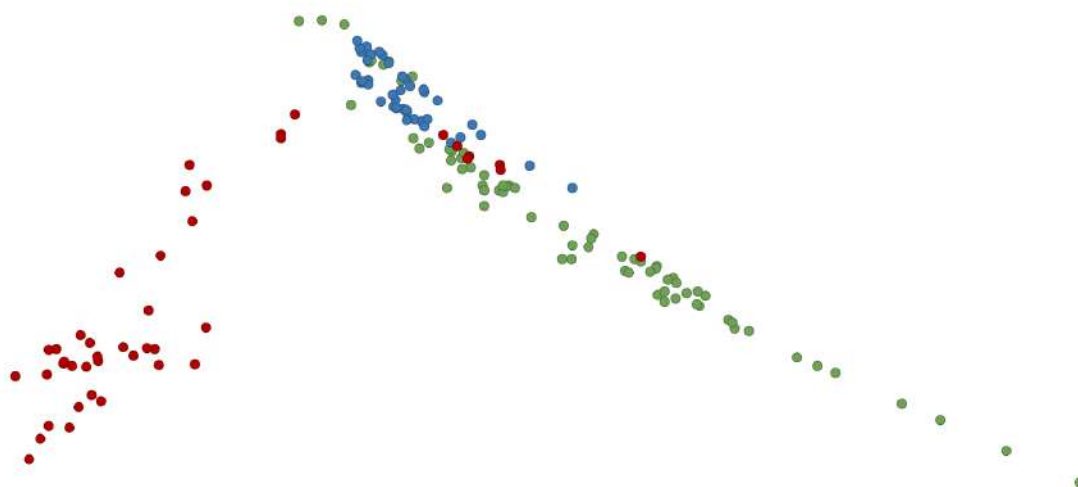




CHALMERS
UNIVERSITY OF TECHNOLOGY



A machine learning approach applied for interpretation of signals from multisensor technique

Electronic tongue for monitoring of fluidized bed quality during combustion

Master's thesis in Innovative and Sustainable Chemical Engineering

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DEPARTMENT OF ENVIRONMENTAL INORGANIC CHEMISTRY

Chalmers University of Technology
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MASTER'S THESIS 2021

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CINDER

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Cover: PCA score plot of ET-signals from bed material leachates constructed in SIMCA-P+16

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Abstract

As the need for more sustainable energy production has increased, the thermochemical conversion of biomass as an alternative to combustion of fossil fuels has gained more attention. One of the most efficient technologies used for combustion of biomass is fluidized bed combustors, since the bed provides a good solid-gas mixing and heat transfer. One of the major problems, related to the technology, is bed material agglomeration; a clustering of bed particles caused by the formation of low-melting compounds such as K- and Na-silicates. The agglomeration causes disturbance in the fluidization of the bed and as a consequence the operation has to be stopped and the bed has to be exchanged, thereby increasing operational costs. In this context, a method used to follow the quality change of the bed could be used to prevent premature stops. This project investigates the feasibility of the use of an electronic tongue (ET); a sensor consisting of electrodes with overlapping selectivities that can be used to analyze quality parameters, as a tool to monitor the bed quality. For this purpose bed samples as well as data from a six months period from the bubbling fluidized bed boiler combusting wood at Idbäcksverket were analyzed. The received data from the plant included fuel composition, operational data and response signals obtained from an ET. The data from the ET, using three working electrodes of Pt, Au and Rh, was gathered by using pulse voltammetry on a leachate solution from used bed material. Chemometrics was used to analyze the response signals from the ET and the used bed material was analyzed using SEM-EDS, AAS and XRF. The analysis of the bed material showed that the ash-forming matter from the fuel is responsible for layer build-up around the bed particles. The layer consists of a Ca-rich outer layer and a Na-rich inner layer. Furthermore, the analysis showed that an increase in the Ca/Si ratio in the fuel resulted in an increase of the Ca/Si ratio in the outer layer which in turn results in, not only Ca-silicates but also other, more leachable, compounds. The results of the analysis, together with the fuel data were used to understand the connection between bed material quality and the response from the ET. From the analysis of the used bed material further experiments were conducted with the same ET on solutions with known concentrations of Ca, K and Na, to determine their influence on the ET signal. The findings in this study indicate that the ET can be used to follow the change of the amount of leachable ions from the bed material. From the studied elements, changes in Ca can be detected by the ET. The results also show that the ET can be used to distinguish between mixtures of several compounds. The conclusion of this study is that the ET is a promising tool for monitoring the quality change of a fluidized bed during combustion. Further investigation of electrolyte, pulse-train, electrodes and leachable compounds as well as experiments on bed material of different quality can add to the optimization of this tool. Nevertheless, the results suggest that the ET could be used to detect changes in the composition of the bed material as well as to predict when the bed has to be replaced in order to avoid agglomeration.

Keywords: agglomeration, ash-forming matter, ash-layers, bed material, biomass, calcium, combustion, electronic tongue, fluidized bed, principal component analysis

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Benjamin Stenbäck Storm, Maria Alejandra Hernández Leal, Gothenburg, June 2021

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1 Introduction

In order to reach society's energy demand without the use of fossil fuels, the thermochemical conversion of biomass and waste is seen as a possible alternative [1]. Internationally, policies have been elaborated to stimulate the use of biomass to reduce the dependency on fossil fuels and meet greenhouse emission targets [2]. Nevertheless, biomass as an alternative is not as effective as the combustion of fossil fuels [3, 4]. To be able to make the transition from fossil fuels to more sustainable fuels one of the important steps is to reduce the operational costs and the additional costs related to the change of fuel, i.e. the use of biomass, and waste, e.g. transportation and landfill.

1.1 Background

One of the most efficient technologies used for the conversion of biomass, such as demolition wood, into energy is fluidized bed combustion [5]. The fluidized bed reactor contains a bed of solid particles which are fluidized by letting a gas flow of primary air flow through it. The advantages of using a fluidized bed (FB) are that there is a high heat transfer, a large contact area and good gas-solid mixing, which leads to a higher combustion efficiency [5, 6]. Common material used as bed material are silica sand [5], olivine [7], limestone [8] or ilmenite [9]. The choice of the bed material is based on its price, its reactivity with the fuel components as well as its mechanical stability and that it is environmentally sound. Silica sand is a cheaper option conventionally used in industrial scale reactors but it tends to interact with alkali metals originated from the fuel [7]. Olivine and limestone are in comparison more expensive and therefore used primarily in pilot-, bench-scale and semi-industrial plants.

1.1.1 Agglomeration in fluidized beds

A major problem with the use of fluidized bed technology, when silica sand is used as bed material, is the agglomeration that occurs in the bed of the reactor. Agglomeration is the formation of grain clusters consisting of bed particles that have interacted with inorganic components from the fuel [10]. The formed clusters restrict the movement of the bed particles and disturb the fluidization [5, 6, 11]. As a consequence of the bed material agglomeration the boiler needs to be stopped and the bed material has to be replaced [10]. This leads to unplanned boiler stops, which increases the operational costs. Therefore, it is of interest to develop methods that can predict the agglomeration in time. The objective of such methods is to avoid premature exchange of bed material and unnecessary downtime caused by agglomeration.

Agglomeration occurs mainly during thermal conversion of fuels containing alkali metals, e.g. sodium or potassium [5]. The reason being that alkali salts react with silicon and form sticky, low-temperature melting compounds that contribute to the agglomeration of the bed and fouling of the superheater tubes [5, 6]. Other elements that affect agglomeration are chlorine, sulfur and phosphorus, where for example chlorine facilitates the release of potassium as gaseous KCl [6] and phosphorus binds to calcium in the form of calcium phosphates, resulting in lower concentration of calcium in the Ca/K mixture which in turn leads to lowered melting point of the silicate mixture [12].

Bed agglomeration is a consequence of complex interaction between fuel-ash elements and bed particles as well as the operational conditions [6]. In order to predict the agglomeration potential,

a multi-component analysis of the bed material would therefore be useful to monitor the quality change of the bed material.

1.1.2 Electronic tongue to predict agglomeration

A method now used in the food industry for liquid analysis is the multisensor technique called electronic tongue (ET) [13, 14]. The method is called electronic tongue since it mimics the human's gustatory system [15] and uses several sensors with overlapping selectivity to analyze quality parameters instead of single parameters (e.g. pH) [13]. By using advanced mathematical signal processing, based on machine learning, the signals from the ET can be interpreted and used to follow the quality parameters [13] and recognize change of the samples [14].

This technique may be used to follow the quality changes in the bed material of the fluidized bed in a way comparable to that of the food industry, which uses the ET for the analysis of quality parameters. This technique has been applied to predict bed agglomeration and has showed promising results; however, the interpretation of the response signals from the ET is still unclear. By evaluating the ET-response signals obtained from bed samples using a machine learning method and thereafter relating these signals to the composition and characteristics of the bed material, a method to monitor the bed quality change during operation could be developed.

1.2 Aim

The aim of this master's thesis project is to investigate if an electronic tongue could be used to monitor the quality changes in the bed material in a fluidized bed and how to interpret the response signal from it during the thermal conversion of demolition wood.

1.3 Objectives

To determine the feasibility of using an electronic tongue for offline monitoring of the quality changes in the bed material of an industrial fluidized bed over a time span of six months, the following objectives have been set:

- Summarize the known mechanisms and causes of agglomeration during combustion of biomass in fluidized beds.
- Evaluate, by means of principal component analysis (PCA), the response signal from an electronic tongue used on bed material samples.
- Analyze and characterize the bed material using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS), Atomic absorption spectroscopy (AAS) and X-ray fluorescence (XRF).
- Analyze the fuel, ash and operational data provided by the plant operators.
- Relate the changes in the fuel and ash as well as the bed material composition to the changes in the response signal from the electronic tongue.
- From the analysis of the bed material, select and dissolve key species in water that are responsible for the changes in bed quality and investigate their effect on the response signal

using the electronic tongue.

- Based on the results of the experiments, draw conclusions about the electronic tongue's response signals from the bed material samples.

1.4 Scope

The focus of this study is to develop a method that can monitor the quality changes of a fluidized bed during combustion of demolition wood. It should be noted that other bed materials are used in biomass combustion but the focus of this study is only silica sand as bed material. The components responsible for agglomeration, as well as their interaction with the bed material and how they affect the agglomeration process during the combustion, will be investigated.

1.4.1 Electronic tongue

The electronic tongue used in this project was constructed at Linköping University. It is based on pulse voltammetry and consists of three working electrodes and a stainless steel electrode that was used as counter electrode. The potentiostat's reference electrode was connected to the electronic tongue's counter electrode. The three working electrodes are made of gold, rhodium and platinum and this investigation will be restricted to the use of these three electrode materials since the data that will be analyzed in this project was collected with these three electrodes. The measurement technique used to collect the data was pulse voltammetry. The electronic tongue will also be used in the experimental part of the project. After the main compounds responsible of the bed agglomeration are identified, known solutions of these compounds will be tested by the use of pulse voltammetry in order to investigate their influence on the response signal of the electronic tongue.

1.4.2 Fluidized bed data

The data from the ash and fuel analysis as well as the operational data and the data from the electronic tongue was gathered from the bubbling fluidized bed (BFB) boiler at Idbäcksverket in Nyköping over a period of six months. Idbäcksverket is a combined heat-and-power plant producing 60 MW_{th} and 35 MW_e from the combustion of 105 MW_{fuel} wood chips, demolition wood and bark. This BFB boiler uses silica sand as bed material with a size distribution between 0.354 mm and 2.800 mm and the boiler is a bubbling-type fluidized bed with a total weight of 120 ton.

1.4.3 Data analysis

The data analysis of the data from the electronic tongue will be conducted using the multivariate method called principal component analysis (PCA) on the software SIMCA-P+16. PCA is an unsupervised learning method used for classification of multivariate data.

2 Theory

This section presents the theory behind fluidized bed technology, agglomeration in fluidized beds, electronic tongue and principal component analysis. The theory is used as a help to understand fluidized bed combustion and agglomeration mechanisms as well as to understand the principles of

the electronic tongue and how it can be used as a sensor to monitor the quality of the bed material in a fluidized bed.

2.1 Fluidized bed technology

A fluidized bed reactor consists of a furnace lined with welded tubing followed by superheaters, economizer and air preheaters. The lower tubes are covered in refractory lining up to approximately 2 m above the furnace bottom to avoid erosion of the wall tubes. The combustion of solid fuels generates hot flue gas which heats the water flowing inside the furnace wall tubes and converts it into steam [16, 17]. The heat transfer is dominated by radiative heat transfer inside the furnace and by convective heat transfer in the convection section (i.e. the superheater, economizer and air preheaters) [18]. Two types of fluidized bed boilers are presented in Figure 1.

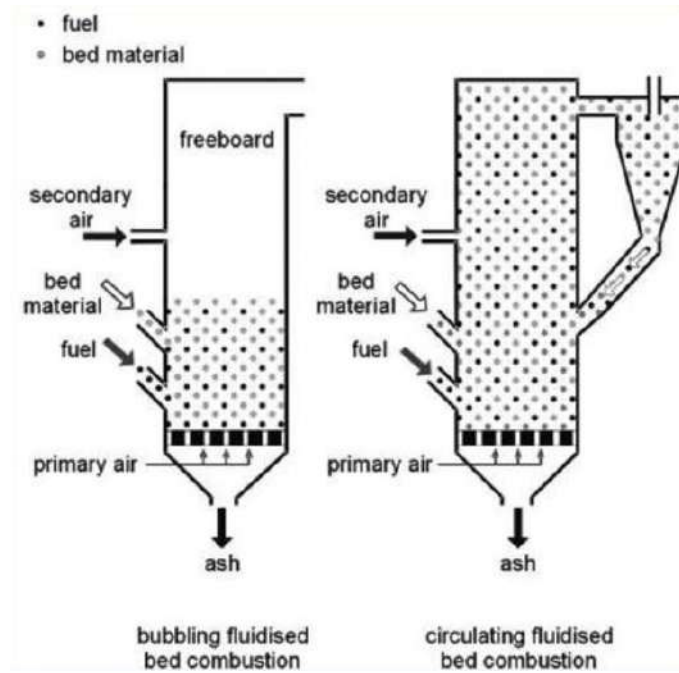


Figure 1: *Bubbling fluidized bed (BFB) boiler and circulating fluidized bed (CFB) boiler [19].*

The bed material in a fluidized bed boiler consists of a layer of sand and ash. The most commonly used bed material during combustion is silica sand [20]. Apart from silica sand other possible bed materials used in fluidized beds are olivine and ilmenite [21, 22]. Ilmenite is investigated as a bed material in oxygen carrier aided combustion (OCAC) [21] while olivine is used during gasification since it has a catalytic effect on the reduction of tars [22]. When the primary air is blown through the bed at a sufficient air velocity the bed particles are suspended and the bed starts to behave like a fluid [16]. The air velocity required for fluidization of the bed is called minimum fluidization velocity. A higher velocity than the minimum fluidization velocity results in excess gas which forms bubbles and causes the bed to bubble. This system is called a bubbling fluidized bed (BFB) [16],

see Figure 1. The total gas velocity ranges from 1.5 to 4 m/s [4]. If the primary air velocity is further increased, a high amount of the bed material is entrained with the flue gas and has to be recycled back to the bed. This is usually carried out using a particle separator in the form of a cyclon. This system is called a circulating fluidized bed (CFB) [16], see Figure 1. The gas velocity through the bed ranges from 3.9 to 9 m/s [17]. A more detail explanation of these two types of boilers can be found below.

2.1.1 Bubbling fluidized bed

In a BFB reactor the bed height ranges from 0.4-0.8 m and the crushed fuels are fed through a screw onto a fuel conveyor which introduces the fuel to the top of the bed [16]. Fuel can also be added from under the bed with a more complex pneumatic system that requires smaller fuel particle size and has the risk of choke and erosion of the feeding pipe [17]. The advantage with this type of feeding is the longer residence time of the fuel resulting in higher conversion efficiency [4]. Primary air is fed at the bottom of the furnace and secondary air ports are situated where the bed ends. The air is fed at temperatures in the range of 20-400 °C [16]. The portion of the furnace from the top down to the secondary air ports are called the freeboard. Higher up in the furnace, tertiary air is injected to lower the NO_x emissions.

During startup the bed is heated using oil or gas supplied by burners located above the bed [16]. The bed is heated to 400-600 °C. During operation the bed temperature is between 700-1000 °C depending on the fuel quality and load. The lower temperature limit is the temperature required for sufficient combustion, while the upper limit is to avoid agglomeration [11, 16]. Bubbling fluidized beds are suitable for combustion of fuels such as wood waste which contain high volatile content. Most of the char combustion occurs in the bed while the gases are combusted in the freeboard. The pressure drop over the bed is usually between 6-12 kPa and the bed density is between 1000-1500 kg/m³ [16]. Compared to a CFB the BFB has a lower energy consumption and is used for sizes less than 100 MW_{th} [17].

2.1.2 Circulating fluidized bed

When the velocity is increased beyond the bubbling regime the bed particles are entrained in the flue gas and need to be returned back to the bed. This system is a so called circulating fluidized bed, presented in Figure 1 right, and requires a gas-solid separator that captures the entrained particles in the flue gas and returns them to the lower furnace [16]. The gas-solid separator is usually a cyclon which captures the bed material and unburned fuel and returns it to the furnace. The cyclon is lined with abrasion resistant refractory material to provide erosion protection [16]. The CFB reactor is constructed in the same way as the BFB reactor regarding the tube covered walls and heat exchangers, however the geometry of the reactors is usually different. The CFB units are taller than the BFB ones, with the height up to 10 times larger than the diameter [4]. In the CFB the heat transfer from flue gas to the wall depends mainly on the suspension behaviour. An advantage using a CFB is that different fuels can be used at the same time [16]. The bed material in a CFB boiler usually has finer particles compared to a BFB boiler and the bed density is 10-100 kg/m³. The pressure drop over the bed is between 10-15 kPa and the circulation causes good mixing and evens out the temperature in the furnace. The low, uniform temperature results in a low emission of NO_x [11, 16]. The CFB boiler has better performance regarding the environmental aspect than the BFB boiler and is used from 50 MW_{el} [17].

2.1.3 Thermal conversion of fuels used in fluidized bed boilers

Fluidized bed boilers can be used in the combustion of different kinds of solid fuels for energy conversion. The most common fuel is coal, but also municipal solid waste (MSW) and biomass can be used as fuel. Biomass and MSW have a high moisture content which results in a low heating value [16]. In a fluidized bed the bed acts as an additional heat source and because of the bed's thermal capacity the drying of the fuel becomes fast and this dampens the difference in fuel quality. The fluidized bed has a good mixing which in turn results in high heat transfer rates [4–6]. Overall, the fluidized bed boilers have a high combustion efficiency and are therefore suitable for low-grade fuels with high moisture content [4].

In a fluidized bed reactor three different types of thermal conversion of fuels can take place; pyrolysis, gasification and combustion. The main difference between these processes is the amount of oxygen present. Pyrolysis is a thermal decomposition where no additional oxygen is added. The temperature in pyrolysis is between 300-600 °C. The main products are oil, tar and char with high content of carbon. Syngas (H_2 and CO) is a byproduct [4]. Gasification is a partial oxidation of the fuel, with a sub-stoichiometric oxygen amount. The aim of this process is to produce fuel gas like methane (CH_4) and syngas. Incombustible solid product is also produced in lower quantity during gasification than during pyrolysis. Gasification temperatures are typically between 800-950 °C for biomass and 950-1100 °C for coal [4]. Finally, in combustion, the fuel is completely oxidized to carbon dioxide (CO_2) and water (H_2O) in the presence of excess air. In this sense, all the chemical energy of the fuel is converted into thermal energy and steam is generated. Only a small amount of chemical energy in the form of unconverted carbon is left in the ashes. Combustion temperatures are above 1000 °C [4].

During operation of the fluidized bed, coarsening of the bed particles occurs due to layer build-up of fuel-ash elements [16]. The average size of the bed particles increases which can result in agglomeration. Bed agglomeration disturbs the fluidization and reduces mixing and efficiency of the combustion process [5]. Solid biofuels usually have low ash content but contain ash elements, like chloride and potassium, which have a relatively low melting point [16]. Agglomeration is partially caused by alkali compounds [6] and it is therefore important to monitor the alkali levels, the bed temperature and to replace the bed material continuously to prevent agglomeration and defluidization of the bed [16].

2.2 Agglomeration of bed material

A major problem in combustion using a fluidized bed reactor is agglomeration of the bed particles, which restricts their movement and thus ultimately results in defluidization of the bed [5, 6, 11]. The agglomeration leads to multi-sized particles which results in channeling since the void fraction of the bed is increased. The channeling decreases the bed pressure which makes the agglomeration process clearly detectable by measuring the bed pressure [6]. When defluidization eventually occurs it is noticed by a sharp and sudden pressure drop [1]. The onset of bed agglomeration results in a decrease in the mixing of bed particles, which causes a non-homogeneous temperature distribution in the bed, resulting in local hotspots [1, 6] and uneven in space combustion process.

2.2.1 Ash-forming matter and its role in agglomeration

There are three different stages of combustion: drying, devolatilization and char oxidation [23]. The fuel particles are first rapidly heated and dried when they reach a temperature around 100 °C as they enter the furnace [23, 24]. Thereafter pyrolysis occurs where organic volatile species are released. During this stage some of the ash-forming elements will be released together with the gases. Lastly char burning begins and the particles temperature can reach 850 - 1000 °C [23]. In the fluidized bed reactor all three steps occur simultaneously throughout the bed. Ash is defined as the non-combustible inorganic part of the fuel that is left as residue after combustion of the fuel [25]. A scheme of the ash particle formation from fuel is presented in Figure 2.

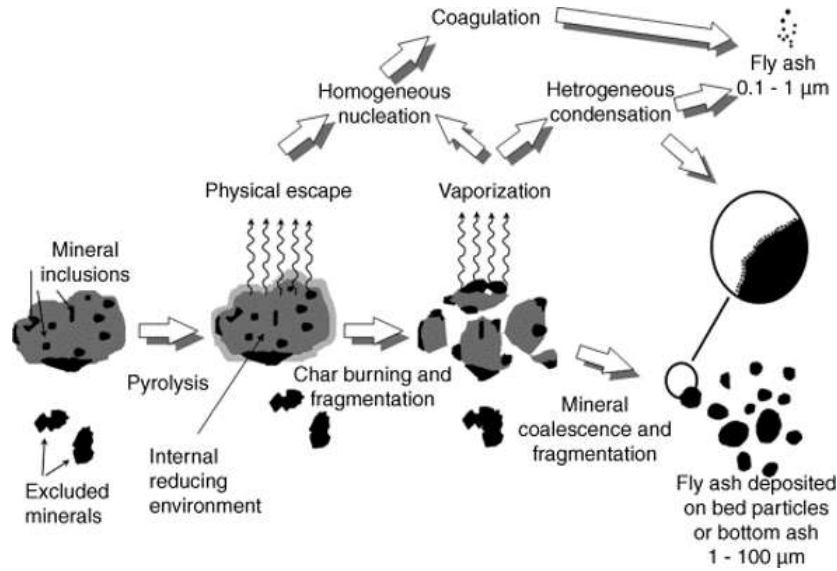


Figure 2: Scheme of ash particle formation from fuel particles [24].

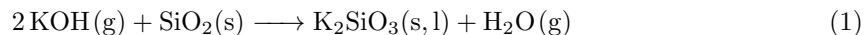
The fuel particles fragment during the thermal conversion process and form ash particles of different sizes, depending on the fuel diameter, the mineral content and its distribution as well as the number of fragments formed [24]. The larger sized ash particles usually include the main portion of the minerals and contamination of the fuel and end up as bottom ash. The smaller sized ash particles are released as fly ash during pyrolysis and char burning and leave the reactor with the flue gases. A portion of the fly ash will coalesce with the bottom ash and bed material [24, 26].

The ash-forming matter consists of organically bound matter, water soluble matter and minerals. The organically bound matter is metal ions bound to organic molecules and includes ions of K, Na, Mn, Ca, Mg, Fe and Al [24]. The water soluble part of the ash-forming elements contains often small inorganic ions such as the cations K^+ , Na^+ and Ca^{2+} and the anions Cl^- , HPO_4^{2-} and SO_4^{2-} [24]. The mineral part of the ash-forming matter in biomass consists of mixed oxide phases, for example silica (SiO_2). In addition to the organically bound matter, the water soluble matter and the minerals of the fuel, biomass is often contaminated by soil minerals including sand and clay minerals like quartz and aluminium silicates bound to alkali metals [24].

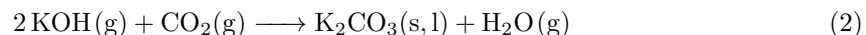
2.2.2 Alkali compounds role in agglomeration

The silica is not in itself a problem during combustion since the ash formed from the silicates has high melting point and stay crystalline during combustion in fluidized bed [24]. However, during combustion of fuels containing alkali compounds, e.g. sodium or potassium, the alkali minerals react with silicon and form sticky, low-melting point alkali silicates that contribute to sintering and agglomeration of the bed and fouling on the superheater tubes [5, 6].

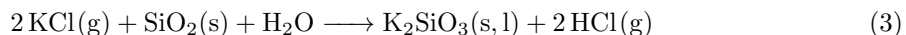
The alkali metals potassium and sodium are the most important ash-forming elements. However, since sodium is usually present in a lower concentration in biomass (an order of magnitude lower) than potassium, the ash-forming element of interest is potassium [24]. Potassium exist in the fuel both as an insoluble fraction and a soluble fraction. The insoluble fraction has its origin in the silicate contamination [24] while the soluble fraction of potassium in the biomass fuels is present as salt, organically bound or as aqueous fluids and will be released as vapours during combustion in the form of KOH(g), K(g) and KCl(g) [23, 24]. An important reaction that form alkali silicates are the reaction between silica and gaseous alkali compounds as shown in reaction 1, [24].



