

**APPLICATION OF CHEMICAL FRACTIONATION METHODS FOR CHARACTERISATION
OF BIOFUELS, WASTE DERIVED FUELS AND CFB CO-COMBUSTION FLY ASHES**

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Abstract

In the important efforts to decrease the net CO₂ emissions to the atmosphere, new, alternative fuels are being included in the fuel mixes used in utility boilers. However, these fuels have ash properties that are different from those of the traditionally used fuels and in some cases technical problems, such as ash fouling and corrosion occur due to this. Therefore, diagnostic and predictive methods are developed and used to avoid such problems. Determination of the chemical association forms of important elements, such as potassium and sodium, in the fuel by chemical fractionation is a method well defined for coal and biofuels, such as wood pellets, bark and forest residues. Chemical fractionation is a step by step leaching method extracting water soluble salts in the first step, ion exchangeable elements, such as organically associated sodium, calcium and magnesium in the second step and acid soluble compounds such as carbonates and sulfates in the third step. The solid residue fraction consists of silicates, oxides, sulfides and other minerals. The compound extracted in the two first steps is considered reactive in the combustion with a few exceptions. In this work, it has been applied to some waste fuels, i.e. sewage sludge, straw and refuse derived fuel (RDF), as well as to coal and wood. The present work also includes results from combustion tests in a fluidised bed boiler where three blends of the investigated fuels were used. The fractionation results for the fuel blends are weighted results of the fractionations of the pure fuels discussed above which are compared with fractionations of their corresponding fly ashes. The co-combustion strategy gave very good results in reducing ash problems. Possible chemical mechanisms involved are discussed in the article.

Sludge, biofuel, refuse derived fuel, alkali, and fluidized bed

1 Introduction

The energy consumption in the world is constantly increasing simultaneously as the problems with global warming are causing serious concerns [1]. This has opened the market for new fuels, more or less classified as bio-fuels and not considered to contribute to the net CO₂ emissions to the atmosphere. Examples of such fuels are municipal sewage sludge, refuse derived fuel (RDF) and agricultural wastes, such as straw. Fluidized bed (FB) boilers are known to be very fuel flexible due to the stable and suitable for co-combustion of different fuels. However, since the combustion usually takes place in a sand bed, interactions between fuel ash components with the bed material may occur. Such processes frequently lead to the formation of compounds with low

melting points. Thus, it can cause severe agglomeration problems and in the worst case a turn down of the boiler operation. To make it possible to avoid such problems, it is crucial that the chemical properties of the ash forming components in the fuels are known. Thus, it is necessary to have tools for predicting the behaviour of the ash forming elements in new fuels and fuel mixes. Investigation of the chemical character of inorganic fuel components by chemical fractionation is a method that has been developed and implemented during the last 20 years. The fractionation is based on differences in solubility between different chemical forms of the elements studied. The fuel is selectively extracted with three solvents in which characteristic groups of compounds are dissolved and can be quantified. This methodology was developed by Benson [2] for application on coals, used by Baxter [3] and finally modified by Zevenhoven [4] to be suitable for biofuels. A database containing fractionation data for hundreds of different biofuels has also been compiled at Åbo Akademi University [5]. This data base was created in order to help researchers and industry to easily find data that can be used to predict the ash properties for new fuel mixes.

Alkali compounds as carbonates, sulfates and chlorides are easily leached out by water and thus separated for analysis. Ammonium acetate extracts Na, K, Ca and Mg associated with organic compounds together with some calcium carbonates.

Compounds extracted by water and ammonium acetate are assumed to be reactive in the combustion and their relative concentrations influences what impact the fuel has on the boiler in terms of corrosion, deposit formation and/or bed agglomeration [6]. Compounds not extracted by these two solvents are considered inert in the combustion, not influencing the combustion behaviour in any significant way. There are some exceptions discussed in this paper as for example the plastic PVC.

In this work two sewage sludges and a pelletised RDF, as well as coal and biofuels already present in the database, were investigated by the chemical fractionation method [5]. In addition, three fuel mixes comprising some of the above mentioned fuels were studied along with the fly ashes produced in co-combusting tests. The results were used to explain the impact of the different fuel blends on the processes involving inorganic fuel species during combustion and on the fly ash composition. Published results from earlier investigations [7, 8] on co-combustion of biofuels with sewage sludge have shown significant reduction of alkali chlorides both in the flue

gas and in deposits in the present FB boiler. This was the case even though the sewage sludge contributed with significant amounts of the potentially troublesome species K, Na and Cl.

2 Experimental background

2.1. *The Fuels*

The six fuels to be studied in this work were chosen to represent the broad spectrum of fuels on the market that are relevant for FB combustion to date. The fuels were: two digested municipal sewage sludges from large waste water treatment plants in Sweden, straw pellets and pellets made from RDF. Coal and wood pellets were included as reference fuels. Standard fuel analyses were carried out according to Swedish and European standards; Sewage sludge by A328:8, SS 028113, ASTM-D 4208, ICP-EAS: Coal by SS 187170, ISO 1171/ASTM-D 5142 mod, EN 13656 mod, Met.OA.4.04, SS028150-2, ASTM-D 4208: Wood pellets, Straw and RDF by A328:8, SS 028113, NMKL161 mod., ICP-AES and -MS, ALC208:201, AAS (Flame), ASTM-D 4208.

2.2. *The CFB unit*

The 12 MWth circulating fluidized bed (CFB) boiler at Chalmers University of Technology (Göteborg, Sweden) was used for the combustion tests, Figure 1.

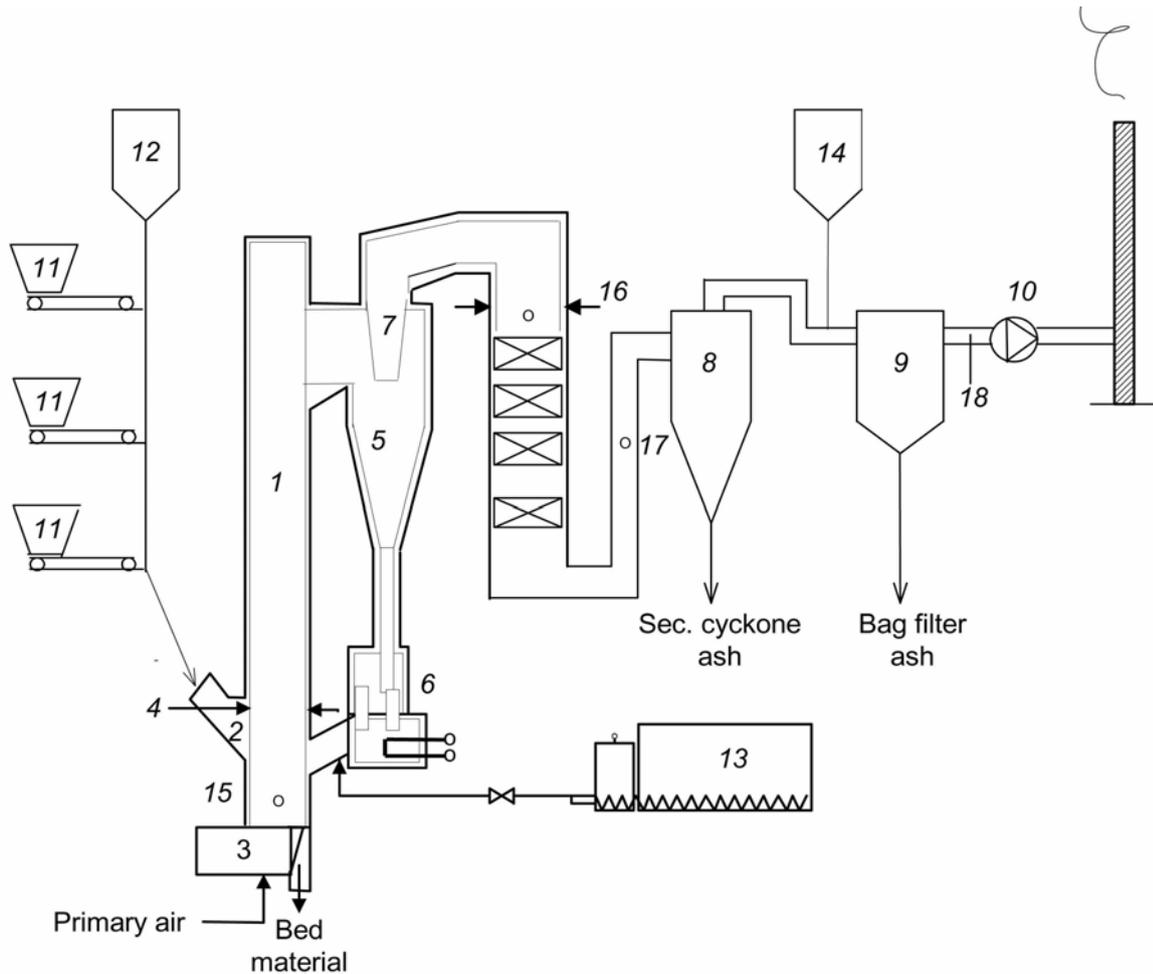


Figure 1: The 12-MW_{th} FBC boiler at Chalmers University of Technology (1) combustion chamber; (2) fuel feed chute; (3) air plenum; (4) secondary air inlet at 2.1 m; (5) hot primary cyclone; (6) loop seal; (7) cyclone exit duct; (8) cold secondary cyclone; (9) bag house filter; (10) flue gas recirculation fan; (11) fuel bunkers; (12) sand bin; (13) sludge pump; (14) hydrated lime bin; (15) bed ash sampling hole; (16) measurement spot (before convection pass) IACM instrument, deposit probe and FTIR; (17) measurement spot (after convection pass) FTIR; (18) measurement spot (stack) FTIR.

The combustion chamber (1) has a square cross-section of about 2.25 m² and a height of 13.6 m. The fuel (wood pellets) is fed to the bottom of the combustion chamber through a fuel chute (2). The mechanically dewatered sludge was supplied by a special sludge pump (reconstructed cement pump) (13) to the return leg where it is mixed with the hot particles coming from the primary cyclone (5) before it enters into the combustion chamber. Primary combustion air is supplied to the bottom of the combustion chamber (3), and secondary air is injected through a nozzle register located just above the fuel chute (4). After passing the exit duct of the cyclone (7), the flue gases are cooled to 150°C in the convection section and about 80% of the coarsest size

fraction of the fly ashes are separated from the flue gases in a secondary cyclone (8) and the remaining fraction of fines is captured in a textile bag filter (9). This is not a common arrangement in commercial CFB boilers, but it has the advantage of giving fly ash samples with different size distributions depending on the collection point. This gives the opportunity to study how the particle size distribution influences the characteristics of the ash.

