REFAWOOD

ERA-NET Bioenergy

REFAWOOD Work package 1: Fuel additive design concepts for reduction of ash related problems in wood waste combustion

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Content

Foreword

The work was carried out within the ERA-Net Bioenergy project "REFAWOOD - Resource-efficient fuel additives for reducing ash related operational problems in waste wood combustion" and has been coordinated by RISE Research Institute of Sweden. The project partners consist of six small and medium-sized enterprises and two large companies related to the supply chain of waste biomass power plants and additives, three research organizations and four universities from 5 different countries (Sweden, Austria Germany, Poland and The Netherlands).

This report is part of the deliverables of WP1 Fuel additive design concepts for reduction of ash related problems in wood waste combustion.

Key words: waste wood, waste-to-energy, additive, combustion, ash formation

Summary

Combustion of waste wood and wood residues pose different operational challenges than those encountered in combustion of stem wood. Industrial challenges such as slagging, fouling, deposit formation and/or corrosion are more likely to occur due to more complex ash transformation reactions taking place. Previous research has shown that various types of additives modifying the total ash composition of a fuel may reduce these problems. Notably, additives or co-combustion fuels containing calcium, sulphur, or aluminium silicates have been proven as suitable additives in combustion of stem wood.

The work conducted by Umeå University (UmU) and Luleå University of Technology (LTU) in Work package 1 (WP1) investigated how three different types of additives (gypsum, iron(II)sulphide, and halloysite) could theoretically affect combustion characteristics of different waste wood from all project partners (demolition wood chips, wood board residues, furniture manufacturing residues) and wood residues (logging residues, wood residuals, bark, wood chips). The total fuel composition together with chemical assessment of additive reaction mechanisms and results from calculations were used as support for choosing suitable additive levels prior to combustion tests carried out by project partners, where different countries used different waste wood fuels and/or additives.

Thorough fuel analyses was made prior to evaluating the fuels using thermodynamic equilibrium calculations. Combustion experiments in an underfed fixed bed boiler carried out jointly by UmU and LTU specifically investigated the effect of recycled gypsum and iron(II)sulphide on the combustion characteristics of demolition wood chips from the Swedish industrial partners ENA Energi AB. The results from these combustion tests were evaluated using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and powder X-ray diffraction (XRD) to determine the effect of respective additive with respect to slagging, fouling, deposits, and flue gas composition.

Recycled gypsum and iron(II)sulphide displayed slightly different reactivity based on burner and bottom ashes. With the addition of gypsum, distinct ash particles with high Ca and S concentrations could be observed in the bottom ash. This was not as prominent for the FeS case suggesting a more efficient decomposition.

The effects both gypsum and FeS on flue gas composition was pronounced; both additive types yielded higher SOx concentrations coupled with HCl. This combination shows that chloride formation has been somewhat replaced by sulphate formation instead which was the intended goal. Interestingly, the major effect was on the deposit probe where Cl concentrations were reduced. Instead, in the particulate matter, the Cl concentrations did not change much possibly suggesting that formed sulphates will be retained in larger particles rather than form through gas-phase nucleation.

The results show that the outlined fuel design strategies for using recycled waste gypsum and FeS to affect the ash formation in combustion of woody waste fuels can be applied. For industrial applications it is important to start with relevant fuel analysis to assess appropriate dosage and to consider how the excess acidic flue gases produced should be managed.

1 Background

Reducing the energy supply from fossil sources requires innovative strategies to reduce reliance on thermochemical conversion of solid or liquid fuels when applicable, and to consider a broader fuel feedstock for the combustion and/or gasification systems that remain. Energy carries from waste streams, such as waste wood, are expected to play a growing part in this shift. If such materials are not suitable for recycling the energy content could at least be utilized.

The importance of utilizing waste streams to their full potential, including energy value, is well recognized within the EU.[1, 2] The replacement of virgin biomass with woody waste in waste-to-energy has created a push for more fuel-flexible combined heat and power plants across Europe. This allows operators to adequately respond to market fluctuations and keep fuel costs low while also contributing to a net reduction of greenhouse gas emissions. Woody waste fuels are already well utilized in the EU but often come with operational challenges for the plant operators. Waste streams may contribute to a circular economy although a simultaneously desired increase in reuse and recycling (see Figure 1) may lead to a more challenging situation for waste-to-energy plant operators.
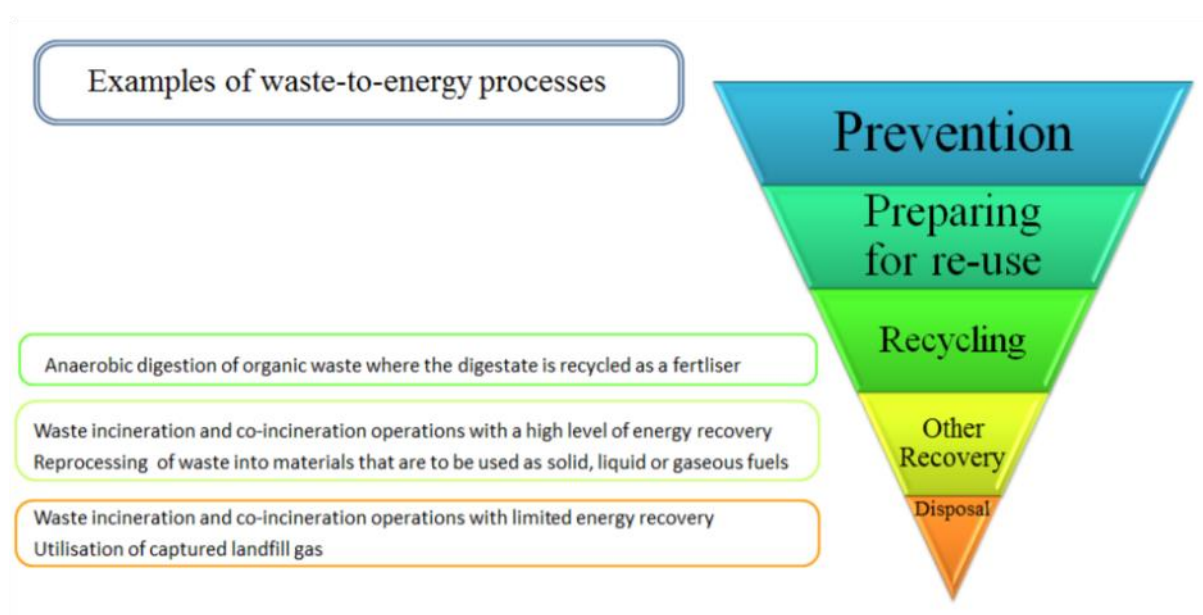
Figure 1 The waste hierarchy and waste-to-energy processes. Figure adapted from Figure 1 in The role of waste-to-energy in the circular economy, Brussels, 26.1.2017 COM(2017) 34 final.[1]

Waste wood fuels pose specific challenges in thermal conversion compared to conventional combustion of clean wood chips, and these often arise from the inorganic content in the fuel. The ash content is typically higher, the concentrations of certain elements such as Zn is often higher due to residues of paint and other materials from construction, and the concentrations of Cl could be high due to inclusion of plastic materials. Altogether, this causes waste wood from demolition in particular to have a challenging composition of ash-forming elements with regards to operational problems such as slagging or corrosion.

Extensive research has been conducted to understand such challenges for complex biomass fuel streams. Some of these results are directly applicable to waste wood where similar challenges arise regarding slagging and chlorine-induced high temperature corrosion. It is fairly well understood that capturing alkali metals (K, Na) in stable structures may reduce issues with slagging and that the addition of sulphur in various forms can reduce issues with corrosion caused by chlorides. These amendments could be amended by fuel design where the total inorganic content of the fuel is altered using additives or co-combustion, depending on what suits the issue best.

Similar solutions based on fuel design could be applied for waste wood, but in these cases it becomes more attractive to include additive sources that are considered waste streams. This could reduce additive costs, reduce the waste produced by society, as well as mitigate ash-related operational problems in combustion of wood waste fuels. In order to achieve efficient strategies for such reuse of waste streams it is vital to understand the underlying chemical mechanisms for the additives used as well as determine suitable additive dosage levels that could reasonably be expected to work from laboratory to industrial scale.

Identifying potential additive strategies based on waste stream compositions could simultaneously address the demand for reuse or other recovery as well as meeting the operational challenges in an increased waste-to-energy strategy. The REFAWOOD project aims to facilitate this shift to a circular economy by selecting a range of resource-efficient additives with a potential for reducing operational-related challenges in waste-to-energy for woody waste fuels. The additives that have been identified as most relevant is this work has a potential to address slagging, fouling, and deposit formation issues in combustion of woody waste fuels through different mechanisms.

2 Aim

Work package 1 of the REFAWOOD project aims to investigate the influence of new cheap and resource efficient fuel additives as recycled gypsum, iron sulphide (sulphide ore waste material), and the aluminosilicate additives halloysite and coal fly ash on important ash transformation processes in fixed bed combustion of wood waste.

This is achieved by determining the underlying chemical mechanisms for how these three additives react with fuel ash and how this may affect ash related operational problems; propose suitable additive approaches depending on wood waste fuel composition; and test these additives in a range of laboratory- and small-scale combustion facilities. The results from Work package 1 serves Work package 3 with input of full-scale experimental operation conditions including interesting fuel-additive blending concepts. This addresses the following two specific aims for the REFAWOOD project:

- To determine the influence of recycled gypsum, iron sulphide and halloysite on important effects of ash transformation processes in combustion of wood waste fuels i.e. bed agglomeration, slagging, fouling and high temperature corrosion.
- To propose efficient fuel additive design concepts for reducing ash related operational problems (corrosion/fouling/slagging) in combustion of wood waste fuels.

3 Additives – a fundamental outlook

3.1 Recycled waste gypsum

3.1.1 Identifying the key component

Gypsum ($CaSO_4 \cdot 1.5H_2O$) decomposes in two steps, first by dehydration into anhydrite ($CaSO_4$) which further decomposes to CaO(s) and SO_3(g), where the latter reaction is more efficient at higher temperatures and low O_2-to-fuel ratios. The decomposition is crucial for its efficiency as an additive. Looking at what effect is desired from the additive for application in waste wood combustion, the addition of CaO(s) will readily assist in increasing melting temperature of formed bed ash already at low additions. The sulphur addition aiming to capture alkali and to some extent Zn and Pb, including that which may be released into gas phase after tertiary ash transformation reactions where Ca substitutes alkali in silicates, should therefore be considered the most important reactive component.

3.1.2 Waste gypsum efficiency limitations

3.1.2.1 Decomposition of gypsum

The efficiency of alkali capture in by sulphur from recycled gypsum cannot be expected to be 100% due to several limiting factors. Previous studies have suggested that small amounts of additive will display a decomposition of gypsum as evident by elevated SO_2 levels, but not to 100% decomposition – with significantly lower results in fluidized beds. Gypsum addition in coal combustion have shown decomposition efficiencies as low as 30% but previous bench-scale studies for grate-fired systems would place this number significantly higher. Therefore, a decomposition of gypsum at 80% was used as an estimate in the present project where fixed bed systems dominated the experimental setups both in laboratories and in industrial-scale experiments.

3.1.2.2 Absorption of emitted sulphur by coarse ash particles

Part of the challenge of estimating gypsum decomposition is that CaO(s) in bottom ash or entrained in flue gases may reabsorb SO_2/SO_3(g) to form anhydrite ($CaSO_4$(s)). This interaction may take place on cooler parts of the grate or if CaO particles are entrained in the flue gas and does compete with the desired alkali sulphate formation. This limits the availability of SO_2/SO_3(g) to interact with compounds containing K or Na in the flue gas to reduce chloride formation.

3.1.2.3 Sulphation reactions in flue gas

Elevated concentrations of SO_2/SO_3(g) have been shown to promote sulphation reactions. Still, some of the gaseous SO_2(g) will remain in the flue gas even if there is still alkali and/or Zn and Pb available for further reaction. For this reason, an efficiency of 80% of sulphur in gas phase will be assumed to bond with K, Na, Zn, and Pb, to reduce chloride formation. This efficiency is a coarse estimation and does require specific

studies targeting the kinetic parameters of sulphate formation, which is beyond the scope of this work.

3.1.3   Additive efficiency

The assumptions made above suggests a stoichiometric efficiency of S for capture of K(+I), Na(+I), Zn(+II), and Pb(+II) to be 80% decomposition · 80% sulphation = 64% of the total S available in the system. While dependent of assumptions of these factors, calculations in FactSage suggest that this weighting of factors should result in sulphation. These assumed efficiencies of decomposition and sulphation will differ heavily dependent of the combustion system used and are very difficult to separate in practice. Further studies would be necessary to separate the two effects and estimate how much each of them account for as a function of parameters such as partial O_2 pressure in the initial fuel conversion, flue gas temperature, separation of bottom ash and flue gas concerning reabsorption, to name a few.

3.1.4   Approach for calculating gypsum additive levels

The stoichiometric amounts of S for capturing total amount of K, Na, Zn, Pb with the above suggested efficiency were used throughout the project. This will provide information whether these low amounts will already have a noticeable effect. The high addition level corresponds to twice the stoichiometric amount of S according to the assumptions made. This is also the additive level relevant for full-scale experiments. The total molar amount of S to be added, S_{add}, can therefore be calculated according to Equation 1:

$$S_{add} = (F_{stoich} \cdot (((K+Na)/2)+Zn+Pb)-0.64 S_{fuel})/0.64 \qquad \text{(Equation 1)}$$

Where S_{add} is the molar amount of S added through gypsum, F_{stoich} is the final molar ratio between available S and K, Na, Zn, Pb molar levels in the fuel based on cation properties, S_{fuel} is the S included with fuel and 0.64 is the factor resulting from the total efficiency estimations.

Using Fstoich = 1 will provide the amount of S_{add} necessary to follow the expectations according to efficiency limitations and may work well in small systems with the additive evenly distributed and in high contact with surrounding fuel particles. Reasonable levels of additive for industrial scale experiments where a few kilograms of additive may get lost in a ton of fuel will perhaps have to be higher, at least for low additive amounts. Until there are studies outlining the actual efficiency in sulphation through gas phase reactions, it is likely more convenient to use F_{stoich} to estimate desired additive levels.

3.2   Iron(II)sulphide

3.2.1   Identifying the key component

The addition of iron(II)sulphide in waste wood combustion only aims to reduce chloride-induced corrosion, similar to the mechanism discussed in waste gypsum. While actual iron sulphide sources may contain Fe(I)S or/and Fe(II)S, this is a suitable starting component to investigate the system. The oxidation of iron(II)sulphide is exothermic since both Fe and S is oxidized in the net reaction, see Reaction 1 for ΔG of oxidizing 1

mol Fe(II)S at 1000 °C. The actual oxidized iron compounds are likely to have a mixture of oxidation states, but the equilibrium heavily favours the decomposition of iron sulphides. Compared to waste gypsum where energy is required to both remove crystalline water and sulphate decomposition, this reaction is likely to be more efficient.