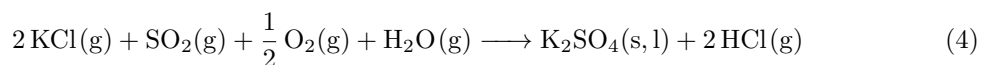
When there is no sulfur available, K(g) and KOH(g) will also form carbonate according to reaction 2.



with a melting temperature around 860 °C. Chlorine exist in the form of salts in biomass fuels. During combustion the chloride is released as chlorine vapours and facilitates the release of potassium as gaseous KCl [6, 23]. KCl will, when sulfur is not available, condense on fly ash and decrease the melting temperature of the fly ash, resulting in a sticky ash at typical furnace temperature [23, 24]. Furthermore, fly ash containing KCl is very corrosive and results in corrosion of superheaters. The chloride vapours react with other ash-forming elements. Alkali chlorides like KCl will react with quartz particles through the reaction 3, [24].



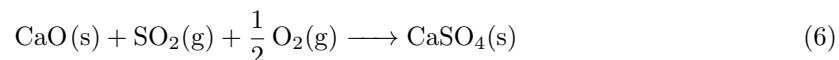
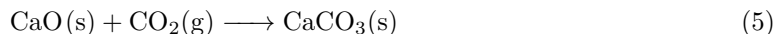
One of the products of the reaction is alkali silicate with a low melting point which forms a sticky coating on bed particles during combustion in a fluidized bed, which in turn promotes sintering [5, 24]. However, when sulfur is present reaction 4 takes place.



resulting in fly ash free from KCl [24].

2.2.3 The role of calcium in agglomeration

In woody biomass calcium is present in high concentration [24]. During combustion, the soluble calcium in biomass will produce calcium oxide which can react with carbon dioxide and sulfur dioxide through the reactions 5 and 6, [23, 24].



The reactions can lead to reaction-induced sintering, where the reaction between particles results in a new compound that forms a neck between the particles [23, 27]. The sulfation of calcium oxide also results in a reduced sulfur concentration which in turn leads to that alkali chlorides will be formed. Calcium does not induce agglomeration just by being present in the combustion [11] since the calcium sulfate formed has a high melting point (about 1400 °C). However, calcium contributes to the growth of the coating around the bed particles, resulting in an increased number of larger particles, which may lead to defluidization [11]. Larger particles tend to result in increased agglomeration since the larger particles have higher minimum fluidization velocity and a lower specific surface area [1]. Therefore, while burning a calcium rich fuel the presence of sulfur dioxide may enhance sintering [27].

2.2.4 Agglomeration mechanisms

Agglomeration can occur through different mechanisms; coating- or melt-induced mechanism, see Figure 3, and is the result of compounds with low-melting point depositing on the surface of the bed particles and gluing them together [5, 10, 11]. Coating induced agglomeration is the result of the deposit of coating layers on the bed material that melts and causes agglomeration, while melt induced agglomeration is caused by liquid bridges of molten ash particles [12]. In commercially operated fluidized bed combustors coating-induced agglomeration is the more common mechanism [10].

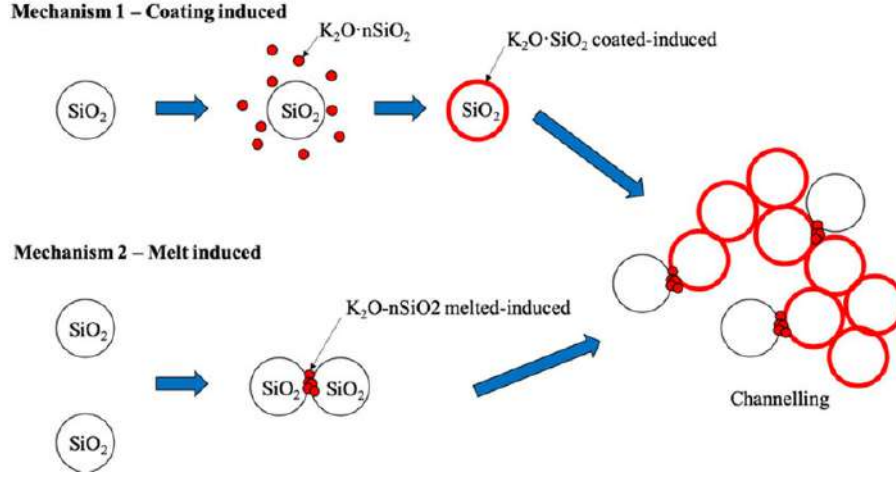


Figure 3: Schematic diagram of agglomeration mechanisms [5].

2.2.5 Ash layers around bed particles

M. Öhman et al. [28] showed that the coating mainly consist of products form within the ternary system $\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$. Chloride and sulfur were shown to not participate in the agglomeration mechanism. In the study it was proposed that homogenization takes place over time in the coating and that the homogenized silicate layer is responsible for the final agglomeration process. It was also shown that the melting behaviour is sensitive to the relative amounts of K and Ca; more potassium relative to calcium will result in more amount of melt. One of the subprocesses of agglomeration suggested was the condensation of gaseous alkali species on the bed particles, amongst which the mentioned species are KCl and K_2SO_4 .

A.-L. Elled et al. [29] found that a dual ash layer is formed around the bed particles. The inner ash layer consists of potassium silicate with a low melting point that forms a sticky layer. The sticky layer induces agglomeration unless it is covered by an outer layer consisting of calcium silicate. It was found that the outer ash layer consisting calcium silicate was crucial to prevent agglomeration.

Ca-silicate rich layer could also result in crack formation in the layer and in the particle [30]. The crack is a result of the microstructural stress from the difference in molar volumes of the different Ca-silicates. Gaseous alkali could thereafter diffuse through the cracks, forming alkali-rich melt. More cracks are formed with increasing age of the bed particles. Older particles will have wider and deeper cracks which eventually can result in that the outer layer and part of the inner layer can break off from the particle as well as fragmentation of the whole particle. This will expose the alkali-rich melt in the particles which in turn can lead to alkali deposition and agglomeration. The proposed scheme of crack formation is presented in Figure 4.

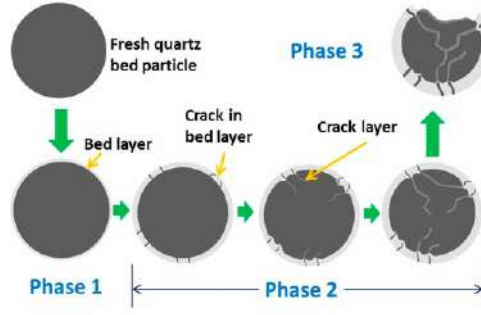


Figure 4: *Proposed scheme of crack layer formation [30].*

In conclusion the interaction between the ash-forming matter and the bed material through crack formation and layer build-up around the bed particles, leads to agglomeration. In order to predict agglomeration, it is therefore important to be able to track the content of ash-forming elements in the bed [24]. By dissolving the ash components that are deposited on the bed material in deionized water, the leachable fraction can be detected and correlated to the quality of the bed. The electronic tongue is an instrument that has a potential use in this application and will be discussed in Section 2.4.

2.3 Electrochemistry

The electronic tongue is a multisensor tool built up of several electrodes. In order to understand the processes occurring when using an electronic tongue, theory behind Faradic and non-Faradic processes as well as conductivity and how redox species behave in water when a potential is applied over the solution are presented.

2.3.1 Faradic and non-Faradic processes

At an electrode both Faradic and non-Faradic processes can take place. Examples of the difference between the Faradic and non-Faradic process are presented in Figure 5.

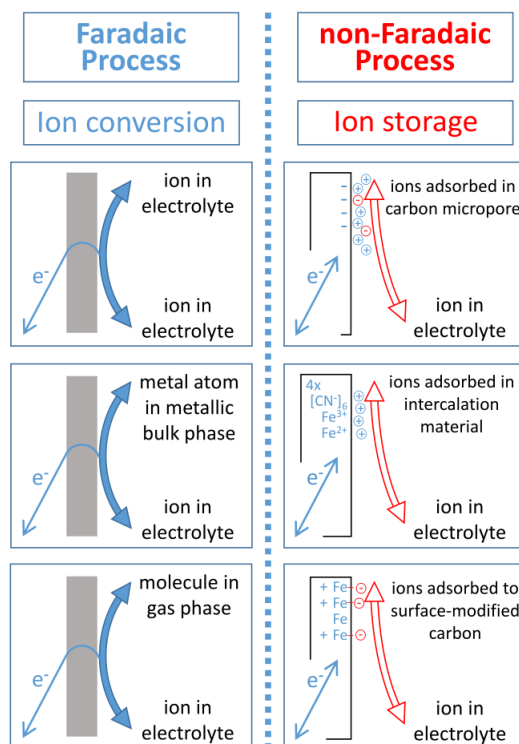


Figure 5: *Ion conversion vs. ion storage as the key difference between Faradaic and non-Faradaic (capacitive) electrode processes, using six examples [31].*

In a Faradic process there occurs an electrochemical reaction in the form of a reduction or oxidation of ions or water [31]. Here there is a transfer of charged particles (ions or electrons) across the electrode and charge is not stored in the electrode. If a process allows for a continuous current it is a Faradic process. In a non-Faradic process the current is a result of charging and discharging of an electrical double layer which behaves like a condenser in series with the resistance of the solution. In the non-Faradic process no reaction occurs and as the current flows, charge is progressively accumulated on the electrode surface since the charges cannot leave the surface.

2.3.2 Conductivity and redox species in water

Conductivity is the ability of a solution to transfer an electrical current [32]. Since the current is transported by ions, an increased number of ions will result in higher conductivity. If electrolytes are added to water the conductivity will therefore increase in the water-solution. Applying a potential over a water-solution will result in hydrogen evolution if high enough potential is applied. The more positive the reduction potential of a compound is, the more likely the substance is to be reduced [33]. Therefore cations with higher redox potential than hydrogen will be reduced before hydrogen and cations with lower redox potential than hydrogen will be reduced after hydrogen.

2.4 Electronic tongue

Electronic tongues are sensors that imitate the human gustatory system [15], this is, the ability to not only recognise one component but several at the same time in a solution. This simultaneous analysis of several components is very useful in analytical chemistry where often the solution to be analyzed contains a mixture of different substances [13]. Electronic tongues have been used since the 1980's mainly in the food and pharmaceutical industry [14]. Applications like differentiation between teas or oils, freshness of milk, water qualitative analysis or detection of microbial species have been found for the electronic tongues [34]. The electronic tongue typically consists of three types of electrodes; working electrodes, called sensing units; a reference electrode and a counter electrode.

F. Winqvist et al. [35] demonstrated how a prototype of an electronic tongue, based on voltammetry and principal component analysis, could be used to classify samples such as fruit juices, still drinks and milk. The prototype was designed at Linköping University and had two working electrodes; Pt and Au. The electronic tongue used in this work is based on that prototype and has three working electrodes; Pt, Au and Rh.

2.4.1 Working Electrodes' characteristics

The material used for the electrodes are noble metals such as gold, platinum, palladium, rhodium and iridium, non-noble metals such as cobalt, copper, silver, nickel, tungsten and titanium and carbon paste electrodes [13]. The working electrodes have different selectivities which results in complementary information [36]. Their specificity, that is, their ability to asses an exact component, is low, but the combination of specificity from all the sensing units can be utilised to extract information about the solution [14, 36]. Instead of measuring a single parameter such as pH or conductivity, the electronic tongue can be used to determine qualities of a sample such as taste information [36].

2.4.2 Electronic tongue configuration and principles

The electrodes are connected to a potentiostat that generates the potential signals and is connected to a computer. The output signal from the sensor is analyzed using pattern recognition and multivariate analysis [13]. Among common chemometric methods used to process the data from the electronic tongue are principle component analysis (PCA), partial least square (PLS) and artificial neural networks (ANN) [37]. PCA is used to find correlations between the samples and classify them [38] and will be explained further in Section 2.5.

Electronic tongues can use different measurement techniques such as conductometry, potentiometry and voltammetry. The latter has some advantages over the others, as it is a simple technique as it allows change in the used potentials and electrodes of choice, making it versatile. Furthermore the voltammetric approach is not effected by electric disturbances and has low detection limits. It does, however, only targets redox-active substances [13].

2.4.3 Voltammetric electronic tongues

Voltammetric electronic tongues are based on the principles of voltammetry. In voltammetry, a voltage is applied over the working and reference electrodes and the current between working and

counter electrode is measured [13]. The electrochemical signal measured originates from the varying fluxes of electrons which are the result of the electroactive analyte being oxidized or reduced on the working electrodes surface as the potential is changed according to a predetermined pattern [36]. The output signal is presented in a voltammogram representing the current in the y-axis and the potential in the x-axis. The voltage can be applied cyclic, by pulses or stripping [36].

Stripping Voltammetry

Stripping voltammetry is a technique used for the detection of organic substances and metal ions at very low concentrations (10^{-10} - 10^{-12} mol/l). It consists on a preconcentration of the analyte on the working electrode surface followed by a potential sweep where the analyte is stripped of the electrode, generating a current response [39].

Cyclic Voltammetry

Cyclic voltammetry is usually the first technique used to have an understanding of the redox behavior of a liquid sample [13]. This consists in applying the potential as a sweep signal (called excitation signal) between two values (called switching potentials) at a chosen scan rate.

In the voltammogram, two different parts can be identified; the cathodic current (positive current) and the anodic current (negative current). The first one is the current measured when the species are being reduced on the surface of the electrode. The latter, on the contrary, is caused when the species are being oxidized.

When the forward scan starts, the current remains zero until a potential able to reduce the species is reached. At this point a fast increase of the current can be seen until a maximum point is reached. This point corresponds to the cathodic peak current (i_{pc}) and cathodic peak potential (E_{pc}) [40]. After that, the current decreases slowly as remaining species are still being reduced. When the switching potential is reached, the reverse scan starts. At the beginning, the current continues diminishing slowly but is still cathodic as some of the species that are left in the solution are still being reduced. Later, a sufficient potential to oxidize the species is reached and the species that were accumulated in the electrode start to oxidize generating anodic current. Again, a maximum is reached corresponding to the anodic peak current (i_{pa}) and potential (E_{pa}) [40].

Pulse voltammetry

Pulse voltammetry can be divided into large amplitude pulse voltammetry (LAPV) and short amplitude pulse voltammetry (SAPV). In LAPV, a sequence of potentials of different amplitude, both negative and positive, are applied, with zero potential applied in between. This is a so called pulse-train. The measure starts with zero potential, producing no chemical reaction in the solution. Then a stepped potential is applied and the current starts flowing through the electrodes. As the species are oxidized or reduced they form a so called Helmholtz double layer on the electrodes that act as a capacitor. As the capacitance increases, the current decreases exponentially until a remaining value, called Faradaic current, is achieved [35, 36]. The measured current depends on the presence and concentration of the redox species in the solution. By changing the amplitude of the voltage, reliability of classification and accuracy of quantification are increased. The choice of the amplitudes combination has an influence in the presence of undesired Faradaic and non-faradaic effects [13].

SAPV consists of applying a continuous direct current (DC) scan to the electrodes with small amplitude voltage impulses. This produces changes in the species concentration deposited on the electrode surface. The current is measured before and after the voltage is applied and its difference is taken as the output signal, represented as peaks [36].

2.4.4 Electronic tongue's advantages and disadvantages

The electronic tongue has a potential application in the analysis of complex samples. The output signal from the electronic tongue depends on the combination of choice of electrode material, potential range and waveform applied to the electrodes [13]. This signal can be analyzed by multivariate data analysis such as PCA. A disadvantage of the instrument is that the electrodes suffer from fouling and must be cleaned and calibrated to assure their correct performance. This is a problem for the process industry as it is a time consuming step. Another drawback is the high amount of data collected and its redundancy, which requires data pretreatment [13, 38].

2.5 Principal Component Analysis

Due to many processes occurring on the electrodes' surfaces, voltammetric data from an electronic tongue is multivariate, complex and nonlinear [35]. To be able to handle the vast amount of data collected by an electronic tongue a multivariate method of analyzing the data is necessary. A multivariate methods that could be used to interpret the data from an electronic tongue is principal component analysis (PCA). PCA is a mathematical method used to find structure and correlation in data. It is also classified as a non-supervised pattern recognition method [41]. It can be used to reduce and classify data, to find outliers in the data, to find correlations between variables and observations and to detect the most influential variables. PCA was first described by Pearson in 1901 and Hotelling in 1933, but it was not until the widespread use of electronic computers, that it found a wide range of applications in almost every field i.e. agriculture, biology, economics, meteorology, psychology, etc. [42]

2.5.1 Principal components

The idea behind the method is to reduce the number of variables by means of creating new, fewer variables called *principal components* (PCs), which are linear combinations of the original values. PCs have the ability to explain most of the variation present in the original values [35]. The first principal component is a vector which describes the direction of the largest variance. The second principal component is vector orthogonal to the first principal component. Principal components are created until most of the variance of the data is explained. In PCA the data is organized in a matrix called X , [43]. The N rows of this matrix are the *observations* and the K columns are the *variables*. The X matrix has the dimension ($N \times K$) and can be written as

$$\mathbf{X} = \begin{bmatrix} x_{1,1} & \cdot & \cdot & \cdot & \cdot & \cdot & x_{1,K} \\ x_{2,1} & \cdot & & & & & \cdot \\ \cdot & & \cdot & & & & \cdot \\ \cdot & & & \cdot & & & \cdot \\ \cdot & & & & \cdot & & \cdot \\ x_{N,1} & \cdot & \cdot & \cdot & \cdot & \cdot & x_{N,K} \end{bmatrix}$$

where each sample x_i has the dimension $(1 \times K)$. In PCA the number of variables are reduced by creating new variables called principal components. The principal components are linear combinations of the original variables. Therefore, if the number of variables should be reduced from K to 2, then a linear transformation mapping

$$x \in \mathbb{R}^K \mapsto z \in \mathbb{R}^2$$

is required, where Z is the matrix with size $(N \times 2)$ containing the the new variables z with the dimension $(N \times 1)$. These two new variables are called principal component 1 and 2. The linear transformation can be written as in Equation (7). [43],

$$z = xU \quad (7)$$

where U is a matrix with dimension $(K \times 2)$. The variance of z can be expressed as in Equation (8), [43],

$$\text{Var}\{z\} = u^T C u \quad (8)$$

where C is the covariance matrix of the original matrix X . To maximize the variance, the right hand side of Equation (8) should be maximized. It can be shown that, under the constraint $u^T u = 1$, the optimization problem can be expressed as Equation (9), [44],

$$C u = \lambda u \quad (9)$$

which is the definition of eigenvectors and eigenvalues if u is the eigenvector and λ is the corresponding eigenvalue of the covariance matrix C . By using Equations (8) and (9), the variance of z can be expressed as in Equation (10),

$$\text{Var}\{z\} = u^T \lambda u \quad (10)$$

and since λ is a scalar and $u^T u = 1$ the expression can be rewritten as Equation (11)

$$\text{Var}\{z\} = \lambda \quad (11)$$

Therefore, to maximize the variance of z , the largest possible value of λ should be used. By choosing the components of U in equation (7) as the eigenvectors corresponding to the largest eigenvalues of the covariance matrix C , in descending order, the components of Z will explain the largest possible variance. In this way the principal components explain the largest variance of the data with the first principal component explaining most of the variance compared to the other components of Z . The data can thereafter be related to the PCs in order to classify the observations and describe the original variables influence on the system.

2.5.2 Loading plot

To describe the original variables influence on the system the loading plot can be investigated [42]. Each point shown in the loading plot correspond to the cosine of the angle formed between an original variable and a PC, see Figure 6. Therefore, the limits of the loading plot is $[-1, 1]$. Values closer to 0 mean that the corresponding variable has little influence [45]. A loading vector (p) describe the relation between all the original variables and one PC. The resulting loading matrix (P) consists of one loading vector per PC. A 2-D loading plot is built by two loading vectors. Variables appearing close to each other in the loading plot have a positive correlation while variables appearing diagonally opposite to each other are negatively correlated.

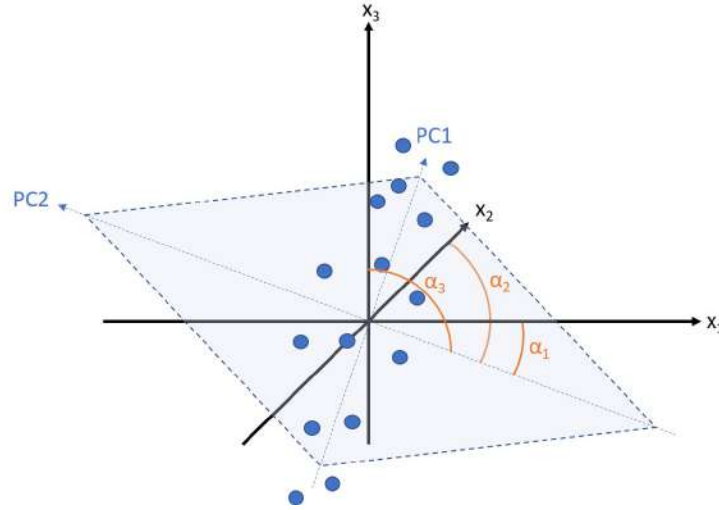


Figure 6: *Visual explanation of the calculation of loading vector values. Cosine of the angle between the original variables and PCs are calculated.*

2.5.3 Score plot

To show the relation between observations and to classify them the score plot is used. Each point shown in the score plot correspond to the projection of the observations onto the plane created by the two PCs, see Figure 7. Each score value is the distance from the origin, along the direction of a PC, until the projection of the observation onto that PC. A score vector (t) describe the relation between all the observations and one PC [35]. The resulting score matrix (T) consists of one score vector per PC. A 2-D score plot is built by two score vectors. Similar observations will cluster together in the score plot. Observations close to the centre of the plot exhibit values close to the average score value, while an observation far away from the centre deviates from the average.

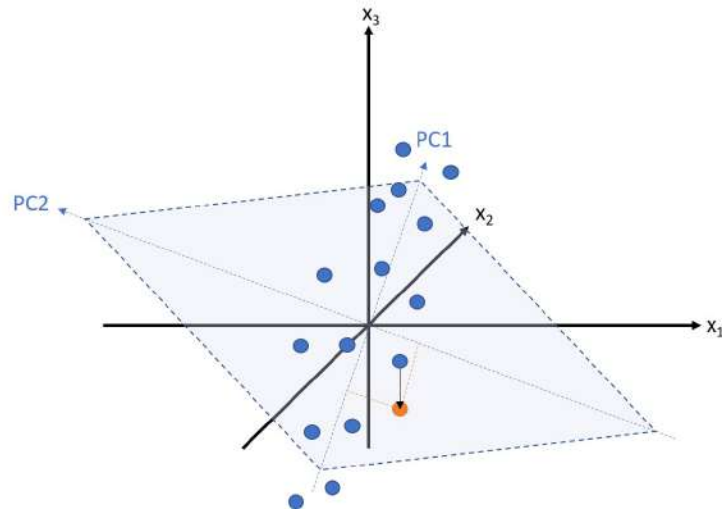


Figure 7: *Visual explanation of the calculation of score vectors. The observations are projected onto the plane built by the PCs.*

A visual explanation of how the score and loading matrices are connected to the original matrix is presented in Figure 8.

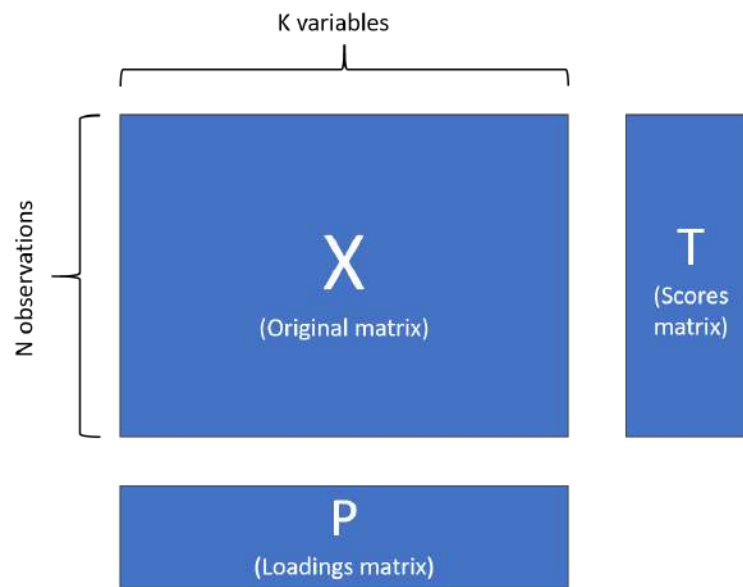


Figure 8: *Visual explanation of how the score and loading matrices are related to the original matrix.*

2.5.4 Interpretation of score and loading plot

Since the scores are linear combination of the data weighted by the loadings, the loading and score plots can be superimposed to draw conclusions about the original variables contribution to the observations. If an observation is located far away from the centre of the score plot, the loading plot can be investigated to determine which original variables explain the deviation from the average. If the observation has a value lower than the average value of a certain variable, that variable will be located in the opposite side of the loading plot. If the observation has a higher value than the average of a variable, that variable will instead be located in the same part of the loading plot as the observation.

