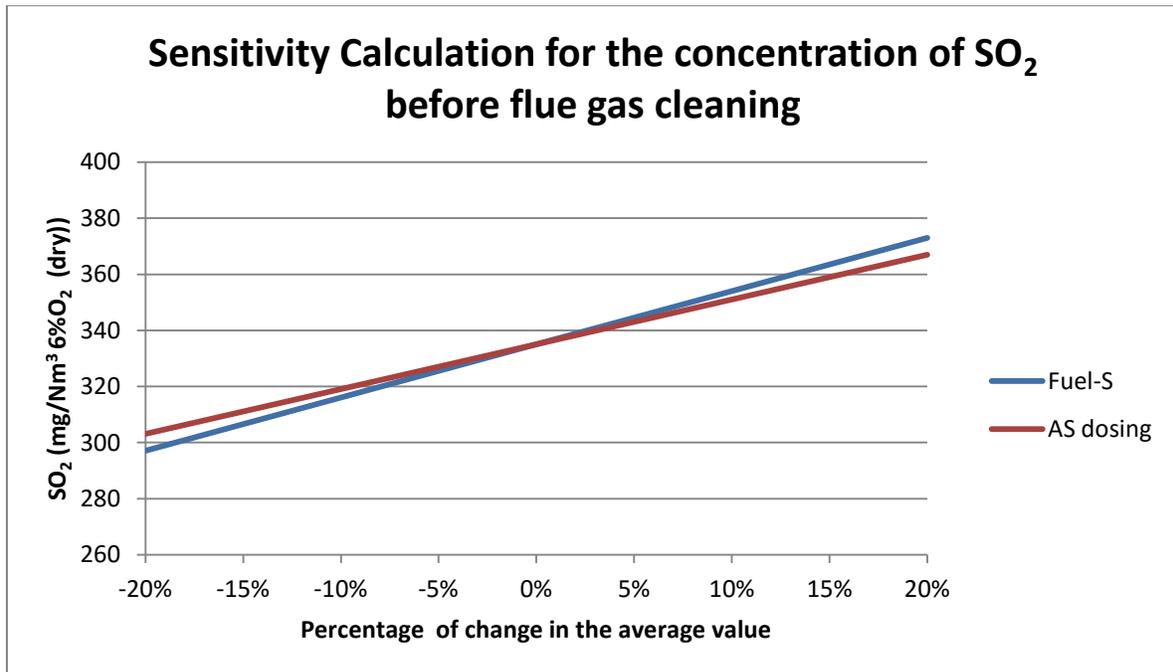


Diagram 27: Sensitivity analysis for the concentration of SO_2 before flue gas cleaning. AS dosing and fuel-S are at their average values and they are increased and decreased up to 20% of their initial value and their impacts are compared. The average value of fuel-S and AS dosing are 0.049 weight% and 65 l/h respectively.

The impacts of AS dosing on the concentration of SO₂ before flue gas cleaning are slightly smaller than the impacts of fuel-S. In order to observe better how the concentration of SO₂ before flue gas cleaning rises as fuel-S and AS dosing increase, a table is created. Table 9 shows the different values that the concentration of SO₂ (*mg/Nm³ 6%O₂ (dry)*) can acquire from fuel-S and AS dosing. The values of fuel-S (*vertical line, wt%*) and AS dosing (*horizontal line, l/h*) in Table 9 are increased and decreased up to 20% of their average values and the concentration of SO₂, before flue gas cleaning, for each combination is shown. The average values of fuel-S, AS dosing and SO₂ are underlined.