$FeS(s) + 1.75 \, O_2(g) \rightleftharpoons \frac{1}{2} \, Fe_2O_3(s) + SO_2(g)$ (Reaction 1)

$\Delta G = -431.66$ kJ at 1000 °C
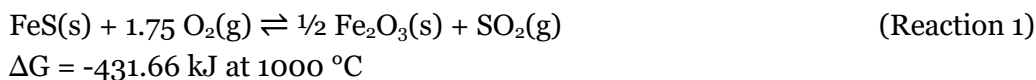
3.2.2   Iron(II)sulphide efficiency limitations

3.2.2.1   Sulphation reactions in flue gas

Similar to waste gypsum additivation, the increased partial pressure of $SO_2/SO_3(g)$ have been shown to promote sulphation of alkali chlorides to reduce high temperature corrosion. For Fe(II)S the interaction will not be inhibited in the same manner by the additive itself. Therefore, the estimation of efficiency will not be adjusted for using any factors as in the gypsum case.

3.2.2.2   Effect of increased Fe on the grate

Increasing the Fe content in the total ash may contribute to lowering the slagging temperature of the formed bottom ash, in particular if it does not oxidize to Fe^{3+}. This was further assessed in the experimental campaigns in REFAWOOD and no increased slagging tendency was immediately identified. Still, it is a parameter that needs to be considered and investigated further in detail.

3.2.3   Approach for calculating iron(II)sulphide additive levels

Since little is known about the efficiency of decomposition of Fe(II)S and subsequent sulphate formation in flue gas, a simple stoichiometric strategy was employed for determining additive amounts. As shown in Equation 2, the total molar concentrations in the fuel for the elements K, Na, Zn, Pb were considered together with amounts of S. Again, an F_{stoich} parameter was included to allow adjusting additive dosage with a known factor where $F_{stoich} = 1$ would correspond to the exact amount of S necessary for complete sulphation of K, Na, Pb, and Zn which is an idealized case.

$S_{add} = F_{stoich} \cdot (((K+Na)/2)+Zn+Pb)-S_{fuel})$ (Equation 2)

3.3   Aluminosilicate additives

3.3.1   Identifying the key component for alkali capture

To find the potential for alkali metal capture of a given aluminium silicate additive we can safely assume that it acts by bonding one K or Na – likely through a tertiary ash transformation reactions with K/Na-OH(g) or possibly by reacting with K_2SiO_3 (s,l) – for each aluminium atom in the aluminium silicate structure. The reaction product of these reactions are compounds such as leucite ($KAlSi_2O_6$), kalsilite ($KAlSiO_4$), microcline ($KAlSi_3O_8$) or analogues containing Na.

While the direct reaction may or may not be targeting the aluminium site specifically, the likely reaction products suggest that one aluminium in the additive corresponds to a possibility to bond one alkali metal ion. The alkali metal ion capture potential, Alk_{cap}, of aluminium silicates should therefore be based on the number of reactive sites originating from the number of moles of aluminium per kilogram of additive (Al_{add}).

3.3.2   Existing cations in the additive

In order to assess the number of reactive sites in an aluminium silicate additive, the amount of already associated components needs to be included or it is likely that the efficiency is overestimated. Suitable minerals as kaolinite or halloysite may already contain certain cations such as K^+, Na^+, Ca^{2+}, and Mg^{2+} (K_{add}, Na_{add}, Ca_{add}, Mg_{add}) when lower qualities are used, and sources such as coal fly ash often contains a complex matrix of cations. Since these cations may already be associated with the reactive sites (Al_{add}) their presence need to be considered when determining the possible number of reactive sites. This does not only apply to mineral additives but may be of relevance for the coal fly ash waste stream as well.

In order to estimate how many reactive sites the Ca^{2+}/Mg^{2+} should be considered to block, one could either consider the formation of anorthite $(Ca,Mg)Al_2Si_2O_8$ or gehlenite $(Ca_2Al_2SiO_7)$. To avoid underestimation of how many reactive sites are lost to Ca^{2+} and Mg^{2+}, the formation of anorthite through direct addition reaction of CaO to metakaolinite $(Al_2Si_2O_7)$ (Reaction 2) and analogues formed after dehydration of aluminium silicates will be used in this work. In summary, K_{add} and Na_{add} will be considered to remove one reactive site each, while Ca_{add} and Mg_{add} will be considered to remove two reactive sites each where their respective abundancy must be calculated in mol/kg of additive.

$$CaO + Al_2Si_2O_7 \rightarrow CaAl_2Si_2O_8 \qquad\qquad\qquad\qquad \text{(Reaction 2)}$$

Based on compounds identified in ash fractions literature it is reasonable to assume that $Fe^{2+/3+}$ does not block access to these sites in the same manner, since Fe in ash from waste combustion typically is found in structures such as Fe_2O_3 or more uncommonly $(Fe,Mg)_2Si_2O_6$ whereas pure Fe-Al-silicates are uncommon. Similarly, other elements such as Ti seemingly presents little opportunity for bonding K or Na, since alkali titanates are rarely reported as identified components.

3.3.3   Aluminosilicate efficiency limitations

The above reasoning assumes 100% alkali capture for each reactive site, which is an ideal assumption, and requires some comparison with empirical studies. Previous work with stem wood and kaolinite as additive has shown the effectivity of kaolinite to be in the range of 0.85 – 0.90, which may also be necessary to apply when assuming additive amounts. The higher value will be used here, assuming 90% efficiency.

The above approach assumes that the aluminosilicate additives has a high reactivity with gaseous alkali compounds. The possibility of reaction with Ca or Mg from the fuel is not included, but such reactions will likely occur. Such alternative reaction pathways would reduce the actual efficiency. Further, coal fly ash as an aluminosilicate source may have a lower actual availability of the reactive sites due to sintering of the material during coal combustion.

3.3.4 Approach for calculating aluminosilicate additive levels

The total Alk_{cap} can, according to the reasons described previously, be calculated as the number of moles of aluminium in the additive, Al_{add}, that is not already associated with cations in the additive (K_{add}, Na_{add}, Ca_{add}, Mg_{add}), in concentrations of mol/kg. This is summarized in Equation 3 below:

$$Alk_{cap} = Al_{add} - (K_{add} + Na_{add} + 2(Ca_{add} + Mg_{add})) \qquad \text{(Equation 3)}$$

Since this is a molar amount, it can be directly compared with amount of alkali metal ions to be captured in the fuel. Basing this on analysis of fuel and additive in mol/kg, either on wet or dry basis for both, and a 90% efficiency provides the following formula to assess how many kg of additive is necessary per kg of fuel (Equation 4):

$$Amount_{add} = ((K_{fuel} + Na_{fuel})/Alk_{cap})/0.90 \qquad \text{(Equation 4)}$$

The resulting fraction from Equation 2 is how many kg of additive is necessary per kg of fuel. This is readily converted into kg/ton or similar units more practical for large scale applications.

4 Materials and methods

4.1 Fuels and additives

4.1.1 Demolition wood chips and recycled waste gypsum

A total of 8 historic demolition wood fuel analyses provided by the Swedish project partner ENA Energi AB were used to calculate average fuel composition of demolition wood chips used in these experiments. The fuels were analysed for ash content (SS-EN 15403:2011), elements C, H, N (SS-EN 15408:2011), S, Cl (SS-EN 15407:2011), and main ash forming elements according to standards SS-EN 15410:2011 and SS-EN 15411:2011. SS-EN 15400:2011 was used to calculate O and for determination of heating values. The average composition of important main ash forming elements as well as Zn and Pb are shown in Figure 2.

The gypsum powder was delivered by Gips Recycling AB that is located in Bålsta, 10 km from the fuel terminal. The company converts gypsum waste into recycled gypsum powder to be used by plasterboards manufacturers. The recycled gypsum substitutes virgin or synthetic (FDG or DSG) gypsum as a raw material. At the recycling facility, a mobile recycling units removes all contaminants and the paper backing of the boards, and grinds the gypsum core into clean recycled gypsum powder. The gypsum was analysed with SS-EN 14774-2 for moisture content, elemental concentration of S using SS-18 71 86, and for other main elements using modified standard ASTM D 3682 with ICP-OES, see Figure 3 for composition.
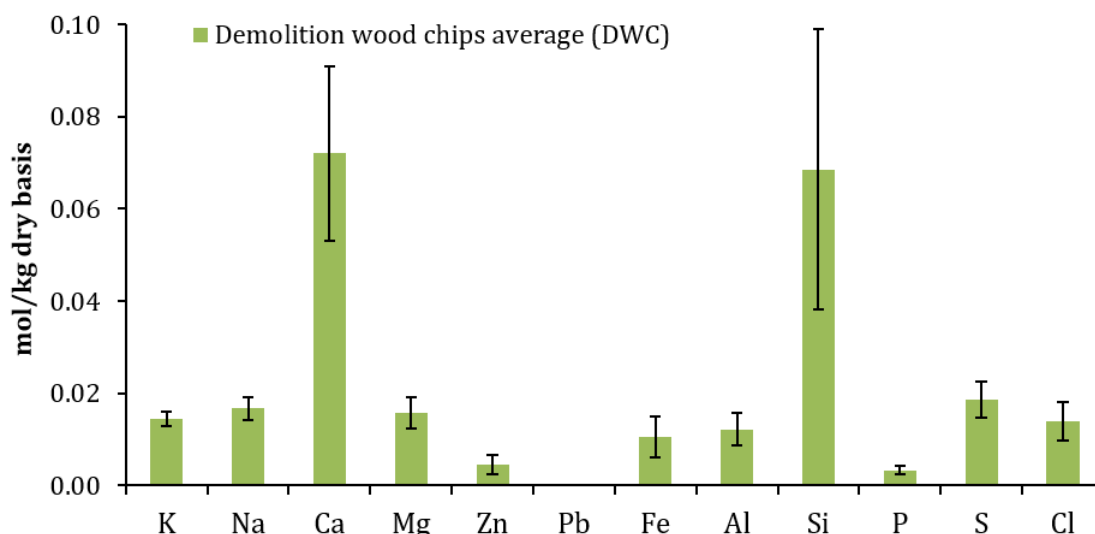
Figure 2 Average elemental composition of demolition wood chips from ENA Energi AB in mol/kg, used for combustion tests in this work package.
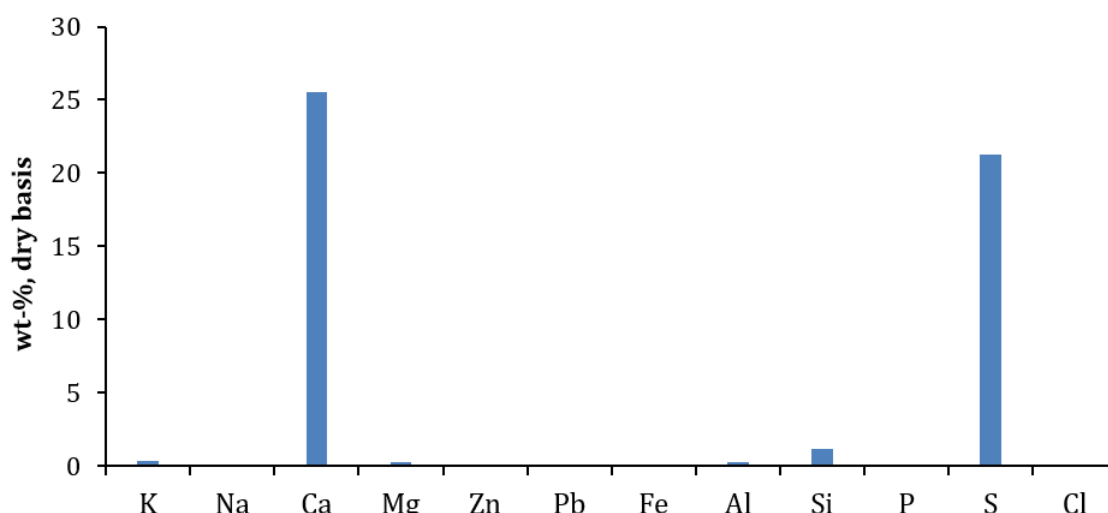
4.1.2   Recycled waste gypsum

Figure 3 Composition of recycled waste gypsum supplied by Gips Recycling AB.

4.1.3   Iron(II)sulphide - FeS

Fe(II)S was purchased as a clean chemical standard for the purpose of preparing fuel blends to perform a feasibility test of its potential as an additive. The compound used was purchased as technical grade from Sigma-Aldrich (CAS no. 1317-37-9) in 250 gram bottles from the same batch.

4.2   Fuel blend preparation

The fuel blends prepared in this work package comprised low and high dosage scenarios for the sulphur-containing additives. Aluminosilicate additives were investigated by other project partners based on the recommendations presented here. The reaction mechanisms and recommended dosage strategies described in Section 3 (Additives – a fundamental outlook) were used in the fuel blend design. Both dosage scenarios assumes

full reactivity of sulphur already carried with the fuel and aims for different stoichiometric ratios according to Equations 2. In this case, the The low dosage scenario was for $F_{stoich} = 1$ and the high dosage scenario was for $F_{stoich} = 2$. The resulting fuel blend compositions are presented in Figure 4. The fuels were blended and pelletized in 6 mm diameter pellets to facilitate fuel feed.
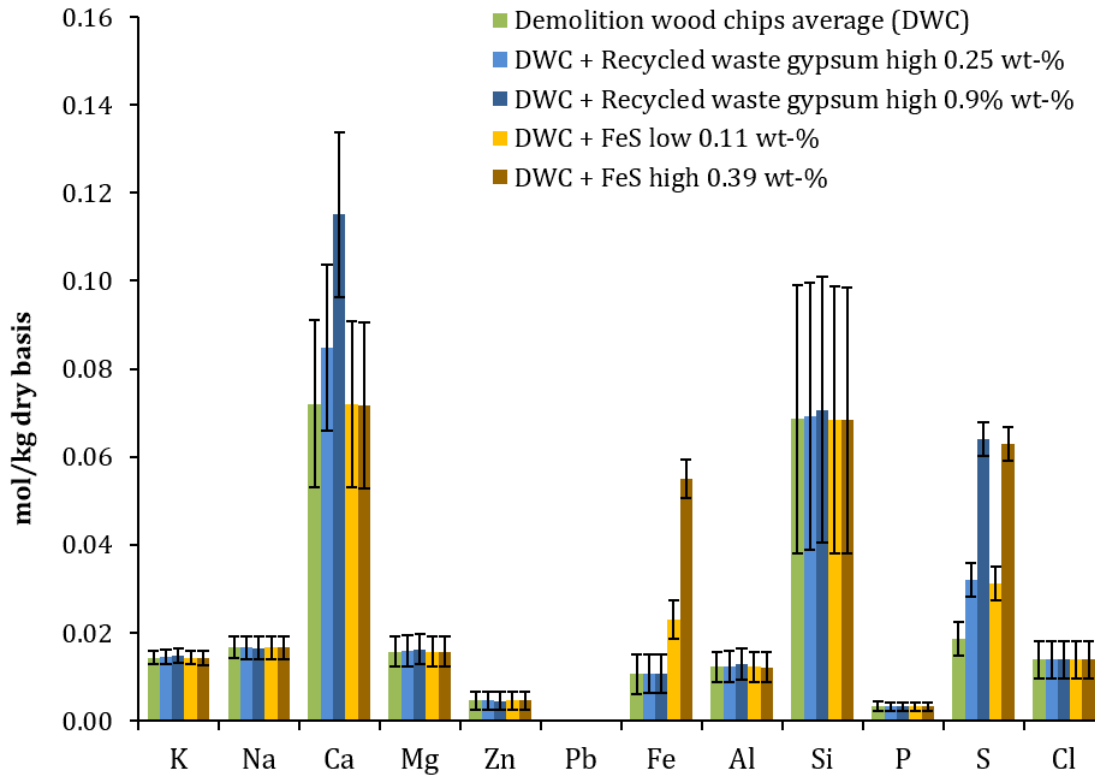

Figure 4 Elemental composition in mol/kg, dry basis, of fuel and fuel blends used in the combustion experiments carried out in work package 1.