2.3. *Combustion tests*

Three co-combustion tests were carried out with different fuel mixes. In the Reference case 79 wt-% wood pellets was co-combusted with 21 wt-% straw pellets to make a fuel blend with a high loading of potassium species. In the case called “Sludge” a mixture of biofuel pellets (67 wt-% wood, 21 wt-% straw) were co-combusted with 12 wt-% sewage sludge. The last test, named “Waste”, was carried out with a fuel blend of 45 wt-% wood pellets, 14 wt-% wood chips, 11 wt-% sewage sludge and 30 wt-% RDF.

For all three co-combustion tests typical operating conditions for a CFB boiler were chosen. This corresponds to a bottom bed temperature of 850 °C, an excess air ratio of 1.2 and a load corresponding to a fluidization velocity of 5 m/s in top of the combustion chamber. Forty percent of the total air supply was injected as secondary air. An in-situ alkali chloride monitor (IACM) was used for the on-line monitoring of the gas-phase KCl and NaCl. This instrument is described in [8]. A Fourier transform infra-red analyser was used for the determination of SO₂ and HCl in the flue gas.

2.4. *Chemical fractionation*

The fly ash samples used in the chemical fractionation was a mix of secondary cyclone and bag filter ash composed in proportion to the measured ash flows during the combustion. The chemical fractionation was carried out according to Zevenhoven [4]. Samples of the pure fuels and samples of fly ashes from the co-combustion tests were prepared by drying at 105°C and grinding to a particle size smaller than 5 mm. After that, the samples were subjected to three successive extractions using different solvents, i.e. water, 1M ammonium acetate and 1M hydrochloric acid. The procedure is schematically described in Reference 4, 5 and 6.

The first step is intended to soak the fuel and to dissolve the water soluble compounds such as alkali metal salts. In the second step ion exchangeable elements, such as organically associated

sodium, calcium and magnesium are replaced with ammonium ions and thus released to the liquid phase. In addition, part of the CaCO_3 in the fuel may become dissolved [4]. The third extraction step includes hydrochloric acid to remove acid soluble compounds such as carbonates and sulfates. The solid residue fraction consists of silicates, oxides, sulfides and other minerals [4].

After each of the leaching steps the solid sample was washed by deionised water two times. Leachate and washing water was collected in the same flask prior to analysis.

The results for pure fuels were then put together according to the fuel mix percentages used in the combustion cases and the calculated results were compared with those for the corresponding fly ashes.

2.5. Analytical methods

Leachates and solid samples were analysed for Ca, Al, Fe, K, Mg, Na, P, Si, S, Cl and Ti using Inductive Coupled Plasma with an Atomic Emission Spectroscopy detector (ICP-AES) or a Mass Spectrometer detector (ICP-MS). All solid samples were totally dissolved according to Swedish standards suitable for their individual characteristics before analysis; Sludge: SS028150-2, Coal: SS 187133, Wood pellets, Straw and RDF: SS 187114/CEN/TS 14780, Ashes: SS 187117.

2.6. SEM-EDX

The topology of fuel and ash particles as well as of the solid residues remaining after chemical fractionation and filtration were examined by Scanning Electron Microscopy (SEM). In addition, the distribution of important elements in the sample structures was examined using Energy Dispersive X-ray Fluorescence spectrometry (EDX). The electron beam induces emission of element specific X-ray wave lengths from the sample and by scanning the specimen surface with the detector element “maps” are obtained. In order to get information about the spatial variations in elements quantities in the samples, semi-quantitative point analyses were made.

In this work both high-vacuum and low-vacuum (environmental SEM or ESEM) electron microscopes were used. The ESEM option gives the advantage that susceptible and non-conducting materials can be examined without sample material damage. The specimen is mounted by spreading on a carbon adhesive tape. No covering by a conducting material is

needed. The charge build up on the sample surface is removed by a small injection of water vapour using the low vacuum mode in the microscope.

2.7. X-ray powder diffractometry

The main crystalline compounds in ash samples from the co-combustion tests were identified by qualitative X-ray powder diffractometry (XRD) using a Siemens D5000 X-ray powder diffractometer with the characteristic Cu radiation and a scintillation detector. The identification of compounds was performed through comparison with standards in the Joint Committee of Powder Diffraction Standards [10].

3 Results and discussion

This investigation was focussed on the ash forming elements most commonly involved in sintering and fouling, i.e. K, Na, and Cl, as well as components which can hinder such problems, i.e. phosphates, aluminium silicates, sulfur and calcium compounds. Table 1 gives the chemical composition of the fuels that were investigated and also includes the composition of the fuel mixes used in the co-combustion tests based on the percentage composition of different fuels as discussed above. The fuels were chosen based on the fact that they have very different chemical compositions and that their special ash components could be used to balance the amount of troublesome ash components in a co-combustion situation. As shown in Table 1, the ash content varied between 0.3 to 50 wt-% and the water content between 7.0 to 74 wt-%. In addition, the alkali metal concentrations spanned over the range 3-110 g/kg dry ash. In biofuels (straw and wood), potassium is the most abundant alkali metal whereas refuse derived fuels (RDF) have higher concentrations of sodium originating for example from food packages contaminated with table salt (NaCl). In coal the concentration of alkali metals was very low and equal amounts of K and Na was found. Although coal has an origin in biological materials, i.e. plant tissues, the long period of coalification and contact with soil water has lead to a significant exchange of potassium with sodium [11].

The Cl concentrations in the fuels ranged from almost zero for wood pellets up to 0.8 wt-% for the RDF.

Sewage sludge contains a lot of phosphorus that has its origin in the waste water [12, 13]. The phosphorus is precipitated and separated from the water phase in the waste water treatment

plants. The sludges included in this study originated from waste water treatment plants using iron sulfate as phosphorus precipitant. In this process different solid iron phosphates, such as FePO_4 , are formed [12].

Table 1: Chemical composition of the fuels and fuel mixes studied in the project.

	Fuels:						Fuel blends:		
	Wood pellets	Sewage sludge 1	Sewage sludge 2	RDF	Straw	Coal	1; Ref	2; Sludge	3; Waste
Proximate analysis									
Water [wt-%. raw]	7.6	74	14.3	6.9	8.8	9.4	8.2	16.1	19.5
Ash [wt-%. dry]	0.3	49.9	34.8	11.6	5.6	8.9	1.4	7.4	9.2
Combustibles [wt-%. dry]	99.7	50.1	65.2	88.4	94.4	91.1	98.6	92.6	90.8
Volatiles [wt-%. daf]	95.2	95.2	91.8	89.9	81.1	34.5	92.2	92.2	91.8
Ultimate analysis [wt-%. Daf]									
C	50.5	52.3	52.3	54.6	49.4	82.1	50.3	50.5	52.0
H	6.1	7.7	7.3	7.3	6.3	4.9	6.1	6.3	6.6
O	43.3	30.9	31.4	35.9	43.4	10.7	43.3	41.8	40.0
S	<0.01	2.4	1.5	0.33	0.1	0.6	0.03	0.31	0.37
N	0.06	6.7	7.5	1.05	0.59	1.4	0.17	0.96	1.08
Cl	<0.01	0.12	0.05	0.83	0.3	0.3	0.07	0.08	0.27
Heating value [MJ kg⁻¹]									
HHV. daf	18.9	20.3	21.3	21.7	18.4	32.2	18.8	19.0	19.9
LHV. raw	17.1	1.0	11.5	17.7	15.6	26.3	16.8	14.8	15.4
Ash analysis [g kg⁻¹ dry ash]									
K	97.4	15	8.4	14.2	110	13	100	90.2	66
Na	9.0	9.4	3.4	24.2	9.0	13	9.0	9.0	13.0
Al	8.0	78.6	51	39.5	6.5	81	7.7	16.2	24.6
Si	40.9	157	84	180	300	210	95	109	92
Fe	8.4	164	140	17.5	2.1	60	7.1	26	27
Ca	200	47.6	51	154	52	73	168	151	174
Mg	33.8	11.2	9.1	10.4	10	38	29	26	25
P	11.7	59	83	2.8	14	1.7	12.2	17.9	15.0
Ti	1.1	4.9	7.2	7.5	0.4	3.7	0.95	1.41	3.3
Ba	3.7	0.8	-	1.0	0.4	1.4	3.0	2.7	2.2

daf= dry and ash free, raw= as received

When considering differences in fuel compositions that may have an influence on the combustion properties it was noted that the fuel mix used in the reference case (Ref) had lower contents of moisture and ash than the other two fuel blends. The significant differences in concentrations of ash elements between the pure fuels were levelled out when the fuels were mixed. Thus, the concentrations of alkali metals and calcium in the fuel blends were rather similar. The principal differences was the lower content of S, Al and Fe in the “Ref” fuel mix and the large amount of chlorine in the “Waste” mix (Table 1). Calculated molar ratios of Cl to Alkali (K, Na) showed that the fuel blend of the “Waste” case had the highest molar ratio with 0.96, whereas the ratio in the “Sludge” case was only 0.38 and the “Ref” case had a molar ratio Cl/Alkali of 0.48. This means that it was theoretically possible for nearly all Cl in the “Waste” case to form alkali chlorides in the combustion while there was just enough chlorine present to make it theoretically possible for about 50% of the alkali metal content in the “Sludge” and “Ref” cases to be present in chloride form.

3.1. Chemical fractionation of single fuels

The results from the chemical fractionation of pure (single) fuels are presented in Table 2 and Figures 2 and 3. Note that there are different scales in Figure 2 and 3. Mass balances over the fractionation experiments were calculated for all elements and generally found to close well, considering the many steps involved. The investigation of chlorine speciation poses a special problem since the acid extraction includes HCl. This made it impossible to determine the amount of acid soluble chlorine. The chlorine content in the solid residue fraction was also unreliable due to the previous HCl step. Hence, the Cl results from HCl-leaching and the residue fraction was left out in Table 2 and Figure 2. More detailed Figures on the leached fractions are found in the Supporting information, Figures S1 and S2.

Table 2: Results from analysis of fuels and solid residue after chemical fractionation.