Fuel- S(wt%)/AS dosing(l/h)	<u>52.00</u>	<u>55.25</u>	<u>58.50</u>	<u>61.75</u>	<u>65.00</u>	<u>68.25</u>	<u>71.50</u>	<u>74.75</u>	<u>78.00</u>
0.039	265.19	273.18	281.16	289.15	297.13	305.12	313.10	321.09	329.07
0.041	274.68	282.67	290.65	298.64	306.62	314.61	322.59	330.57	338.56
0.044	284.17	292.16	300.14	308.13	316.12	324.09	332.08	340.06	348.05
0.046	293.66	301.65	309.63	317.61	325.60	333.58	341.57	349.55	357.53
<u>0.049</u>	303.15	311.13	319.12	327.10	<u>335.08</u>	343.07	351.05	359.03	367.02
0.051	312.64	320.62	328.60	336.59	344.57	352.55	360.54	368.52	376.50
0.054	322.12	330.11	338.09	346.07	354.06	362.04	370.02	378.01	385.99
0.056	331.61	339.59	347.58	355.56	363.54	371.53	379.51	387.49	395.48
0.058	341.10	349.08	357.06	365.05	373.03	381.01	389.00	396.98	404.96

Table 9: This table shows the values that the concentration of SO₂ can take, in mg/Nm³ 6%O₂ (dry), from the different combinations of fuel-S and AS dosing. The values of fuel-S and AS dosing are decreased and increased by 20% of their average value. The average values of fuel-S, AS dosing and SO₂ are underlined.

The maximum concentration of SO₂ in this table is 404.96 mg/Nm³ 6%O₂ (dry) while the minimum 265.19 mg/Nm³ 6%O₂ (dry). It can be also observed that fuel-S has slightly bigger impacts on the concentration of SO₂ than AS dosing.

Similar diagram with SO₂ is drawn for the concentration of HCl before flue gas cleaning, even though the concentration of HCl in the flue gas is influenced mostly by fuel-Cl. In Diagram 28, this influence is shown by decreasing and increasing the average value of fuel-Cl by 20%

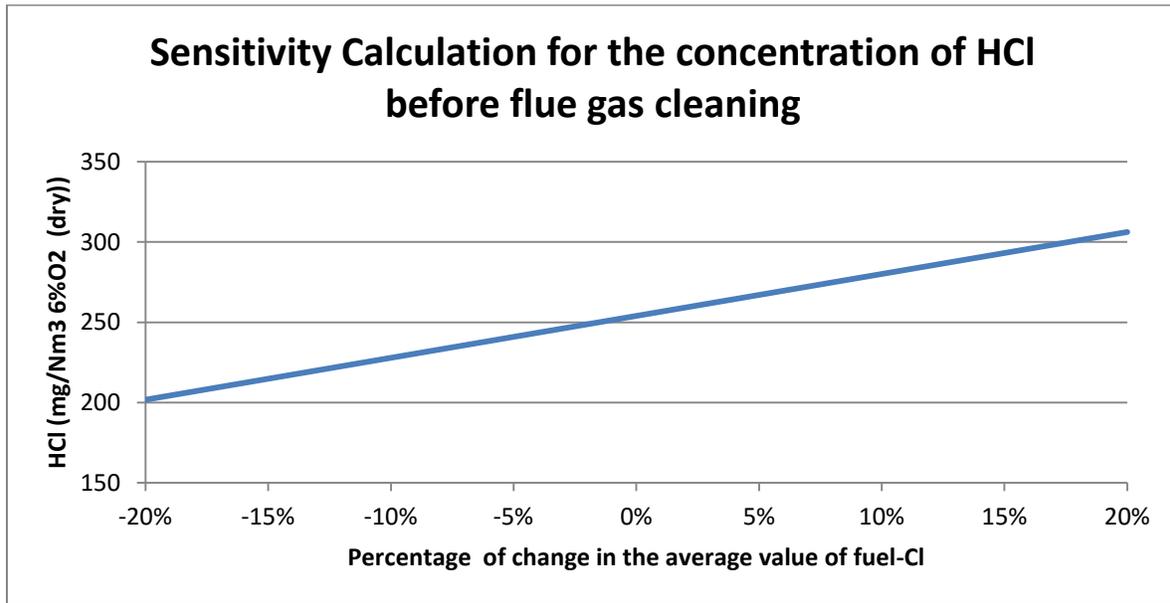


Diagram 28: Sensitivity analysis for the concentration of HCl before flue gas cleaning. Fuel-Cl is at its average value and it is increased and decreased up to 20% of its initial value and its impacts are observed. The average value of fuel-Cl is 0,129 weight%

A more analytical presentation of the results can be found in Table 10. The average values of fuel-Cl and HCl are underlined.