4.3 Combustion experiments

4.3.1 Combustion system

The fixed bed burner in this study, was represented by a circular underfed pellet burner (Ecotec Bioline 20-25, 20 kW), installed in a boiler (Combifire 2 20kW), see Figure 1. The pelletized fuel and fuel blends were continuously added to the fuel supply during the experiment and fed to the burner by an automatic feed screw. The burner was fed with primary air from the sides and secondary air was added above the burner. The fuel feed and air supply rate was adjusted to achieve an even combustion environment and reach steady state for particulate matter sampling.

The ash formed during combustion is removed from the burner cup with a rotating top ring. Formed slag particles either remain the burner cup or can be removed by the rotating ring. Ash and slag that is removed land on the water-jacketed bottom and are rapidly cooled down. The flue gases are rapidly cooled down in the water-jacketed boiler and through the top heat exchanger, which also removes most of the particulate matter larger than 1 µm prior to particulate matter sampling.
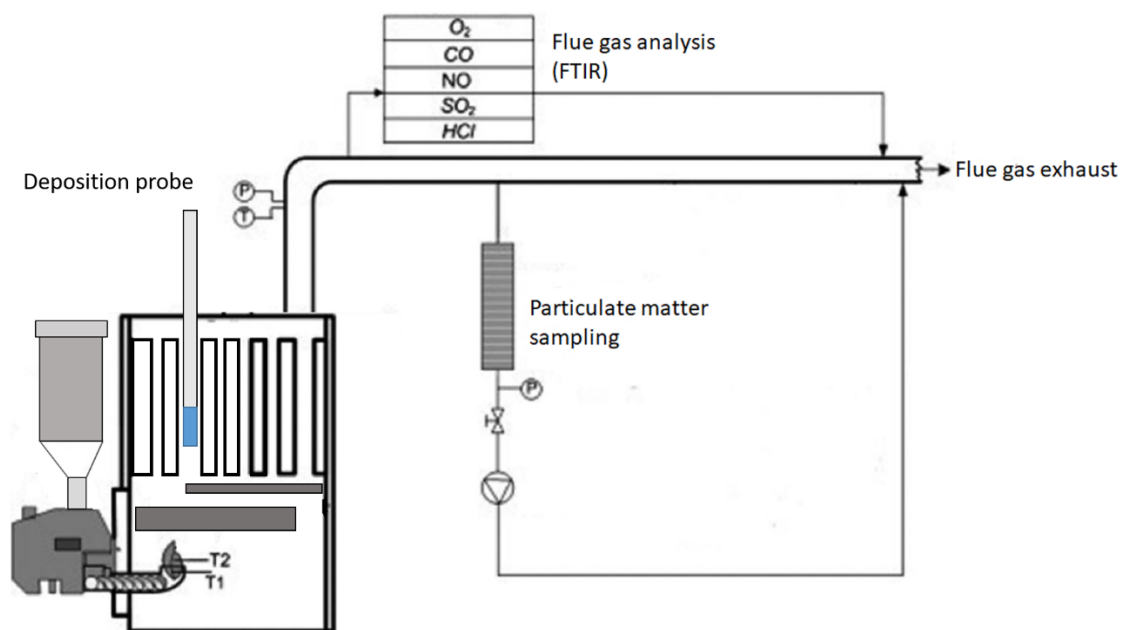
Figure 5 Schematic of the underfed pellet burner, water-jacketed boiler and sampling points for flue gas composition and particulate matter. Thermocouples T1 and T2 were operated during these experiments to monitor the combustion temperature close to the fuel particles. The air-cooled deposition probe was inserted in the heat exchanger region from the top.

4.3.2   Combustion experiments and sampling procedure

A total of five different combustion experiments were carried out in the described system. The combustion period lasted 6 hours for each experiment with an average fuel feed of 2.8-3.4 kg/h depending on flue gas composition. The temperature in the burner was logged at two places during the whole experiment, in connection to the fuel bed and slightly above the burner (see Figure 5). This, together with CO concentrations in flue gas were used to adjust the fuel feed to avoid severe slagging in the more ash-rich co-combustion fuels since the burner is originally designed for clean wood chips.

The composition of the flue gas was determined during the whole experiment by a Gasmet DX-4000Fourier Transform IR-spectroscopy (FTIR), the amount of O2 was detected by a Zirconium-cell. The resulting gas data was used to determine when steady state had been achieved, after this the particulate matter sampling was performed.

Particulate matter size-fractionated sampling was carried with a low pressure impactor from Dekati (DLPI) with aluminum foils as substrates. The DLPI separates the particles by aerodynamic diameter in 13 size steps in the range 0.03–10 μm, enabling a separation of the particulate matter into coarse (>1 μm) and fine (<1 μm) mode. In this study, the DLPI samples were primarily used to study sub-micron particulate matter (PM_1) due to the removal of larger particulate matter particles in the water-jacketed boiler and heat exchanger sections.

An air-cooled deposition probe was inserted in the narrow passes of the heat exchanger section to assess the composition of deposit formation on heat exchangers. Due to the parallel configuration of deposition probe rings and the flue gas direction, the deposit build-up rate could not be assessed using this technique.

The system was left to cool down after completed combustion tests before two different ash fractions were collected; burner ash and bottom ash. Ash and slag was collected from the bottom and the burner and regarded separately during the subsequent analysis. The burner ash was collected from the grate in the burner, and the bottom ash from the bottom of the combustion chamber in the boiler. The ash and slag was separated by sieving, where particles larger than 3.15 mm was classified as slag according to a procedure described in previous works.[3]

4.4 Analysis of ash fractions

4.4.1 Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS)

The morphology of the samples was characterized using variable-pressure scanning electron microscopy (VP-SEM; Carl Zeiss Evo LS-15), using a backscattered electron detector at an accelerating voltage of 20 kV and probe current of 500 pA. The elemental composition was quantified using an energy-dispersive X-ray spectrometer (EDS; Oxford Instruments X-Max 80 mm²). These analyses were performed at Umeå Core Facility for Electron Microscopy (UCEM), Chemical Biological Centre (KBC), Umeå University (Umeå, Sweden).

Three replicate samples were used for each original ash sample from burner and boiler bottom ash. These were encased in epoxy and polished prior to analysis. For PM1 and deposit probes small amounts of samples were transferred to carbon tape prior to analysis since these amounts are in the ranges of milligrams. Area and point analysis were performed from different parts of the samples. For the average composition, all three replicates of the samples and three areas of 1.500 x 1.125 mm from at least three different parts of the samples were used. Chlorine was excluded from the EDS analysis for the samples embedded in epoxy because the epoxy resin contains chlorine and thus provides a background signal making quantification of low amounts impossible when excluding C and O.

5 Results

5.1 Combustion characteristics

5.1.1 Flue gas composition

The overall flue gas composition is presented in Table 1. It should be noted that the CO levels fluctuate most for the gypsum combustion tests, which may indicate challenges with the fuel for this burner type. The SOx increases for all cases with sulphur additives where higher SO_3 was noted for FeS at both additive levels. HCl emissions increase significantly for FeS addition and gypsum low, whereas the DWC and high gypsum addition are not significantly different although the gypsum addition indicate a higher average concentration. The resulting increases in SOx and HCl emissions are shown in Figure 6, where the difference for additivation is seen.

Table 1 Flue gas composition with respect to H_2O, O_2, CO_2 in vol-% and average gaseous emissions on dry basis, normalized against 10% O_2, for CO, SO_2, SO_3 and HCl.

Component	Unit	DWC	Gypsum low	Gypsum high	FeS low	FeS high
H_2O	Vol-%	8.2±0.4	7.2±0.7	7.2±0.4	6.3±0.3	7.4±0.3
O_2	Vol-%, db	10.3±0.7	11.9±1.1	13.2±0.7	12.8±0.6	12.7±0.5
CO_2	Vol-%, db	10.3±0.7	9.1±1.1	8.3±0.6	8.5±0.6	8.5±0.6
CO	mg/m^3, db	153±55	246±263	312±123	237±78	217±79
SO_2	mg/m^3, db	77.8±3.7	133±10	297±37	76.6±6.6	191±20.2
SO_3	mg/m^3, db	0±0.0	0.5±0.7	11.1±1.8	25.4±1.5	9.3±1.0
HCl	mg/m^3, db	10.4±0.8	14.2±2.0	14.6±4.1	20.8±1.9	19.4±1.8
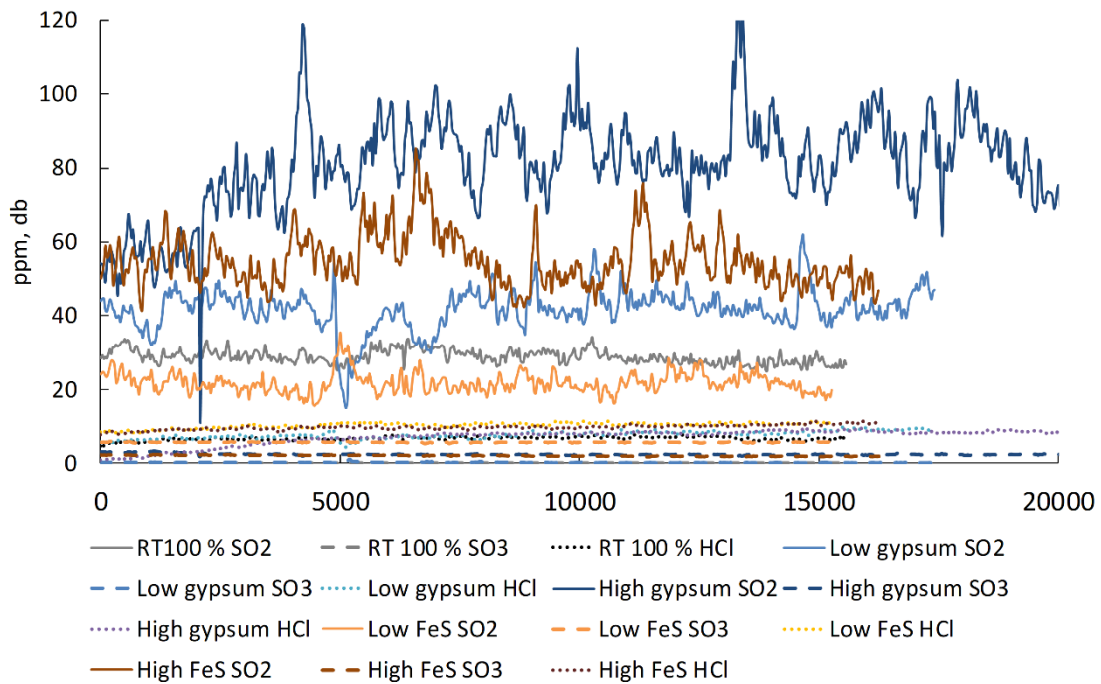
Figure 6 SO_2, SO_3, and HCl concentrations in flue gas during steady state combustion for the fuels and fuel blends.

5.1.2   Particulate matter size distribution

The main part of the particulate matter comprised PM1 as expected due to the construction of the combustion system, see Figure 7. Adding gypsum or FeS increased the total concentrations of PM1 for both cases. It is unknown whether this was affected by the combustion behaviour and potential soot formation, as the analytical techniques cannot analyse carbon separately in the small amounts of PM sampled.

An important feature is that the sulphur addition based on total fuel stoichiometric composition resulted in near-identical particulate matter size distribution curves for the submicron particles. This points towards similar shifts in the formation mechanism for submicron particles regardless of which sulphur-containing additive that was used.
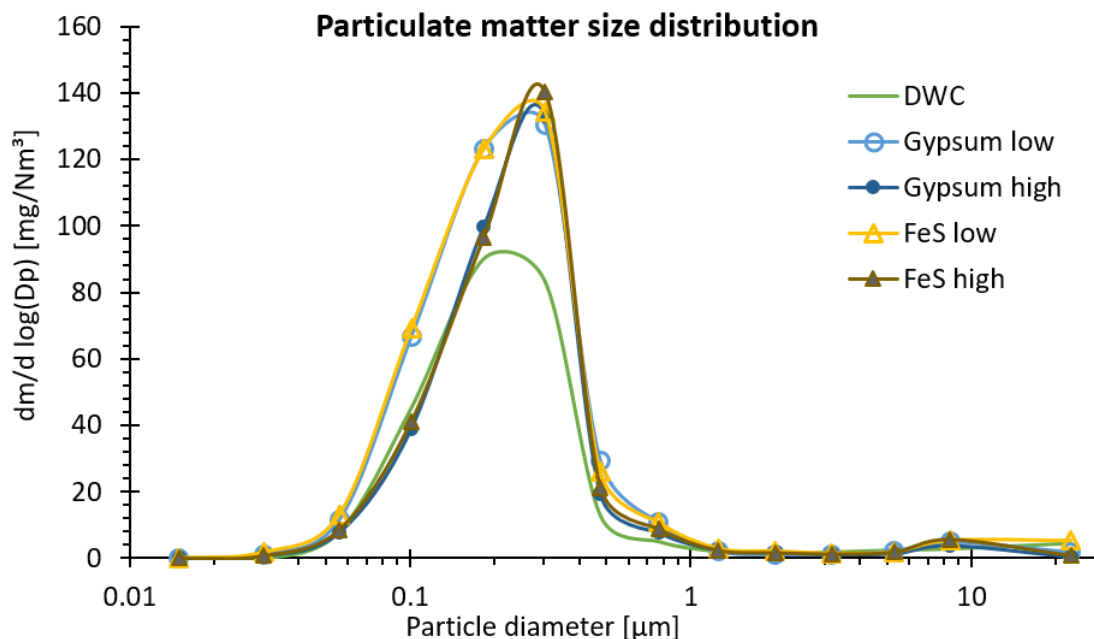
Figure 7 Particulate matter size distribution in mg/Nm3 for the fuel and fuel blends.