Element concentration	Wood pellets		Sewage sludge 1		Sewage sludge 2		RDF		Straw		Coal	
	Fuel	Solid residue	Fuel	Solid residue	Fuel	Solid residue	Fuel	Solid residue	Fuel	Solid residue	Fuel	Solid residue
[g kg ⁻¹ TS]												
K	0.40	0.035	2.1	0.44	2.7	0.18	2.3	0.75	8,7	0.076	0.97	0.62
Na	0.043	0.018	0.77	0.077	0.94	0.056	3.7	2.04	0.18	0.037	0.72	0.22
Al	0.024	0.028	27	1.4	23	0.9	10	5.2	0.095	0.12	7.0	4.4
Si	0.58	0.35	53	44	35	36	26	26	18	17	14	10
Fe	0.034	0.01	89	2.1	73	0.5	4.6	0.72	0.074	0.025	3.5	1.65
Ca	0.89	0.21	17	0.18	30	0.17	25	1.2	4.1	0.082	5.3	0.12
Mg	0.14	0.035	3.3	0.23	3.7	0.1	1.9	0.88	0.7	0.03	2.5	0.095
P	0.048	0.01	25	0.99	44	1.0	0.61	0.14	0.62	0.018	0.11	0.026
Ti	0.0087	0.013	1.0	0.26	2.2	0.13	1.5	2.0	0.007	0.014	0.28	0.00063
S	0.089	0.01	8.9	3.6	9.7	7.0	2.3	0.57	0,95	0.25	3.2	3.2
Cl	0.1	n.a.	0.5	n.a.	0.2	n.a.	5.4	n.a.	2.5	n.a.	2.6	n.a.

n.a. = not analysed

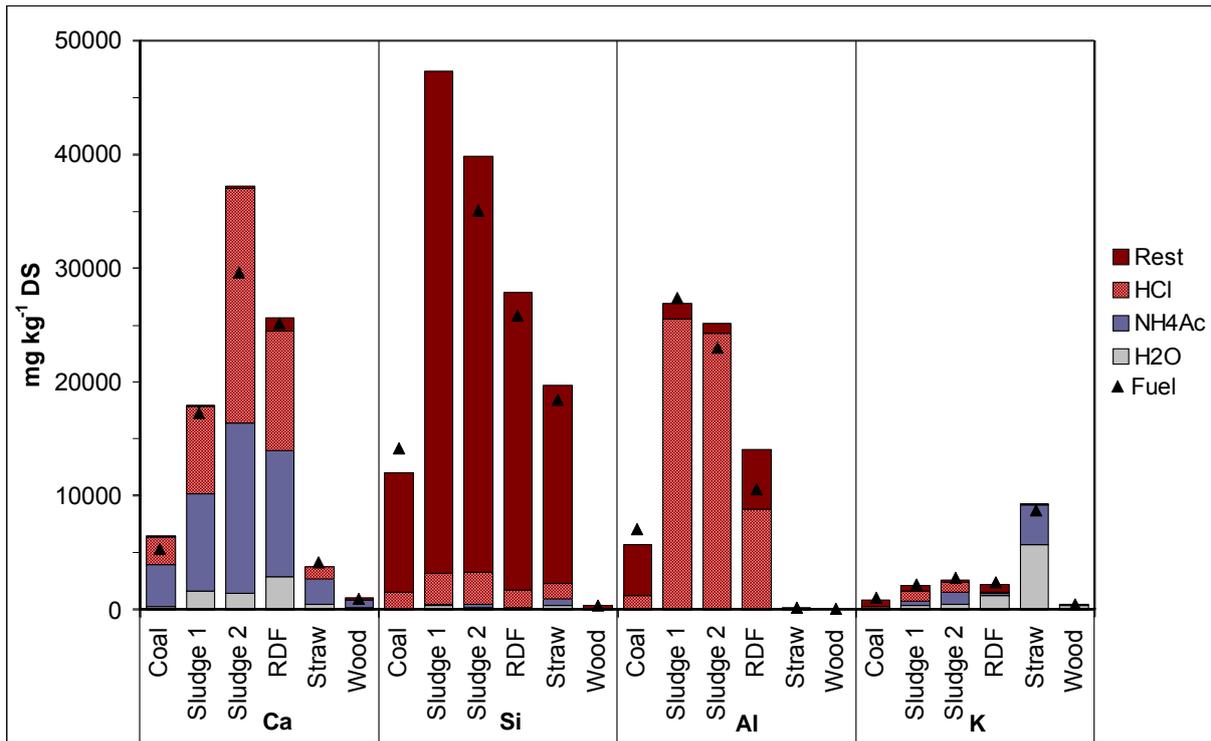


Figure 2: Chemical fractionation analysis results from coal, two municipal sewage sludges RDF, straw and wood pellets. Triangles represent the total concentration of the element in the fuel.

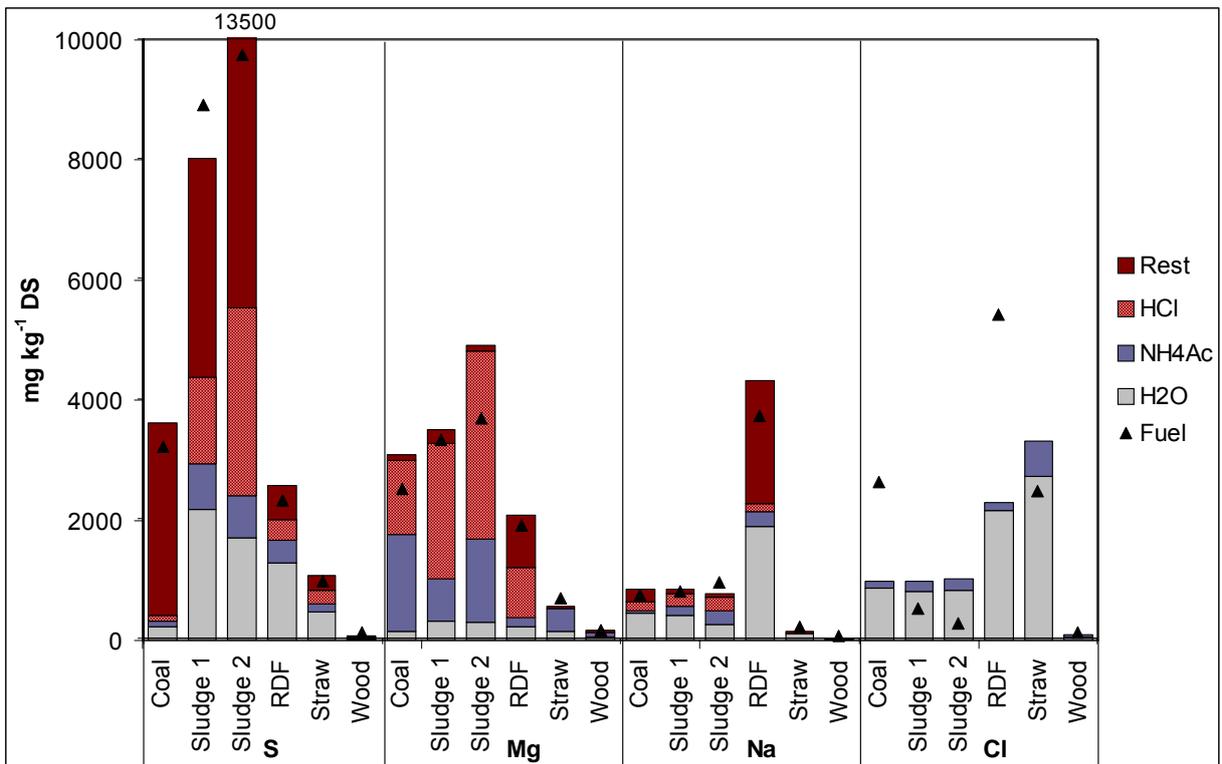


Figure 3: Chemical fractionation analysis results from coal, two municipal sewage sludges RDF, straw and wood pellets. The leaching result for Cl only includes H2O and NH4Ac. Triangles represent the total concentration of the element in the fuel.

3.1.1. *Coal*

The inorganic species in coal can be divided into two groups: those occurring in minerals and those bound in organic associations in the coal matrix. There is also a small fraction of water in the pores of the coal matrix and this water phase generally contains some dissolved salts, such as NaCl. A large number of minerals have been identified in coal samples [11, 14]. Different clay minerals and carbonates are by far the most abundant. In the chemical fractionation procedure, the carbonates would dissolve in the ammonium acetate and the hydrochloric acid step, whereas the clays, i.e. aluminium silicates, would stay in the residue. The coal that was studied here contains calcium mainly in carboxylic groups in the organic matrix and as carbonate. Only a small fraction is present in silicate form and some in water soluble salts. The potassium speciation was dominated by non-soluble forms, probably clay minerals. Sodium, however, was present in water soluble salts, probably NaCl as discussed above. The availability of potassium in different coals vary very much with the lowest availability (proximal 5%) found in high rank coals and an increased availability with decreased rank of the coal. In low rank coals as much as 50% of the potassium is available [3]. Only 40% of the chlorine in the coal was dissolved by water and acetate. This result is in accordance with the results of leaching studies on bituminous coals [15] showing that a large fraction of the Cl is organically associated in high rank coals. The coal contained an amount of sulphur that corresponds to about 7% of the dry ash (21% calculated as sulfate). This sulphur mainly ended up in the insoluble residue which shows that sulphur occurs in minerals with low solubility, such as FeS₂ and ZnS [14].

3.1.2. *Sewage sludge*

There were some differences in the composition of the two sewage sludges, but those were not large and the elements showed similar solubility patterns (Figures 2, 3, S1 and S2).

Sewage sludge is not known to be a difficult fuel with respect to alkali related problems in spite of rather large concentrations of alkali metals and chlorine. The chlorine in the sludges studied here was mainly soluble, but the potassium was present in both soluble and more stable forms, an observation that can explain the absence of ash problems.

Sewage sludge contains high concentrations of aluminium silicates derived from the waste water. Aluminium silicates (zeolites) are used as components in washing powder and are intended to de-harden the water [16]. The original zeolites have their metal binding sites occupied by Na^+ ions which are more or less exchanged for Ca^{2+} and Mg^{2+} in the washing water. During the waste water treatment the zeolites continue to be involved in ion exchange processes, for example by capturing potassium. The zeolites are then included in the sewage sludge formed by flocculation and filtration. Since many zeolites have good adsorption properties at high temperature it may be possible that zeolites present in sewage sludge can bind vaporous metal species in combustion. Kaolin, which is a layer-form aluminium silicate, has been shown to be a good absorbent for alkali metals at combustion temperatures [17, 18]. The zeolites used in detergents are not layer formed but have a structure with channel formed cavities, apart from that they have a chemistry that is related to that of kaolin. The aluminium present in the sludge samples was mainly soluble in the hydrochloric acid (1 mole/litre solution). The zeolites are decomposed in this low pH in the acid extraction step and release their content of calcium and aluminium [19]. The aluminium that remained in the solid phase after the acid extraction step was probably present in feldspars and similar minerals.