Fuel-Cl (wt%)	0.103	0.109	0.116	0.122	<u>0.129</u>	0.135	0.141	0.148	0.154
HCl (mg/Nm³ 6%O₂ (dry))	201.65	214.72	227.78	240.85	<u>253.92</u>	266.99	280.06	293.13	306.20

Table 10: Numerical results from the sensitivity analysis for the concentration of HCl before flue gas cleaning. Fuel-Cl is at its average value and it is increased and decreased up to 20% of its initial value and its impacts are observed. The average values of fuel-Cl and HCl are underlined.

The maximum concentration of HCl in this table is 306.2 mg/Nm³ 6%O₂ (dry) while the minimum 201.65 mg/Nm³ 6%O₂ (dry). An increase of fuel-Cl by 20% results in a rise of HCl by ~50 mg/Nm³ 6%O₂ (dry).

Now that the ranges in the concentrations of the major acidic components are known, the impacts in the flue gas cleaning must be observed. In Diagram 29, the Ca/(S+Cl) ratio is correlated with the fuel-S, fuel-Cl, AS dosing and hydrated lime injection. Their impacts on the Ca/(S+Cl) ratio are evaluated by decreasing and increasing their average value up to 20%.

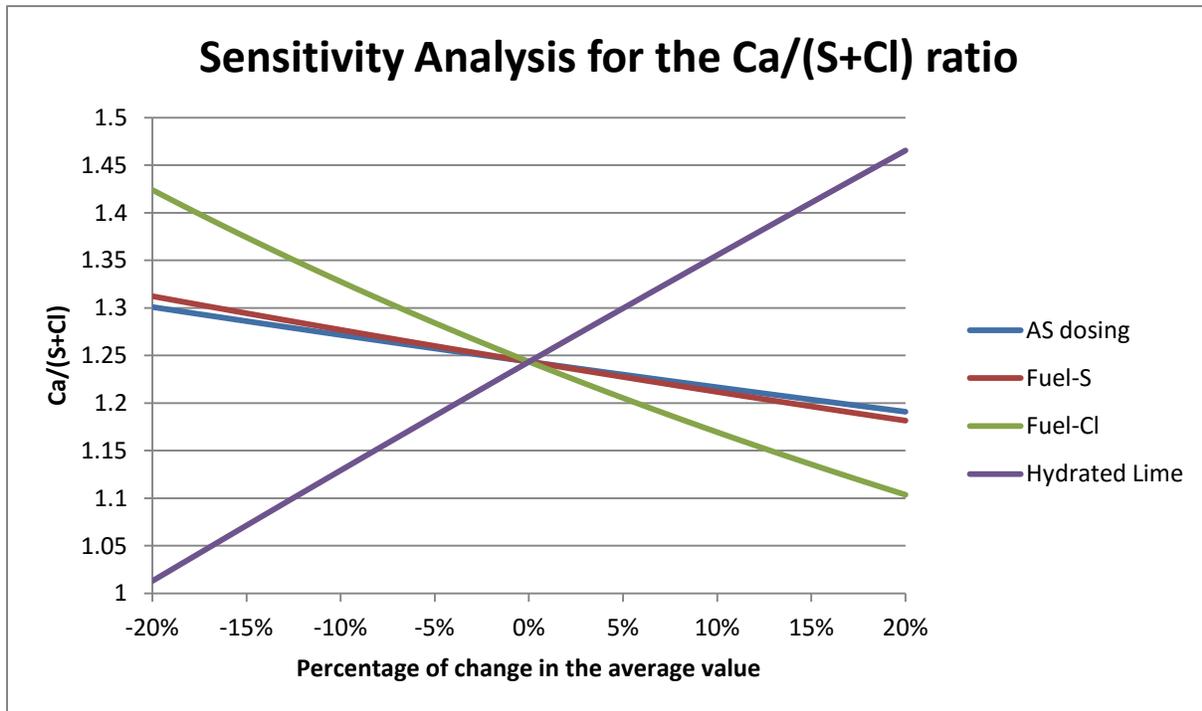


Diagram 29: Sensitivity analysis for the Ca/(S+Cl) ratio. AS dosing, fuel-S, fuel-Cl and hydrated lime are at their average values and they are increased and decreased up to 20% of their initial value and their impacts are compared. The average values of AS dosing, fuel-S, fuel-Cl and hydrated lime are 65l/h, 0.049 weight%, 0.129 weight% and 100kg/h respectively.

In order to show these impacts better, two tables are created. In Table 11, the different values that the Ca/(S+Cl) ratio can acquire from fuel-S and hydrated lime are presented while in Table 12, the influence of fuel-Cl and hydrated lime to the Ca/(S+Cl) ratio is shown. The values of fuel-S (*vertical line, wt%*) and