5.2 SEM-EDS analysis results

5.2.1 General morphology and composition of ash and slag

Notable amounts of unburned fuel particles were found in the bottom and burner ashes from all fuels and both sieve sizes. In Figure 8, SEM images with overviews from the ash samples can be seen. Those are heterogeneous with a lot of unburned fuel in the samples and ash rich particles of different sizes. The ash particles from the larger sieve size were embedded in epoxy and cross-sections of the ash samples are shown in Figure 9. The samples were heterogeneous and contained unburned particles, which were not readily visible in the epoxy. Figure 10 show cross sections of the slag samples in epoxy.

Figure 11 show the average relative content of the ash forming elements for the ash (<1.18 mm) and Figure 12 for the ashes with sieve size of 1.18-3.15 in epoxy. Figure 13 show the average relative content of the ash forming elements for the slag.

The morphology of ash and slag particles were largely similar for all cases, suggesting that the additives did not affect the burner and bottom ash or slag to any larger extent. This also suggests that the addition of Ca from gypsum and Fe from FeS did seemingly not affect the burner or bottom ash composition adversely.
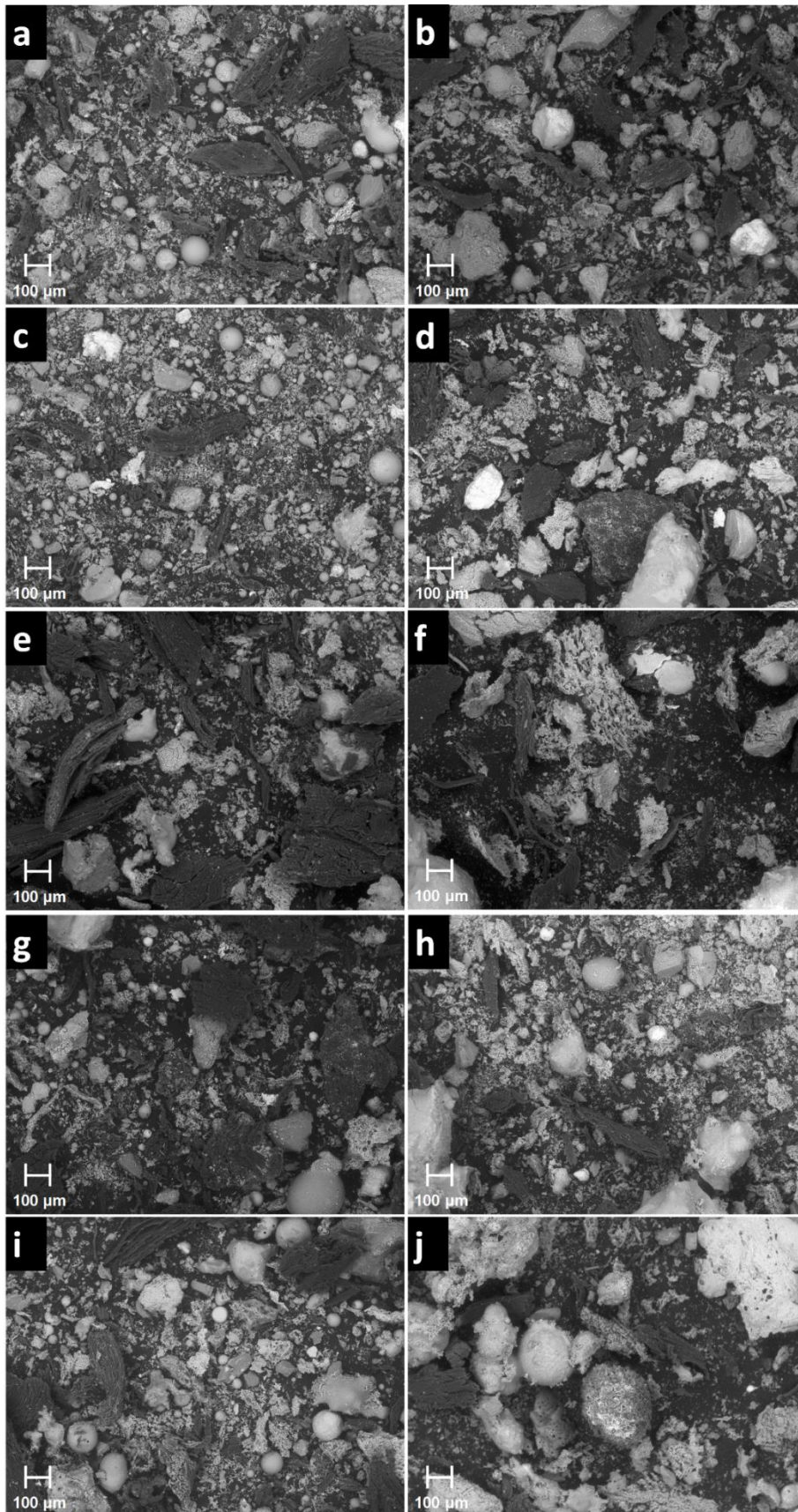
Figure 8 Overview of the ash samples with a) Reference bottom ash, b) Reference burner ash, c) Low gypsum bottom ash, d) Low gypsum burner ash, e) High gypsum bottom ash, f) High gypsum

burner ash, g) Low FeS bottom ash, h) Low FeS burner ash, i) High FeS bottom ash, j) High FeS burner ash.
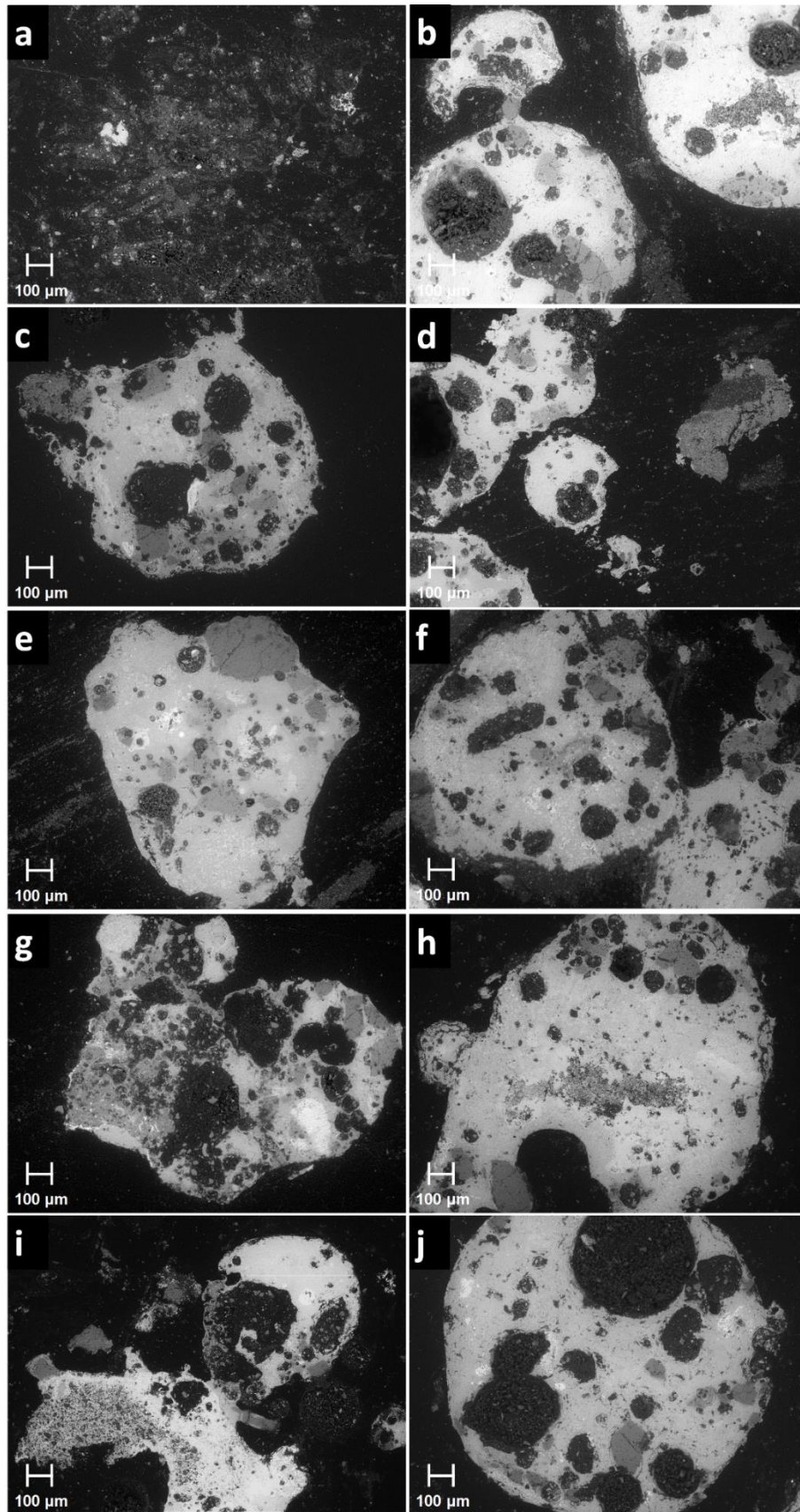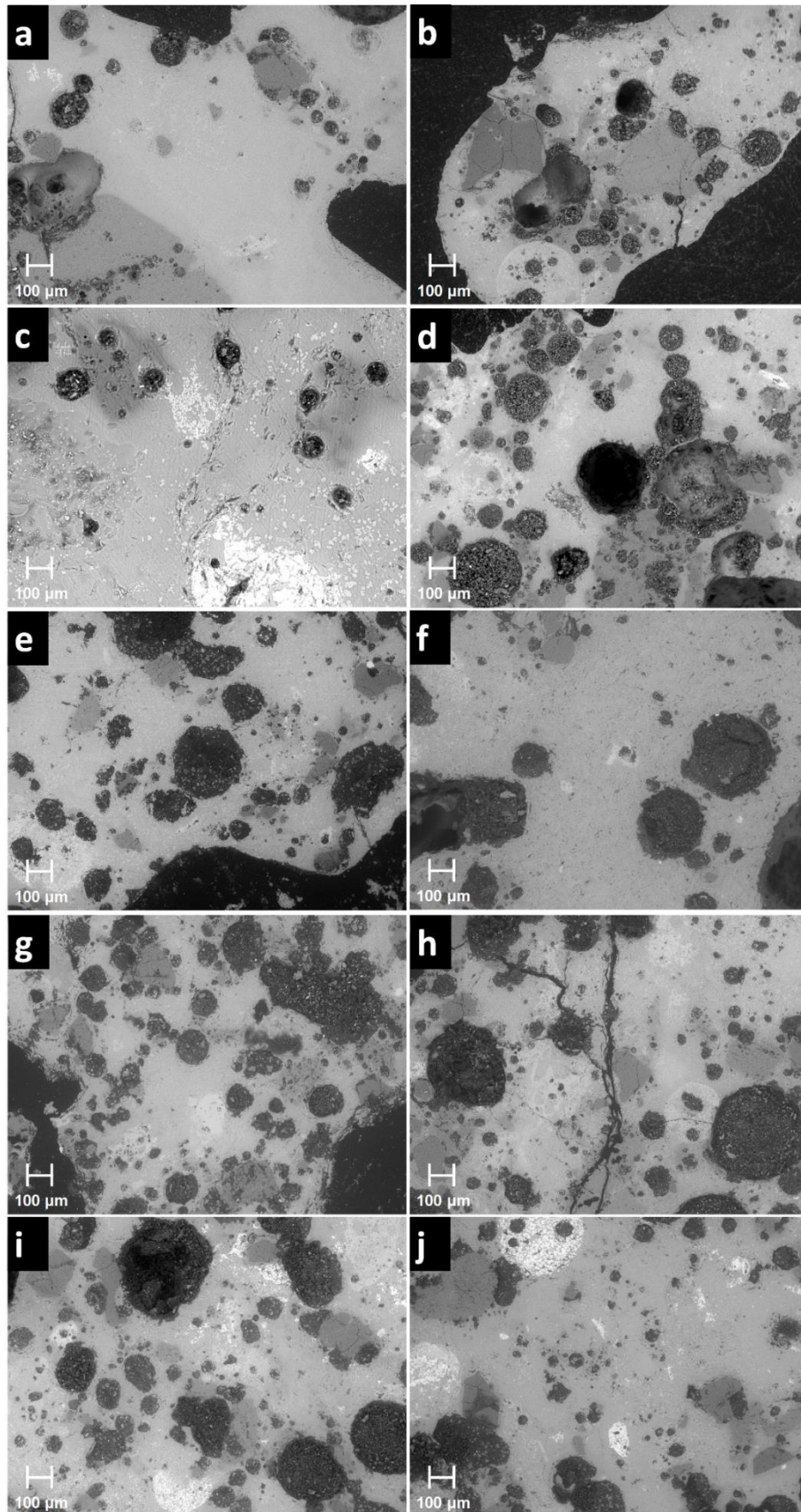
Figure 9 Cross sections of the ash samples from the sieve size of 1.18-3.15 in epoxy, with a) Reference bottom ash, b) Reference burner ash, c) Low gypsum bottom ash, d) Low gypsum burner ash, e) High gypsum bottom ash, f) High gypsum burner ash, g) Low FeS bottom ash, h) Low FeS burner ash, i) High FeS bottom ash, j) High FeS burner ash.