The sludges had the highest sulphur concentrations followed by coal and RDF. The sulphur in RDF, straw and wood pellets was found to be 40-50 % water soluble, in contrast to the sulphur in sewage sludge which was mainly not soluble at neutral or slightly acid pH. However, the combustion tests have shown that sulphur is released at high temperature as SO_2 anyhow.

3.1.3. *Solid waste (RDF)*

The RDF had an ash content of about 11% and important components of this inorganic part were Si, Ca, Na, K and Cl. The RDF consisted mainly of paper, plastics and wood, but also materials as rubber and textiles. Different metals were also found that were not properly removed prior to the manufacturing of the RDF. The RDF fuel had the highest chlorine concentrations among the investigated fuels. Many types of plastics, as for example PVC, contain Cl. The chlorine in the plastics is released in the combustion, but is not soluble with water or acetate making the fractionation method unreliable for the PVC fraction [8, 20]. As much as 55% of the chlorine in the RDF was not soluble and thus believed to derive from different plastics. Food packages with remaining salt were probably the source for soluble sodium and chlorine.

Aluminium was present only in acid soluble and non-soluble forms in this RDF. The non-soluble part of the aluminium might be present as oxide or silicate. It is common that municipal solid waste contains some aluminium metal which often is transported through the whole combustion chamber unit without being fully oxidised [21]. Aluminium metal is soluble at low pH (about pH 3) and would therefore be included in the HCl extraction step. Aluminium metal does not generally cause ash fouling, but it adds a risk to the ash handling since the aluminium metal remaining there will be hydrolysed as the ash is mixed with water and hydrogen gas will be evolved.

3.1.4. *Straw*

Straw is known to cause alkali related problems, such as bed agglomeration as well as building up corrosive deposits on the boiler tubes, during combustion [22, 23]. Most of these problems are caused by formation of volatile KCl and viscous potassium silicate melts. The results obtained here showed that the straw had by far the highest content of potassium of all fuels studied and nearly all of it was dissolved with water or acetate solution.

Calcium is the third important ash forming element in straw, next to potassium and silicon. Straw, as other biofuels contain calcium as calcium oxalate and other calcium salts of carboxylic acids. These calcium compounds are soluble in water and acetate [24]. In the results obtained here 70% of the calcium content belonged to this group. The CaC_2O_4 decomposes in two steps during combustion. The first step gives CaCO_3 and CO and in the next step the carbonate decomposes to CaO and CO_2 . [25]. Neither of these reactions causes any sintering or fouling problems.

3.1.5. *Wood*

The potassium and chlorine present in the wood fuel was almost entirely found in species soluble in water or acetate solution. Calcium, magnesium and sulphur were present in soluble forms to 50% or more, whereas silicon and aluminium occurred mainly in insoluble forms. Sodium seemed to be associated in both types of compounds. These results are in accordance with earlier results [4]. Probable potassium compounds are KCl and other potassium salts dissolved in the cell fluid. Silicon occurs mainly in supportive tissues, such as bark, as silicic acid and is thus expected to be insoluble. The speciation of sodium is less obvious, but some contamination with soil minerals, such as feldspars, is probable.

3.2. Chemical fractionation of fuel blends and ashes

As mentioned before, the fractionation results for the fuel blends are weighted results of the fractionations of the pure fuels used in the combustion tests producing the investigated ashes. After each of the leaching steps the pH was measured giving that all the leachates from the water and acetate steps had pH with in the range of pH 6-7 for all the fuels and the leachates from the HCl step pH <1. This supports the assumption that the weighted results from pure fuels can be used to represent the fuel mixes. Three different combustion tests with different fuel mixes were made. The fly ash (a mix of secondary cyclone and bag filter ash) was fractionated in the same way as the single fuels. The results are presented in Table 3.

Table 3: Results from fly ash analysis and fractionation.

Case	Fuel mix	H ₂ O	NH ₄ Ac	HCl	Residue	Case	Ash	H ₂ O	NH ₄ Ac	HCl	Residue
Fuel Ref (mg kg⁻¹ DS)						Ash Ref (mg kg⁻¹ DS)					
Cl	44000	47000	11000	n.a.	n.a.	Cl	19000	19000	190	n.a.	n.a.
Al	2700	240	53	1900	3300	Al	20000	-	1	9100	8500
Ca	110000	18000	68000	19000	13000	Ca	110000	6300	27000	55000	5700
Fe	3000	150	54	4000	930	Fe	27000	1	1	14000	9700
K	150000	100000	54000	57	3100	K	69000	30000	3500	12000	15000
Mg	17000	5000	9800	28	2400	Mg	17000	19	5400	10000	1400
Na	5100	2300	28	28	1500	Na	5500	1400	380	1300	2100
P	12000	4900	3600	2600	860	P	18000	5	58	11000	350
Si	280000	6100	9100	22000	260000	Si	230000	630	1200	3000	230000
S	21000	9000	3300	4500	4600	S	13000	11000	1900	1000	280
Ti	600	-	-	250	950	Ti	1800	1	2	360	1600
Fuel Sludge (mg kg⁻¹ DS)						Ash Sludge (mg kg⁻¹ DS)					
Cl	9000	10000	2200	n.a.	n.a.	Cl	580	990	35	n.a.	n.a.
Al	58000	76	65	44000	2800	Al	70000	40	1	46000	16000
Ca	51000	5000	24000	16000	1500	Ca	65000	2500	8000	39000	3000
Fe	150000	170	170	140000	3800	Fe	140000	-	1	51000	72000
K	35000	18000	11000	1500	1100	K	44000	4000	1200	24000	8300
Mg	10000	1200	2600	3900	640	Mg	12000	200	1700	8700	1600
Na	5000	1000	240	320	310	Na	5800	310	170	3400	2000
P	50000	1000	1000	52000	1800	P	63000	6	1200	48000	1000
Si	170000	1700	2000	8700	130000	Si	180000	25	860	5600	150000
S	22000	5400	1900	3300	7100	S	12000	4200	1200	630	100
Ti	3000	2	4	640	540	Ti	4900	-	-	920	3500
Fuel Waste (mg kg⁻¹ DS)						Ash Waste (mg kg⁻¹ DS)					
Cl	14000	7200	710	n.a.	n.a.	Cl	11000	13000	710	n.a.	n.a.
Al	68000	100	66	50000	12000	Al	54000	20	110	39000	20000
Ca	89000	10000	41000	36000	4100	Ca	190000	22000	140000	66000	5600
Fe	120000	180	170	130000	4300	Fe	84000	-	2	39000	91000
K	13000	5000	1500	1200	2600	K	34000	2600	940	11000	8500
Mg	11000	1200	1600	4800	2500	Mg	9900	-	780	8100	2000
Na	12000	5500	790	610	5500	Na	8300	850	280	4400	3700
P	37000	430	400	39000	1600	P	29000	-	-	24000	1000
Si	150000	680	550	7800	130000	Si	96000	15	25	14000	170000
S	19000	6200	2000	2900	6100	S	11000	430	12000	2700	900
Ti	5800	2	5	550	4800	Ti	4400	-	-	780	7800

- = under detection limit; n.a. = not analysed

3.2.1. *Reference*

During combustion of the reference fuel mix (wood and straw as shown in Table 3 and in “Supporting Information” Figure S3 and S4) calcium, magnesium, potassium and sodium seemed to be transformed into more stable (less soluble) compounds in contrast to sulphur and chlorine which were more soluble in the ash than in the fuel. However, these results did not show the whole situation because it was not possible to close the element balance over the boiler well for this case. Especially K, S and Cl were accumulated in the boiler as deposits which will be discussed below.

3.2.2. *Sludge*

A comparison of the fractionation results of the fuel blends in which sewage sludge was used (Sludge and Waste) and the corresponding fly ashes showed that most of the alkali (Na, K) was harder bound after combustion, see Table 3 and Supporting information Figures S3 and S4. For K the part found in the solid residue and in the HCl leachate increased from 8% to 90% and for Na from 35% to 95%. The hard bound alkali fraction in this ash was much larger than the fraction in the “Ref” case which may suggest that aluminium silicates had captured alkali in the combustion. No change was noted for chlorine which still was easily released in the water and acetate solutions from ash. Si and Al were also unchanged and these species were found in the HCl and residue fractions in the ash as well as in the fuel.

The only element that was found to be more soluble after combustion was sulphur. The fraction of sulphur ending up in the HCl leachate and solid residue decreased from 59% for the fuel to 13% for the fly ash. The water soluble fraction of S increased from 30% of the total S content to 67%. Since the amount of sulphur in the solid residue decreased from 40% to 3% a transformation of sulphides to sulfates may have taken place. The amount found in the NH₄Ac- and HCl-leachates increases/decreases with 10% respectively.

3.2.3. *Waste*

Just as for the other two fuel mixes, the alkali metals become less soluble and the sulphur more soluble after combustion of the Waste fuel mix. The acid soluble and non soluble fraction of K and Na increased with 80% and 40% respectively, nearly as much as in the “Sludge” case, and that of S decreased with 30%. The “Waste” ash had a large concentration of Ca due to addition of

Ca(OH)₂ upstream of the bag filter in order to neutralise acid gases, i.e. HCl and SO₂, in the flue gas. This made it difficult to compare the solubility of Ca between fuel and ash. There was a significant difference in amount of Si between the totally dissolved ash and the fractions obtained in the fractionation experiments. This could depend on sampling problems, inhomogeneous samples or inefficient dissolution of the sample intended for total content analysis. The analytical results for sulphur and chlorine showed major deviations as well despite that the main samples were carefully divided to yield representative sub samples for analysis.

3.2.4. *Fly ashes*

The fly ash analyses and fractionation results of the fly ash fractions of the three combustion cases are presented in Table 3. The fractionation results are also shown in Supporting Information Figures S5 and S6. Due to uncertainties in the ash analysis the total content determinations were repeated. The average of the ash analyses are shown in Supporting Information Figures S5 and S6 as well.

Element balances over the boiler were calculated for all three cases, Table 4. For the “Ref” case the closure of the element balance was poor. During the “Ref” case there was a significant amount of deposits formed on the heat exchanger tubes in the convection section. Figures S7a and b in the Supporting Information show the deposit probe used at the entrance of the convection section after the experiments. The deposit shown in Figure S7a belongs to the “Ref” case and consisted mainly of K, Cl, Ca and Si [8] and some Na, S and P. Hence, part of the alkali metals, chlorine, calcium and sulphur was captured and did not reach the secondary cyclone, bag filter or flue gas. Regarding the “Sludge” case, however, the element balances agreed very well considering the size of the boiler with an average deviation of $\pm 8.5\%$ and there was no deposit formation, just a fine dust layer on the deposit probe, Figure S7b [8]. The element balances over the boiler in the “Waste” case had a good closure as well, Table 4, but no deposit probe was inserted during this combustion test.