hydrated lime dosing (*horizontal line, l/h*) in Table 11 and the values of fuel-Cl (*vertical line, wt%*) and hydrated lime dosing (*horizontal line, l/h*) in Table 12 are increased and decreased up to 20% of their average values and the Ca/(S+Cl) ratio, for each different combination, is displayed. The average values of fuel-S, AS dosing, fuel-Cl, hydrated lime and Ca/(S+Cl) ratio are underlined.

Fuel- S(wt%)/Hydrated Lime(kg/h)	80	85	90	95	<u>100</u>	105	110	115	120
0.039	1.070	1.132	1.192	1.253	1.312	1.371	1.430	1.488	1.545
0.041	1.055	1.116	1.176	1.235	1.294	1.353	1.410	1.468	1.524
0.044	1.041	1.101	1.160	1.219	1.277	1.334	1.392	1.448	1.504
0.046	1.027	1.086	1.144	1.202	1.260	1.317	1.373	1.429	1.484
<u>0.049</u>	1.013	1.071	1.129	1.187	<u>1.243</u>	1.300	1.355	1.411	1.465
0.051	1.000	1.057	1.115	1.171	1.227	1.283	1.338	1.393	1.447
0.054	0.987	1.044	1.100	1.156	1.212	1.267	1.321	1.375	1.429
0.056	0.974	1.030	1.086	1.141	1.196	1.251	1.304	1.358	1.411
0.058	0.962	1.017	1.072	1.127	1.181	1.235	1.288	1.341	1.394

Table 11: This table shows the values that the Ca/(S+Cl) ratio can acquire, from the different combinations of fuel-S and hydrated lime. The values of fuel-S and hydrated lime are decreased and increased by 20% of their average value. The average values of fuel-S, hydrated lime injection and Ca/(S+Cl) ratio are underlined.

Tables 11 and 12 are calculated by using the average value of AS dosing (65 l/h). Here, the maximum value of Ca/(S+Cl) ratio in this table is 1.545 and the minimum 0.962. The optimum ratio is close to 1.2 as it was mentioned in the literature review. It seems that when the hydrated lime is at 95 - 105 kg/h, it can handle the ratio close to the optimum for each decrease or increase of fuel-S up to 20%.