Figure 10 Cross sections of the slag samples in epoxy, with a) Reference bottom slag, b) Reference burner slag, c) Low gypsum bottom slag, d) Low gypsum burner slag, e) High gypsum bottom slag, f) High gypsum burner slag, g) Low FeS bottom slag, h) Low FeS burner, i) High FeS bottom slag, j) High FeS burner slag.
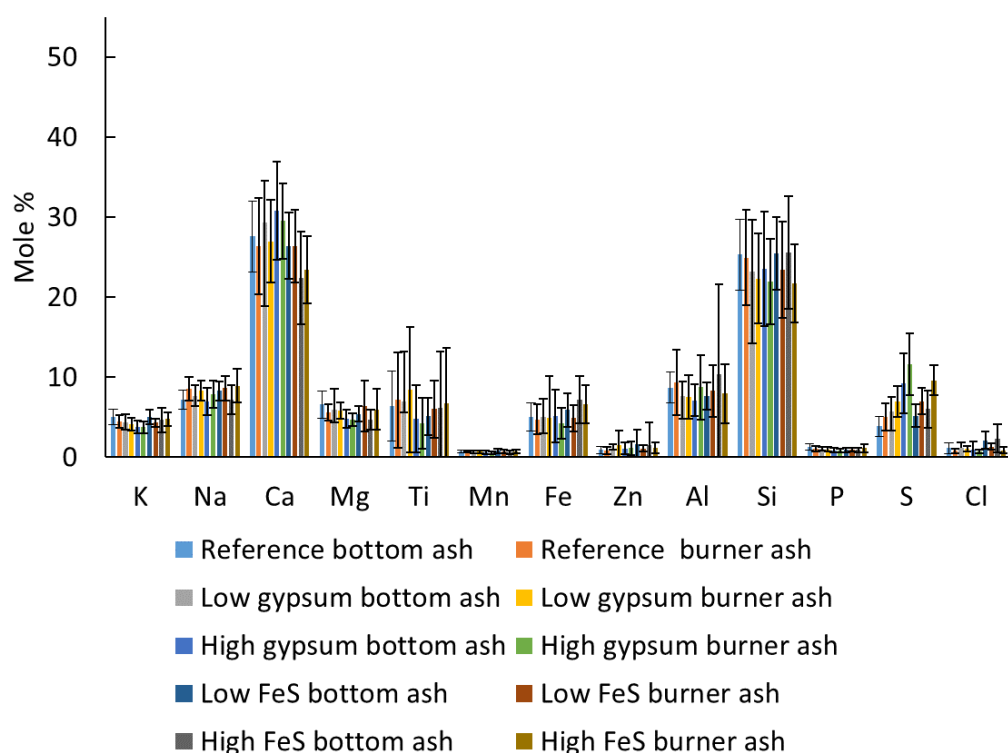
Figure 11 The average relative composition of the ash forming elements for the ash (<1.18 mm), given in O and C free basis for the ashes under size of 1.18 mm. Standard deviation showing the deviations between the averages of the sites/areas as error bars.
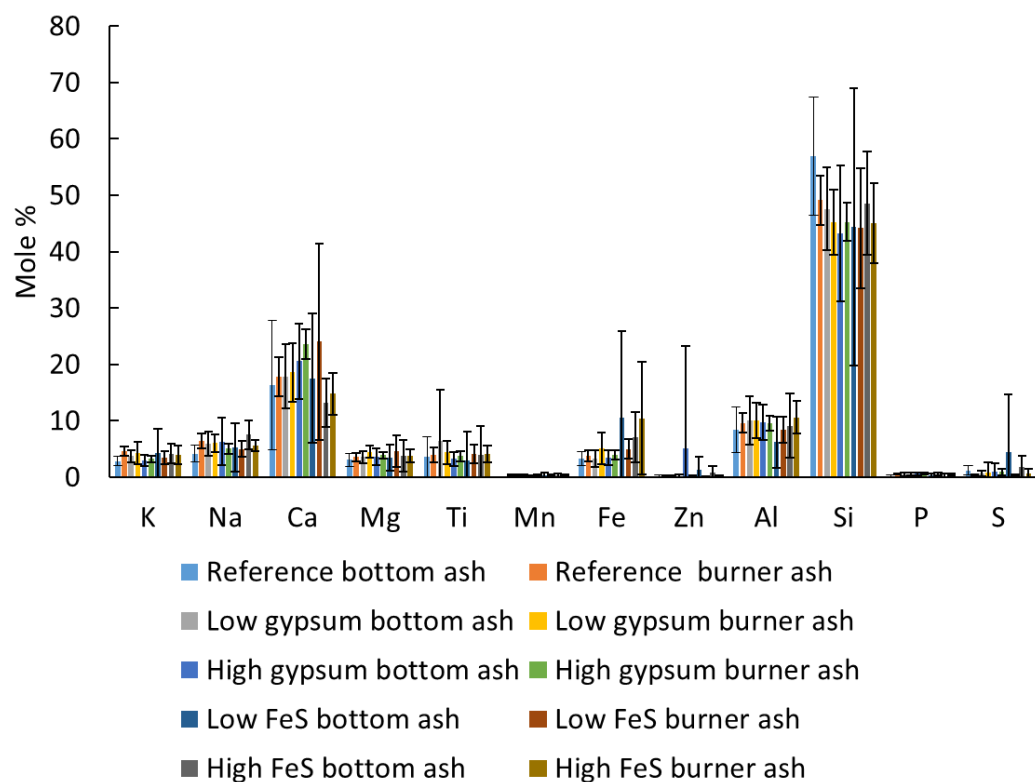
Figure 12 The average relative composition of the ash forming elements for the ash samples from the sieve size of 1.18-3.15 in epoxy, given in O and C free basis. Standard deviation showing the deviations between the averages of the sites/areas as error bars.
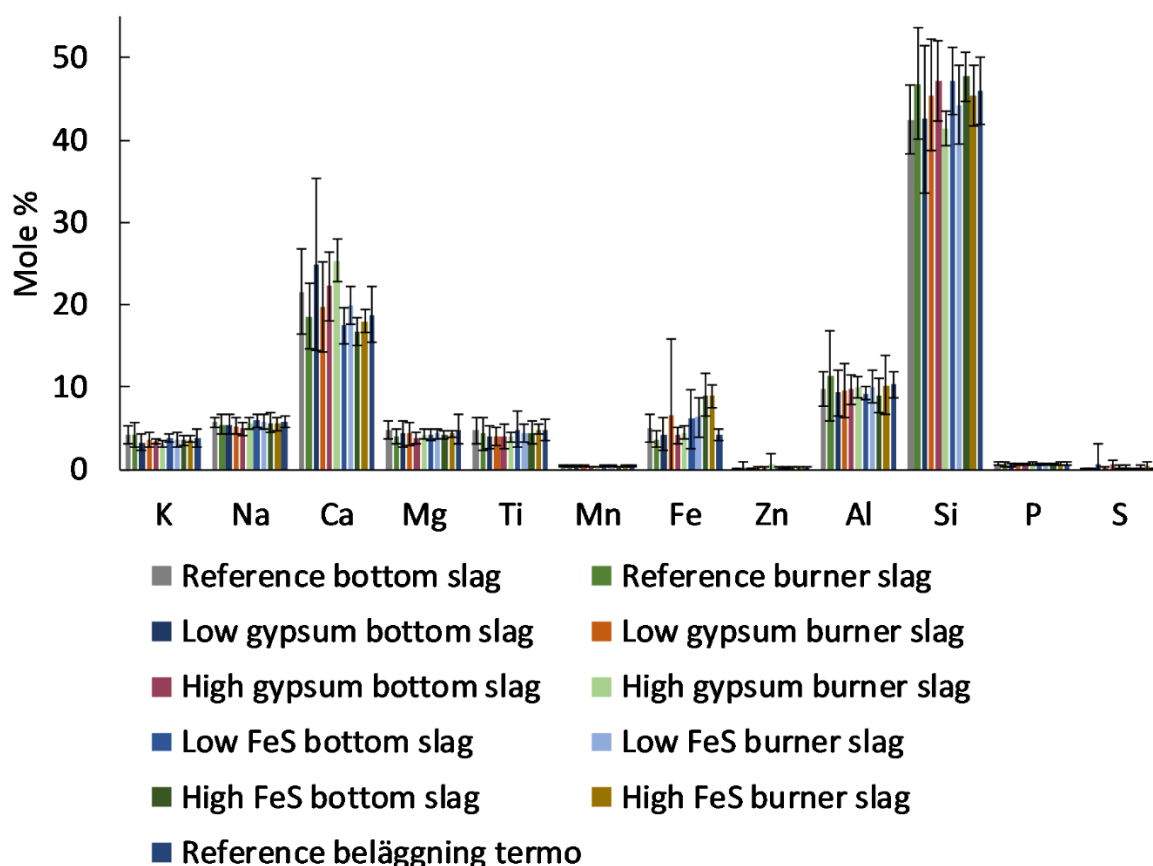
Figure 13 The average relative composition of the ash forming elements, given in O and C free basis for the bottom- and burner slag. Standard deviation showing the deviations between the average of the sites/areas as error bars.

5.2.2   Burner and bottom ash particles – morphology and composition

5.2.2.1   Ash particles <1.18 mm sieving size

The reference experiment contained discrete particles with high Ca, S, and some alkali which may originate from gypsum particles included in the DWC fuel (Figure 14, points 1-3). The heterogeneity of the formed ash particles is obvious from Figure 14 - Figure 19. Gypsum fuel blends showed S was in both the burner and the bottom ash with sieve size under 1.18, also identified in particles during SEM-EDS analysis. As expected, the amounts of S was higher for higher amounts of additive. Particles with a lot of Ca and S was found for both cases (example: Figure 15, number 4 and Figure 16, number 1), indicating that some gypsum probably not have been decomposed. Figure 14, number 3 show a particle with Ca and S together with K, indicating that alkali has reacted with gypsum. When FeS was introduced as an additive, S was found in both the burner and the bottom ash with sieve size under 1.18. Higher amounts was found with more additive, as expected, but in that case to a bit lower amount than for the gypsum additive (Figure 15). Ca was commonly found together with S (Figure 17, number 4 and Figure 18, number 3) and in some case also joined by alkali (Figure 17, number 1).
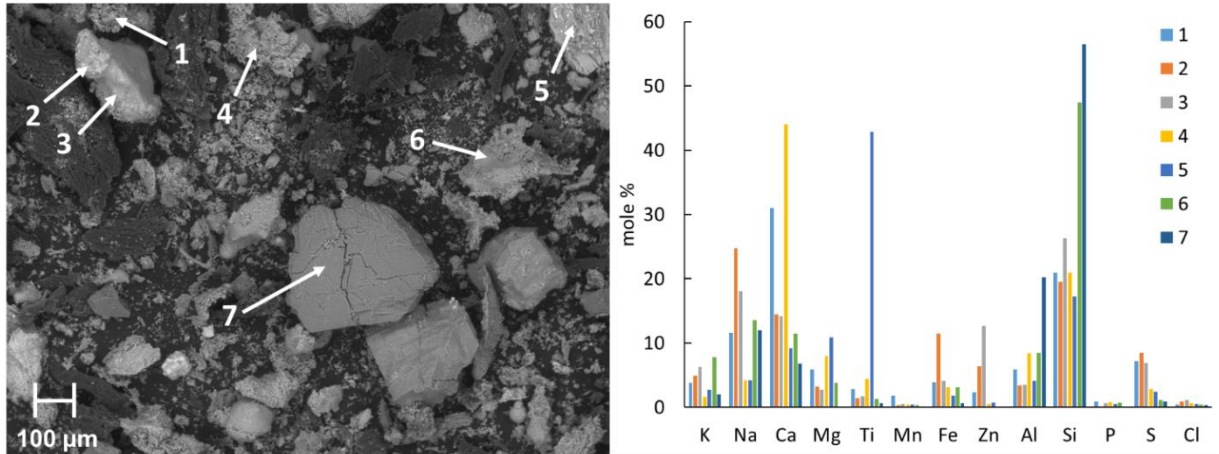
Figure 14 Burner ash, with particles sieved to under 1.18 mm, sample from the reference run with 100 % waste wood.
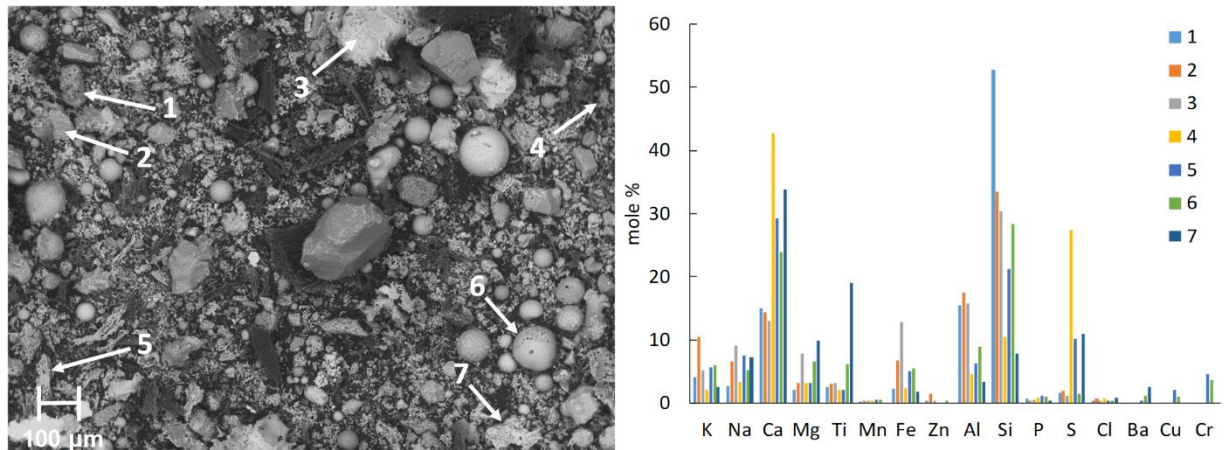

Figure 15. Bottom ash, with particles sieved to under 1.18 mm, sample from the run with low amounts of gypsum as additive.
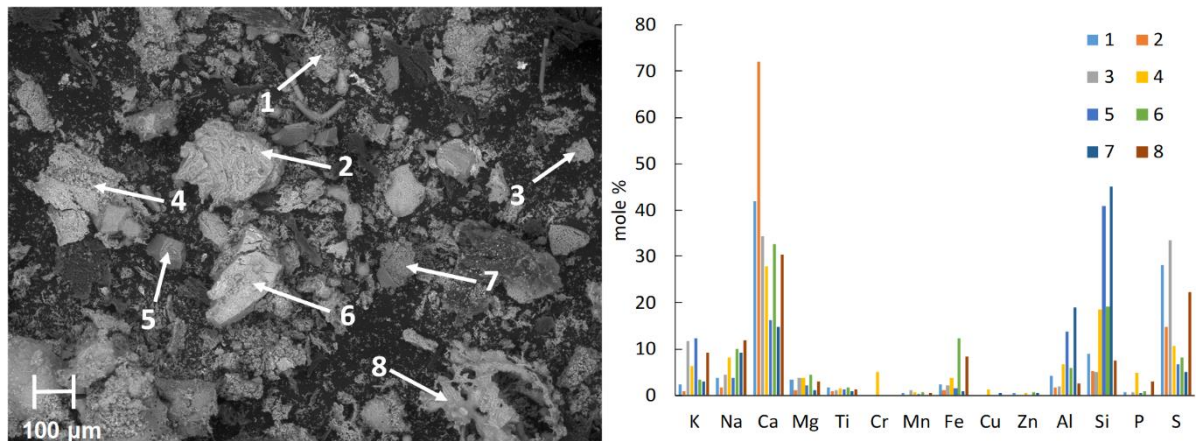