The element distributions and molar flows for Na, K, Ca, Al, S and Cl in the different ash fractions in the three cases are shown in Table 4. As mentioned above, there were clear differences between the cases regarding the distribution of potassium. In the “Ref” case only 76% of the K introduced with the fuel was found in the ashes in contrast to the “Sludge” and “Waste”

cases were all K was found in the ashes. In these cases most of the potassium ended up in the secondary cyclone ash with minor parts being found in the bag filter ash and the bottom bed material in contradiction to the “Ref” case where most K was found in the bed ash.

Table 4: Element distribution in the ash fractions.

Case	Ref %	Sludge %	Waste %	Case	Ref %	Sludge %	Waste %
$K_{out} K_{in}^{-1}$	76.4	102.7	115.4	$Al_{out} Al_{in}^{-1}$	1015	102.7	82.9
$Na_{out} Na_{in}^{-1}$	191.0	114.2	82.0	$S_{out} S_{in}^{-1}$	88.9	104.7	96.6
$Ca_{out} Ca_{in}^{-1}$	143.0	109.6	86.8	$Cl_{out} Cl_{in}^{-1}$	71.3	108.2	107.3
Sec. cyclone (wt-% of tot out)				Sec. cyclone (mole h⁻¹)			
K	28.3	72.4	81.7	K	14.2	61	50
Na	34.6	71.9	72.9	Na	2.5	16	36
Ca	31.1	57.8	68.6	Ca	20.5	75	170
Al	46.8	78.4	73.7	Al	8.1	160	190
S	23.0	3.5	20.0	S	2.1	2.2	14
Cl	8.2	0.7	3.6	Cl	1.2	0.2	2.1
Bag filter (wt-% of tot out)				Bag filter (mole h⁻¹)			
K	9.0	14.8	11.1	K	4.5	12	6.8
Na	7.4	7.5	11.5	Na	0.5	1.7	5.6
Ca	11.6	18.3	Lime add.	Ca	7.6	24	790
Al	4.5	9.1	17.4	Al	0.8	19	45
S	0.3	10.9	64.5	S	0.03	6.8	46
Cl	26.1	0.4	89.2	Cl	3.7	0.1	53
Bottom bed (wt-% of tot out)				Bottom bed (mole h⁻¹)			
K	62.7	12.8	7.2	K	31.4	11	4.4
Na	58.0	20.6	15.6	Na	4.1	4.7	7.6
Ca	57.3	23.9	14.6	Ca	37.8	31	37
Al	48.7	12.5	8.9	Al	8.4	25	23
S	13.1	2.1	0.8	S	1.2	1.3	0.5
Cl	1.9	0.9	0.2	Cl	0.3	0.2	0.1
Fluegas (wt-% of tot out)				Fluegas (mole h⁻¹)			
S	63.5	83.5	14.7	S	5.7	51.7	10
Cl	63.8	98.0	7.0	Cl	9.1	25.5	4.2

The distribution of Na, Ca and Al in the ashes is much the same as for K. These elements were primarily found in the secondary cyclone ash in the “Sludge” and “Waste” cases and in the bed ash in the “Ref” case. The element balance closure for Al in the “Ref” case was poor and indicated that much more aluminium came out than was added to the boiler with the fuel. This may arise either from inhomogeneous fuel samples with low concentrations of aluminium or errors in calculations due to low flows or by memory effects from previous combustion tests with sewage sludge where Al may have been accumulated in the boiler. However, the boiler had been

operated on wood chips for five days between these tests so effects of accumulated aluminium seem unlikely. Sulphur and chlorine was measured in the flue gas as SO₂ and HCl.

Approximately 64% of the sulfur and chlorine leaving the boiler in the “Ref” case was found in the flue gas. Of the fractions found in the ashes most of the sulphur was included in the secondary cyclone ash, whereas most of the chlorine was carried over to the bag filter. When sewage sludge was included in the fuel mix, however, as much as 84% of the total S and 98% of the total Cl was found in the flue gas. Most of the remaining sulphur was collected in the bag filter as CaSO₄ (Table 5). Phosphorous, which is a significant component of the sludge, probably formed various phosphates with calcium, potassium and iron. A calcium-iron-phosphate and a calcium-magnesium-potassium-phosphate were identified with XRD (Table 5). The binding of calcium by the phosphate in sewage sludge is an important mechanism since it interferes with the formation of calcium sulfate and leads to increased SO₂ levels in the flue gas. On the other hand, the sewage sludge seems to bind potassium, which is a positive effect. The amount of KCl vapour measured before the convection pass with the IACM decreased to zero during the “Sludge” case which means that there is a decreased tendency to ash deposit formation and corrosion. The fact that no deposits were found on the deposit probe supports this.

The results obtained indicate that potassium is involved in different reaction mechanisms in the three investigated combustion cases. Chlorination and sulphatation of K are important in the “Ref” case whereas in the “Sludge” and “Waste” cases the Cl is released to the gas phase as HCl and the K is found in the secondary cyclone ash together with most of the Si and Al. The Chemical fractionation shows that this K is hard bound in the ash from these cases but not in the “Ref” case, Table 3. The XRD results for the ash samples verified that this is the case. Potassium chloride and potassium sulfate were identified in ash from the Reference case but not in ashes from the other cases. There, potassium was instead present only in the feldspar form (KAlSi₃O₈). However, in this discussion it is important to remember the limitations of XRD: it shows only crystalline compounds and compounds occurring in crystallites that are not too small with a detection limit of about 2-3 wt-%. Nanometre sized crystallites are too small and will not give a good diffraction pattern. In addition, compounds which have a tendency to become amorphous at high temperature are not possible to identify. Zeolites and other silicates are examples of this type of compounds. The zeolite normally used in detergents (ZeoliteMAP) is not very stable at high temperature and a significant part of it has probably become amorphous during combustion.

There were, however, diffraction patterns showing the presence of a significant amount of zeolite type sodium and/or potassium silicates in the secondary cyclone ash from the Sludge case.

Table 5: Qualitative XRD results for ashes. The markings Trace, Minor and Major give a comparative measure of the amount of each compound. Trace means approx. 3%, Minor approx. 10% and Major more than 10%.

	Ref		Sludge		Waste	
	Sec.cyc. ash	Bag filter ash	Sec.cyc. ash	Bag filter ash	Sec.cyc. ash	Bag filter ash
Sodium silicates			Major ¹			
α -SiO ₂ (quartz)	Major	Major	Major	Major	Major	Major
SiO ₂ (Christobalite)	Trace					
Fe ₂ O ₃ (haematite)			Minor	Major	Major	
Ca ₉ Fe(PO ₄) ₇				Major		
Ca ₉ MgK(PO ₄) ₇				Minor		
Fe ₇ (PO ₄) ₆				Minor		
Ca(OH) ₂						Major
CaCO ₃	Minor	Minor			Minor	Minor
CaSO ₄	Trace	Major	Trace	Major	Trace	Trace
CaSiO ₃		Minor				
Ca ₃ Al ₂ O ₆					possible trace	possible trace
Ca ₂ Al ₂ SiO ₇					Minor	
CaAl ₂ Si ₂ O ₈				Minor	Minor	possible trace
NaAlSi ₃ O ₈			Minor			
KAlSi ₃ O ₈	Trace		Trace ²	Minor	Trace	
KCl		Major				
NaCl		Trace				
K ₂ SO ₄	Trace					
Al-metal					Trace	Trace

¹Sodium silicate hydrates, such as NaSi₂O₃(OH)₃*H₂O (Makatite), Na₂Al₂Si₃₋₃O_{10.6}*7H₂O (Faujasite) or Na₂Al₂Si₃O₁₀*3H₂O (Paranatrolite).

²TiO₂ (Rutile) possible trace amount or KAlSi₃O₈ Trace

The sand used as bed material in the boiler was analysed by XRD as well. The only crystalline compound found was quartz (SiO₂), which was consistent with the element analysis for the sand, indicating a quartz content higher than 99%.

3.3. SEM-EDX analysis

The use of a programmed mapping of the specimen surface by an EDX detector can provide information about possible element associations in the sample material. The occurrence of an element is shown as bright spots and a brighter spot generally means higher concentration of the element in question. However, the fluorescence response is different for different elements and the brightness of the spots in maps for different elements are not comparable. In addition, the fluorescence signals only provide semi quantitative results.

EDX mappings presented in the Supporting Information (Figures S8 and S9) showed a number of elements in Sludge 1 and Sludge 2. Similar element maps for the solid waste fuel are shown in Figure S10. These results indicated the presence of aluminium silicates with potassium in both sewage sludges and the solid waste fuel. The presence of Al, Si and Na in the same structure in the RDF fuel sample might be showing that the structure was a ceramic particle or a small stone. The EDX element maps of the sludges showed correlations between Fe and P which was consistent with the formation of FePO_4 in the waste water treatment. Both sludges investigated here came from waste water treatment plants using ferric salt to precipitate phosphorus from the waste water stream.

EDX element maps for samples of secondary cyclone ashes of the three co-combustion cases are shown in the Supporting Information (Figures S11 and S13). The results for the secondary cyclone ash (Figure S11) and similar results obtained for the bag filter ash from the “Ref” case showed clear correlations between K and S indicating the presence of K_2SO_4 . The potassium sulfate was present in needle like crystals, but there was also a more diffuse structure containing both K and Cl. This indicated that KCl was more evenly distributed in the ash particles and that K_2SO_4 had been formed as a secondary phase through reaction between SO_2 in the flue gas and KCl in the ash matrix. As was discussed above, K_2SO_4 , but not KCl, was identified by XRD for the Ref case ashes which further supports that the chloride was distributed in very small crystallites in the ash matrix.

The EDX results for the ashes from the two combustion cases both containing sludge (the “Sludge” case and the “Waste” case) gave very much the same result with clear correlations between Al, Si and K and no correlations between K and S. Even though the bag filter ash from the “Waste” case was totally dominated by Ca from the hydrated lime addition, it was possible to see the formations of K-aluminium-silicates. Since the sand used as bed material in the fluidised bed boiler was a pure quartz sand with very few inclusions of feldspar minerals, these potassium

aluminium silicates have probably been formed during combustion or are remnants of inorganic materials, such as ceramics or zeolites in the fuels.

Clear correlations between Fe, P and Al was also found for the “Sludge” and “Waste” ashes indicating that the FePO_4 from the waste water treatment had not been decomposed during combustion. Formation of aluminium phosphate is suggested as a candidate for decomposed FePO_4 if there is a lack of calcium [26] although no aluminium phosphate was identified by XRD in the ash samples. Iron containing phosphates were found in ash from the case “Sludge” (Table 5). Some very bright particles in the Si, Al and Fe-maps of the ash from the waste case showed the presence of silica (SiO_2) along with aluminium and iron in metal or oxide forms, which were confirmed by XRD results.