Fuel- Cl(wt%)/Hydrated Lime(kg/h)	80	85	90	95	<u>100</u>	105	110	115	120
0.103	1.163	1.230	1.295	1.360	1.424	1.487	1.550	1.612	1.674
0.109	1.122	1.186	1.249	1.312	1.374	1.436	1.496	1.557	1.616
0.116	1.083	1.145	1.206	1.267	1.328	1.387	1.446	1.505	1.563
0.122	1.047	1.107	1.167	1.226	1.284	1.342	1.399	1.456	1.512
<u>0.129</u>	1.013	1.071	1.129	1.187	<u>1.243</u>	1.300	1.355	1.411	1.465
0.135	0.981	1.038	1.094	1.150	1.205	1.260	1.314	1.368	1.421
0.141	0.952	1.007	1.061	1.116	1.169	1.222	1.275	1.328	1.379
0.148	0.924	0.977	1.030	1.083	1.135	1.187	1.239	1.290	1.340
0.154	0.897	0.949	1.001	1.053	1.103	1.154	1.204	1.254	1.303

Table 12: This table shows the values that the Ca/(S+Cl) ratio can acquire, from the different combinations of fuel-Cl and hydrated lime. The values of fuel-Cl and hydrated lime are decreased and increased by 20% of their average value. The average values of fuel-Cl, hydrated lime injection and Ca/(S+Cl) ratio are underlined.

In Table 12, the maximum value of $\text{Ca}/(\text{S}+\text{Cl})$ ratio in this table is 1.674 and the minimum 0.897, a bit far from the optimum ratio 1.2. From the results it can be validated that fuel-Cl has more impacts to the $\text{Ca}/(\text{S}+\text{Cl})$ ratio than fuel-S. However, when the hydrated lime is at 100 - 105 kg/h, a fair approach to the value 1.2 occurs for each decrease or increase of fuel-S up to 20%.

16. Conclusions.

Fuel quality plays an important role in the concentration of the acidic components in the flue gas. The challenge in determining the fuel quality influence on the emission performance, is in the significant variation of the fuel acidic components especially fuel-Cl of the recycled wood fuels. It may not be easy to keep the ratio of $\text{Ca}/(\text{S}+\text{Cl})$ over 1,2 when a peak of HCl occurs in the flue gas due to a significant increase in fuel-Cl. The flue gas cleaning (lime dosing specifically) should provide enough alkaline buffer in the cake of the fabric filter in order to properly control the emissions of SO_2 and HCl if the fuel-Cl has temporarily increases. Besides fuel-Cl, fuel-S combined with the SO_2 decomposed from AS dosing, which is highly dependent on fuel-Cl during the operation in the boiler, affects the flue gas cleaning and SO_2 emissions. Though the impacts of fuel-S on S/Cl and $\text{Ca}/(\text{S}+\text{Cl})$ ratio will be decreased when fuel-Cl increases, the overall impacts on SO_2 emissions would be increased regardless of fuel-Cl. Furthermore, the retention of S and Cl by the summary of bottom ash (empty draft ash and economizer ash) is not significant (normally <5%) which also implies that the retention of S and Cl by deposition in the surface of heat exchangers should not be very significant. Additionally, because fuel-Cl has great impacts on corrosion and flue gas cleaning, chemical dosing is highly affected by fuel-Cl and its variation, which will define the demands of both AS dosing and hydrated lime dosing. The efficiency of the chemical dosing can be easily estimated by the

modeling for specific fuel quality and operation conditions. Moreover, control of NH_3 slip for SNCR could limit the contribution of secondary de- NO_x measures (SNCR) for the overall de- NO_x demand. Efficient primary de- NO_x process should be implemented for the fuels with higher fuel-N content which can be estimated by the modeling and define how difficult it can be achieved as fuel-N increases. Last but not least, the recirculation of the pollutants from the flue gas quench process has limited impact on the flue gas compositions, few percentage increases in SO_2 , HCl and NH_3 before flue gas cleaning, for the cases used in the simulations. The impacts of the recirculation contaminants from the quench water can be handled by existing flue gas cleaning (i.e. SNCR, hydrate lime dosing and bag-house filtration).

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