Figure 16. Burner ash, with particles sieved to under 1.18 mm, sample from the run with high amounts of gypsum as additive.
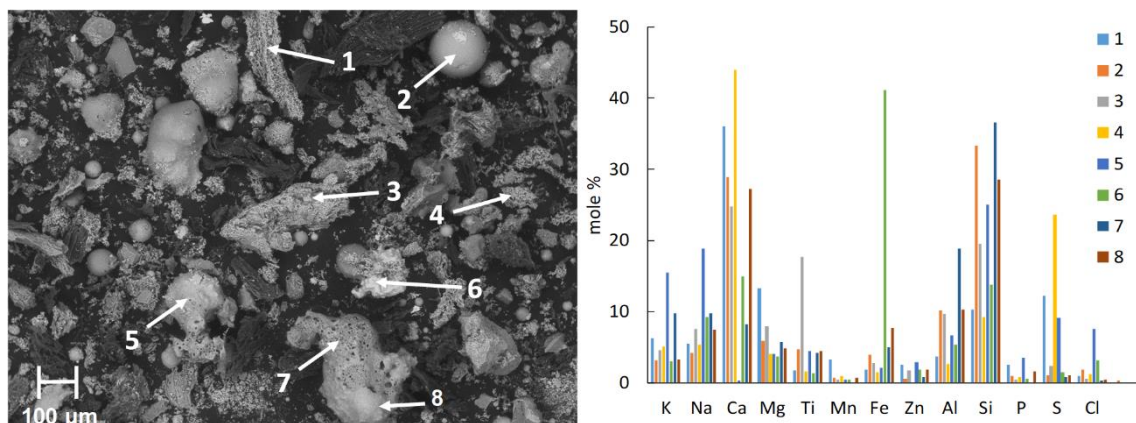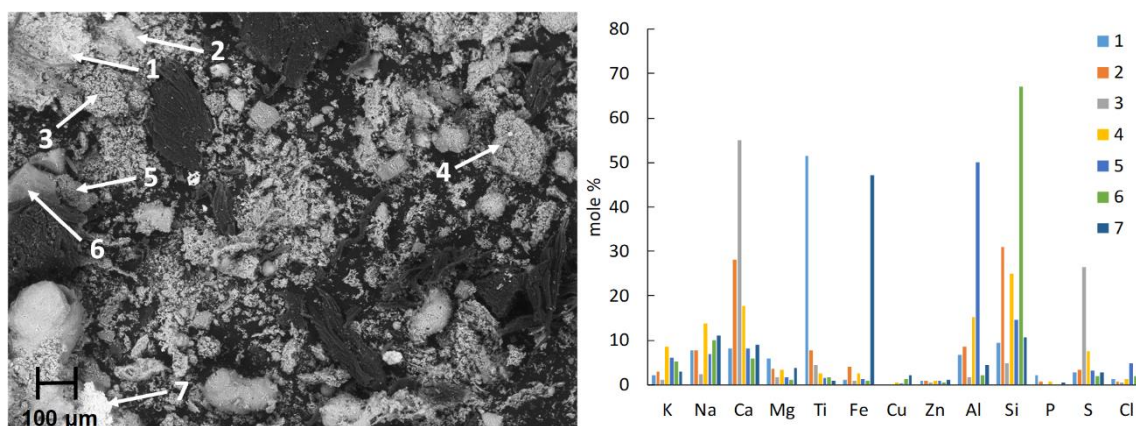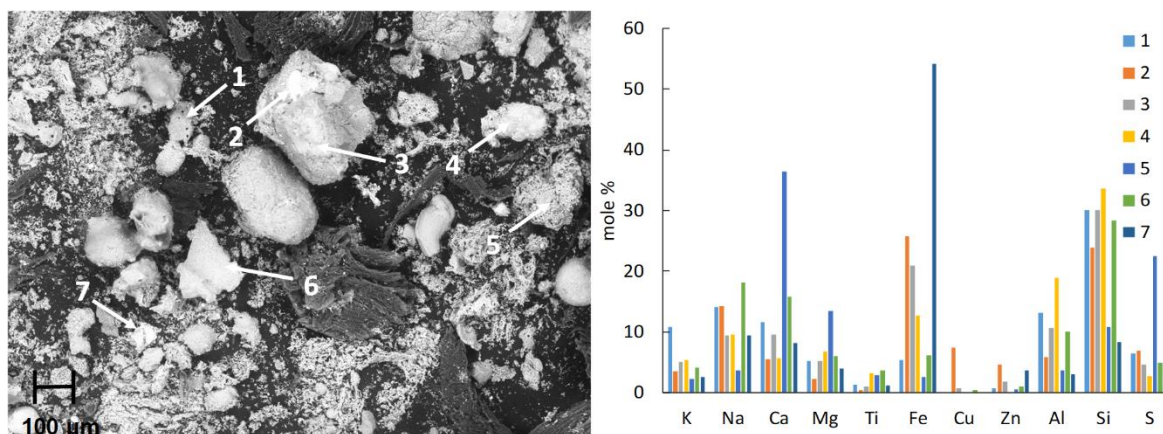
Figure 17. Bottom ash, with particles sieved to under 1.18 mm, sample from the run with low amounts of FeS as additive.

Figure 18. Burner ash, with particles sieved to under 1.18 mm, sample from the run with low amounts of FeS as additive.

Figure 19. Burner ash, with particles sieved to under 1.18 mm, sample from the run with high amounts of FeS as additive. Number 5 might be a particle originating from the gypsum in the fuel.

5.2.2.2 Ash particles 1.18 – 3.15 mm sieving size

For the ashes of the larger sieve size (1.18-3.15 mm, Figure 20 - Figure 23), almost no S was found in average composition (Figure 5) for By then, when studying single particles places with a lot of Ca and S was found, that seems to be small gypsum particles that has not been decomposed (Figure 20, number 6 and 7). Also particles/areas enriched in S

and Ca together with alkali was found (Figure 20, number 1). Some particles rich in both Fe and S was found, exemplified with the sample from the run with low amounts of FeS as additive (Figure 21), were A show a common particle with high amounts of Fe in number 5 and 6, and B show Fe and S rich particle.
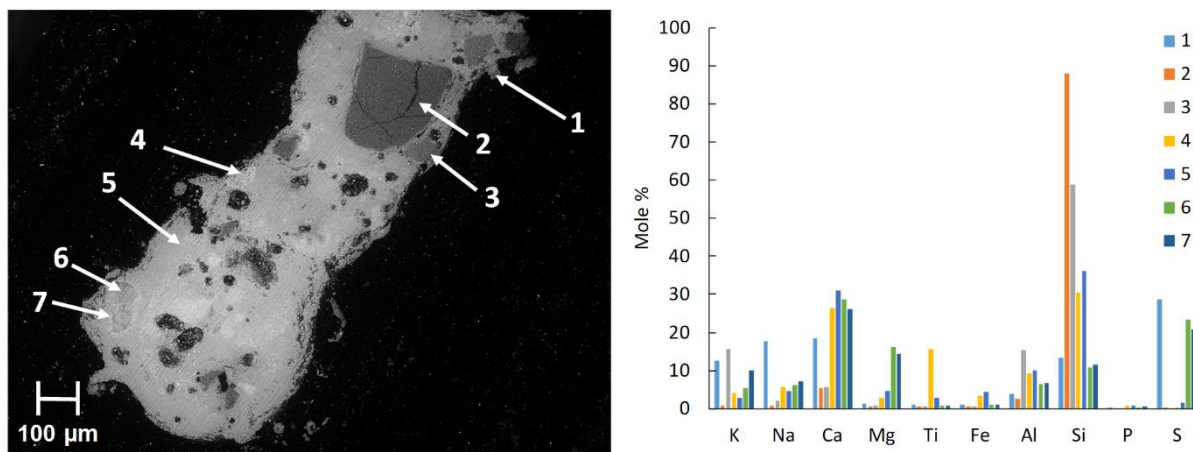

Figure 20. Burner ash, with particles sieved to 1.18-3.15 mm, sample from the run with high amounts of gypsum as additive. Number 6 and 7, with high concentrations of S and Ca might be small gypsum particle that has not been fully decomposed and instead encapsulated in the melt. Number 1 is also enriched in S and Ca, but more alkali appear to be included.
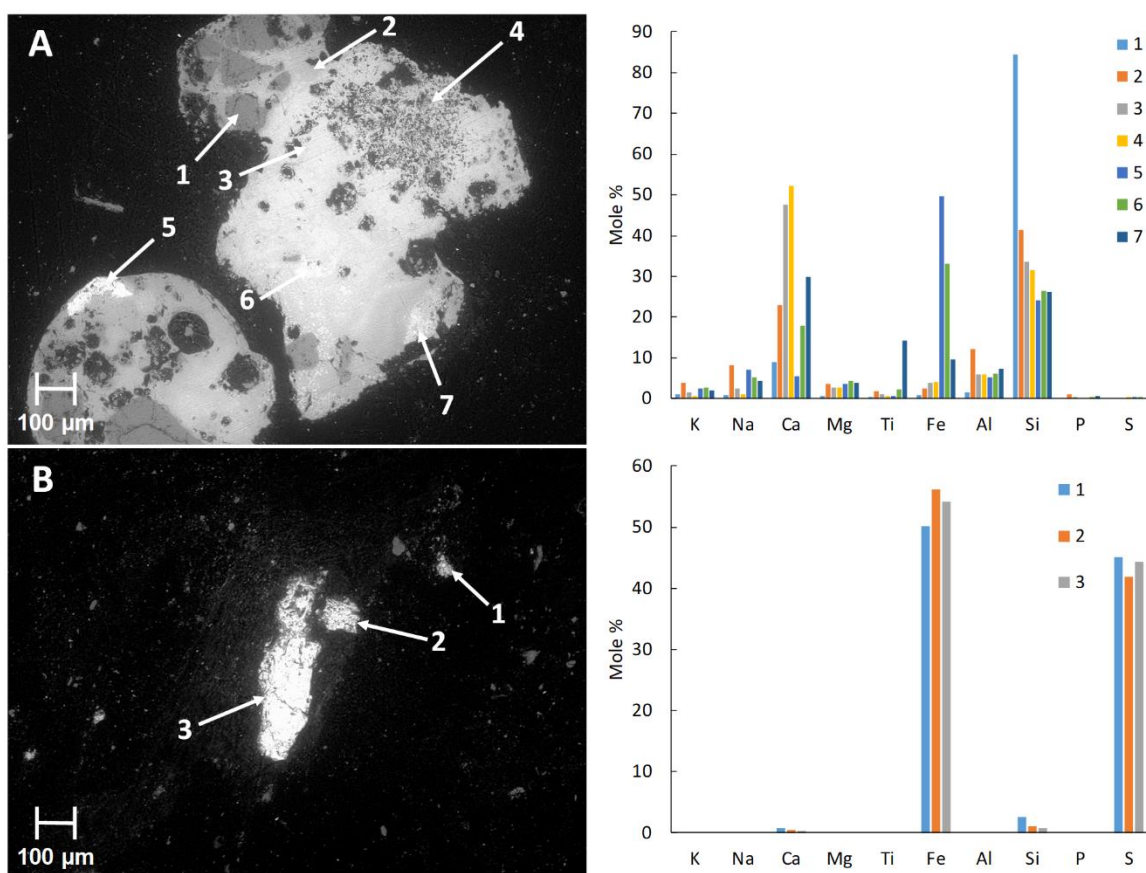

Figure 21. Bottom ash, with particles sieved to 1.18-3.15 mm, sample from the run with low amounts of FeS as additive. A show a common particle with high amounts of Fe in number 5 and 6. B show Fe and S rich particles. Probably unreacted additive.
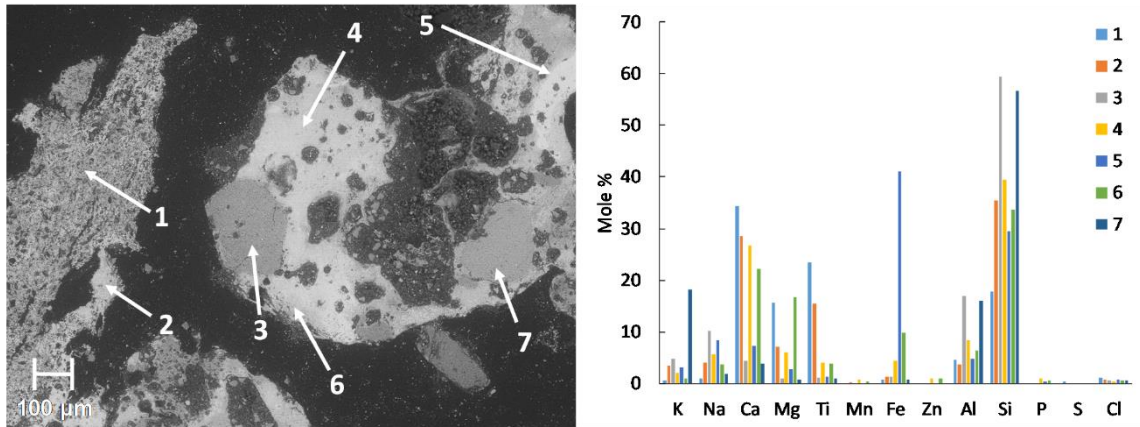
Figure 22. Burner ash, with particles sieved to 1.18-3.15 mm, sample from the run with low amounts of FeS as additive.
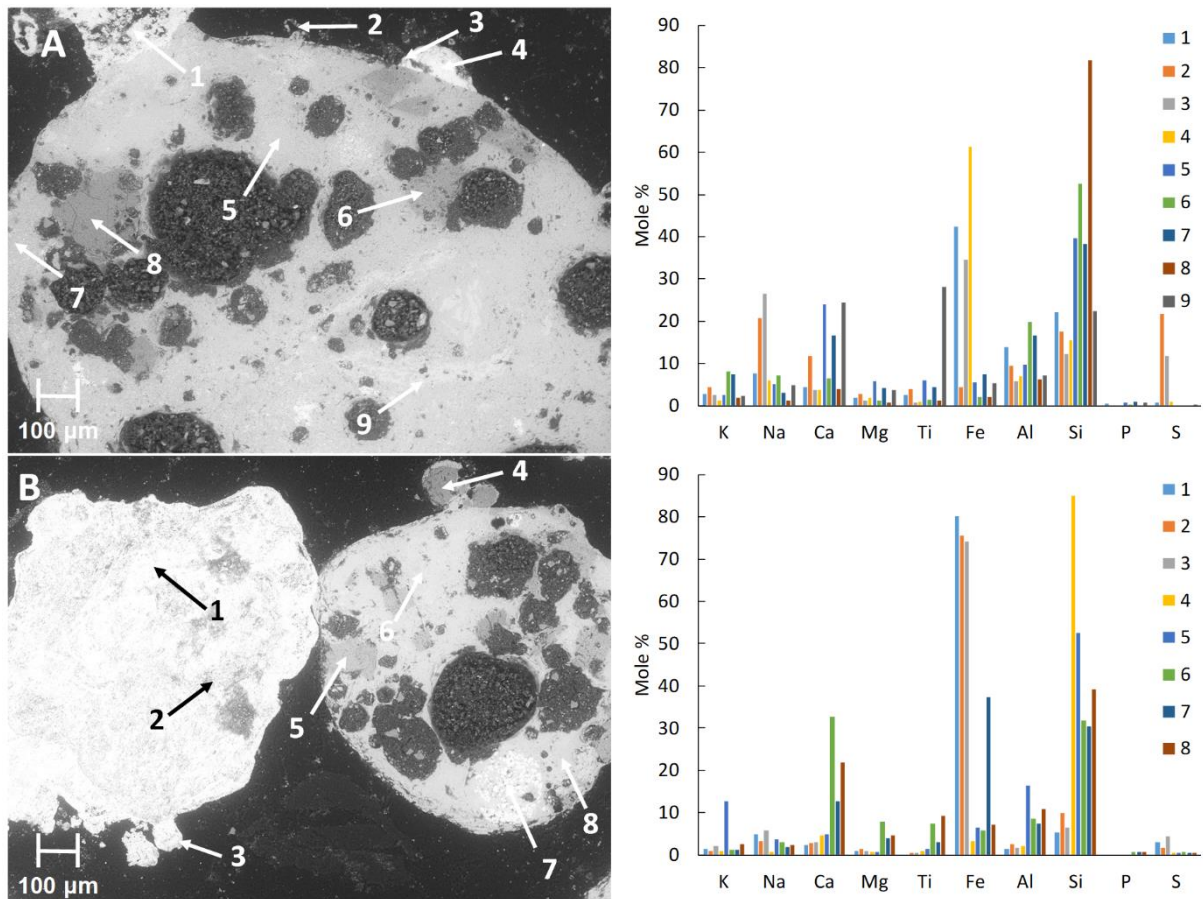