The XRD results showed CaSO_4 , K_2SO_4 and SiO_2 as components of ashes from the Ref case. The results of the spot analyses carried out during the electron microscopy (SEM) investigation of the secondary cyclone ashes are reported in the Supporting Information (Table S1 and Figure S14). These results showed, as the element mapping results also did, clear correlations between Ca, K and S. Silicon occurred as a major element in all spot analyses which was mainly due to the presence of quartz sand elutriated from the fluidised bed, but also from silica in the fuels.

When phosphorus occurred, it occurred together with Fe, K and Ca which could be expected since these cations, especially Ca, have a strong tendency to form phosphates together with potassium [27]. In addition, Fe_2O_3 (haematite), $\text{Ca}_9\text{Fe}(\text{PO}_4)_7$, $\text{Fe}_7(\text{PO}_4)_6$ were identified in the secondary cyclone ash (Table 5) and Fe_2O_3 in the filter ash which also confirmed earlier results [12].

The results for the cyclone ash from the Sludge case given in Table S1 agrees well with the XRD results (Table 5) since they showed Al, Si, K, Ca, P and Fe as important elements in most spots analysed. Occasionally (spot 8 in Table S1), Al, Si and K with only traces of P and Fe was found. This was most probably a KAlSi_3O_8 crystal that may have been formed through high temperature transformation of a potassium exchanged zeolite.

The result for the spot analyses of the sec. cyclone ash from the “Waste” case agreed well with the composition of the fuel blend and the fractionation results for the ashes, Table 3. All of the sec. cyclone ashes were inhomogeneous consisting of very different particles and the “Waste” ash was the one with the largest differences, Figure S14. Spot 1 was a spherical calcium silicate,

whereas spot 2 included all elements in the list. No particles containing any significant amounts of S or Cl was found as expected considering the results in Table 4 and 5.

The filter ash from this case contained nearly 90 wt-% of the Cl introduced to the combustion with the fuel, Table 4. Mappings and spot analyses show that this chlorine is found in particles mainly consisting of Ca and O, but also some S, Si, Al, Mg and Fe. The molar ratio of Ca/S in these particles varies but is in average around 3. The Cl in the filter ash originates from HCl transported with the flue gas. It reacts with the lime in the filter cake to form CaCl_2 or CaOHCl [21]. The hydrated lime addition increases the filter ash flow with nearly 5 times its weight.

Conclusions

The fuels investigated in this study had very different properties both in composition and behaviour during combustion. RDF had the highest concentrations of chlorine and sodium among these investigated fuels and also high concentrations of potassium. About 50% of the amount of these components was soluble by H_2O and NH_4Ac , thus considered available during combustion. The only fuel having higher concentrations of potassium and chlorine available was the straw fuel.

The fractionation results for the two different sewage sludges showed similar solubility patterns. They contain high concentrations of potassium of which 40 to 60% are easily soluble. The results from fractionation of the fuels are supposed to predict the tendency for an element to create problems such as sintering and fouling. The alkali metals along with chlorine and sulphur are usually involved in such processes. In this work, the fractionation results for the bio fuel showed significant amounts of these elements in forms with a problematic behaviour which also was observed in the combustion tests. In the Ref case 50% of the sulphur and chlorine were lost as deposits in the boiler and 50% of the remaining share was found in the flue gas. On the other hand, K, Na and Cl were pointed out as potential ash deposit formers by the fractionation results for fuel mixes Sludge and Waste as well, but no deposits or any other problems were observed. Thus, the fuel mixes used in this work gave favourable combinations of ash forming compounds with ability to capture alkali metal species and decrease sintering and fouling.

Fractionation of the fly ashes from the combustion tests was made with the aim to compare the stability of the elements before and after combustion. The results indicated that a number of transformation reactions occur. The elements potassium, sodium, calcium and magnesium were found in more stable forms in the ash flows after combustion in all three cases, whereas sulphur and to some extent chlorine were more stable prior to combustion.

In the cases studied here, the sewage sludge probably provided some ash forming components, most likely aluminium silicates, iron compounds and different phosphates, that worked favourably by immobilising K, Na and Cl. The reduction of vaporous KCl was nearly total in both secondary cyclone ash and bag filter ash when co-firing with sludge. In the “Sludge” case 98% of the Cl was found in the flue gas. In the “Waste” case the HCl in the gases was captured by the hydrated lime addition prior the bag filter, thus collected in the filter ash. The fly ashes from the combustion of fuel mixes with sludge showed the presence of KAlSi_3O_8 , $\text{NaAlSi}_3\text{O}_8$ and zeolite residues. Thus, a binding of K in zeolites in combustion is indicated. The exact mechanism is not clear but a laboratory investigation has been initiated with the aim to clarify this.

Chemical fractionation is a good predictor of sintering tendencies of coals and most bio fuels and mixes of these fuels, estimating the amount of reactive alkali and chlorine. However, the results obtained in this work show that the method is not suitable for waste fuels, such as sewage sludge and RDF. For waste fuels chemical fractionation of the fly ashes produced in an test combustion probably is a more promising method to show if the alkali metals can be expected to be absorbed and bound by other ash compounds during combustion.

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Supporting Information Available

The following information has been placed in Supporting Information:

Figures S1 and S2, Chemical fractionation results from coal, sludge, RDF, straw and wood pellets. Percentage found in the four fractions: H_2O , NH_4Ac , HCl and solid residue.

Figures S3 and S4, Chemical fractionation analysis results from fuel blends used in the combustion cases and their corresponding fly ashes. Percentage found in the four fractions: H_2O , NH_4Ac , HCl and solid rest.

Figures S5 and S6, Chemical fractionation analysis results from the calculated fuel mixes and fly ashes obtained from the three combustion cases; Ref, Sludge and Waste.

Figure S7, pictures of the deposit probes from the “Ref” and “Sludge” case with deposits after the experiments.

Figures S8 to S10, SEM-EDX mappings on sludge 1, sludge 2 and RDF.

Figures S11 to S13, SEM-EDX mappings on secondary cyclone ashes from the “Ref”, “Sludge” and “Waste” cases.

Figure S14, pictures on the ashes with markings showing the SEM-EDX-spots.

Table S1, the results of the spot analyses of the three different combustion cases “Ref”, “Sludge” and “Waste”.

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SUPPORTING INFORMATION FOR:

**APPLICATION OF CHEMICAL FRACTIONATION METHODS FOR
CHARACTERISATION OF BIOFUELS, WASTE DERIVED FUELS AND CFB
CO-COMBUSTION FLY ASHES**

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The supporting information contains figures (Figure S1 to S6) showing the fractionation results on fuels, fuel blends and ashes, pictures of the deposit probes (Figure S7), SEM-EDX maps on sludge 1, sludge 2 and RDF (Figures S8 to S10), SEM-EDX maps on secondary cyclone ashes (Figure S11 to S13), Pictures showing the spot analysis on the secondary cyclone ashes (Figure S14) and a table (Table S1) showing the spot analysis results of the secondary cyclone ashes.

Chemical fractionation of single fuels

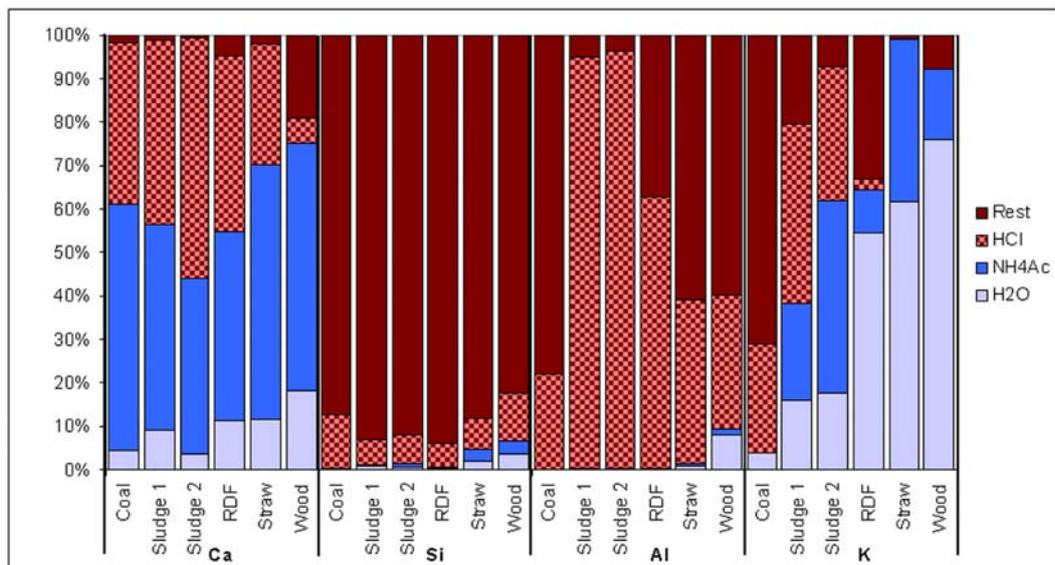


Figure S1: Chemical fractionation analysis results from coal, two sludges, RDF, straw and wood pellets. Percentage found in the four fractions: H₂O, NH₄Ac, HCl and solid rest.

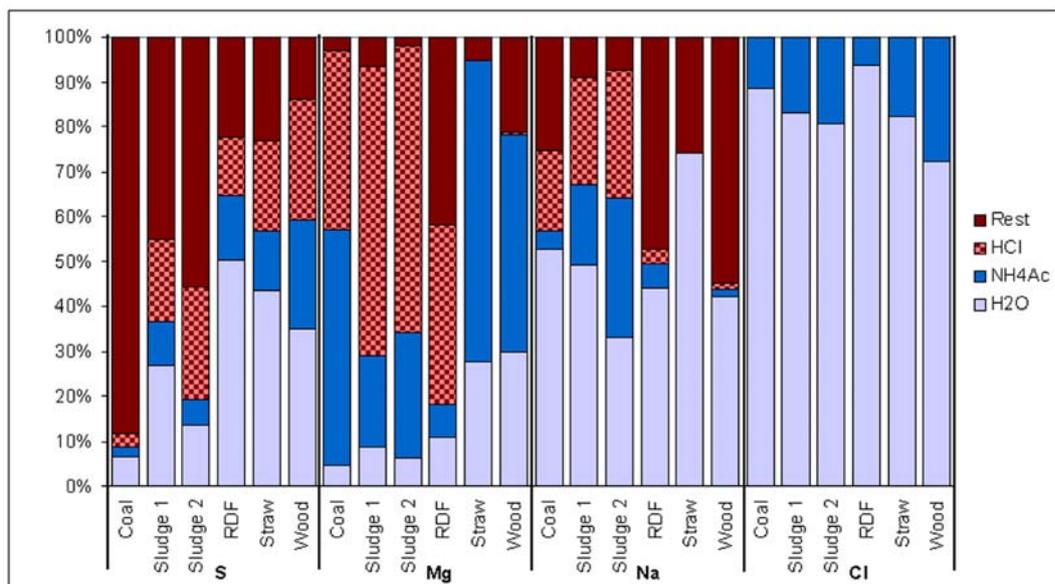


Figure S2: Chemical fractionation analysis results from coal, two sludges, RDF, straw and wood pellets. Percentage found in the four fractions: H₂O, NH₄Ac, HCl and solid rest. The leaching result for Cl only includes H₂O and NH₄Ac.