3 BFB boiler at Idbäcksverket

In this project, data collected from the bubbling fluidized bed combustor at Idbäcksverket in Nyköping, was analyzed. Idbäcksverket is a combined heat-and-power plant producing 60 MW_{th} and 35 MW_e from the combustion of 105 MW_{fuel} wood chips, demolition wood and bark. In Figure 9 the inside of the furnace is presented. The furnace bottom has a cross-sectional area of $5.3 \times 9.3 \text{ m}$. The height between the bottom of the furnace and the fuel inlet is 1.5 m . The amount of sand normally inside the furnace is 120 ton and the average bed height is 0.58 m . The fluidized bed uses silica sand as bed material with a particle size distribution between 0.354 mm and 2.800 mm .

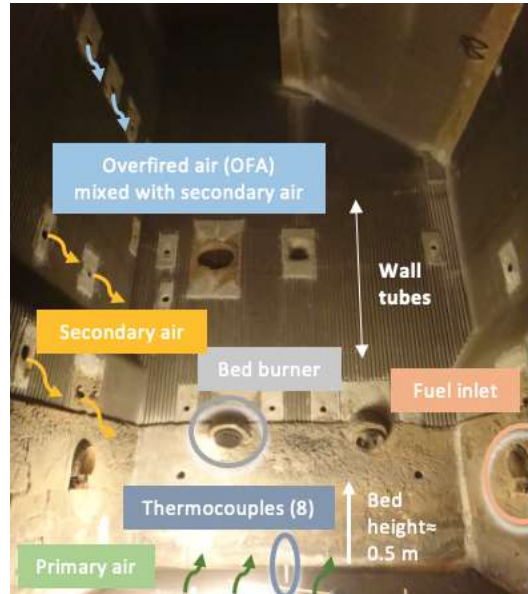


Figure 9: *Illustration of the different parts of the Idbäcksverkets BFB combustion reactor.*

3.1 Plant conditions

The BFB boiler at Idbäcken is operated at a temperature between 800-840°C and a pressure drop of 6-7 kPa. The data collection for this study started on 11th of December 2019 and ended on 4th of June 2020. This data has been divided into three chronological operation periods; period 1, period 2 and period 3. Between these periods the boiler was stopped. Period 1 goes from 11th of December to 19th of February (71 days), period 2 from 26th of February to 14th of April (49 days) and finally period 3 goes from 24th of April to 4th of June (42 days). Information obtained from the operation periods including temperature, pressure and ash forming matter content present in the fuel are presented in Appendix A.

The BFB boiler has two in-flows of bed material; fresh bed material and recirculated bed material and an out-flow of bed material, which is a mix between used bed material and bottom ash. The out-flow of the mix between recirculated bed material and bottom ash is sieved and particles above a certain size are re-directed to a reject silo, while the smaller particles are returned to the storage silo of recirculated bed material before they re-enter the boiler. At the start of period 1 the bed material was completely replaced. At the start of period 2, 2/3 of the bed material was replaced while at the start of period 3, the bed material was completely replaced. The load of the boiler in period 1, increased to high load. At the end of period 2 the load started to decrease and period 3 had a low load. This is related to the energy demand of the seasons of the year. A graph with the detailed load of the periods can be seen in Appendix A.

3.2 Analysis of bed material using an electronic tongue

An electronic tongue was used to analyze bed material from the BFB boiler at Idbäcksverket. Bed material samples were collected from 6th December 2019 to 4th June 2020, resulting in 153 bed material samples. The date when each sample was collected as well as an ID connected to each sample is presented in Appendix B. The investigated bed samples were collected at the outlet of the recirculated bed material silo, before the bed material re-entered the furnace again, see Figure 10.

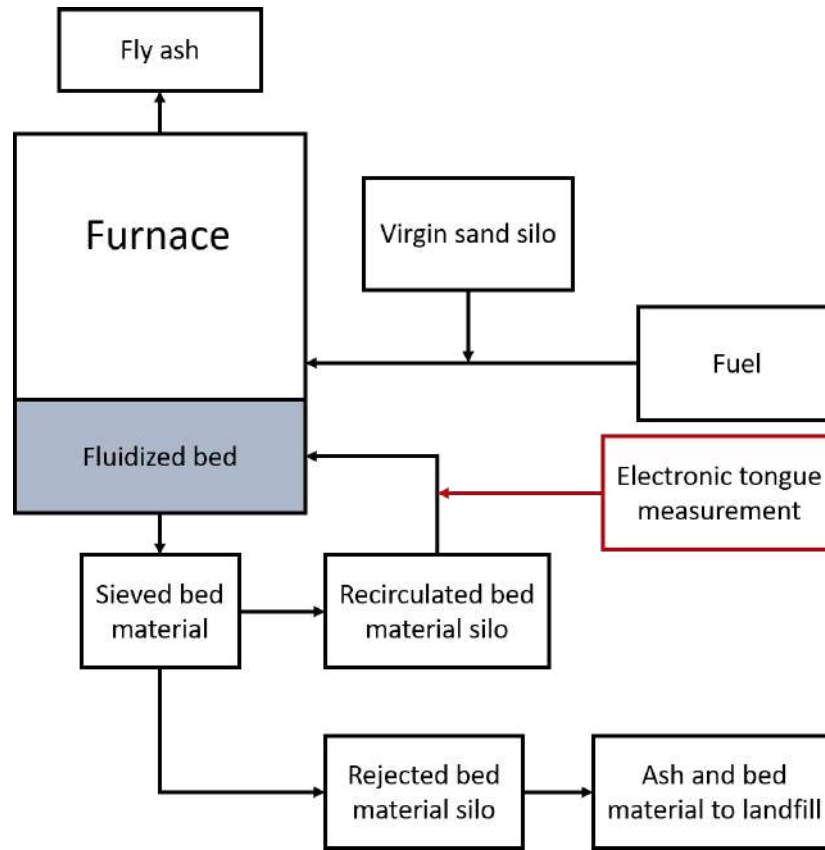


Figure 10: *Simplified schematic of the fluidized bed boiler at Idbäcken. The place where the bed material was collected for analysis is marked in red.*

Each sample was analyzed using large amplitude pulse voltammetry (LAPV). The method used to analyze the bed samples from Idbäcksverket was to leach the bed material in a deionized water in a plastic beaker, using a magnetic stirrer, while at the same time measuring the leachate using the electronic tongue. The electronic tongue used for the experiment had a stainless steel electrode used as counter electrode and three working electrodes; platinum, gold and rhodium. During the experiments all three working electrodes were connected at the same time. One measurement consisted of 600 pulse-trains and lasted for approximately 6 minutes. The pulse-train is presented in Figure 11.



Figure 11: *Pulse-train used to analyze bed material from Idbäcksverket.*

4 Bed material characterization

Bed samples collected from December 2019 to June 2020 were investigated using Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM-EDS), Atomic Absorption Spectroscopy (AAS), X-ray Fluorescence Spectrometry (XRF) and electronic tongue (ET). Based on the principal component analysis of the 153 samples, 10 representative samples were selected to be further investigated. SEM-EDS was used to qualitatively investigate the particles and to measure the ash-layer composition and thickness around the bed particles. The results from the SEM-EDS were used as the basis for the AAS analysis; the elements found to be abundant in the particle layers, (Ca, K, Na and Mg), were investigated further. The result from the AAS showed the leachable fraction of the elements of interest in the different samples. XRF was then used to find the total composition of the bed material. The result from XRF and AAS were thereafter used as a base for the experimental setup for the experiments with the ET. A flowchart of the experimental procedure is presented in Appendix C

For the experiments with the ET a method similar to the one used for the 153 bed samples was applied. However, the same potentiostat and pulse-train procedure was not available. Therefore a new procedure, resembling the old one, had to be built and instead of measuring with all working electrodes at the same time one electrode at a time was connected to the potentiostat. The potentiostat used for the bed samples gave a response signal in potential [V] while the one used for the known samples gave a response signal in current [A].

In the following sections the instruments as well as the preparation of samples and conduction of experiments are presented.

4.1 Instrument description

In the following section a brief description of the instruments SEM-EDS, AAS, XRF and ET is presented.

4.1.1 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

To obtain chemical information and topographic images of micro- and nano-structures a Scanning Electron Microscopy (SEM) was used. When a sample is studied with SEM a focused beam of high energy electrons is generated from an electron source consisting of one cathode, an anode and a Wehnelt cylinder. The cathode emits an electron that is released towards an anode and the density and brightness of the beam is controlled by the cylinder [46]. The electrons are focused using a series of lenses, and a magnetic field in deflection coil causes the electron beam to scan the sample [47]. A schematic of the SEM is presented in Figure 12.

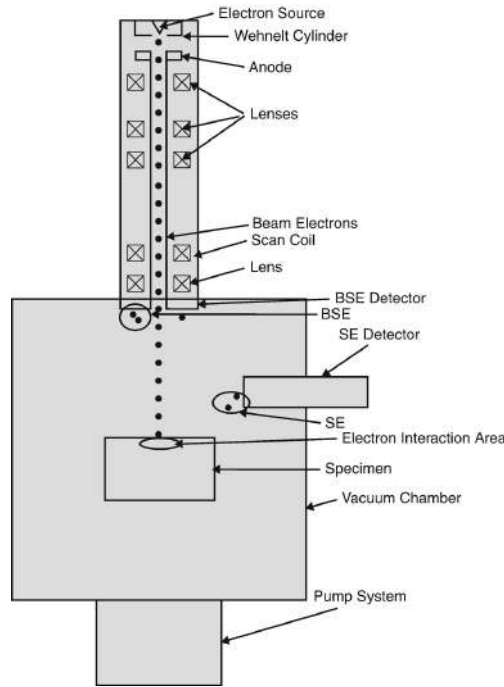


Figure 12: *Schematic diagram of a scanning electron microscope (SEM) [46].*

The interaction of the electron beam and the surface of the sample results in several signals among which back scattered electrons (BSE) and secondary electrons (SE) can be detected using BSE and SE detectors [46]. The SE are the result of inelastic scattering process while BSE are the result of an elastic backscattering. Since there is a higher probability of backscattering in areas with higher mean atomic number those areas will appear as brighter in the images [46]. To obtain surface images the BSE and SE are counted for each point that the beam is scanning, resulting in a gray-scale image. The more BSE and SE in that is counted in a point the brighter that area in the image will

be. To analyze the composition of a sample Energy Dispersive X-Ray Spectroscopy (EDS) is used. X-rays represent another signal resulting from the interaction of the electron beam and the surface of the analyzed sample. The electron beam knocks out electrons from the inner shell when the kinetic energy of the electron from the beam is higher than the binding energy. The vacant space is thereafter filled by an electron from a higher shell, the energy difference is emitted as X-ray radiation [46]. Since every element has its characteristic X-ray spectrum the signal gives information about the elemental composition of the sample. In this way, point scan is used to analyze the sample at a specific point; linescan is used to analyze the gradient of elements in a straight line and intensity mapping gives an overview of the difference in composition in a micrograph.

4.1.2 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy is an analytical method used to quantitatively detect dissolved ions in a liquid sample. It is a highly sensitive method with a detection limit of elements on a part per million and billion scale, however it does not allow for multicomponent analysis and requires one analyte to be determined at a time [48, 49]. The method is based on the principle that ground-state metal atoms absorb light at a specific wavelength [50]. This wavelength corresponds to the energy required for the electronic transition in the electron orbitals. The AAS consists of a light source, a flame atomizer, a nebulizer, and a detector [51]. The sample solution is provided by the nebulizer is atomized in the flame and the light source, a hollow cathode tube containing the element of interest, emits a light with the same wavelength as the element that is being investigated. The amount of absorbed light is proportional to the concentration of the element.

4.1.3 X-ray Fluorescence Spectrometry

X-ray fluorescence spectrometry is a quantitative, nondestructive technique used to determine the elemental composition of a material [52]. Material composition ranging from 0.1% to 100% can be detected [53]. The sample is excited by primary high-energy X-ray and secondary X-rays of lower energy, also called X-ray fluorescence, is emitted from the sample. The fluorescent X-rays emitted are characteristic for the energy levels of each atomic species and the intensity of the rays are proportional to the amount of the elements in the sample [54, 55].

4.1.4 Electronic Tongue

As mentioned in Section 2.4, the electronic tongue is a sensor that imitates the human gustatory system. It has the ability to recognise several components in a solution, but has a very low specificity. Instead of measuring a single parameter the ET can be used to determine qualities of a sample. As explained, the ET consists of three types of electrodes; working electrodes, a reference electrode and a counter electrode. The ET used for the experiments had three working electrodes: a platinum, a gold, and a rhodium electrode, and a stainless steel electrode that was used as counter electrode. The potentiostat's reference electrode was connected to the ET's counter electrode. The ET was connected to a potentiostat (AUTOLAB AUT72461) that was used to control the ET and the program NOVA 2.0.2 was used to create the pulse voltammetry procedure used for the experiments.

4.2 Method

The preparation of samples as well as how the experiments were conducted are presented in the following section.

4.2.1 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

The samples to be examined in the microscope are prepared by mounting them in an epoxy resin where the surface is later grinded and polished to get a flat cross section of the bed material. Bed samples from each chosen time period were analyzed; two samples per period. First, a general visual scan of the sample was carried out and representative micrographs were captured. Three different magnifications were used when obtaining the micrograph; 450x to have an overview of several particles at the same place and 1500x and 3500x for a closer capture of the layers. The atomic percentage of the layers was determined by a combination of line and spot scans. Finally, to get an overview of where the elements were located in the particles, EDS-mapping was done.

4.2.2 Atomic Absorption Spectroscopy

Samples of bed material (three for period 1 and 2, and four for period 3) were prepared by adding 10 g of the sample to 40 ml of milli-Q water in a glass beaker and the sample was leached for 6 minutes using a magnetic stirrer. The solution was thereafter filtered through a filterpaper using a funnel. The content of K, Na, Ca and Mg in the leachate was measured using AAS. A calibration curve fitted to three points was created for each element using calibration solutions and concentrations presented in Appendix D. In order for the sample concentration to fit within the range of the calibration curve the leachate of each sample was diluted 10 times by taking 1 ml of the sample and adding 9 ml of milli-Q water. Samples which did not fall within the range after 10 times of dilution were diluted an additional 4 times, resulting in a 40 times dilution of the original sample, see Appendix D. The lamps, filters and wavelengths used as well as the detection range for the measurements of each component are presented in Appendix D. Each result was replicated three times during one measurement and the final result was taken as an average of the three replications. Milli-Q water was used as a blank sample before and in between the measurements of the samples.

4.2.3 X-ray Fluorescence Spectroscopy

XRF was used to determine the elemental composition of each sample. The samples were prepared by grinding the bed material to a fine powder in order to make the entire bed material accessible and not only the outer sections of the particles. The grinded samples were then added to the sample holders. Each sample holder was filled with approximately 4 g of bed material; enough to cover the entire bottom of the sample holder. The samples analyzed using XRF as well as the amount of sample used for the analysis are presented in Appendix E.

4.2.4 Pulse voltammetry using Electronic Tongue

Experiments performed by pulse voltammetry, using the ET, were divided into two different setups. The first setup consisted of monocomponent solutions of Ca(OH)_2 , KOH and NaOH with the concentrations 20, 40 and 80 mg/l for each solution, resulting in nine different solutions. Each

sample was prepared for the pulse voltammetry by adding 30 ml of sample to a beaker which was placed on a magnetic stirrer.

The second setup consisted of eight different mixtures of Ca(OH)_2 , KOH and NaOH with different combinations of concentrations of the three compounds. Further information about the setups can be found in Appendix F. During the experiments the electronic tongue was connected to the potentiostat, mounted on a lab stand and lowered into the solution, see Figure 13.



Figure 13: *Set up of the ET for the experiments. The three working electrodes can be seen in the close-up.*

The working electrodes were connected one at a time and 100 pulse-trains were used per electrode. The signal from the 100th pulse-train was later analyzed. These signals are current measurements that respond to an applied voltage signal from the pulse-train. The train consists of 15 voltage pulses of different amplitude, both positive and negative, which were sampled 5 times each following the pulse voltammetry technique. This results in a total of 75 measurements done by the three electrodes, generating a total of 225 response signals. The information about the pulse-train can be found in Appendix F.

5 Results

The results of the PCA carried out on the signal responses from the ET used to analyze the 153 bed samples from Idbäcksverket are presented in the following section together with the results from the

bed material characterization using SEM-EDS, AAS and XRF. The PCA analysis performed on the data from the experiments conducted with the ET of the known samples are presented hereafter, followed by a summary of all the results.

5.1 Principal component analysis (PCA)

The response signal from the 600th-pulse-train from each sample obtained from the ET between December 2019 and June 2020 was collected in a matrix. This matrix had 153 rows (one for each, almost daily, sample) and 225 columns (one for each variable of the pulse-train). A PCA was performed on the data resulting in nine principal components, explaining 99.7 % of the variance of the data, where the three first principal components explained 94.3 % of the variance.

5.1.1 Score plot

The score plot of the PCA is presented in Figure 14. The IDs are in consecutive order of time, from December 2019 to June 2020.

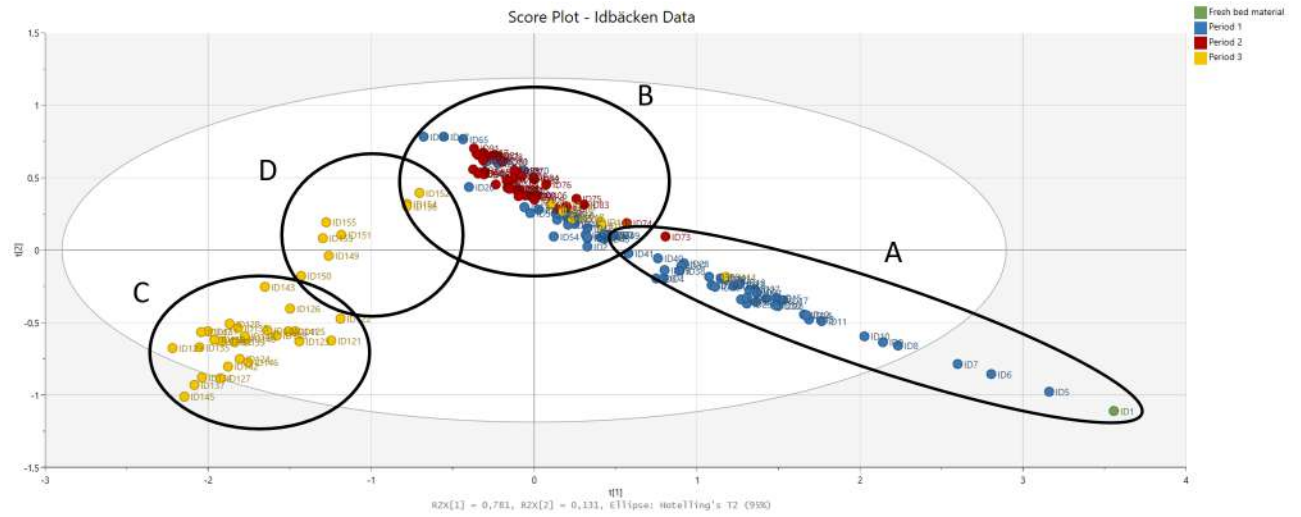


Figure 14: Score plot (t_1 vs. t_2) of the response signal of the 600th pulse-train from the electronic tongue for each sample from December 2019 to June 2020. Pre-processing of data was carried out by centering the data points to the mean and component-wise scale to unit variance. The colors represent operation periods and the circles mark areas of interest.

The score plot of the ET-response shows that the samples from period 1 are more difficult to group than the samples of period 2 and 3. The scattered samples of period 1 suggests that the ET-signal changes during that period. Consequently, this suggests that the concentration of the species that is detected by the ET is also changing during the first period. In the beginning of period 1 the bed material was completely exchanged to fresh bed material with a more narrow particle size distribution, meaning that at first the bed material only consists of silica sand, the sample labelled as *ID1* in the score plot represents the fresh bed material. Over time ash-forming matter from the

fuel starts to build up an ash layer on the bed particles in the bed, resulting in a gradual change in the ET response during period 1.

The end of period 1 and all of period 2, (marked as B in the score plot), have signals from the ET that are grouped together, suggesting that the concentration of the key species being detected by the ET did not change in the bed. The ET samples from most of period 3, (marked as C in the score plot), are grouped together fairly well, but are separated from the other samples. This suggests that the concentration of the key species changed in the bed from period 2 to period 3. The separation of the samples of period 3 from the other samples might be explained by that during period 3 a fuel with different quality was used.

Furthermore the last samples of period 3, (marked as D in the score plot) are separated from the rest of the samples. However, to easier see this, the score plot consisting of the first and third principal component could be investigated, see Figure 15.

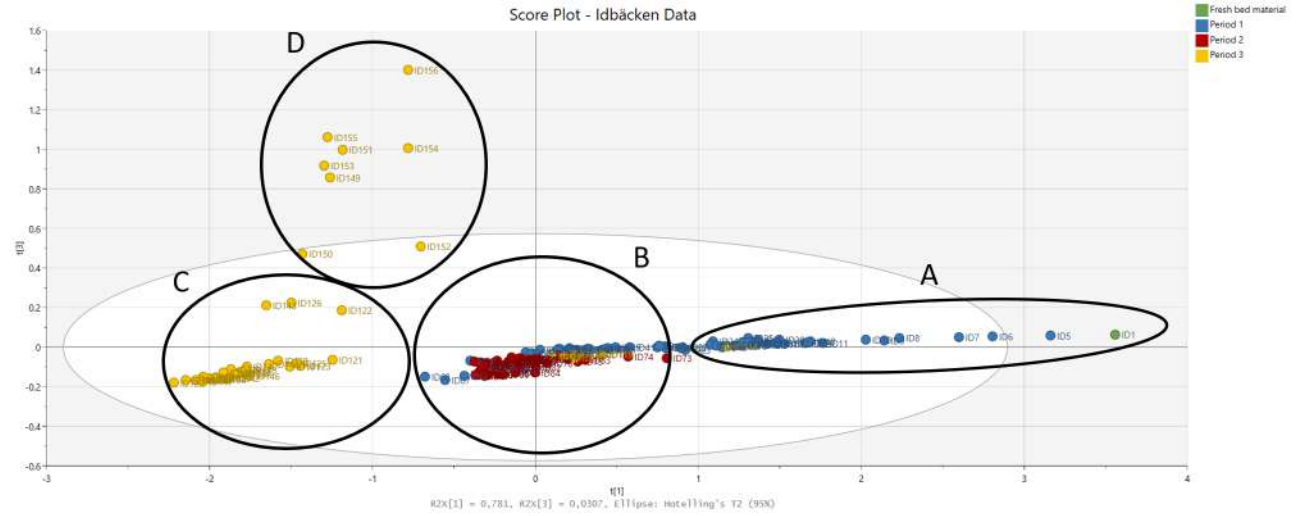


Figure 15: Score plot ($t1$ vs $t3$) of the response signal of the 600th pulse-train from the electronic tongue for each sample from December 2019 to June 2020. Pre-processing of data was carried out by centering the data points to the mean and component-wise scale to unit variance. The colors represent operation periods and the circles mark areas of interest.

5.1.2 Comparison of score plot and accumulated ash forming matter

The distribution of the data in the direction of PC1 could be explained by the accumulation of ash-forming matter in the bed. The analysis of the ET-data suggests that there is change of the bed quality during period 1 as well as in period 3. By analyzing the accumulation of ash-forming matter in the bed that is added from the fuel, (see Figure 16), it can be seen that there was an increase in ash-forming matter during period 1. After the initial increase the content was kept between certain constant levels by periodically exchanging part of the bed. This is in accordance with the observation that the ET-signals from the end of period 1 and the entire period 2 are grouped together in the score plot (marked as B in Figure 14).

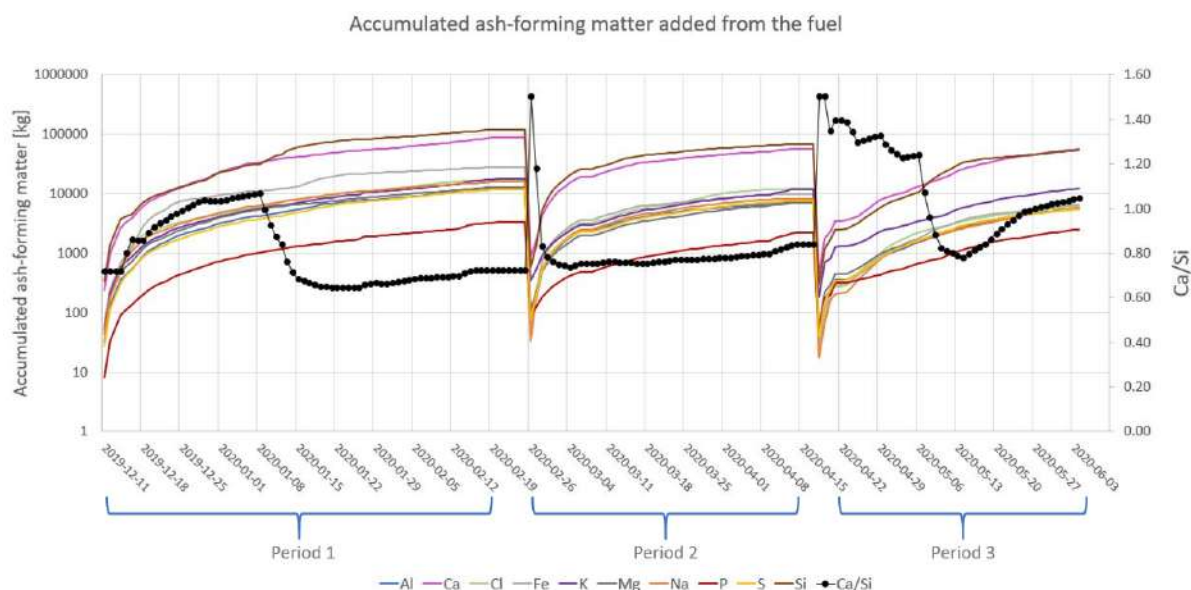


Figure 16: Accumulated ash-forming matter added to the bed from the fuel from December 2019 - June 2020. The ratio between Ca and Si is shown by a black dotted line.