Figure 23. Burner ash, with particles sieved to 1.18-3.15 mm, sample from the run with high amounts of FeS as additive. A show a common particle with high amounts of Fe in number 1 and 4, in number 3 both Fe and S were found together with Na, and number 2 show high amount of S together with Na. B show one Fe dominated particle to the left, with small amounts of S left. To the right, Fe were enriched in a part of the particle (number 7).

5.2.3   Slag particles – morphology and composition

What is assumed to be unreacted gypsum particles could be seen in the slag from both high and low gypsum additive cases. As an example, Figure 26 show bottom slag from the run with low amounts of gypsum as additive, and in the middle (number 3), a Ca and S rich area might be a large gypsum particle that has not been decomposed and instead encapsulated in the slag. Similar, but a lot smaller particles, could be seen in all other slag samples, with example from the burner slag from the run with low amounts of gypsum as additive (Figure 27, number 2). Fe was commonly included in the slag and more Fe with higher amount of additive. Fe was found in the slag as enrichment in a part of the sample (for example see Figure 24, point 3 and Figure 30). The presence of S was low, but in the bottom slag from the run with low amounts of FeS as additive (Figure 29), some S was found in number 6.
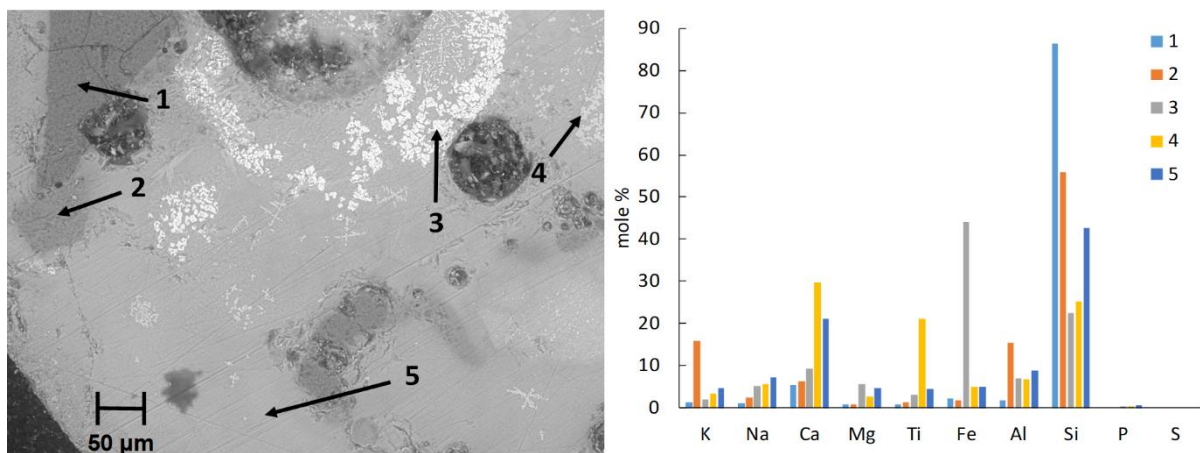
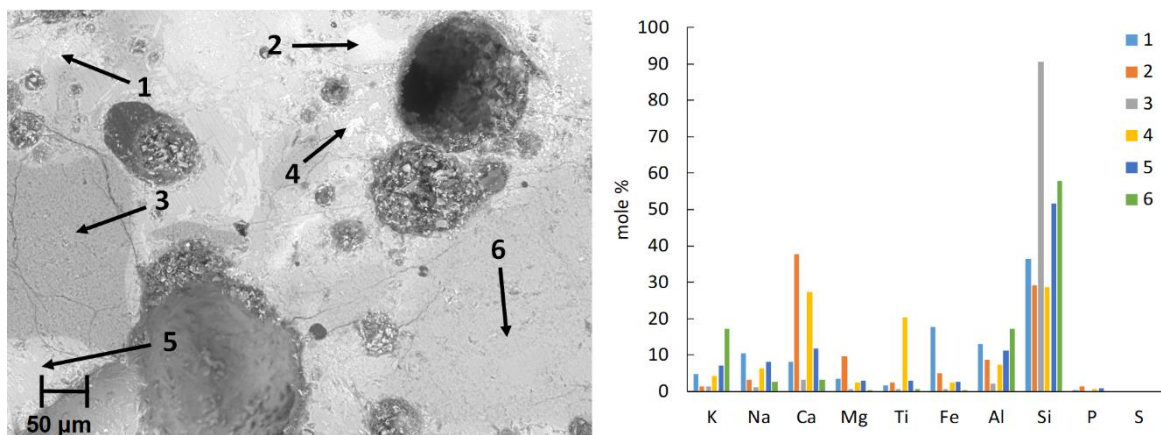

Figure 24. Bottom slag from the reference run.

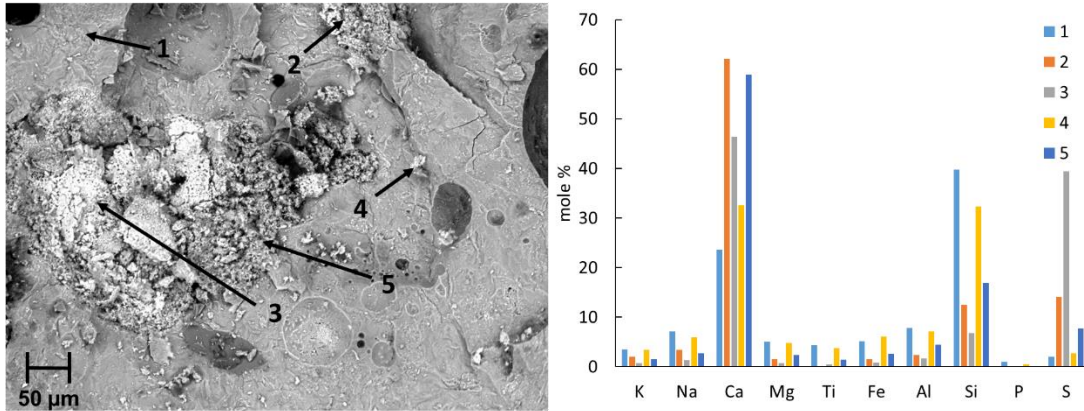Figure 25. Burner slag from the reference run.

Figure 26. Bottom slag from the run with low amounts of gypsum as additive. In the middle, number 3 in the image, with a lot of S and Ca might be a large gypsum particle that has not been decomposed and instead encapsulated in the slag.
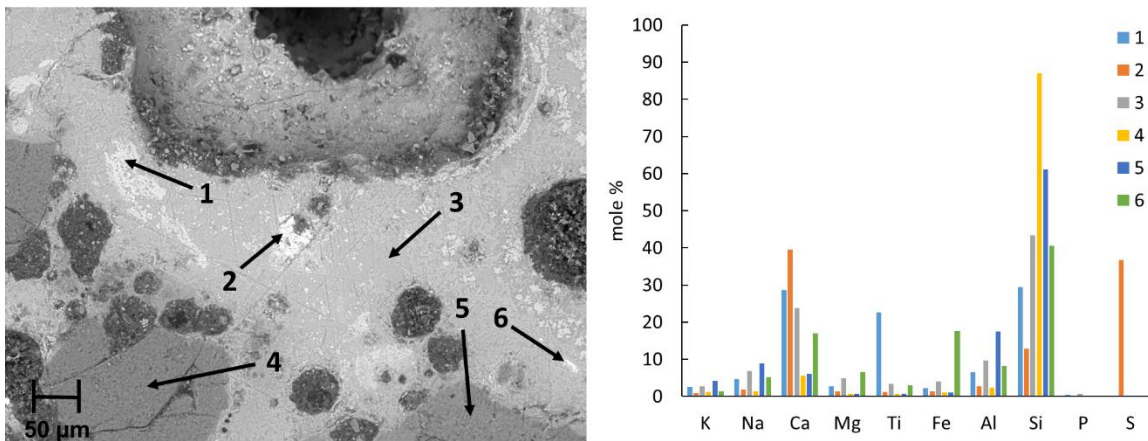

Figure 27. Burner slag from the run with low amounts of gypsum as additive. In the middle, number 2 in the image, with a lot of S and Ca might be a small gypsum particle that has not been decomposed and instead encapsulated in the slag.
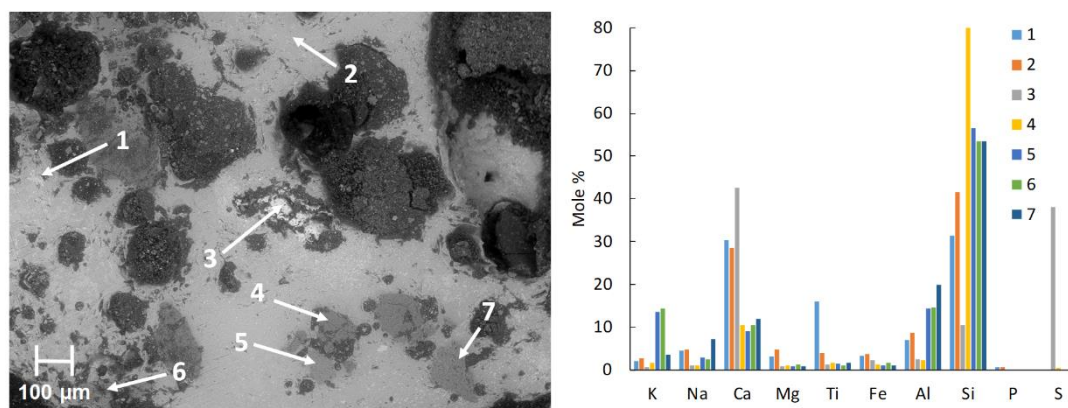

Figure 28. Bottom slag from the run with high amounts of gypsum as additive. In the middle, number 3 in the image, with a lot of S and Ca might be a large gypsum particle that has not been decomposed and instead encapsulated in the slag.
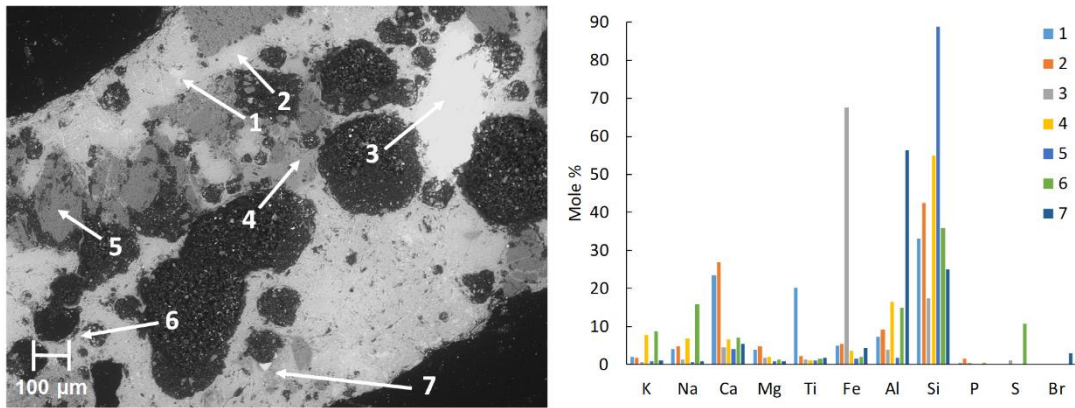
Figure 29. Bottom slag from the run with low amounts of FeS as additive.
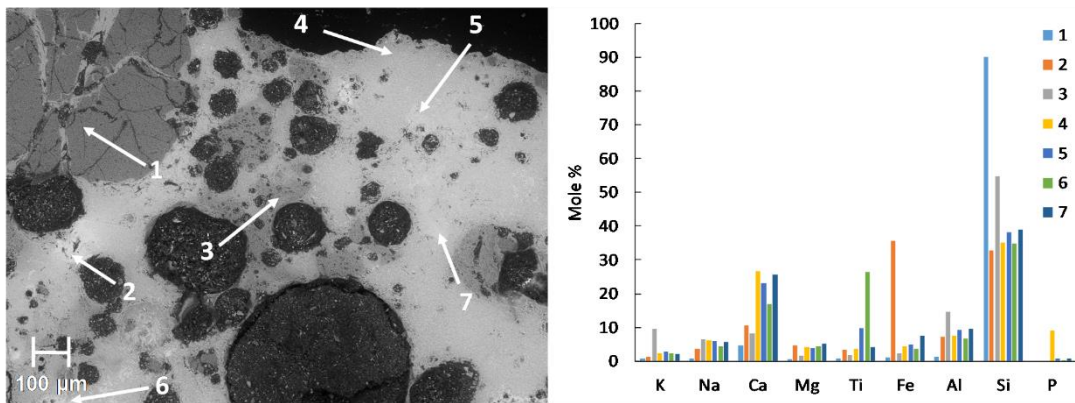

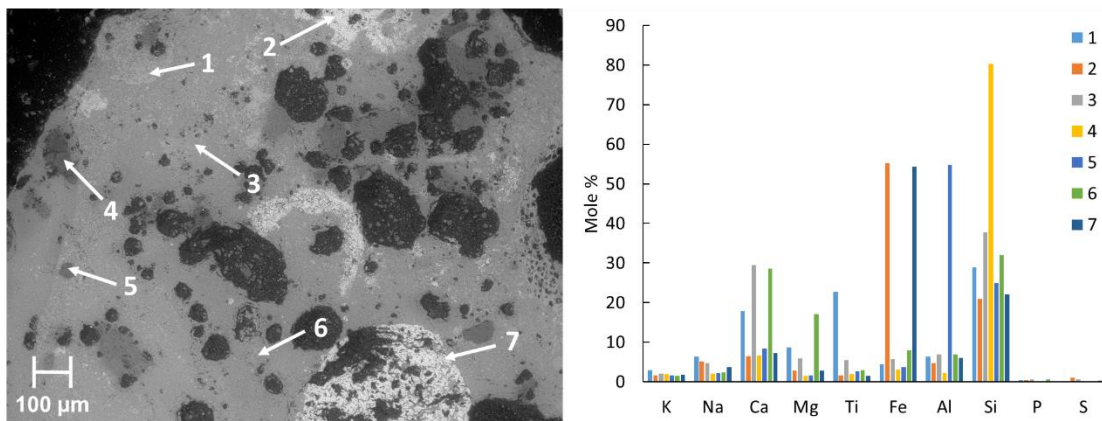Figure 30. Burner slag from the run with low amounts of FeS as additive.