Chemical fractionation of fuel blends and ashes

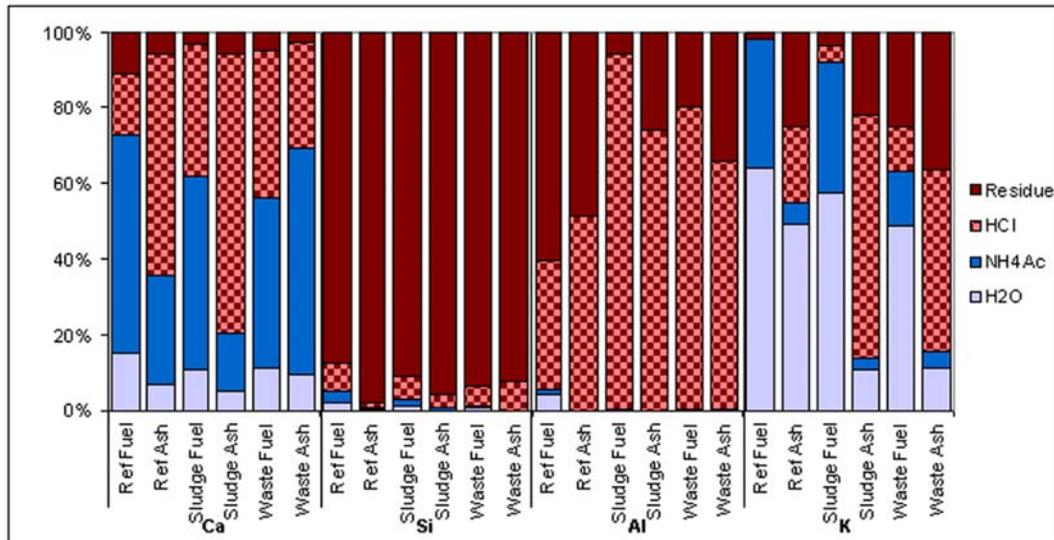


Figure S3: Chemical fractionation analysis results from fuel blends used in the combustion cases and their corresponding fly ashes. Percentage found in the four fractions: H₂O, NH₄Ac, HCl and solid rest.

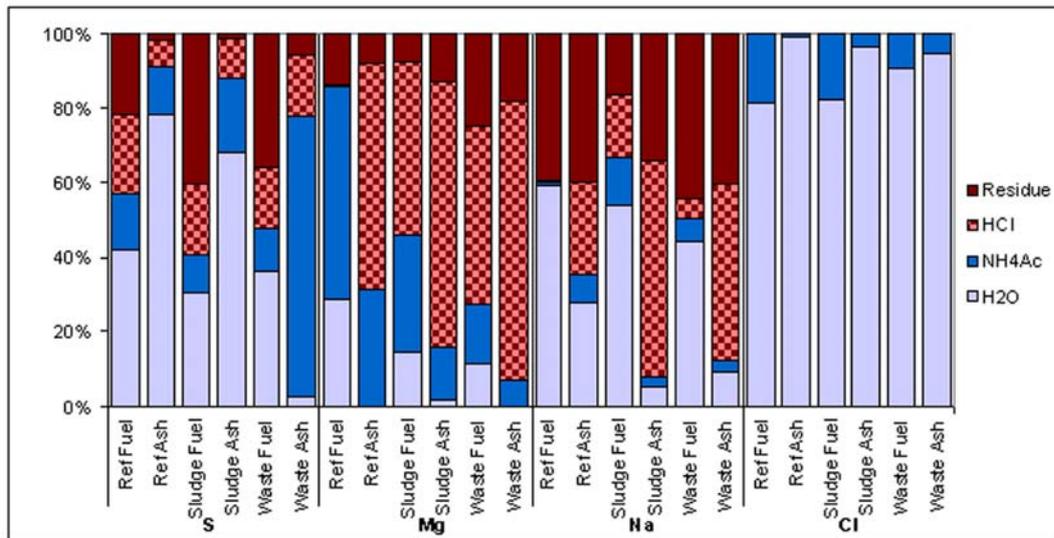


Figure S4: Chemical fractionation analysis results from fuel blends used in the combustion cases and their corresponding fly ashes. Percentage found in the four fractions: H₂O, NH₄Ac, HCl and solid rest. The leaching result for Cl only includes H₂O and NH₄Ac.

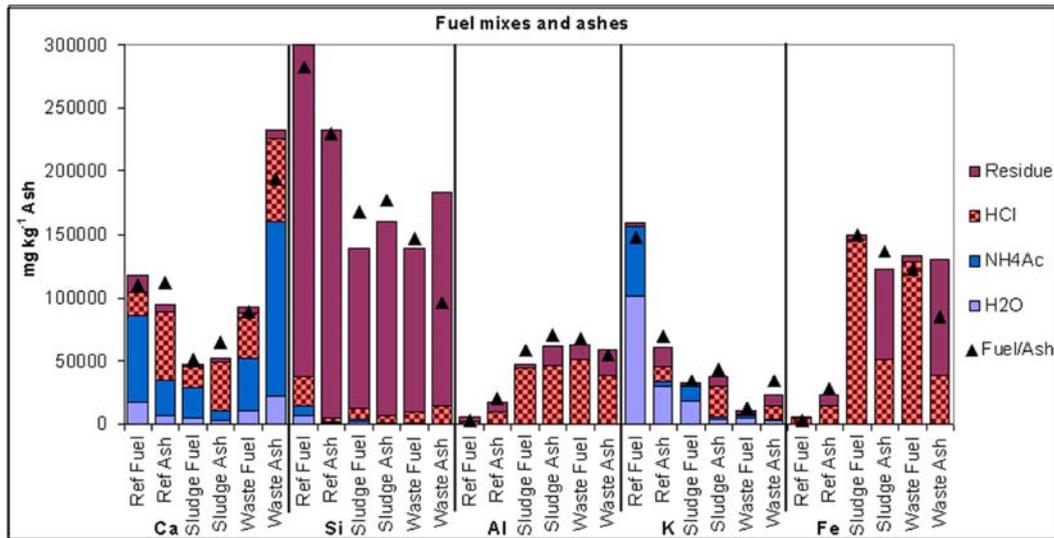


Figure S5: Chemical fractionation analysis results from the calculated fuel mixes and fly ashes obtained from the three combustion cases; Ref, Sludge and Waste. Triangles represent the total concentration of the element in the fuel/ash.

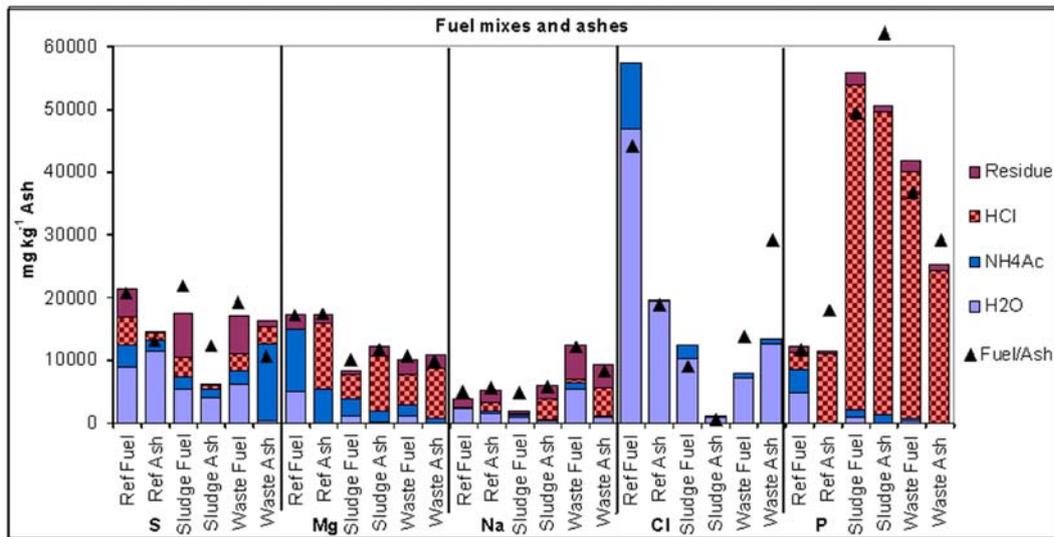


Figure S6: Chemical fractionation analysis results from the calculated fuel mixes and fly ashes obtained from the three combustion cases; Ref, Sludge and Waste. Triangles represent the total concentration of the element in the fuel/ash. The leaching result for Cl only includes H₂O and NH₄Ac.

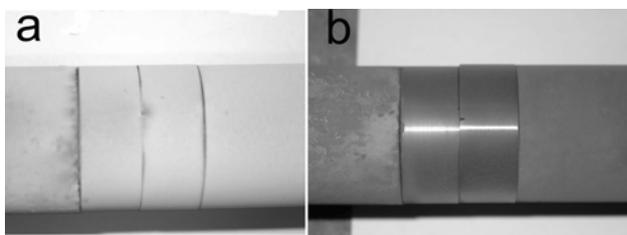


Figure S7: Deposit probes with deposits after the experiments. a; Ref case, b; Sludge case.