As can be seen in Figure 16, the Ca/Si is higher in the beginning of period 1 and during period 3. This could be the reason for the separation of the data in the direction of PC2, that occurs during the same time in the score plot, see Figure 14.

5.1.3 Further analysis of period 3

From the analysis of the accumulated ash-forming matter from the fuel it is not clear why the time period 3, (in Figure 14), is separated from the other periods in the score plot. However it may be noted that the accumulation of potassium in period 3 is larger relative to the other elements than it is in period 1 and 2. The ratio between the accumulated calcium and silicon is also larger in period 3 compared to end of period 1 and the entire period 2.

5.1.4 Loading plot

The loading plot from the PCA was analyzed to investigate the effect of each electrode as well as the significance of each pulse. The loading plot is presented in Figure 17 and describes the variables influence on the system.

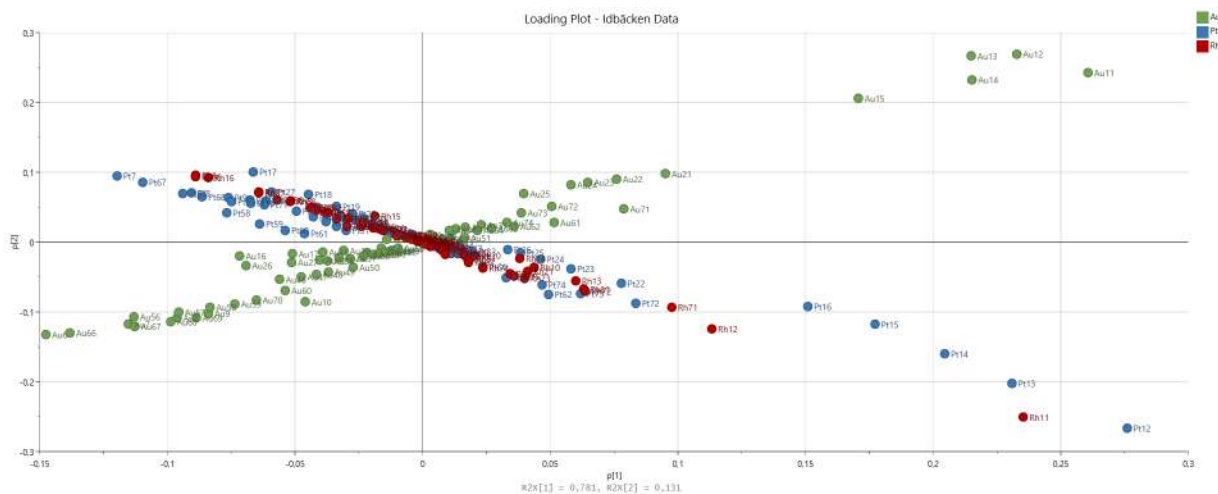


Figure 17: Loading plot corresponding to the score plot of Figure 14. Each variable is marked by its corresponding electrode and response signal number of the pulse-train.

Each pulse-train consists of 15 pulses that are being sampled 5 times each, resulting in 75 response signals per electrode. Each response signal represents a variable and since there are three electrodes, the final number of variables are 225. In the loading plot each variable is marked with the corresponding electrode and sample. For example Au15 means the 15th response signal of the pulse-train using the gold electrode.

The result from the loading plot shows that the data from the rhodium and platinum electrodes are very close to each other, suggesting that both contribute with similar information. However, the data from gold electrode is clearly separated from the other data points and thus contributes with different information. From the loading plot it can also be seen that the information content is largest from the platinum and gold electrode during the pulse corresponding to the variables 12 - 16 as well as the pulse corresponding to the variables 66 - 70 since those variables are furthest away from zero. For a clearer view of these variables see Figure 18.

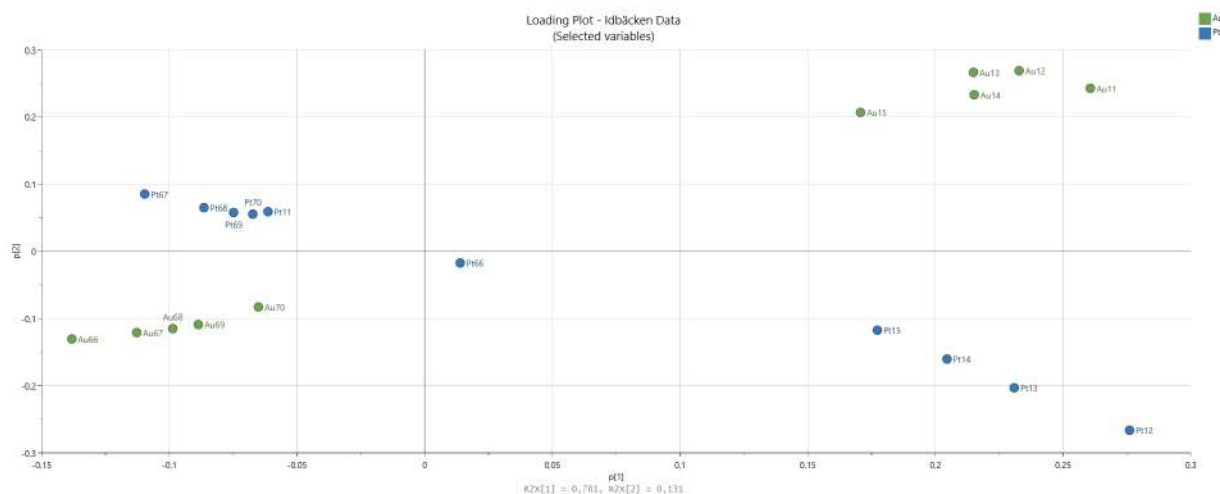


Figure 18: *Modified loading plot showing only the influential variables.*

In the score plot, Figure 14, the samples from beginning of period 1 (marked as A) and the samples of period 3 (marked as C) are separated from the other samples in both horizontal and vertical direction. The variables far from zero in horizontal and vertical direction of the loading plot would therefore be the variables responsible for the separation of the classes in the score plot. This suggests that pulses corresponding to the samples 11 - 15 and 66 - 70 from the gold and platinum electrodes are responsible for the detection of the change in the key species in the bed material.

By investigating the loading plot consisting of the principal component 1 and 3, (see Figure 19), it can be seen that the variables Au11 - Au13 are separated from the rest of the variables in horizontal direction. These variables might therefore be the variables responsible for the separation of group D from the other groups in the score plot seen in Figure 15.

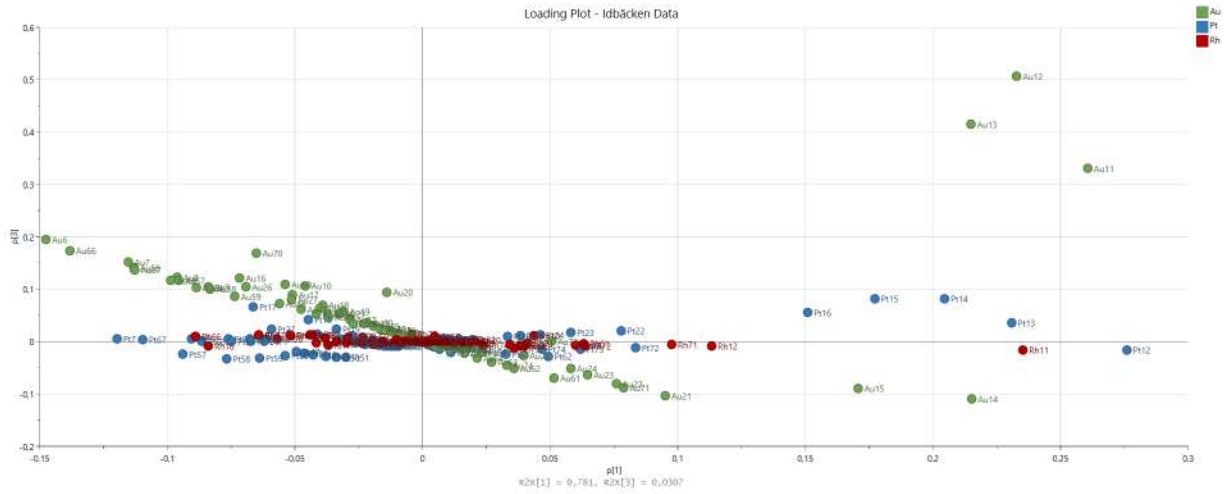


Figure 19: Loading plot (p_1 vs. p_3) corresponding to the score plot of Figure 15. Each variable is marked by its corresponding electrode and response signal number of the pulse-train.

By plotting the changes in the response signal over time, for each variable, the changes in the response signal can be visualized more clearly, see Figure 20.

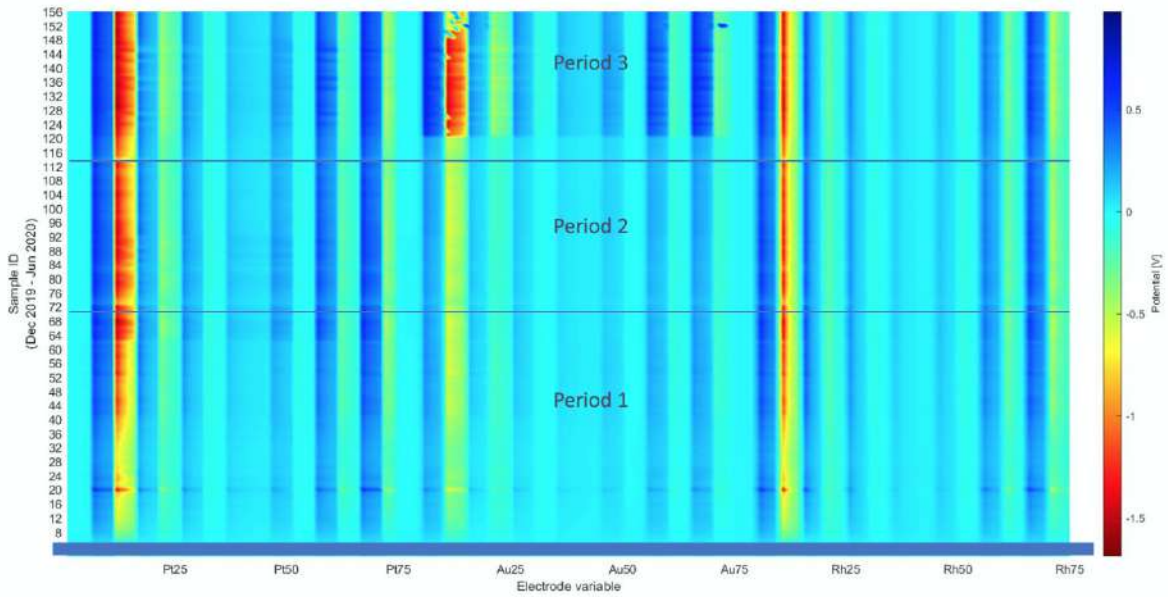


Figure 20: A waterfall plot showing the response signal over all periods for all variables.

It can be seen that the variables corresponding to the pulse from the Au-electrode with amplitude -1V (Au11 - Au15) experience a sharp increase in response towards the end of the season (period 3). It can also be seen that the same pulse for the Pt- and Rh-electrode has a more gradual increase beginning at the start of the season (period 1) and is kept constant throughout the remaining periods. This can explain the increase in the concentration of key elements throughout the periods. Furthermore, it may be noted that there is a disturbance in the signal from the Au-electrode in the final samples (ID149-156) which is a consequence of that the Au-electrode was not connected properly during those experiments. These samples correspond to the samples that are located in cluster D in Figure 15. The separation of the last samples might therefore be explained by a measurement error. The response signals plotted as potential vs variables can be seen in Appendix G.

5.1.5 Conclusion of principal component analysis

The principal component analysis shows that the signal from the ET changes over the three periods suggesting that the signal can be used to follow the change in the bed material. It can be seen that the signals from period 1 are harder to classify than the signals from period 2 and 3. This result is expected since the bed consisted of fresh bed material in the beginning of period 1 and was thereafter exposed to ash material that accumulated on the bed particles throughout the period, changing the content of the bed material analyzed with the ET. At the stop between period 1 and 2, 2/3 of the bed material was replaced, which can be seen in the score plot. However, overall period 2 was easier to classify since the content of the bed was kept more constant. Finally period 3 deviates from the other periods. This can be explained by that a fuel with different composition was used during this period. Looking at the loading plot it could be seen that the variable responsible for classifying period 3 differently than the signals from the end of period 1 and the entire period 2, is the pulse from the Au-electrode with amplitude -1V. Analyzing the variable further it could be seen that the signal had a sudden, sharp increase during period 3. This suggests that there is a change in composition of the bed material occurred during period 3, which might be a result of the different fuel used. To determine which element that might cause the signal from the ET the bed material and the layer build-up around the bed particle were investigated using SEM-EDS.

5.2 SEM-EDS analysis

An elemental analysis, using EDS point scans, line scans and mapping, was done on the bed samples to identify the main components of the layers as well as any other interesting element that could be detected further on by the electronic tongue in a liquid solution. The elements Si, Ca, Na, K, Fe, Al and Mg were selected as elements of interest for comparison in the study as they were the most abundant in the samples' layer. Appendix H contains a summary table with the atomic concentration and thickness of the layers as well as a more detailed table with micrographs, line scans and composition. A more visual representation of the most relevant data can be seen in Figure 21, where Si, Ca, Na and K are compared.

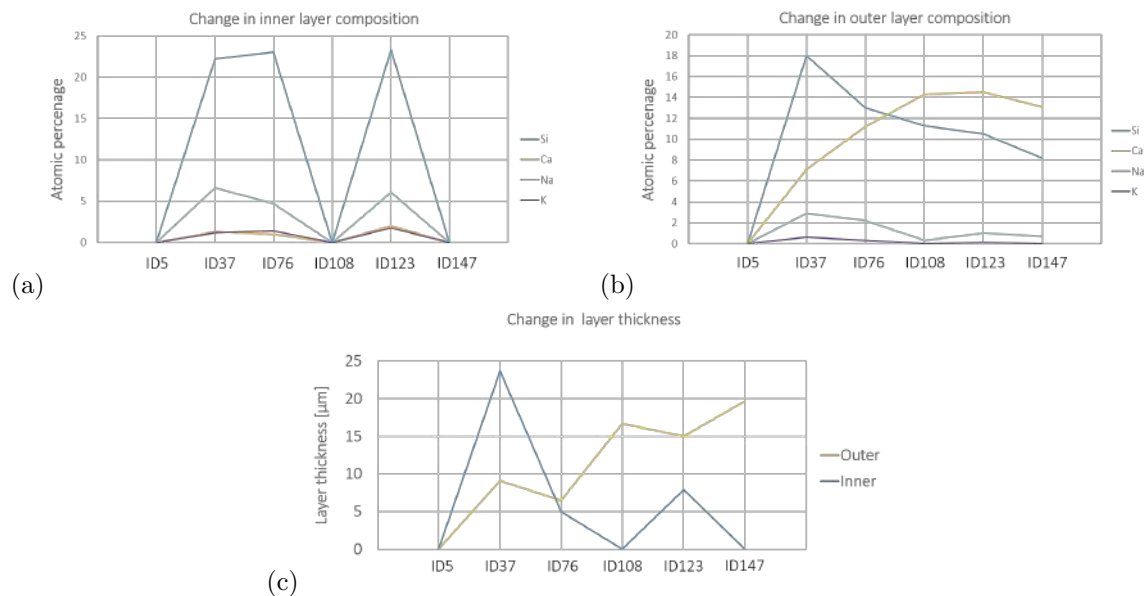


Figure 21: Summary of the data collected by SEM-EDS. a) Change in inner layer composition. b) Change in outer layer composition. c) Change in layer thickness

The layers surrounding the particles are divided into an inner and an outer layer. Apart from Si and O, the inner layer mainly consists of Na and the outer layer consists mainly of Ca. Therefore, the inner layer thickness is measured from EDS-linescans of Na and the outer layer thickness is measured from EDS-linescans of Ca. A representative linescan of a layer around a silica particle, starting from outside the particle and going into the particle, is presented in Figure 22.

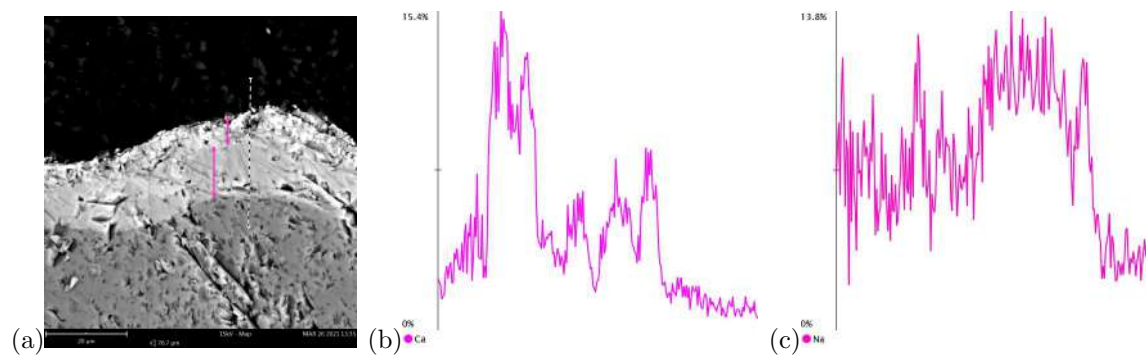


Figure 22: Representative EDS-linescan of a layer around a silica particle (ID38). a) Micrograph of the surface where the linescan was done. Colored arrows mark the inner and outer layer. b) Variation of Ca across the linescan. c) Variation of Na across the linescan.

From Figure 22a it can be seen that there is an outer and an inner layer of the formed ash coating on the bed particle. From Figure 22b-c it is clear that Ca has a peak in the outer layer and Na has a peak in the inner layer. It may also be noted that the Ca/Si ratio in the outer layer increased during the three periods. Further results from the SEM-EDS analysis are presented in Appendix H.

5.2.1 Analysis of samples from period 1

As can be seen in Figure 21c the ash layers are building up over time. Between sample ID5 and ID38, 32 days passed. The first sample, which was taken at the beginning of period 1 right after the entire bed material had been replaced by a fresh bed material, has no, or very low, layer build-up. Further in to period 1 both an inner and an outer layer have formed around the bed particles, see Figure 23. Moreover, other elements such as Fe, Al and Mg have started to accumulate in the outer layer, see Appendix H.

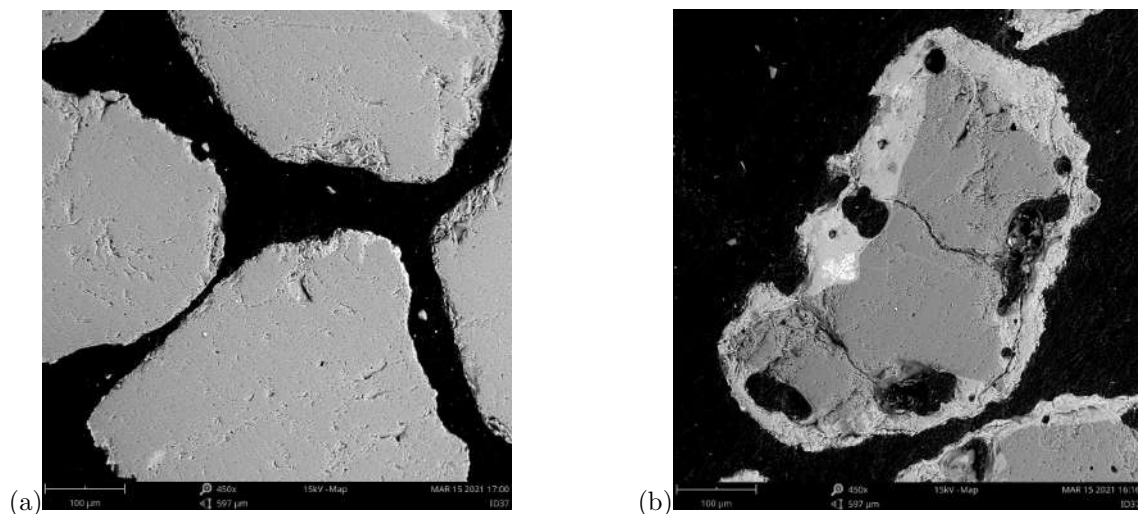


Figure 23: SEM-micrographs showing bed material from period 1. a) SEM-micrograph of a particle without layer from sample ID5. b) SEM-micrograph of a particle with a layer build-up from sample ID38.

5.2.2 Analysis of samples from period 2

Period 2 started with a bed material composition of 2/3 of fresh bed material and 1/3 of old and recirculated bed material from period 1. This results in that there are still bed particles that have an outer and an inner layer around the particles in the bed material at the start of period 2 (ID76). At the end of period 2 (ID108) the outer layer has increased in thickness as well as the concentration of Ca. The number of days in between the sample ID76 and ID108 were 35. Furthermore there seems to be an increase of Fe, Al and Mg in the outer Ca-layer, see Appendix H. As seen in Figure 21c, the outer layer has kept growing throughout period 2, however, there are no, or very few, defined particles with an inner layer at the end of the period. This might be explained by the fact that the particles with an inner Na-layer have agglomerated, see Figure 24.

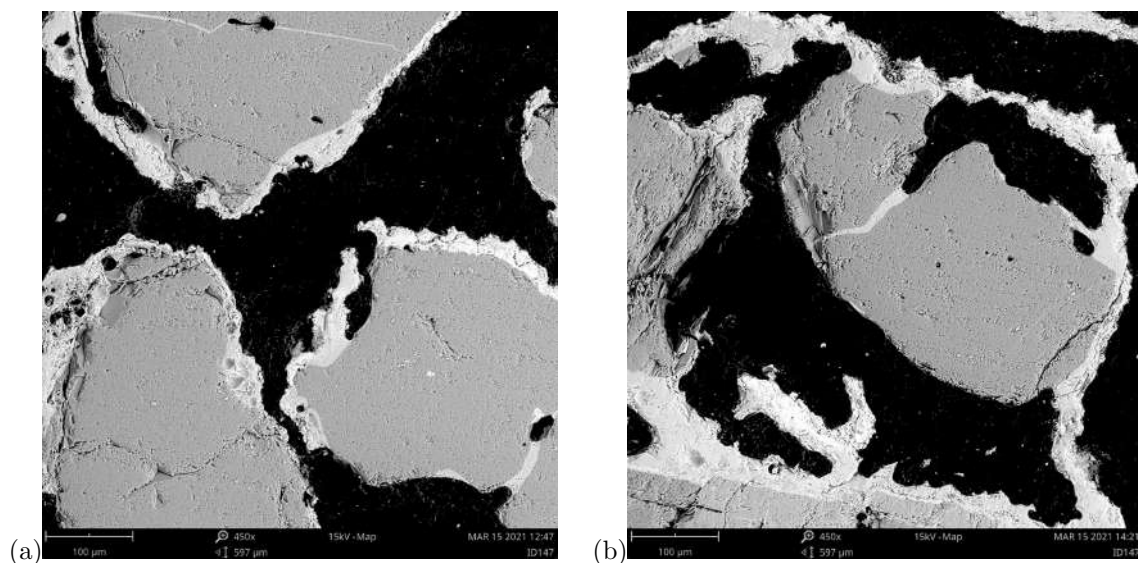


Figure 24: SEM-micrographs showing bed material from the end of period 2 (ID108). a) SEM-micrograph of particle without an outer Ca-layer. b) SEM-micrograph of particles agglomerated in sample ID108.

The micrograph in Figure 24a shows particles with only an outer Ca-layer while Figure 24b shows particles agglomerated through necks consisting of mainly Na.

5.2.3 Analysis of samples from period 3

Period 3 started with a complete replacement of the bed material. From the replacement of the bed material until the sample with ID123 was taken, 11 days passed. This is a shorter time span than the time span between the samples of period 1 (32 days) and period 2 (35 days). However, as can be seen in Figure 21a-b, the concentration of Ca and Na in outer and inner layer, respectively, as well as the Ca-layer thickness in sample ID123 have already reached the same, or surpassed the values reported from the end of period 1 and 2. This suggests that the layer build-up was faster during period 3 than during both period 1 and 2. Furthermore the accumulation of Fe and Al has increased in the Ca-layer compared to previous periods.

The time between sample ID123 and ID147 was 24 days. During that time span the outer layer thickness increased as well as the concentration of Fe and Mg in the layer. However, as was also seen during the end of period 2, there are fewer particles with a well-defined inner layer in sample ID147. As in sample ID108, this might be the result of that the particles with inner layers were participating in agglomeration. This hypothesis is strengthened by the presence of agglomerates, see Figure 25.