Figure 31. Burner slag from the run with high amounts of FeS as additive.

5.2.4   Particulate matter and deposit composition

The elemental composition of PM_1 is shown in Figure 32 and in Figure 33 the composition of deposits on cooled surfaces is shown. Gypsum additive resulted in an increase in S and K, and decrease in Cl and Na was detected, especially for the high runs with high amount of gypsum. The elemental analysis suggests that increased amount of Zn are captured in particulate matter and deposits if gypsum is used as an additive. Na displays an interesting behaviour since its concentrations are lowered by FeS addition in particulate matter, suggesting that it instead captured in larger particles.

The effect of both gypsum and FeS can be seen as an increased share of S in the particulate matter. The Cl concentration is mostly affected in deposits which is interesting and also important from a corrosion perspective. The small but present levels of Pb may be problematic from a corrosion and fouling point of view due to its tendency to lower the melting point of formed salts.

Figure 32. The average relative composition of the main ash forming elements, given in O and C free basis for the particulate matter collected with the impactor. Standard deviation showing the deviations between the average of the sites/areas as error bars.
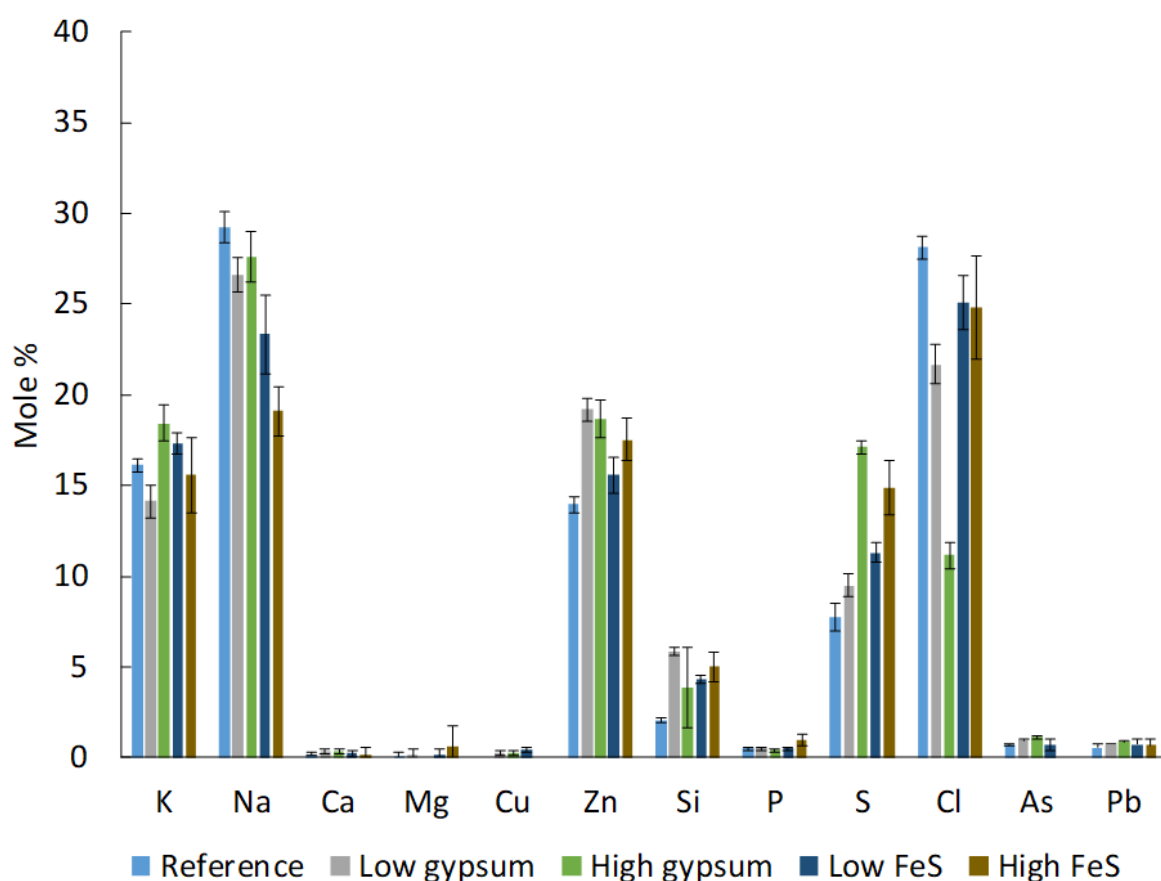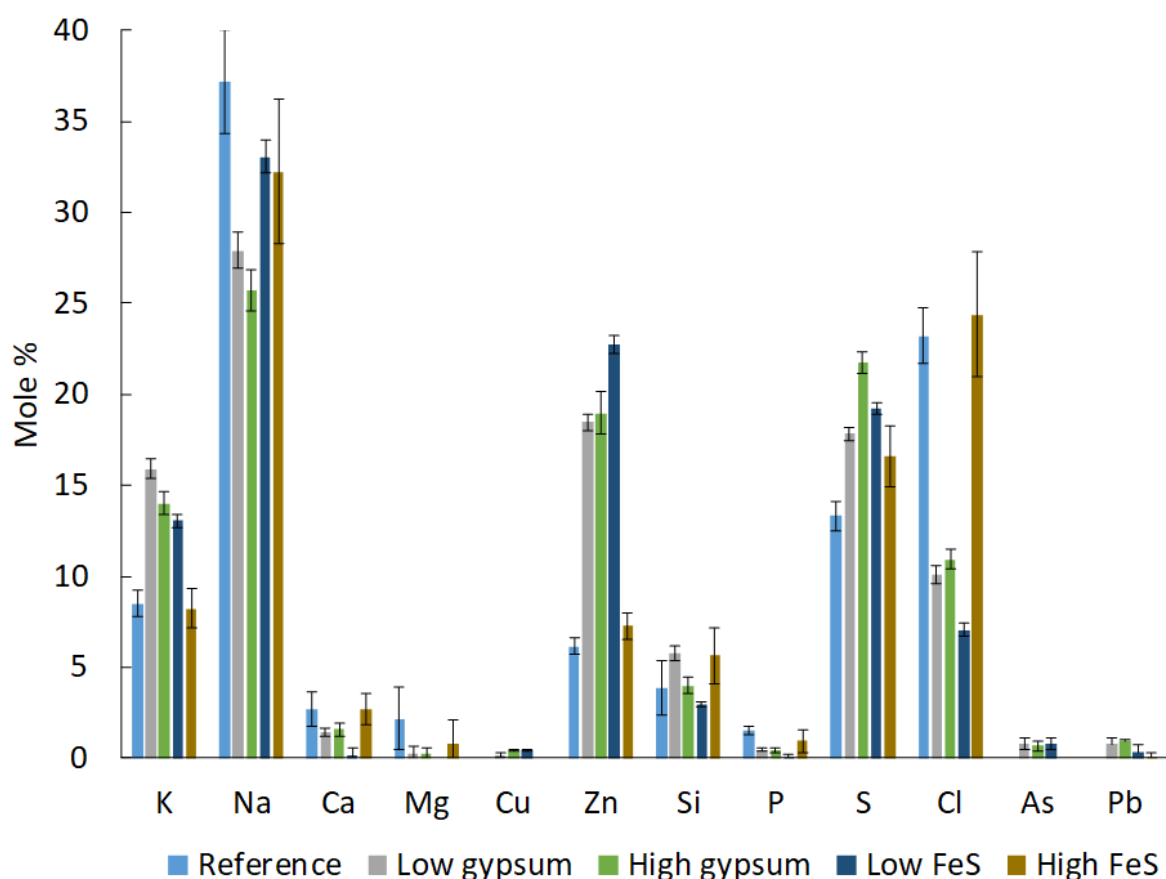
Figure 33. The average relative composition of the main ash forming elements, given in O and C free basis for the particulate matter collected with the deposit probe. Standard deviation showing the deviations between the average of the sites/areas as error bars.

6 Discussion

6.1 Woody waste fuel and additive

The woody waste fuel used in this study, DWC, is cleaning on-site at ENA Energi AB which was reflected in its composition, Figure 2. It does contain some alkali metals and Zn but not to very high levels. Further, the S concentration is higher than Cl showing that there is already some sulphation potential. The main concerns are still slagging induced by alkali silicate melts as well as chloride formation. Some of the included Ca and S are likely originating from gypsum particles present in the DWC, meaning that it to some extent carries one of the tested additives. The recycled waste gypsum contains Ca and S (Figure 3) but also some Si, with other contaminants at very low concentrations.

The DWC used in this work is cleaned before it is used at the industrial site. With Ca already having a significantly higher concentration than alkali metals the expected effect on slagging by gypsum may be minor. Further, excess of Ca could cause absorption of SO_x in the cooler bottom ash or slag, thereby reducing the effect of SOx from gypsum on the formation of chlorides. The fuel blends prepared with additives are in this case likely to mainly affect chloride formation in deposits.

6.2   Combustion characteristics

The resulting flue gas compositions (**Fel! Hittar inte referenskälla.**) clearly show that gypsum and FeS does decompose to release SO_x in the gas phase in these combustion experiments. The general combustion conditions were somewhat more challenging in the additive cases as noted by elevated CO concentrations despite higher O_2. This is because the underfed burner is not optimized for woody waste fuels with increasingly higher ash content, but rather is designed for clean wood chips.

Importantly, the decomposition of gypsum and FeS is not only shown by the elevated SOx concentrations. Based on the increased HCl concentrations there is less Cl captured in solid particles and instead it remains in the gas phase. These two observations show that there is an intended effect on chloride formation. This effect is most prominent for the pure FeS cases. Still, the more acidic flue gases need to be considered for implementation in industrial scale applications and may warrant increased flue gas cleaning.

Particulate matter concentration and size distribution were affected by the additives. The total PM_1 concentrations increased for all cases but interestingly, almost identically so between the low and high concentrations regardless of additive. This may suggest that both gypsum and FeS are limited by the same reactions for actual sulphation in submicron particles.

6.3   Additive effect on ash formation

The general composition obtained by SEM-EDS of ash and slag fractions from the burner and bottom ash was largely unaffected by the addition of gypsum and FeS. No significant differences could be observed for the bulk material although it was noted that discrete particles that had not decomposed could be found for both gypsum and FeS.

This suggests that the low additive levels of gypsum applied here were not enough to significantly improve slagging behaviour. On the other hand, this is the commonly used woody waste fuel that is currently used in industrial-scale operation so there may not be a slagging problem to actually remedy. The results concerning whether gypsum may reduce slagging tendencies are therefore inconclusive in this case. This should be further investigated with waste streams that have a more problematic initial composition.

The composition of PM1 (Figure 32) was largely unaffected despite the higher SOx concentrations in the flue gas, suggesting that the reduction of chloride formation indicated by higher HCl concentrations in the flue gas was to be found elsewhere.

The lower Cl concentrations in the small amounts of deposits (Figure 33) suggest that the observed higher SO_X levels did primarily reduce chloride formation in the heat exchanger section of the system. Since this would be the boiler section most sensitive to chloride-induced corrosion, both additives may have improved the overall fuel properties by lowering the corrosion risk in heat exchangers.

7 Conclusions

Fundamental reaction mechanisms behind different resource-efficient additives that could be derived from waste streams or low-quality sources have been described. These were used to create strategies for dosage of such additives, which are discussed in detail, and some key equations have been provided for industrial users to do so. The strategies were tested experimentally with inconclusive results for slag formation but promising results concerning reduction of chlorides in deposits. Some specific findings are provided below:

- The woody waste fuel used in this study may not have had slagging issues that could be addressed by CaO addition from decomposition of gypsum.
- Both gypsum and FeS did provide significantly higher SO_x and HCl in the flue gas, pointing to increased formation of sulphates instead of chlorides
- Stoichiometrically identical addition of S through gypsum and FeS affected particulate matter distribution in similar ways.
- Sulphation effects of both gypsum and FeS was pronounced in deposits but did not change the overall composition in submicron particulate matter.
- Recycled waste gypsum and FeS should be considered as potential additives in waste-to-energy plants in the circular economy.

8 Recommendations

Implementation of these results in industrial scale requires up-to-date information on fuel composition to calculate appropriate dosage levels. This is especially important in sulphur dosage since more acidic flue gases may incur additional costs in the flue gas cleaning. This would in turn likely not benefit the role of waste-to-energy in a circular economy.

Of the two additives tested here, gypsum is the one closest to industrial use – as has been done in work package 3 of the REFAWOOD project. Iron sulphide as a sulphur additive may become more interesting in the future, especially if less plastic is landfilled and is included in waste-to-energy instead. Considering the fuel used in this study, users that have more challenges with silicate slagging may benefit from gypsum addition. This is a likely outcome from but would require industrial-scale experiments with those types of fuels.

9 References

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2. Towards a better exploitation of the technical potential of waste-to-energy, JRC Science for Policy report, Hans Saveyn, Peter Eder, Mark Ramsay, Grégoire Thonier, Kathryn Warren, Mathieu Hestin, 2016. In.
3. Diaz-Ramirez, M.; Boman, C.; Sebastian, F.; Royo, J.; Xiong, S. J.; Boström, D., Ash Characterization and Transformation Behavior of the Fixed-Bed Combustion of Novel Crops: Poplar, Brassica, and Cassava Fuels. *Energy & Fuels* **2012,** 26, (6), 3218-3229.

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