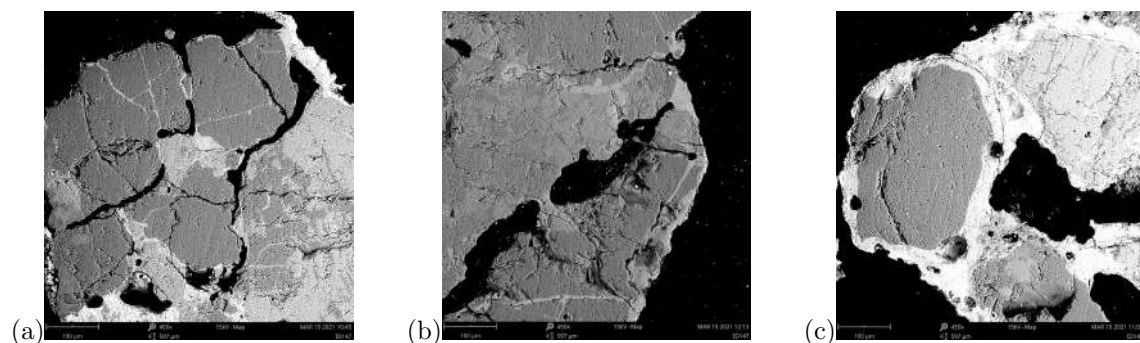


Figure 25: *Micrographs showing agglomeration in sample ID147. The particles are connected by necks containing Na.*

The micrographs presented in Figure 25 shows agglomeration of bed particles. To clearer see how the elements are distributed in the agglomerate a EDS-mapping was carried out on the particles in Figure 25c, see Figure 26.

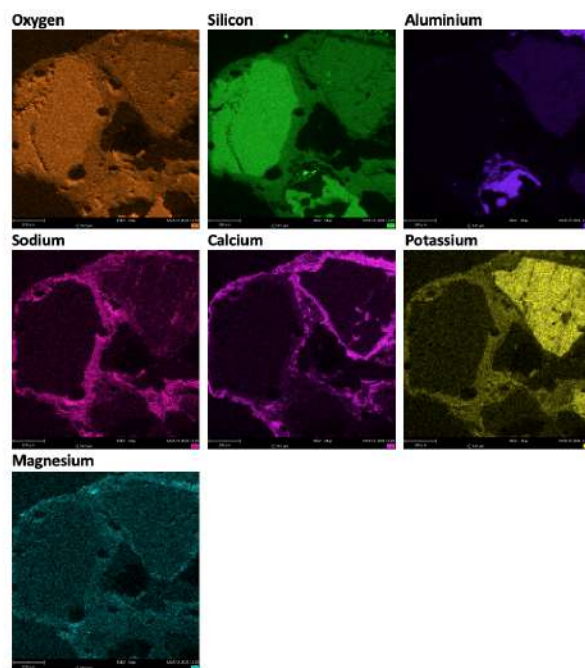


Figure 26: *EDS-mapping of agglomerated particles in sample ID147.*

Firstly it may be noted that the EDS-mapping of K shows that the particle in the upper right corner most likely is a K-feldspar particle, while the distribution of Si shows that the other two particles are silica particles. The mapping shows that the Ca-layer is distributed around the cluster

while the Na-layer, also containing some K, is the layer that is mainly connecting the particles. The mapping suggests that it is the inner, Na-rich layer that is responsible for the agglomeration.

5.2.4 Crack formation

As mentioned, the ratio between Ca and Si in the outer layer is constantly increasing throughout these three periods, see Figure 27.

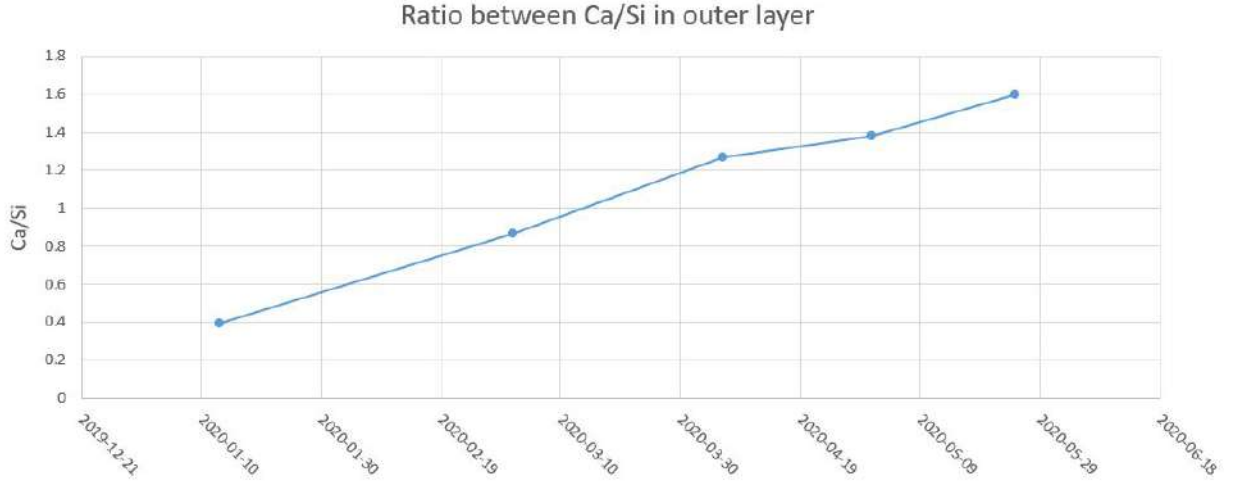


Figure 27: *Ratio between Ca and Si in the outer layer.*

When the amount of Ca-silicates increases in the bed particle layer, formation of cracks in the layer can occur. The crack is a result of the microstructural stress as a result of the different molar volumes of the different Ca-silicates. Gaseous alkali can thereafter diffuse through the cracks, forming alkali-melts. The cracks might eventually result in that the outer layer is detached from the particle or that the bed particle is fragmented. Micrographs of particles with a crack formation in the end of each period are presented in Figure 28.

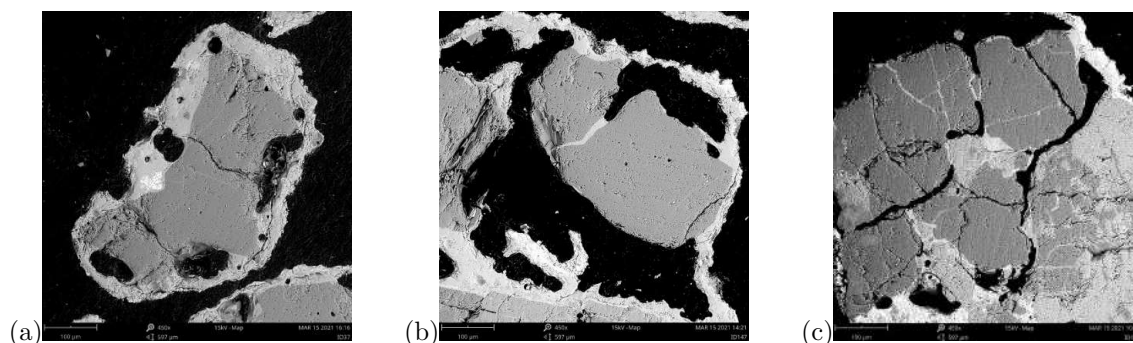


Figure 28: Micrographs showing crack layer formation in the three different samples. a) Period 1, sample ID38; b) Period 2, sample ID108; c) Period 3, sample ID147.

As can be seen in the micrographs, all particles have appearance of crack formations which have been filled by alkali melt and in all particles the outer layer has detached or partially detached from the particle. The crack formation gets progressively more severe along the periods. In the later samples (Figure 28b-c) the crack formation has also resulted in agglomeration. Particularly in the last period, Figure 28c, the crack formation and agglomeration is clear.

5.2.5 Conclusion of SEM-EDS analysis

The conclusions that can be drawn from the SEM-EDS analysis are that there is layer growth around the bed particles during combustion. The layers can be divided into an inner and an outer layer, where the inner layer is dominated by Na and the outer layer is dominated by Ca (disregarding Si and O). The concentration of the elements as well as the layer thickness increases during use of the bed material and eventually the particles with an inner Na-rich layer agglomerate where the Na-rich layer acts as a glue between particles. From the SEM-EDS analysis it can also be seen that elements such as Fe, Al and Mg are accumulated in the outer layer. Furthermore it seems like the rate by which the layer is growing might depend on the fuel added since the layer growth was faster during period 3, where a fuel with different composition compared to previous periods was used.

The principal component analysis showed that period 3 was classified differently than the other two periods. From the analysis it was shown that the Au-electrode with a pulse of amplitude -1V was the main variable responsible for the different classification. Connecting the PCA to the results from the SEM-EDS analysis, it can be noted that the increase in signal from the Pt- and Rh-electrode throughout period 1 coincides with the build-up of layers around the bed particles. Also the easier classified period 2 coincides with the more constant elemental concentration in the layers during period 2. Finally, looking at the SEM-EDS results from period 3, it can be noted that the Ca and Na content, as well as the layer thickness of the particles resemble the layers from period 2. However, the elements accumulating in the Ca-layer; Fe, Al and Mg, are increasing each period and have their highest value during period 3.

The accumulation of elements in the Ca-layer might lead to that the elemental concentration of Fe, Al or Mg surpasses the detection limit of the Au-electrode, resulting in a sudden increased signal from the electrode. Another reason for the sudden increase in signal from the Au-electrode might be

that the elements detected have higher affinity to the Pt and Rh electrode, but that the amount of the element has increased to the point where the Pt- and Rh-electrode are saturated. When the Pt- and Rh-electrode are saturated the Au-electrode start giving a current response to the compound of interest.

To further investigate what elements might explain the reason behind the response signal from the ET, the concentration of a few potentially leachable candidates was investigated. This analysis is carried out with AAS on the leachate from the different bed samples.

5.3 AAS analysis

AAS analysis was carried out on the leachate from the different bed samples to determine the concentration of the leachable elements from the bed material. In Table 1 a summary of the atomic concentrations found in the bed samples is presented. The elements Ca, Na, K and Mg as ions were selected as interesting for comparison in the study. The samples are organized in chronological order, from period 1 to period 3.

Table 1: *Elemental concentrations in the leachate of bed material obtained by AAS analysis of 10 samples from period 1 - period 3.*

Period	Sample ID	Ca [mg/l]	Mg [mg/l]	Na [mg/l]	K [mg/l]
1	ID5	10.56	0.45	1.57	2.92
1	ID38	39.64	0.42	9.44	2.07
1	ID72	45.83	0.10	7.89	3.69
2	ID76	33.20	0.19	5.28	2.10
2	ID92	46.58	0.12	6.22	2.19
2	ID108	49.93	0.19	9.22	3.38
3	ID116	31.30	0.17	2.75	2.99
3	ID123	33.11	0.26	4.32	2.95
3	ID147	77.75	0.01	6.57	2.63
3	ID156	77.27	0.01	6.28	2.58

From Table 1 it can be seen that Ca and Na follow a trend where the amount of leachable Ca and Na increases throughout the period and decreases at the beginning of the following period as the bed material is partially or fully replaced. K follows this pattern in period 1 and 2, while in period 3 the amount of leachable K decreases throughout the period. Mg does not seem to follow the same trend but is instead decreasing throughout all periods.

Table 1 shows that Ca is leached in largest amount. This corresponds to the fact that, a part from Si, Ca was the most abundant element in the fuel. It should also be noted that there is a sharp increase in concentration of Ca in the last two samples of period 3 (ID147 and ID156).

Na does, as mentioned, follow the trend of increasing each period. However K does not follow this trend in the last period. The amount of K in the fuel, as well as in the inner layer, is largest in period 3. There is also least K in the outer layer in period 3. The reason for the decreasing trend of leachable K might be a result of that the Ca-layer acts as a diffusion barrier that prevents K to

be leached from the inner layer. The result from the AAS analysis are plotted in Figure 29.

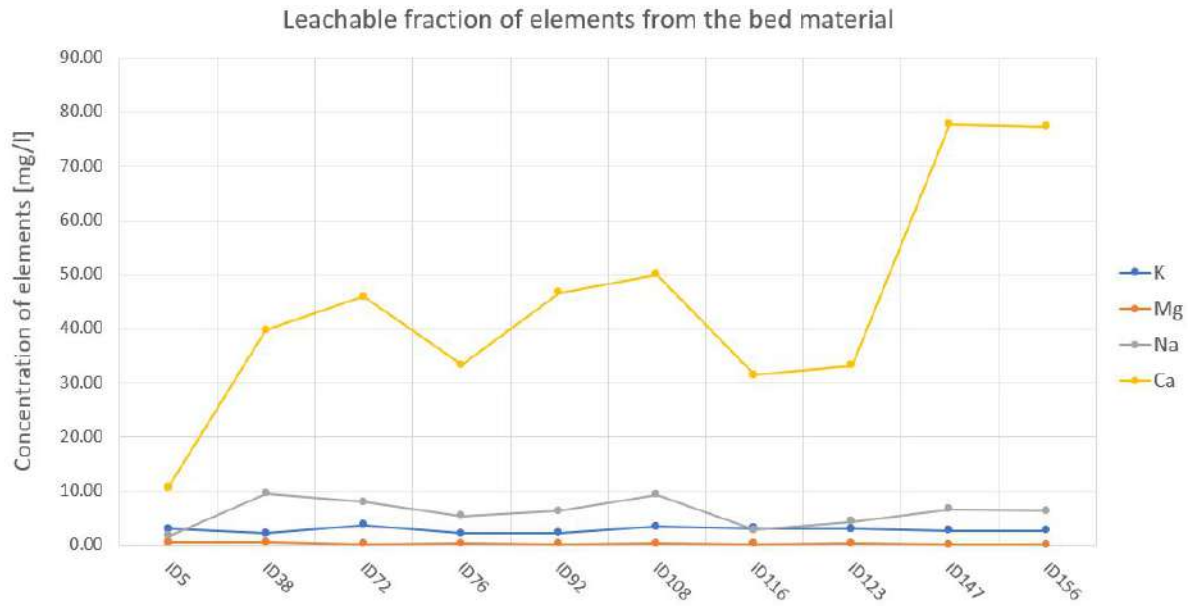


Figure 29: Concentration of elements in the leachate after leaching the bed material for 6 minutes.

5.3.1 Comparison of AAS-data to ET-data

The concentration of leachable Ca has a sharp increase at the end of period 3. This is also seen in the signal response from the Au-electrode, see Figure 20. The signal response from variable Au13 is plotted together with the concentration of leachable Ca in Figure 30.

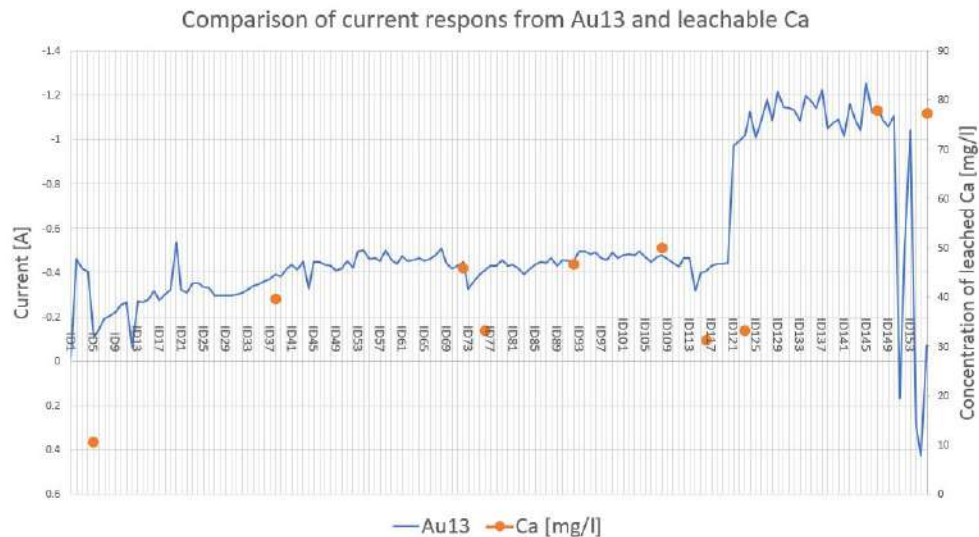


Figure 30: Comparison between the amount of leachable Ca from the bed material and the current response from variable Au13.

As can be seen the change in response signal and leachable Ca is similar. This might suggest that Ca or a compound consisting of Ca is responsible for the response from the Au electrode.

As can be seen in the waterfall plot of the response signals (Figure 20) the other two electrodes (Pt and Rh) have an increased signal in the beginning of period 1 and thereafter the response signal levels out and changes only slightly as the bed material is replaced. This suggests that the components responsible for the Pt and Rh response signals follows the same trend as Na. Furthermore this suggests that Na or a compounds consisting of Na are responsible for the response signals from the Pt and Rh electrode.

5.3.2 Comparison of AAS-data to SEM-data

Since the ratio of Ca to Si gives insight to what Ca-compounds that might be formed the Ca/Si ratio was plotted and compared to the amount of leachable Ca, see Figure 31.

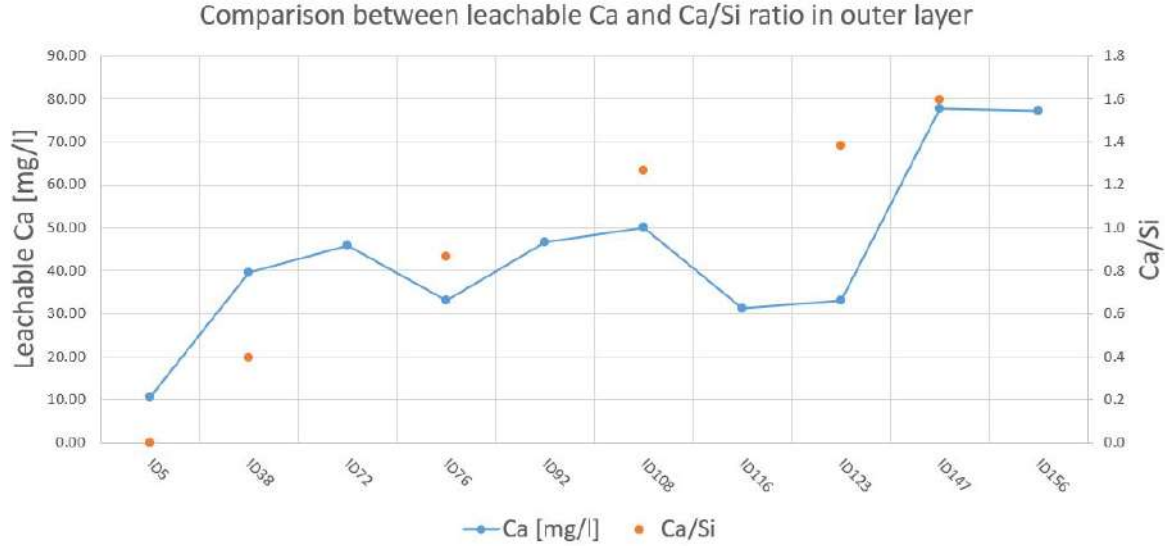


Figure 31: A comparison between the amount of leachable Ca from the bed material and the ratio between Ca and Si in the outer layer of the bed particles.

The increasing Ca/Si ratio might explain the sudden increase of leachable Ca, since the increased ratio would result in that Ca not only will be present as Ca-silicates but also more soluble compounds such as CaO. The increase in Ca/Si is a result of the fuel in period 3 which has a higher Ca to Si ratio. The increasing ratio might also explain the crack formation that occurs in the particles and their layers. After a certain amount of time the cracks might result in fragmentation of the particles and that the outer, Ca-rich layer, breaks off and exposes the layers consisting of alkali-silicates. This in turn may cause agglomeration.

5.4 XRF analysis

The results from XRF give information of the total elemental composition of the samples in atomic percentage. The difference between SEM and XRF measurements is that SEM focuses on layer composition while XRF focuses on the composition of the entire sample. Interesting elements for the present work such as Si, Ca, Na, K, Fe, Al, Mg, S and P are discussed in this section. The detailed data of the samples is found in Appendix E.

The XRF analysis showed that the most abundant element is Si (average 22.3%), which is mostly present in SiO₂ but can also come from formation of silicates formed from Na, K and Ca. Al is the second most abundant element, with an average of 5%, which is present in feldspar. The next most abundant element is Ca (average 4.1%), which increases over time within the periods, having its maximum value at the end of period 3 (6.8%). This suggest a deposition of the Ca coming from the burned wood into the bed particles over time. The next most abundant elements are K and Na which have similar values (average 2.2% and 2.1% respectively). Their presence in the samples shows opposite trends within a period; K decreases while Na increases. Fe and Mg are in

very low quantity (average 0.7% for both) and have very similar values all the time. Also, both increase within the period. The atomic percentage of P and S is insignificant in all periods (average 0.2% and 0% respectively). With this information, sulphates and phosphates compounds are not considered for further analysis of the leachable fraction.

The experiments with the ET resulted in a 17×225 data matrix where the rows are the samples and the columns are the variables of the pulse-train. The current response of the two experimental setups can be found in Appendix F. For a better understanding of the current response, multivariate data analysis tool PCA was again used, resulting in three principal components, explaining 97.3% of the variance in the data. The two first components explain 96.2%. The score plot of the PCA is presented in Figure 32.

Figure 32: Score plot (t_1 vs. t_2) of the response signal of the 100th pulse-train from the electronic tongue for each sample of the two experiments. Pre-processing of data was carried out by centering the data points to the mean and component-wise scale to unit variance. The mixtures are represented by one color while the mono-components solutions are colored according to elements. The points in the score plot of mixtures and mono-component solutions are labeled by element name of the hydroxide cation followed by the concentration in mg/l.

The analysis of the mixtures showed that mixtures with a higher concentration of ions are located further to the left in the score plot. Mixtures with higher concentrations of ions are more separated

from each other than the mixtures with lower concentration of ions. This suggests that the ET can more easily distinguish between mixtures with higher concentration of ions.

To investigate the influence of each electrode on the obtained signals the loading plot was studied. The loading plot of the PCA is presented in Figure 33.

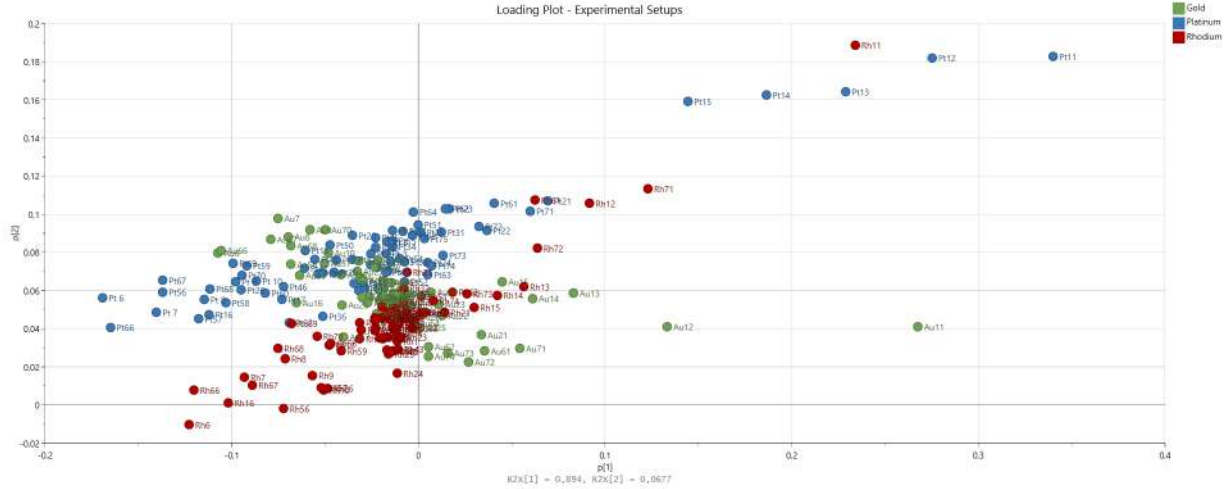


Figure 33: Loading plot corresponding to the score plot of Figure 32. Each variable is marked by its corresponding electrode and response signal number of the pulse-train.

By analyzing this plot, it can be seen that electrode-wise, all electrodes have approximately the same influence on the data since they overlap in the centre of the plot. Pulses corresponding to Pt11-15, Rh11 and Au11 have the most influence. These pulses correspond to the highest negative voltage applied to the samples (-1V).

5.6 Summary of results

The response signal from the experiments conducted at the BFB boiler at Idbäcken showed changes in the signal obtained from the bed material over the operation periods, suggesting that an ET can be used to follow the changes in the bed material quality. To explain what caused the signal changes, a score plot made from the response signal was further investigated. A separation between the signal from period 3 and the rest of the operation periods was found. The separation could be explained by an increase in signal from the Au-electrode throughout this period. To further investigate what caused the change in signal from the Au-electrode the accumulated fuel content in the bed was analyzed. The conclusion of the analysis was that the bed material in period 3 contained more K than in the other periods and that the ratio between Ca and Si had increased. The bed material from each period was thereafter analyzed using SEM-EDS. The analysis showed the build-up of an inner Na/K-layer and an outer Ca-layer around the bed particles. Samples from period 3 did not show a higher amount of K in comparison to the other periods as expected. However, an increased Ca/Si ratio was seen in the outer layer of particles from period 3. The increase in Ca/Si ratio suggests that Ca in the outer layer might exist in other, more leachable forms, than Ca-silicates.

An increased amount of leachable Ca in the end of period 3 was confirmed using AAS. From the AAS analysis it could be calculated that the concentration of Na was about 2 - 10 times and for K it was 4 - 30 times lower than the Ca concentration.

The use of a XRF to analyze the total elemental composition of the bed material showed that the amount of P and S in the samples (from the analysis) was non-significant (0 - 0.2 at%), a result that made it easy to discard them as possible leachable compounds from the bed material. Since Ca forms CaO during combustion it is reasonable to think that the leachable Ca existed in the form of CaO. When CaO is dissolved in water it reacts to form $\text{Ca}(\text{OH})_2$. Therefore $\text{Ca}(\text{OH})_2$ was chosen to be investigated further using the ET. Since Na and K are part of the layer build-up and involved in the agglomeration mechanisms they were also included in the experimental matrix. To be able to make a better comparison between the different elements effect on the response signal from the ET the hydroxide form was chosen for all three elements.

The experiments with mono-component solutions showed that the ET could differentiate between the different elements. The experiments also showed that the ET could separate the Ca mono-component solutions according to concentration more easily than the Na and K solutions. Furthermore, the experiments with mixtures showed that the ET mainly separated solutions according to the amount of ions rather than the composition of the mixture. However, the result also suggests that the ET might be able to distinguish between mixtures with higher concentrations of ions. Finally, the analysis of the different electrodes showed that they gave similar information, unlike the experiments conducted on the bed samples where the Au-electrode gave different signal information than the Pt- and Rh-electrode.

The theory of electrochemistry can be used to further explain the results of what is happening between the electrode and the solution. Dissolving ash build-ups from used bed material in water will result in a water-solution containing, among other ions, Ca^{2+} , K^+ and Na^+ . All three ions have a lower redox potential than hydrogen [56]. Therefore it will not be possible to cause a reduction of the ions in a water solution by applying a potential using an electronic tongue. The response signal from the ET will instead be caused by a non-Faradic process and the current response will increase as the concentration of ions increase due to the ions causing an increased conductivity.

The distribution of the points, in the t_1 direction, presented in the score plot made from the experiments conducted on the used bed material from the BFB boiler in Idbäcken can therefore be explained by that the amount of leachable ions increased over time as the bed material is being used. The change in signal, in the direction of t_2 , could be explained by the Ca/Si ratio. The change in signal that happened in the end of period 3 could be explained by the change of fuel composition, causing more leachable Ca and in turn more available ions in the leachate. However, which compounds that caused the increased response signal of the Au-electrode in period 3 is unclear. The experiments performed with known solutions show no difference between the three different electrodes. This was expected since all three electrode materials are good conductors and the processes occurring in the solution were non-Faradic. However, there are some possible explanations to the change in signal from the Au-electrode in the bed samples from Idbäcken. One explanation is that in the known experiments the pulse-train was run with one electrode at a time, while during the experiments conducted on bed material from Idbäcken all three electrodes were connected at the same time. This could affect the signal in the sense that the ions are not competing for the same electrodes' surface. Furthermore, if there is a higher affinity of the ions to one electrode

and all electrodes are connected at the same time, the distribution of the ion in the different surfaces would be noted in the intensity of the signal. Another explanation is that, compared to the known solutions, containing Ca, Na and K, the bed material contains several other elements that could affect the signal and cause Faradic effects. For example Fe was found in the bed particle layers and could therefore be in the form Fe^{2+} in the leachate. The applied potential from the ET could cause the reduction of Fe^{2+} to Fe and in that way also cause Faradic effects. Finally, measurement error cannot be excluded.

6 Conclusion

After the analysis of the used bed material and the experiments conducted in the laboratory using an electronic tongue, combined with literature studies of agglomeration mechanisms in a fluidized bed and electrochemistry principles, the following conclusions can be drawn.

Bed material

- The analysis of the used bed material from Idbäcksverket shows that the ash-forming elements in the fuel are responsible for layer build-up around the bed particles. The formed ash layer consists of a Ca-rich outer layer and a Na-rich inner layer.
- Ca, Na and K are involved in the agglomeration of the bed material. Na and K form low-melting silicates which cause agglomeration while Ca forms a protective outer layer around the particles, preventing agglomeration.
- An increased Ca/Si ratio in the fuel will result in an increased Ca/Si ratio in the outer layer around the bed material particles. The increased Ca/Si ratio in the outer layer will in turn result in that Ca not only is present as Ca-silicates in the layer, but also other, more water leachable compounds.

Principles of the electronic tongue

- The response from the electronic tongue in the present case is a result of non-Faradic effects causing the ions in the solutions to build up an electrical double layer at the electrodes' surface which acts as a capacitor. The signal detected is the current flow, which starts with a peak that decreases over time as the charge flow to the layer decreases.
- An increase of ions in the solution causes an increased signal from the electronic tongue. This is a result of an increased conductivity due to the increase in the number of ions.
- The electronic tongue can differentiate between different elements of mono-component solutions.
- Ca is the ash-forming element with the highest concentration in the bed samples of this study. When being analyzed by the electronic tongue, it is the element that gives the highest response. The results suggest that the electronic tongue can differentiate between different concentrations of Ca in a mono-component solution.
- When a mixture of compounds is analyzed, the electronic tongue can distinguish between the different mixtures more easily at higher concentration of ions.
- The investigation indicates that change in signal from the Au-electrode that occurred in period 3 is caused by an increase amount of leachable Ca. This increase in leachable Ca is connected to a change in fuel composition.
- The principal component analysis of the data from Idbäcksverket shows that the electronic tongue can separate samples depending on ion concentration and Ca/Si ratio.

Use of the electronic tongue

- The experiments showed that the electronic tongue was able to detect change in composition of a mixture of elements as well as change in concentration of certain elements. A possible use of the sensor would therefore be as an indicator for when changes in the bed material composition occurs due to change in, for example, the fuel composition.
- The results suggest that the ash-forming matter accumulated in the bed material faster in period 3 compared to the other periods. Hence, the electronic tongue could be used to monitor the time it takes for the ash-forming matter in the fuel to accumulate in the bed. This information could thereafter be used to predict when the bed has to be exchanged in order to avoid agglomeration.

The results of this study indicate that the electronic tongue can be used to follow the change of the amount of leachable ions in a fluidized bed. It has also been shown that the electronic tongue can be used to detect certain changes in the composition of the bed material. The results suggest that the electronic tongue could be used as a sensor to detect changes in bed material composition as well as to predict when the bed has to be exchanged in order to avoid agglomeration.

7 Future work

After the study carried out in this project, some limitations were found and some suggestions for further work have been identified and are presented below.

- Ca, K and Na will not be part of redox reactions when dissolved in water since their redox potential is lower than that of hydrogen. An increased potential will reduce hydrogen, producing $\text{H}_2(\text{g})$, instead of reducing the Ca, K and Na ions. To be able to reduce Ca, K and Na, a non-aqueous electrolyte should be used in order to broaden the window of the reduction potentials.
- When no redox reactions occur the different electrodes will not give significantly different information about the solution. In the case of this study, platinum and rhodium electrodes gave very similar information and therefore the omission of one of them and the use of a different material will be interesting for further investigation.
- Furthermore, it was also noted that the lower voltage amplitudes did not add large information. Voltage of -1 and 0.7, the highest used in the pulse-train, gave the most significant information. Therefore a different pulse-train could be of interest to investigate.
- In order to use the electronic tongue to predict agglomeration a model based on a large amount of data from different bed qualities has to be constructed. Experiments with the electronic tongue on bed material with quality from unused bed to severe agglomeration should therefore be conducted in order to investigate the change in the signal.
- The leachable fraction of the bed samples is a complex multicomponent solution. This project focused on the study of Na, K and Ca hydroxides. Further investigation with other compounds and mixtures would give a more accurate information of what the electronic tongue responds to.

The investigation shows that the electronic tongue is a promising tool for monitoring the quality change of a fluidized bed during combustion. Further investigation of electrolyte, pulse-train, electrodes and leachable compounds as well as experiments on bed material of different quality can add to the optimization of this tool. Nevertheless, the results suggest that the electronic tongue could be used to detect changes in the composition of the bed material as well as to predict when the bed has to be exchanged in order to avoid agglomeration.

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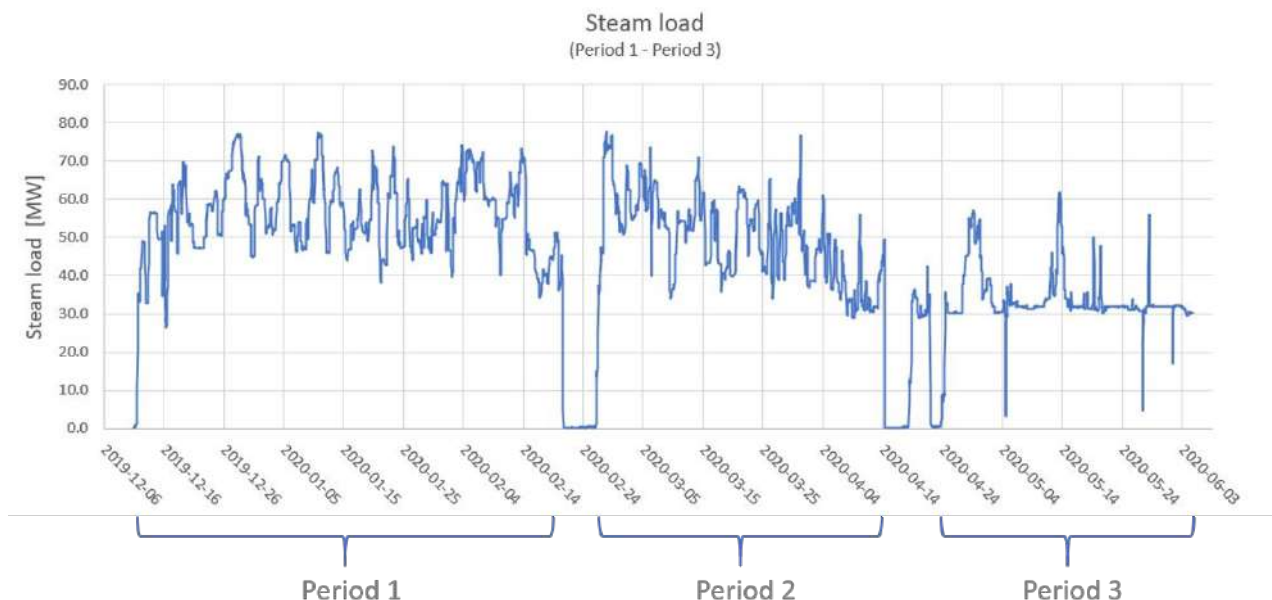
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Appendix

A Operation periods: Idbäcksverket

The information obtained from the operation periods includes steam load, temperature, pressure and ash forming matter content present in the fuel. These has been organized and presented in graphs. The bed temperature is measured by 8 thermocouples (type K) that are located 20 cm above the primary air nozzles in the bottom of the furnace. The two pressure gauges measured the primary air pressure in the bottom of the furnace and are located at the same level as the primary air nozzles. The ash-forming elements in the fuel: Cl; S; P; Si; K; Na; Ca; Fe; and Al are plotted in the graphs below. Si and Ca are present in higher quantities than the rest of the elements and therefore are plotted in a separated graph. In this section, a description and analysis of the working conditions and fuel composition of each period is done. The steam load over the three operation periods are presented bellow.

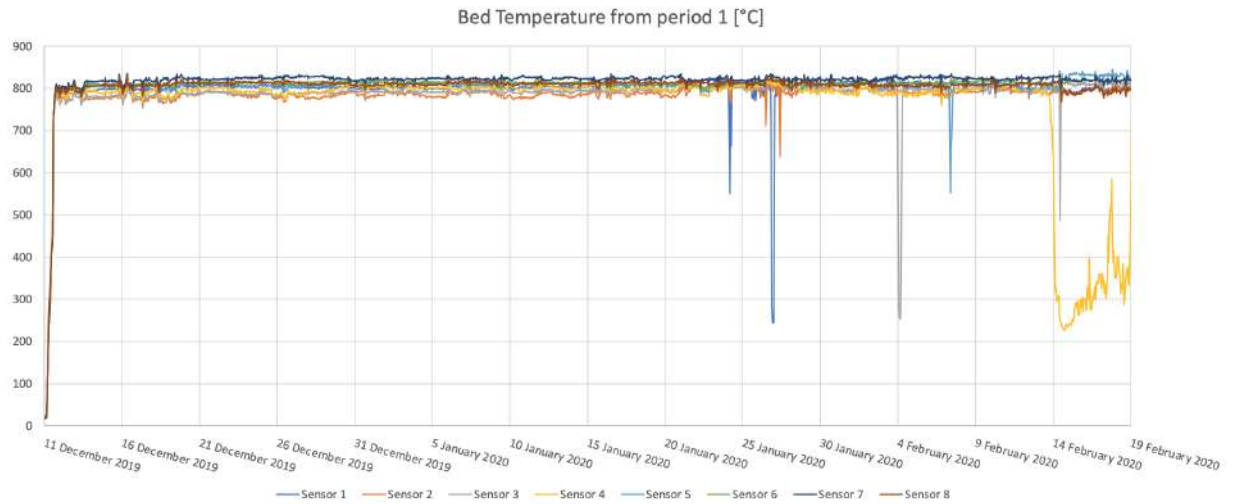


Steam load of the boiler at Idbäcksverket, recorded hourly, from 11th of december 2019 until 4th of june 2020 (period 1 - period 3).

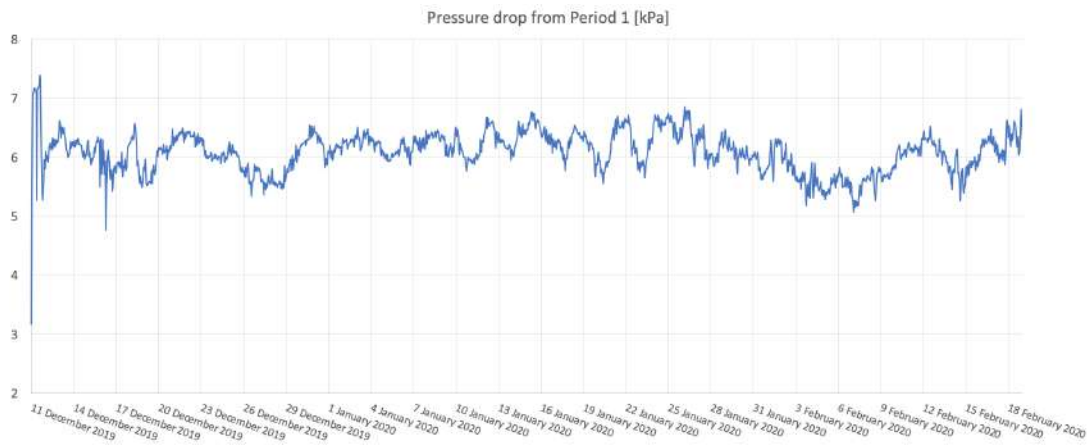
Period 1

At the beginning of this period the bed material was completely replaced and therefore the ash-forming matter started to accumulate from zero. The temperature during this period is very stable at the beginning but at the end of the period, 5 different thermocouples started to register short drops in the temperature. During the last five days of the Period 1, thermocouple 4 started to register a longer temperature drop that continued until the boiler was stopped for cleaning. The

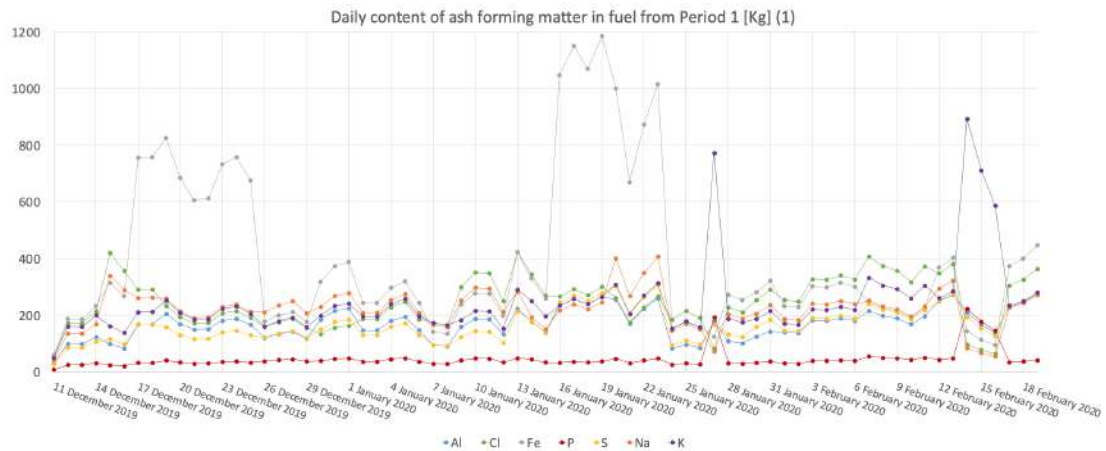
pressure measured in the bottom of the bed showed a slight continuous decrease around the same time as the bed temperature experienced some drops. Nevertheless it is within the pressure drop range of the whole period. Regarding fuel content, the graph shows that Fe was high in several fuel batches at the beginning (17-25th of Dec) and middle of the period (16-23th of Dec). Towards the end, some fuel batches have an uncommonly higher amount of K and P (27th Jan, 14-16th Feb). Ca and Si are usually similar in content in most of the fuels but there is a noticeable increase of Si from the 9th to 23th of January, being 3 to 5 times more than Ca.



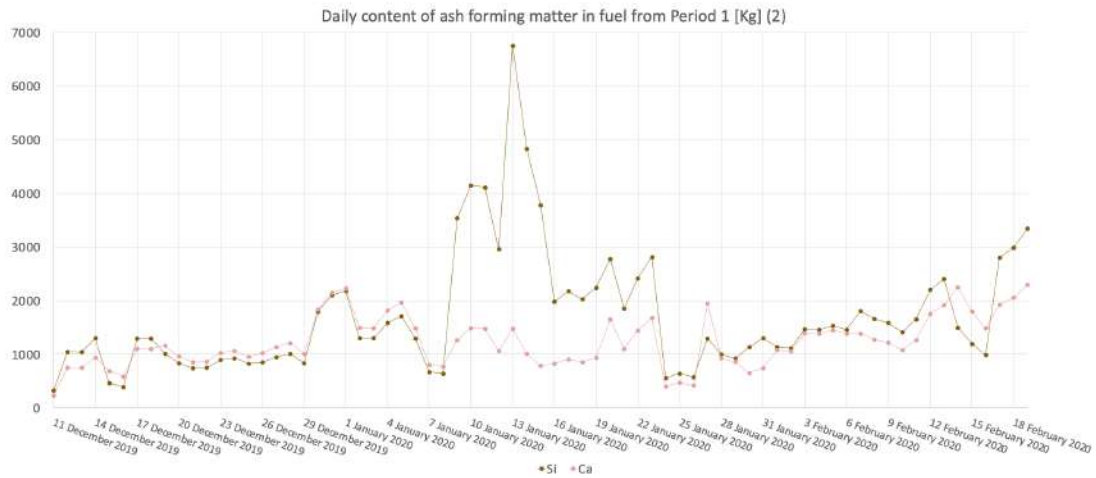
Temperature over period 1



Pressure drop period 1



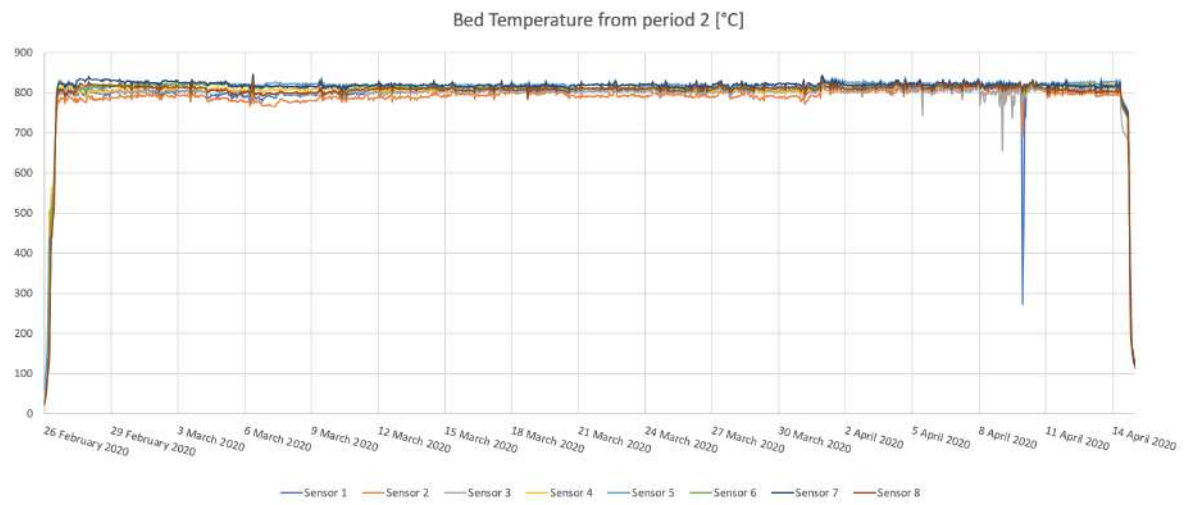
Ash forming matter content in fuel (1)



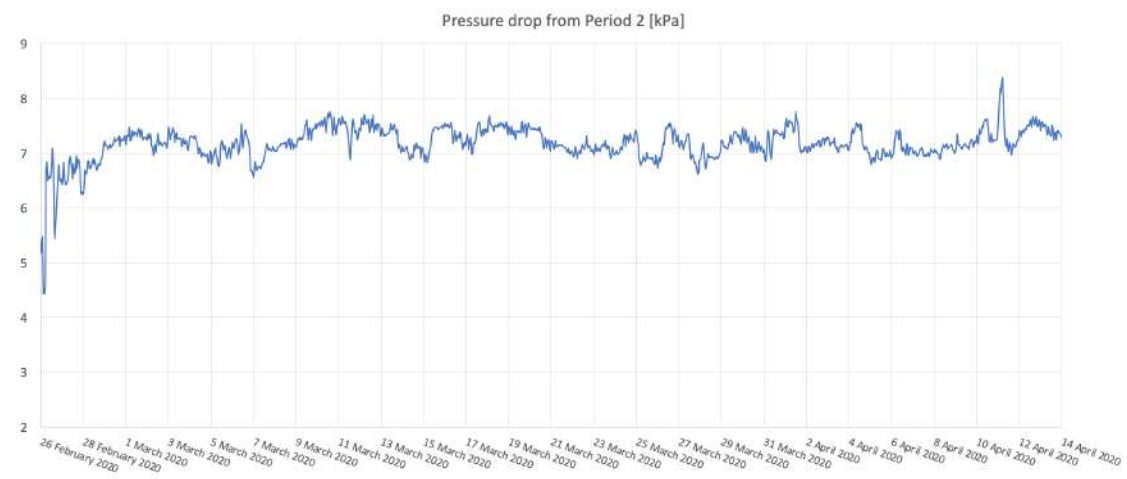
Ash forming matter content in fuel (2)

Period 2

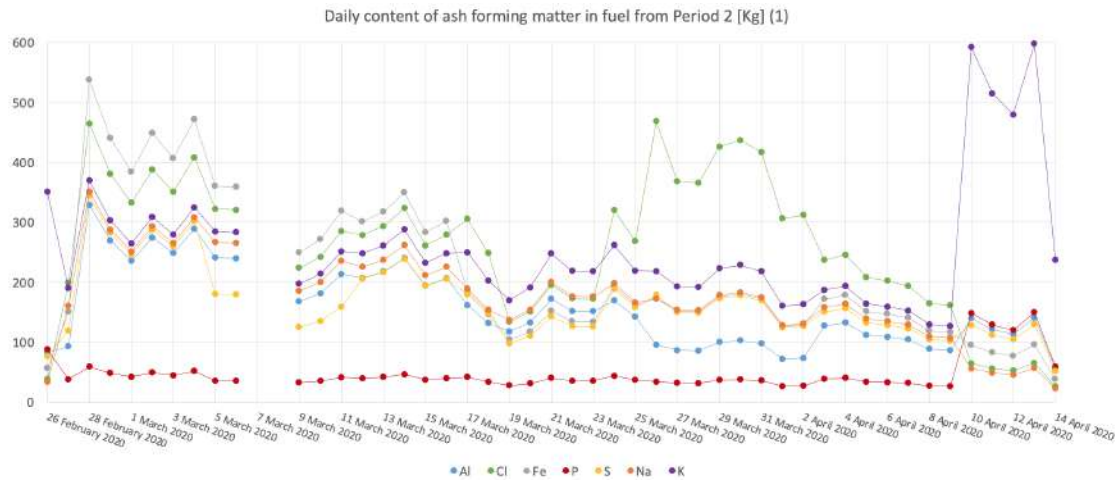
The bed temperature during period 2 was very stable. Two of the thermocouples (2 and 3) registered smaller drops in the bed temperature towards the end of the period. Thermocouple 1 also registered a larger but shorter drop in the bed temperature at the end of the period. The pressure measured in the bottom of the bed during Period 2 is higher than during period 1 in average and appears to be very stable. The fuel in this period has a higher amount of Cl compared to last period. The Fe content is moderate. At the beginning of the period the amount of Si and Ca is higher than in the rest of the period (28th Feb-6th March). The last five days before the stop, the amount of K added was significantly higher, as well as the P.



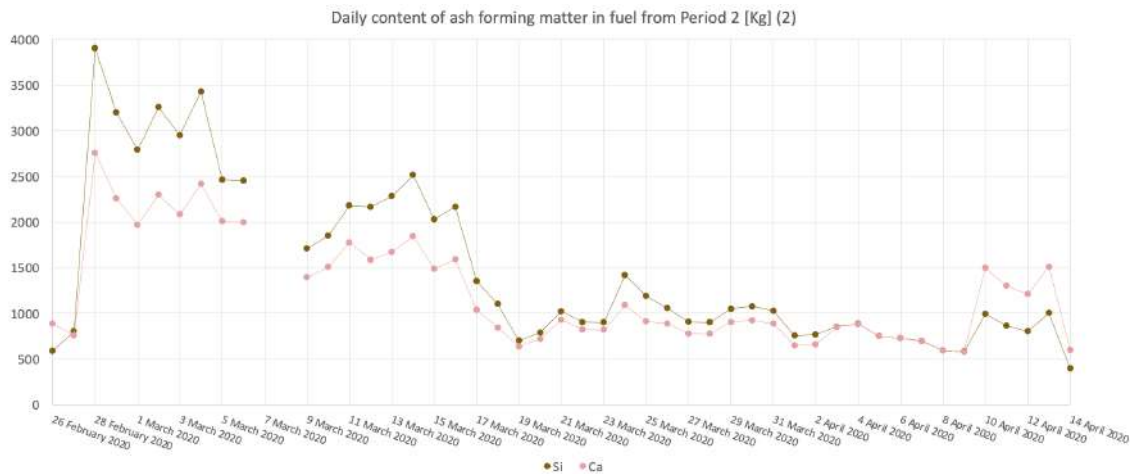
Temperature over period 2



Pressure drop period 2



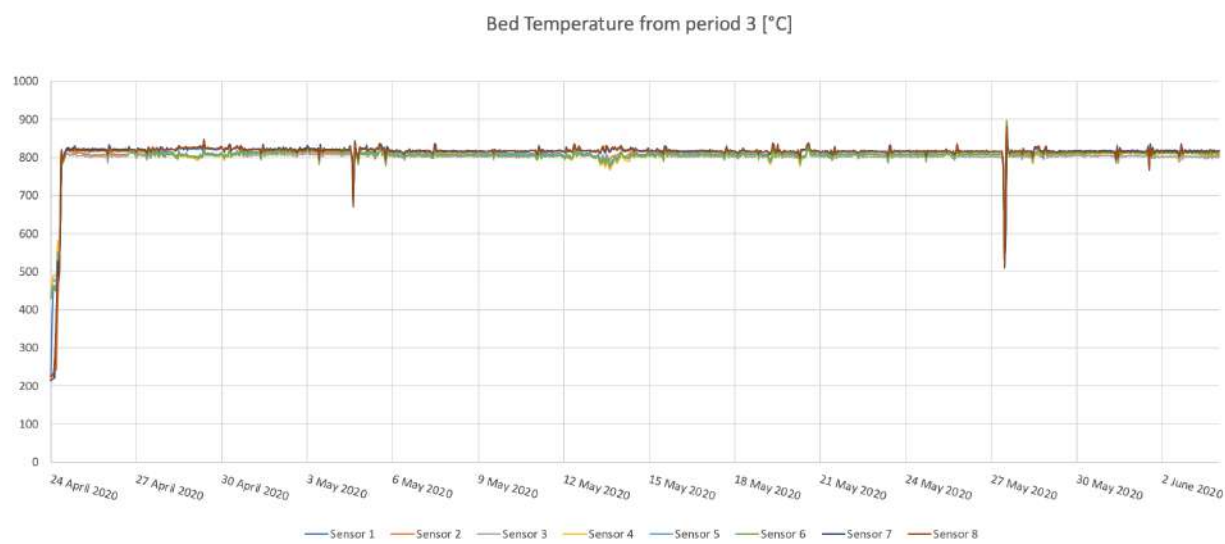
Ash forming matter content in fuel (1)



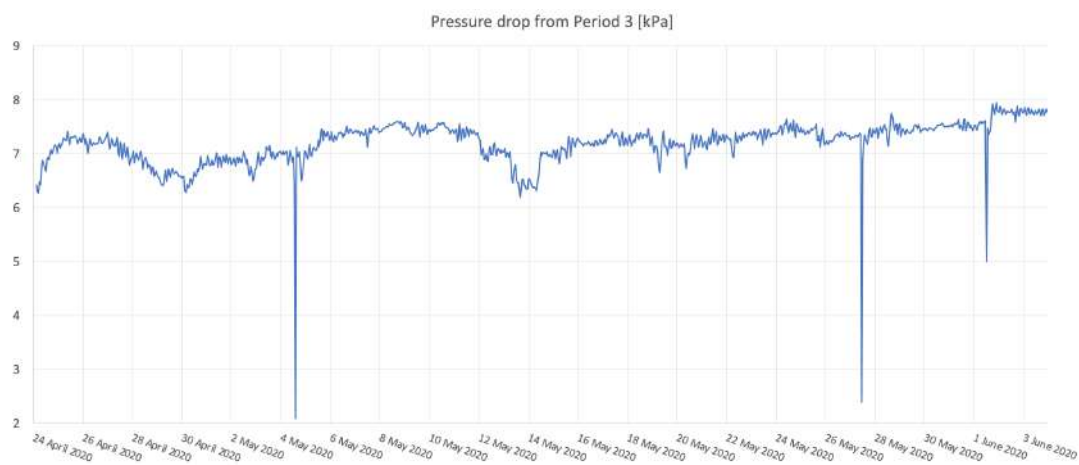
Ash forming matter content in fuel (2)

Period 3

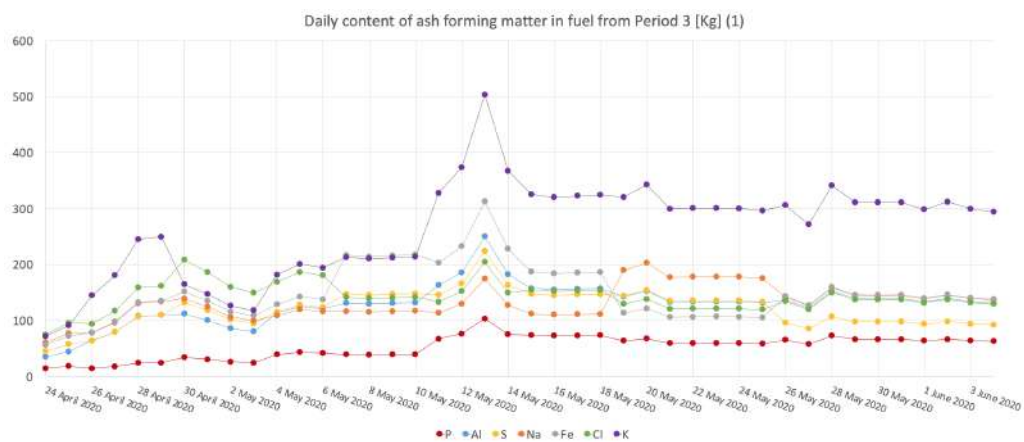
The temperature measured in the bed with the thermocouples during period 3 registered a more homogeneous bed temperature throughout the bed. There are two smaller and shorter temperature drops that also coincide with bed pressure (4th and 27th of May). Additionally, there is a smaller pressure drop on 2nd June. Fuel in this period characteristically contained high amount of K. The amount of Si and Ca is high in batches from the 6th to 14th of May, and here the ratio Si/Ca is higher than 1. From 19-25th May the Si/Ca ratio is lower than 1.



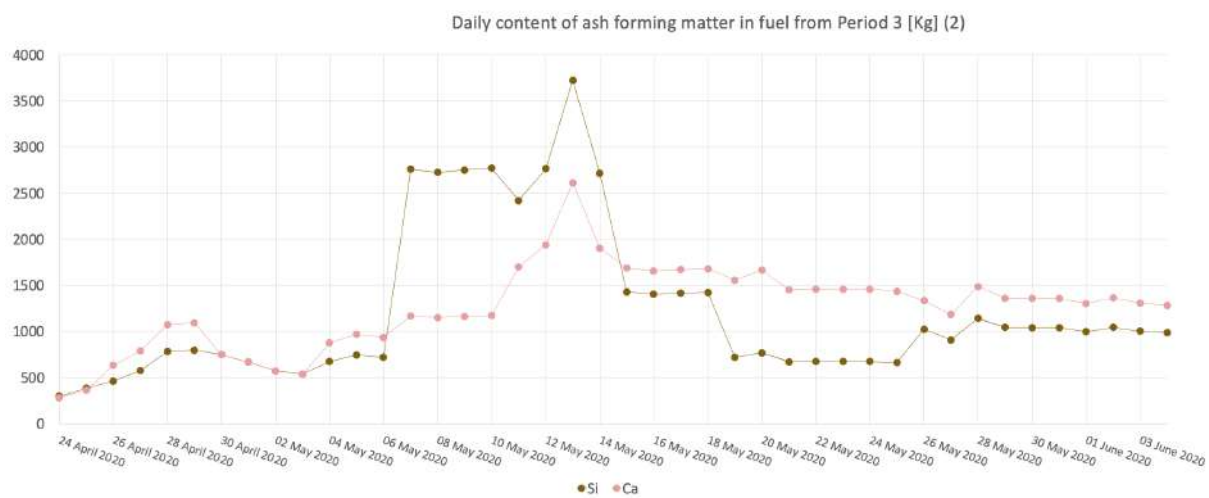
Temperature over period 3



Pressure drop period 3



Ash forming matter content in fuel (1)



Ash forming matter content in fuel (2)

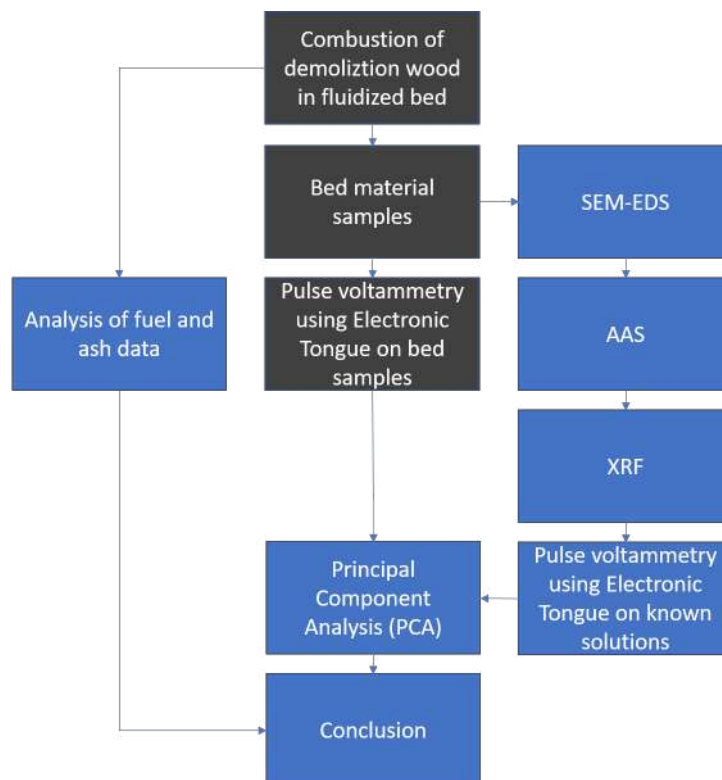
B Bed material sample from Idbäcksverket

The table shows when each sample was taken from Idbäcksverket. Red represents the samples that were excluded from the investigation since they were outside the period 1 - period 3. Blue represents samples that were further investigated using SEM-EDS, AAS and XRF. ID1 is a fresh bed sample.

ID	Date	ID	Date	ID	Date	ID	Date
ID1	2019-12-06	ID40	2020-01-15	ID79	2020-03-06	ID118	2020-04-26
ID2	2019-12-06	ID41	2020-01-16	ID80	2020-03-07	ID119	2020-04-27
ID3	2019-12-07	ID42	2020-01-17	ID81	2020-03-08	ID120	2020-04-28
ID4	2019-12-08	ID43	2020-01-18	ID82	2020-03-09	ID121	2020-04-29
ID5	2019-12-12	ID44	2020-01-19	ID83	2020-03-09	ID122	2020-04-30
ID6	2019-12-13	ID45	2020-01-23	ID84	2020-03-10	ID123	2020-05-01
ID7	2019-12-14	ID46	2020-01-24	ID85	2020-03-11	ID124	2020-05-02
ID8	2019-12-15	ID47	2020-01-25	ID86	2020-03-13	ID125	2020-05-02
ID9	2019-12-16	ID48	2020-01-26	ID87	2020-03-14	ID126	2020-05-03
ID10	2019-12-17	ID49	2020-01-27	ID88	2020-03-15	ID127	2020-05-03
ID11	2019-12-19	ID50	2020-01-28	ID89	2020-03-16	ID128	2020-05-04
ID12	2019-12-20	ID51	2020-01-29	ID90	2020-03-17	ID129	2020-05-05
ID13	2019-12-21	ID52	2020-01-30	ID91	2020-03-18	ID130	2020-05-06
ID14	2019-12-22	ID53	2020-01-31	ID92	2020-03-19	ID131	2020-05-07
ID15	2019-12-23	ID54	2020-02-01	ID93	2020-03-20	ID132	2020-05-10
ID16	2019-12-24	ID55	2020-02-02	ID94	2020-03-21	ID133	2020-05-11
ID17	2019-12-25	ID56	2020-02-03	ID95	2020-03-22	ID134	2020-05-12
ID18	2019-12-26	ID57	2020-02-04	ID96	2020-03-23	ID135	2020-05-13
ID19	2019-12-27	ID58	2020-02-05	ID97	2020-03-24	ID136	2020-05-14
ID20	2019-12-27	ID59	2020-02-06	ID98	2020-03-25	ID137	2020-05-15
ID21	2019-12-28	ID60	2020-02-07	ID99	2020-03-26	ID138	2020-05-16
ID22	2019-12-28	ID61	2020-02-08	ID100	2020-03-27	ID139	2020-05-17
ID23	2019-12-29	ID62	2020-02-09	ID101	2020-03-28	ID140	2020-05-18
ID24	2019-12-30	ID63	2020-02-10	ID102	2020-03-29	ID141	2020-05-19
ID25	2019-12-31	ID64	2020-02-11	ID103	2020-03-30	ID142	2020-05-20
ID26	2020-01-01	ID65	2020-02-12	ID104	2020-03-31	ID143	2020-05-21
ID27	2020-01-02	ID66	2020-02-13	ID105	2020-04-02	ID144	2020-05-22
ID28	2020-01-03	ID67	2020-02-14	ID106	2020-04-03	ID145	2020-05-23
ID29	2020-01-04	ID68	2020-02-15	ID107	2020-04-04	ID146	2020-05-24
ID30	2020-01-05	ID69	2020-02-16	ID108	2020-04-06	ID147	2020-05-25
ID31	2020-01-06	ID70	2020-02-17	ID109	2020-04-07	ID148	2020-05-26
ID32	2020-01-07	ID71	2020-02-18	ID110	2020-04-08	ID149	2020-05-27
ID33	2020-01-08	ID72	2020-02-19	ID111	2020-04-10	ID150	2020-05-28
ID34	2020-01-09	ID73	2020-02-28	ID112	2020-04-12	ID151	2020-05-29
ID35	2020-01-10	ID74	2020-02-29	ID113	2020-04-13	ID152	2020-05-30
ID36	2020-01-11	ID75	2020-03-01	ID114	2020-04-20	ID153	2020-05-31
ID37	2020-01-12	ID76	2020-03-02	ID115	2020-04-21	ID154	2020-06-02
ID38	2020-01-13	ID77	2020-03-03	ID116	2020-04-24	ID155	2020-06-03
ID39	2020-01-14	ID78	2020-03-04	ID117	2020-04-25	ID156	2020-06-04

C Flow chart of experimental procedure

The flowchart shows the different steps of the project. Demolition wood was combusted at Id-bäcksverket's bubbling fluidized bed boiler and 153 samples of recirculated bed material were collected over a time period from December 2019 to June 2020.



Flowchart of experimental procedure. Grey boxes represent steps that had already been done before the project.

The bed material collected had been analyzed using pulse voltammetry with an electronic tongue and the data from the pulse voltammetry were investigated using PCA. Based on the principal component analysis, 10 representative bed samples were selected from the 153 samples and analyzed using SEM-EDS, AAS and XRF. Based on the results from the analysis, known solutions were prepared and experiments, using pulse voltammetry with the electronic tongue, were conducted on the known solutions. The results from the experiments of the known solutions were also analyzed using PCA. Conclusions were drawn from the PCAs, the experiments and the analysis of fuel and ash data.

D Atomic Absorption Spectroscopy

Data of the amount of sample, dilution of leachate and number of replicates used in the analysis using AAS is presented in the table bellow.

Data of samples analyzed using AAS.

Sample ID	Weighed sample [g]	Dilution of leachate	Number of Replicates used for average K/Na/Ca/Mg
ID5	10	$\times 10$	3/3/3/3
ID38	10	$\times 10$	3/3/3/3
ID72	10	$\times 10$	2/3/3/2
ID76	10	$\times 10$	1/3/3/3
ID92	10	$\times 10$	3/3/3/3
ID108	10	$\times 10$	3/3/3/3
ID116	10	$\times 10$	2/3/3/3
ID123	10	$\times 10$	3/3/3/3
ID147	10	$\times 10$ (40) ^a	3/3/3/3
ID156	10	$\times 10$ (40) ^a	3/3/3/3

a) The sample was diluted 40 times when measuring the content of Ca.

In the following table information of the calibration solutions used to create the calibration curves as well as the wavelengths, detection ranges and lamps used for the AAS analysis is presented.

Data of calibration solutions, wavelengths, detection ranges and lamps used in the AAS analysis.

Element	Standard solution [mg/L]	Low/middle/high [mg/L]	Wavelength [nm]	Detection range [mg/l]	Hollow cathod lamp
K	1	0.1/1/2	766.5	0.043 - 2.0	K ^a
Na	1	0.1/0.5/1	589	0.012 - 1.0	Na
Ca	1	0.5/2.5/5	422.7	0.092 - 5.0	Ca - Mg
Mg	1	0.01/0.1/0.5	285.2	0.0078 - 0.50	Ca - Mg

a) A red filter which absorbs radiation below 650 nm was used.

An example of how the calibration solutions were prepared

The three calibration solutions used to analyze the concentration of Ca in the leachate were prepared from a standard solution with the concentration 1000 mg/l (C_1). A calibration solution with concentration 5 mg/l (C_2) containing 60 ml (V_2) were prepared by diluting the standard solution with milli-Q water. To calculate the amount of standard solution needed (V_1) following equations were used,

$$V_1 \times C_1 = V_2 \times C_2$$

$$V_1 = \frac{V_2 \times C_2}{C_1} = \frac{60 \text{ ml} \times 5 \text{ mg/l}}{1000 \text{ mg/l}} = 0.3 \text{ ml}$$

resulting in that 0.3 ml of the standard solution was required to obtain 60 ml of solution with concentration 5 mg/l. The calibration solution were split in two equal parts containing 30 ml. One of the 30 ml solutions were diluted to 2.5 mg/l. To calculate the amount of milli-Q water needed, the following equation was used.

$$V_3 = \frac{30 \text{ ml} \times 5 \text{ mg/l}}{2.5 \text{ mg/l}} = 60 \text{ ml}$$

By adding 30 ml of milli-Q water to one of the two 30 ml solutions a 60 ml calibration solution with the concentration 2.5 mg/l was obtained. The 2.5 mg/l solution was thereafter divided in two parts and the same procedure was repeated according to following equation,

$$V_4 = \frac{30 \text{ ml} \times 2.5 \text{ mg/l}}{0.5 \text{ mg/l}} = 150 \text{ ml}$$

to obtain a third solution of 150 ml with the concentration 0.5 mg/l.

E X-ray Fluorescence Spectrometry

The samples, its weight and the results from the analysis using XRF are presented in the table.

Data of samples analyzed using XRF.

Sample ID	Weight[g]	Si [%]	Ca[%]	Na[%]	K[%]	Fe[%]	Al[%]	Mg[%]	P[%]	S[%]
ID5	4.121	26.00	0.71	1.70	2.05	0.46	5.03	0.30	0.08	0.01
ID38	4.375	21.12	5.26	2.64	1.72	0.88	4.50	0.86	0.21	0.01
ID72	4.185	21.50	4.62	2.32	2.37	0.75	5.11	0.77	0.29	0.02
ID76	4.097	23.80	2.23	1.95	2.45	0.58	5.46	0.50	0.14	0.01
ID92	4.181	22.26	3.95	2.15	2.41	0.75	5.29	0.55	0.17	0.01
ID108	4.154	21.23	5.61	2.18	2.02	0.80	4.73	0.72	0.22	0.02
ID116	4.188	24.00	2.34	1.77	2.53	0.46	5.31	0.46	0.21	0.01
ID123	4.393	22.44	3.66	1.98	2.47	0.66	5.42	0.67	0.19	0.02
ID147	4.122	20.58	6.07	2.24	2.09	0.71	4.82	0.83	0.29	0.04
ID156	4.242	20.09	6.77	2.18	1.94	0.74	4.72	0.91	0.32	0.03

F Pulse voltammetry using Electronic Tongue

The pulse-train used during the experiments with the electronic tongue is presented in the figure bellow.



The pulse-train used for the experiments with the electronic tongue.

Each pulse-train consisted of 0.02 s long pulses of negative and positive potentials that ranged from -1 V to 0.7 V. Each pulse was sampled 5 times with 0.004 s in between each sample. The pulse-train lasted for 0.3 s. The three working electrodes used for the experiments were of platinum, gold and rhodium.

Set up of experiments

First set up: Hydroxides

The weight of the compounds used for the hydroxide solutions are presented in the following table.

Data of compounds used for ET analysis.

Compounds	Weighted sample [g]
CaO	0.100
NaOH	0.102
KOH	0.105

Each compounds was dissolved in milli-Q water and diluted to obtain three different concentrations: 20, 40 and 80 mg/l.

An example of how the solutions were prepared

The solution was prepared by weighing 0.1 g of CaO and adding it to a beaker. The beaker was filled

to 100 ml, resulting in a concentration of 1000 mg/l (C_1). Thereafter 10 ml (V_1) of the solution was added to a new beaker and an additional 115 ml of milli-Q water was added to give a concentration of 80 mg/l (C_2) and a volume of 125 ml (V_2). Example calculation are presented below.

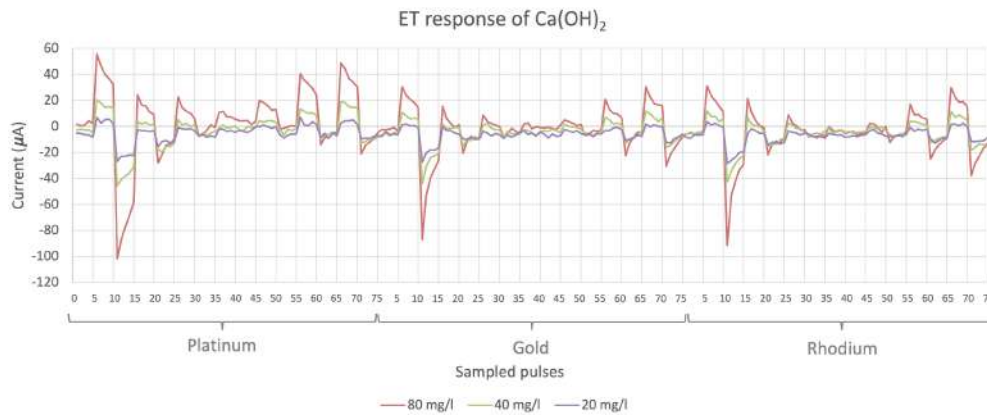
$$C_1 \times V_1 = C_2 \times V_2$$

$$\frac{1000 \text{ mg}}{l} \times 10 \text{ ml} \times \frac{l}{80 \text{ mg}} = 125 \text{ ml}$$

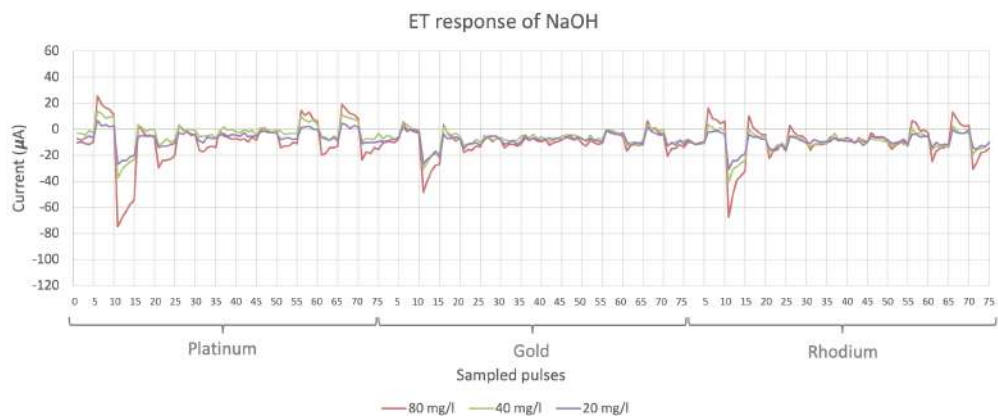
When the 80 mg/l solution was prepared, 50 ml of that solution was diluted to 100 ml to obtain a 40 mg/l solution and the same procedure was repeated to obtain the 20 mg/l solution.

Current response graphs

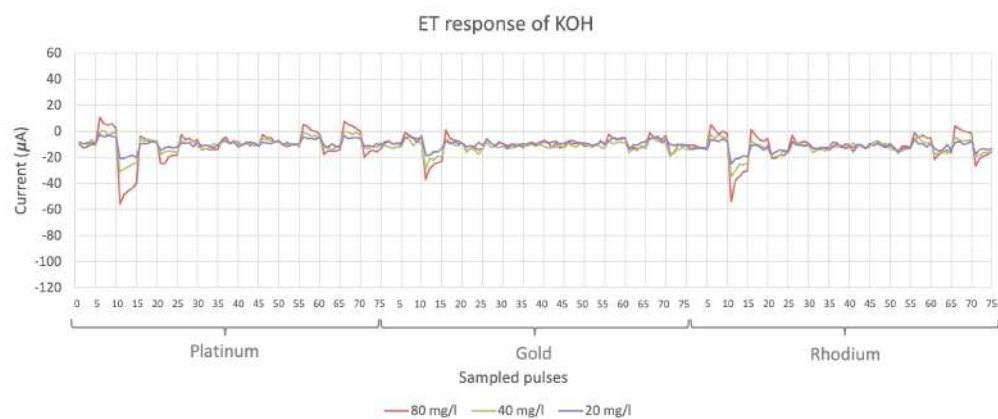
The current response of the different hydroxides is presented in the following graphs.



ET-response to different concentrations of $\text{Ca}(\text{OH})_2$



ET-response to different concentrations of NaOH



ET-response to different concentrations of KOH

Second set up: Mixture of hydroxides

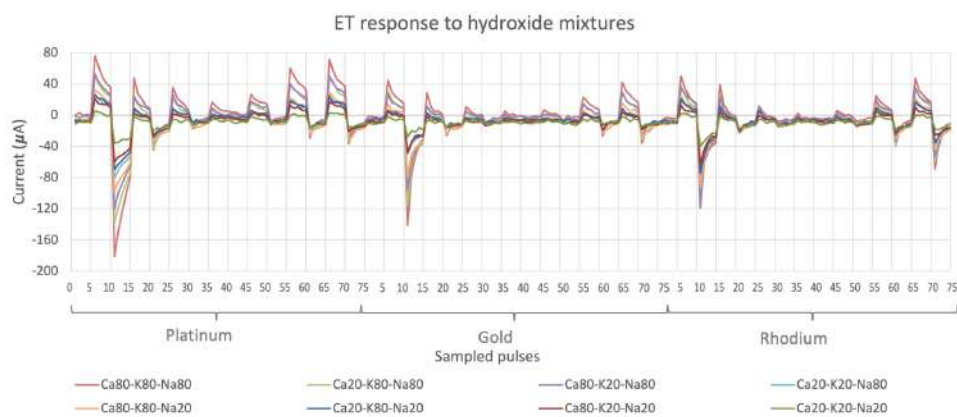
The concentration of hydroxides for the experiments containing a mix of hydroxides are presented in the following table.

Experimental matrix

	Ca(OH) ₂	NaOH	KOH
1	80	80	80
2	20	80	80
3	80	20	80
4	20	20	80
5	80	80	20
6	20	80	20
7	80	20	20
8	20	20	20

Current response graphs

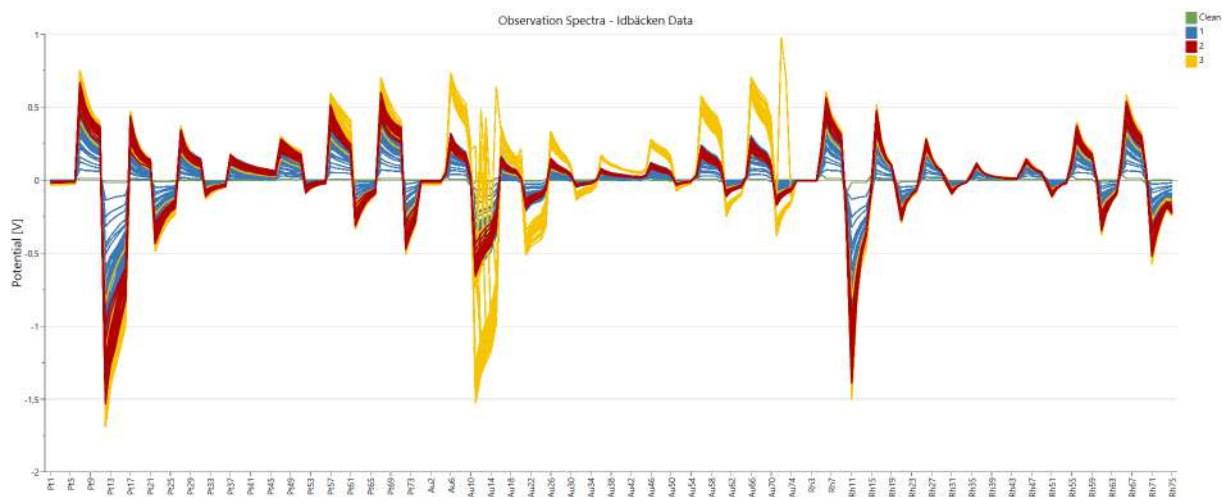
The current response of the experimental matrix is presented in the following graphs.



ET-response to hydroxides mixtures from experimental matrix

G Response signal

The response signal from the electronic tongue obtained from the bed material from Idbäcksverket is presented in the figure.



The response signal from the electronic tongue obtained from the leachate of 153 samples of bed material from Idbäcken. Each operation period is presented by a color.

H Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

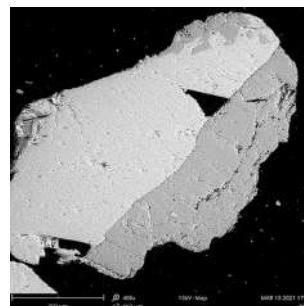
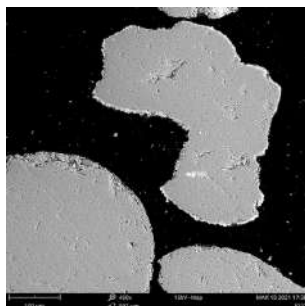
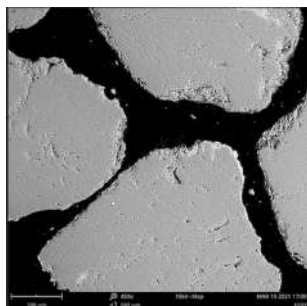
Elemental concentration and thickness of the layers around the bed particles obtained by SEM-EDS analysis of 6 samples from period 1 - period 3. The detection limit of the EDS is 1 at%. Values lower than 1 at% are therefore only presented to show gradients between the layers.

Silica sand				
Period	Sample	Inner layer [at%] Si/Ca/Na/K/Fe/Al/Mg	Outer layer [at%] Si/Ca/Na/K/Fe/Al/Mg	Layer thickness [μm] Ca/Na/Total
1 (Start)	ID5	-	-	-
1 (Middle)	ID38	22.2/1.3/6.6/1.2/0.4/1.3/0.8	18/7.1/2.9/0.6/0.8/1.8/1.7	9.1/23.7/28.3
2 (Start)	ID76	23/1.0/4.7/1.4/0.7/0.9/0.9	13/11.2/2.2/0.3/0.7/1.6/3.2	6.5/5/7
2 (End)	ID108	-	11.3/14.3/0.3/0/0.6/1.5/3.4	16.7/0/15.7
3 (Start)	ID123	23.3/2.0/6.1/1.8/0/1.1/1.3	10.5/14.5/1.0/0.1/0.9/2.9/2.9	15.0/7.9/17.8
3 (End)	ID147	-	8.2/13.1/0.7/0/1.1/2.3/6.1	19.7/0/18.1

a) If the particle only had one layer it is reported in the column named outer layer.

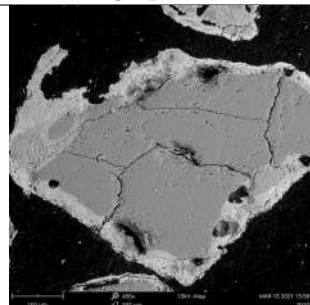
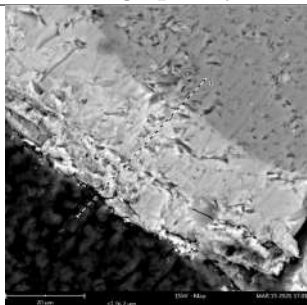
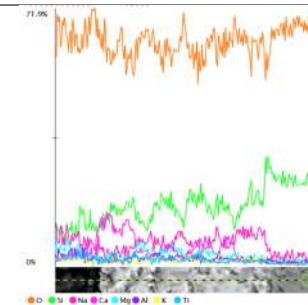
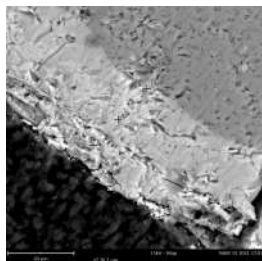
Micrographs and line scans from 2 bed samples of each period (1-3) are presented in this section.

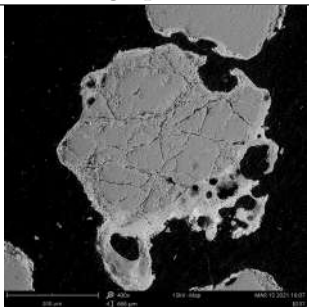
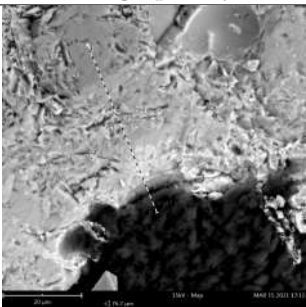
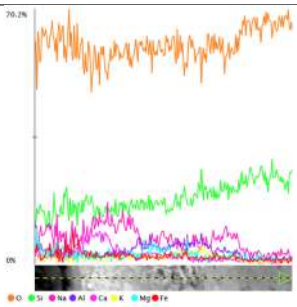
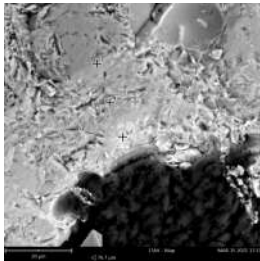
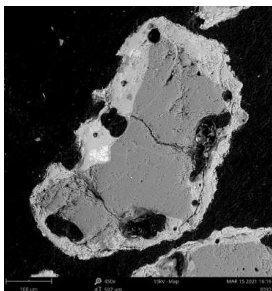
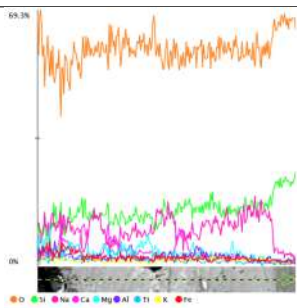
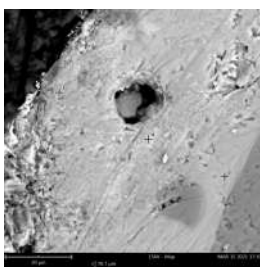
Period 1- ID5



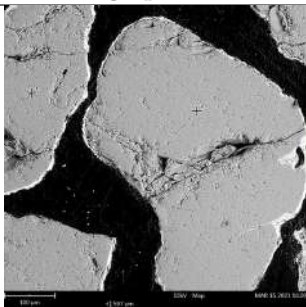
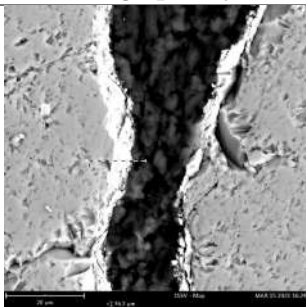
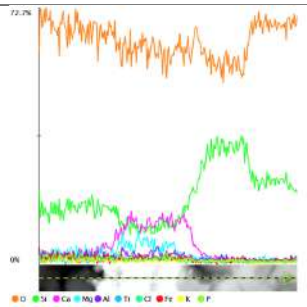
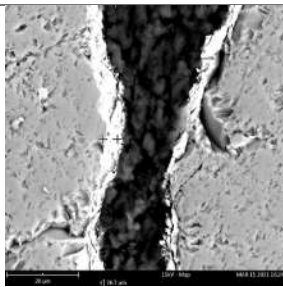
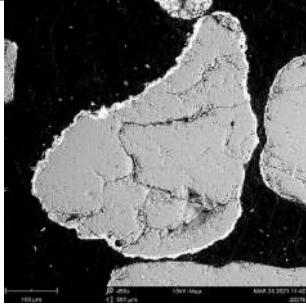
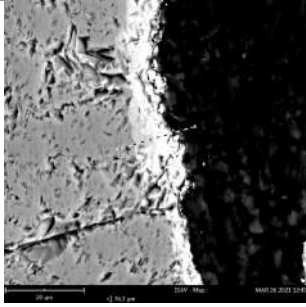
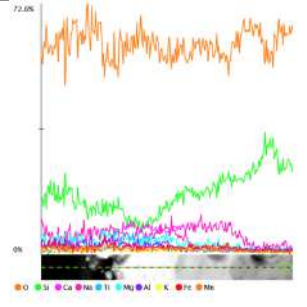
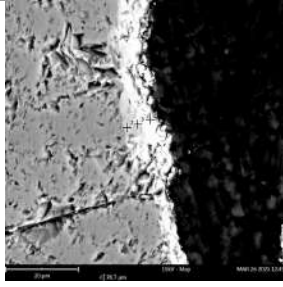
Representative micrographs of sample ID5. Particles present no layers.

Period 1- ID38

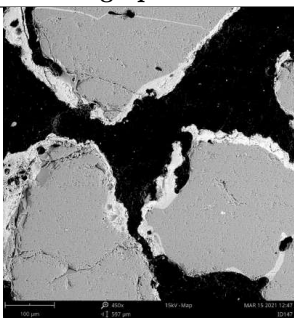
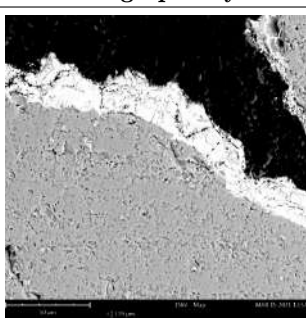
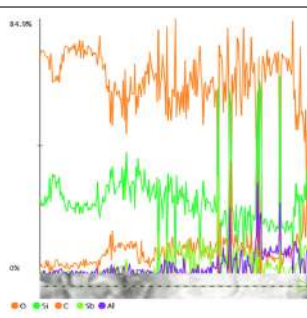
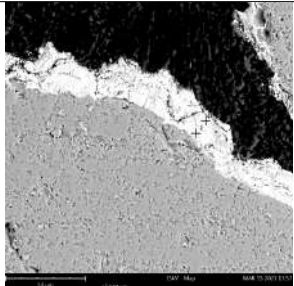
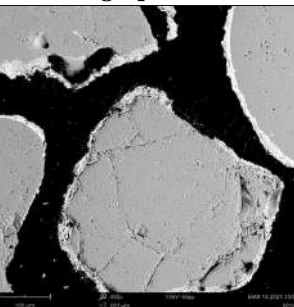
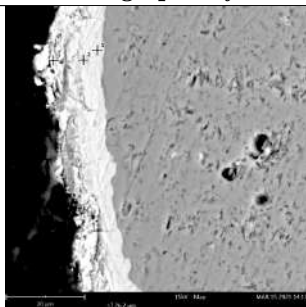
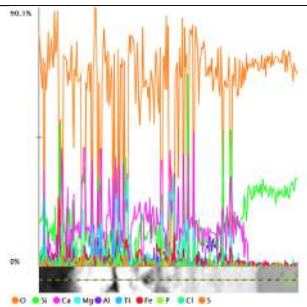
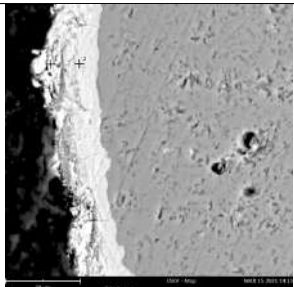
Micrograph Particle	Micrograph Layer		line scan	
				
Point scan	Element	Spot 3	Spot 4	Spot 5
	O	68.12	66.24	66.81
	Si	23.49	18.31	18.78
	Ca	1.04	8.14	4.13
	Na	4.55	3.76	4.87
	K	0.91	0.76	1.19
	Al	0.56	1.36	2.49
	Mg	0.53	0.65	0.26
	Fe	0.5	-	0.60
Other	-	P: 0.35	Ti: 0.61, Mn: 0.25	

Micrograph Particle	Micrograph Layer		line scan	
				
Point scan	Element	Spot 3	Spot 4	Spot 5
	O	68.41	63.40	68.04
	Si	22.89	20.67	17.35
	Ca	0.45	2.49	6.87
	Na	3.89	3.36	-
	K	1.18	2.07	0.75
	Al	2.43	4.54	2.07
	Mg	-	2.66	0.84
	Fe	0.75	0.80	1.09
Other	-	-	Zn: 2.61	
Micrograph Particle	Micrograph Layer		line scan	
				
Point scan	Element	Spot 3	Spot 4	Spot 5
	O	64.48	66.26	63.74
	Si	21.30	18.08	18.25
	Ca	1.24	10.10	9.40
	Na	11.24	-	3.75
	K	1.15	0.42	0.29
	Al	0.58	0.91	0.73
	Mg	-	0.91	2.04
	Fe	-	0.80	1.02
Other	-	-	Zn: 2.52	Ti: 0.77

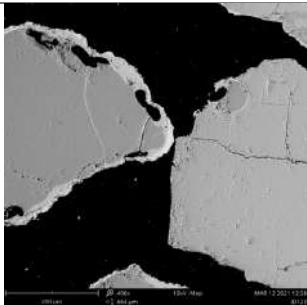
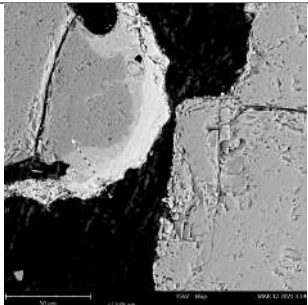
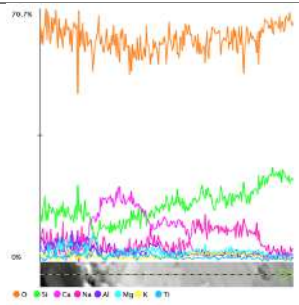
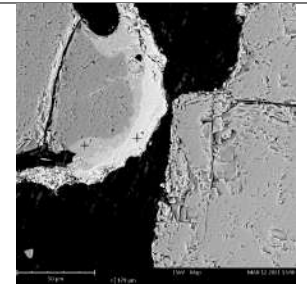
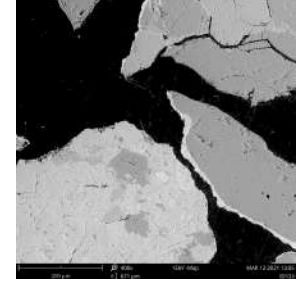
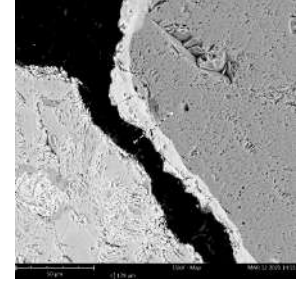
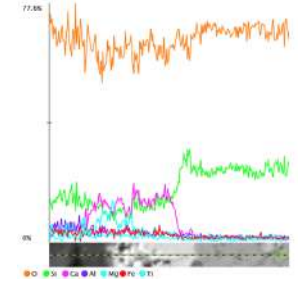
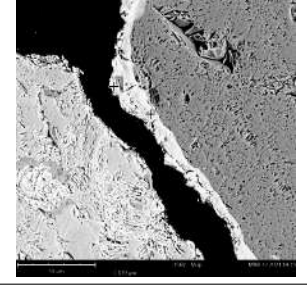
Period 2- ID76

Micrograph Particle		Micrograph Layer		line scan	
					
Point scan		Element		Spot 3	Spot 4
		O		72.69	63.67
		Si		24.74	12.07
		Ca		2.18	13.38
		Na		0.10	0.14
		K		-	0.01
		Al		0.1	1.81
		Mg		0.06	5.34
		Fe		0.04	0.72
		Other		-	Ti: 0.77
Micrograph Particle		Micrograph Layer		line scan	
					
Point scan		Element	Spot 2	Spot 3	Spot 4
		O	66.91	66.24	74.34
		Si	22.96	20.50	10.29
		Ca	1.00	8.30	7.82
		Na	4.69	2.23	2.13
		K	1.37	0.66	0.02
		Al	0.88	0.55	1.09
		Mg	0.87	0.60	1.98
		Fe	0.65	0.38	0.32
		Other	Mn: 0.22	Mn: 0.31, Ti: 0.22	Ti: 2.00

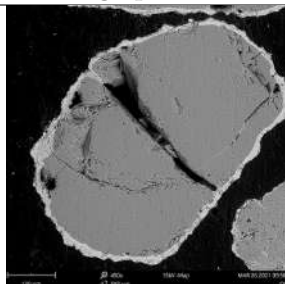
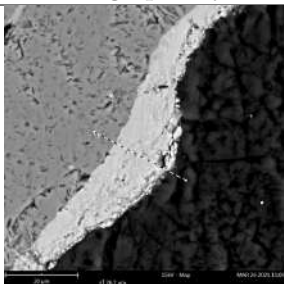
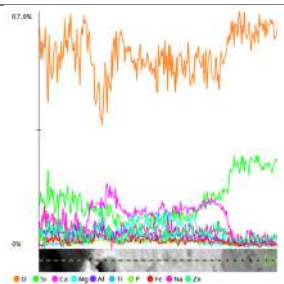
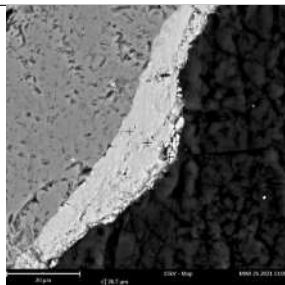
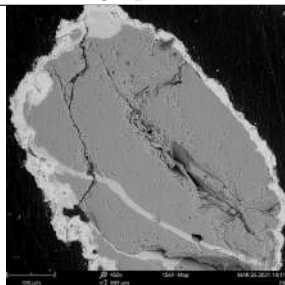
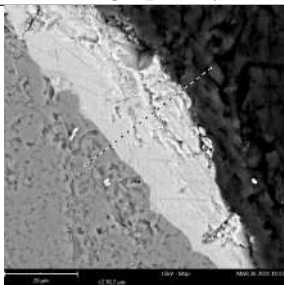
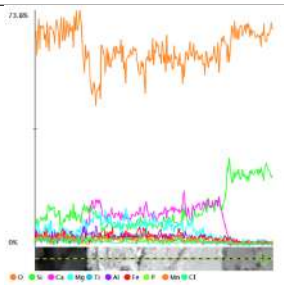
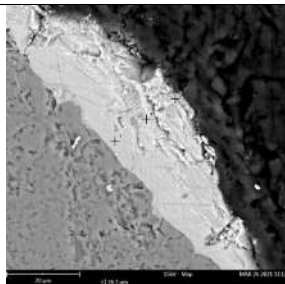
Period 2- ID108

Micrograph Particle	Micrograph Layer	line scan		
				
Point scan	Element	Spot 2	Spot 3	
	O	68.12	70.19	
	Si	13.91	9.02	
	Ca	16.09	10.16	
	Na	-	0.42	
	K	-	0.09	
	Al	0.25	2.42	
	Mg	0.56	3.63	
	Fe	0.77	0.71	
	Other	Ti: 0.23, P: 0.06	Ti: 1.79, P: 0.96	
Micrograph Particle	Micrograph Layer	line scan		
				
Point scan	Element	Spot 1	Spot 2	Spot 5
	O	68.20	65.24	65.58
	Si	8.58	10.74	15.08
	Ca	12.39	13.92	15.91
	Na	0.18	0.21	0.13
	K	0.06	-	0.06
	Al	2.02	2.83	0.74
	Mg	3.28	2.91	1.46
	Fe	0.83	0.66	0.23
	Other	Ti: 2.11, Cl: 1.53	Ti: 1.85, Cl: 0.82	Ti: 0.29, Cl: 0.27

Period 3 - ID123

Micrograph Particle	Micrograph Layer	line scan	
			
Point scan	Element	Spot 3	Spot 4
	O	64.12	60.40
	Si	23.30	8.16
	Ca	2.01	12.78
	Na	6.10	1.13
	K	1.80	-
	Al	1.11	3.30
	Mg	1.34	5.62
	Fe	-	1.08
	Other	Ti: 0.22	Ti: 2.58
Micrograph Particle	Micrograph Layer	line scan	
			
Point scan	Element	Spot 3	Spot 5
	O	63.00	67.29
	Si	12.82	9.66
	Ca	15.97	15.12
	Na	-	-
	K	-	0.07
	Al	3.22	2.58
	Mg	0.74	3.02
	Fe	0.65	0.71
	Other	P:0.46	P:1.27

Period 3 - ID147

Micrograph Particle	Micrograph Layer		line scan	
				
Point scan	Element	Spot 3	Spot 4	Spot 5
	O	66.01	65.55	63.71
	Si	12.84	8.92	7.87
	Ca	16.59	13.83	12.18
	Na	0.58	0.95	1.32
	K	0.03	-	-
	Al	1.20	1.48	2.59
	Mg	1.00	5.40	6.87
	Fe	0.37	0.78	1.31
Other	Ti: 0.9, P:0	Ti: 1.45, P: 1.14	Ti: 2.21, P:1.27	
Micrograph Particle	Micrograph Layer		line scan	
				
Point scan	Element	Spot 3	Spot 4	Spot 5
	O	66.49	67.01	55.97
	Si	14.13	7.59	8.95
	Ca	16.63	12.78	15.19
	Na	-	0.32	1.00
	K	0.03	-	-
	Al	0.67	1.83	3.62
	Mg	1.29	5.78	7.57
	Fe	0.43	0.93	1.37
Other	Ti: 0.16, P:0	Ti: 1.35, P: 1.51	Ti: 2.60, P:1.88	