SEM-EDX analysis

Fuels

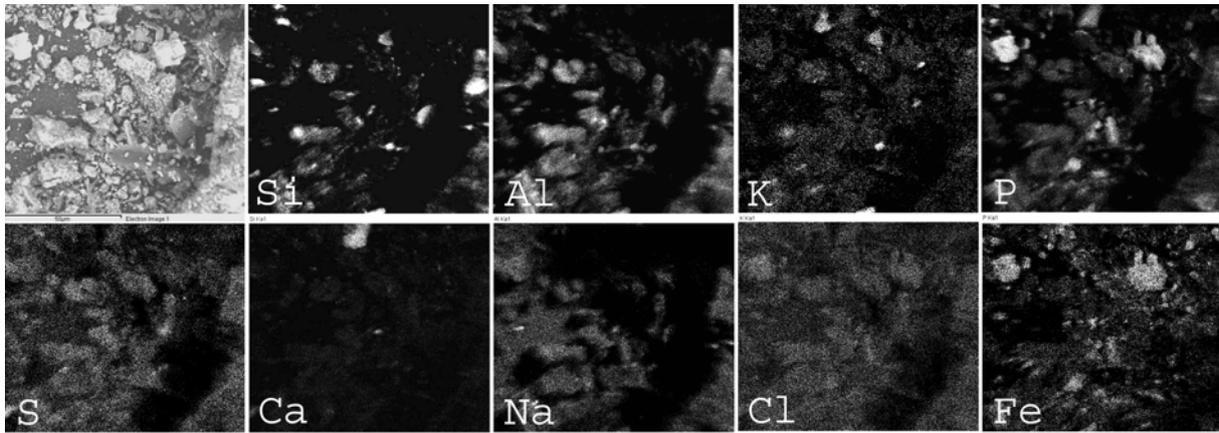


Figure S8: SEM-EDX mapping on Sludge 1. Picture and nine element maps of the same area.

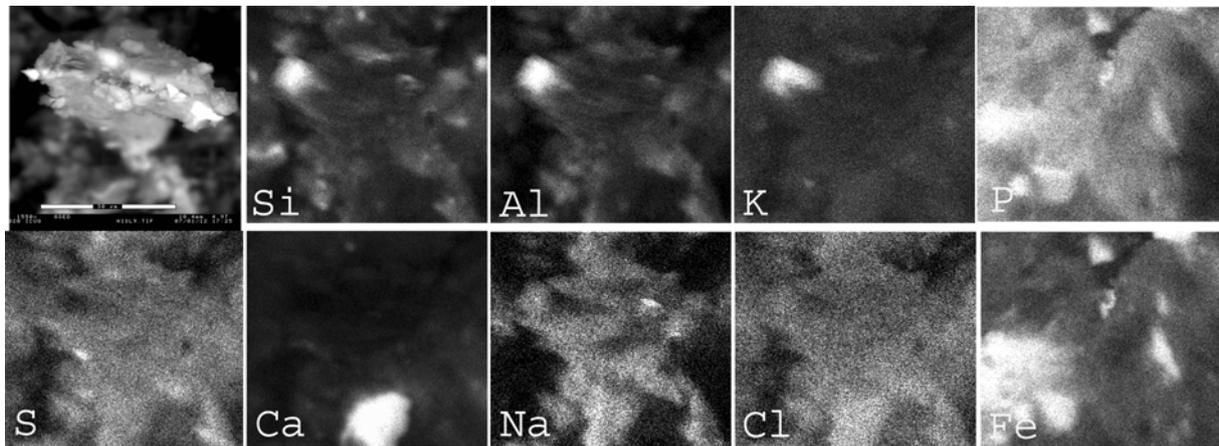


Figure S9: SEM-EDX mapping on Sludge 2. Picture and nine element maps of the same area.

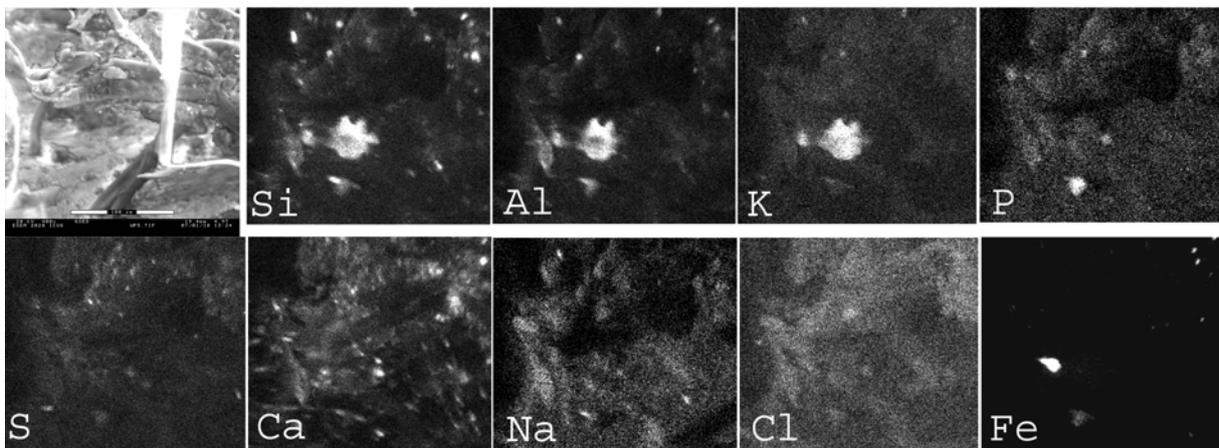


Figure S10: SEM-EDX mapping on RDF. Picture and nine element maps of the same area.

Ashes

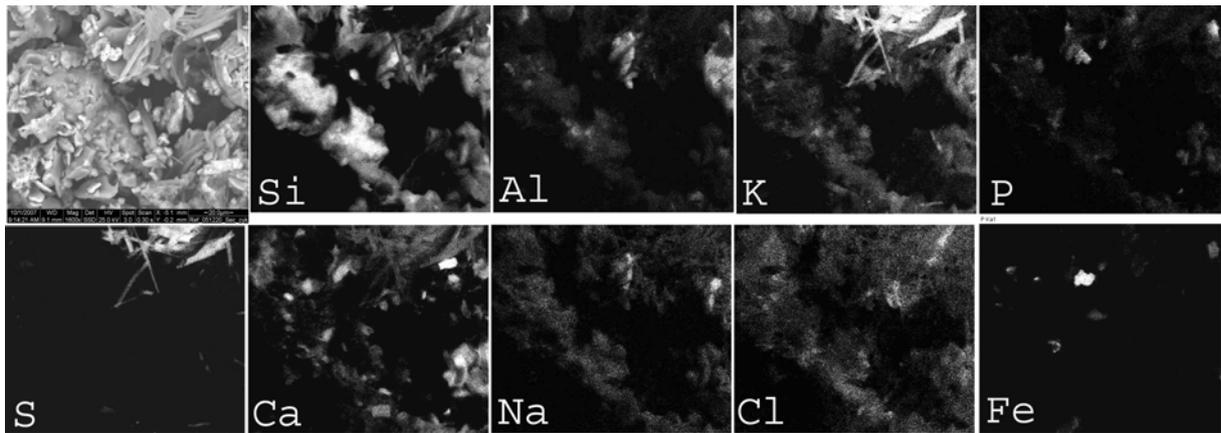


Figure S11: SEM-EDX mapping on Secondary cyclone ash from the “Ref” case. Picture and nine element maps of the same area.

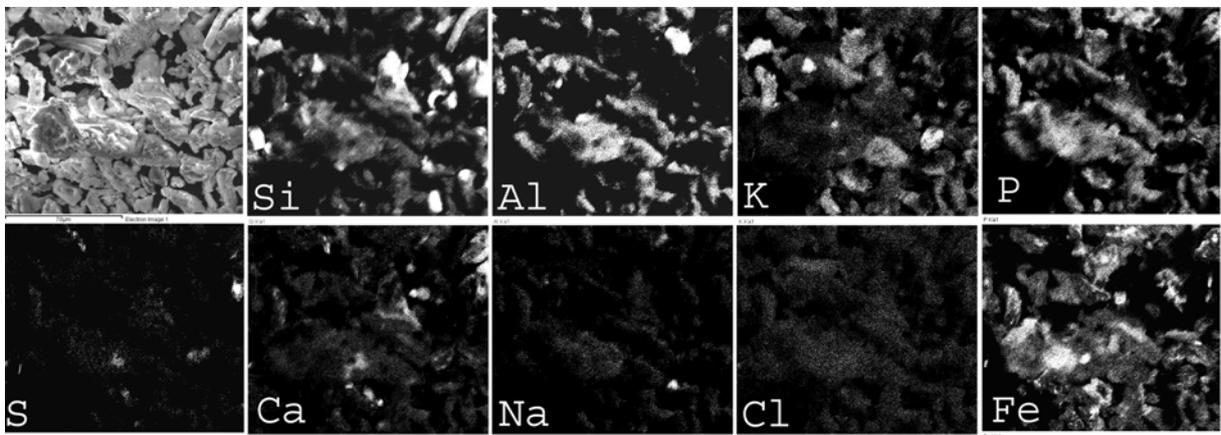


Figure S12: SEM-EDX mapping on Secondary cyclone ash from the “Sludge” case. Picture and nine element maps of the same area.

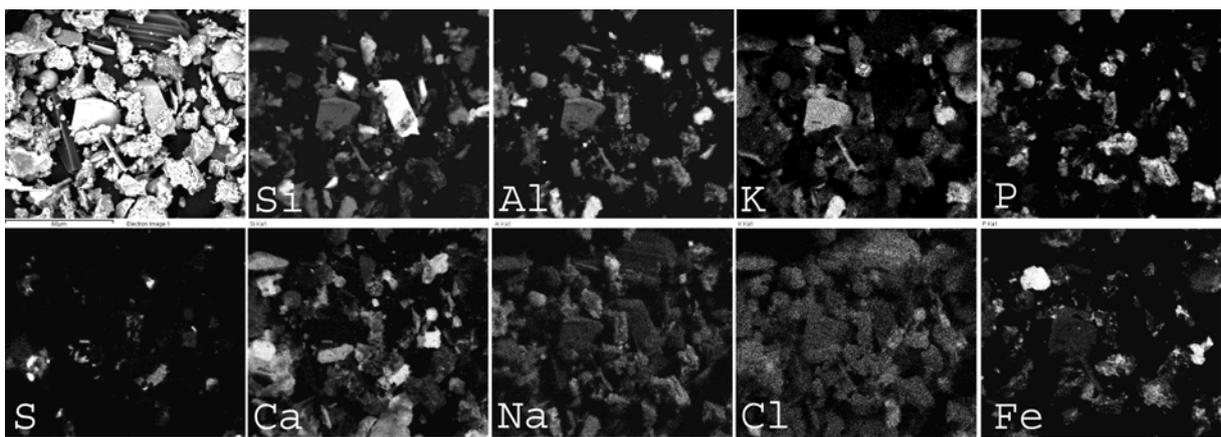


Figure S13: SEM-EDX mapping on Secondary cyclone ash from the “Waste” case. Picture and nine element maps of the same area.

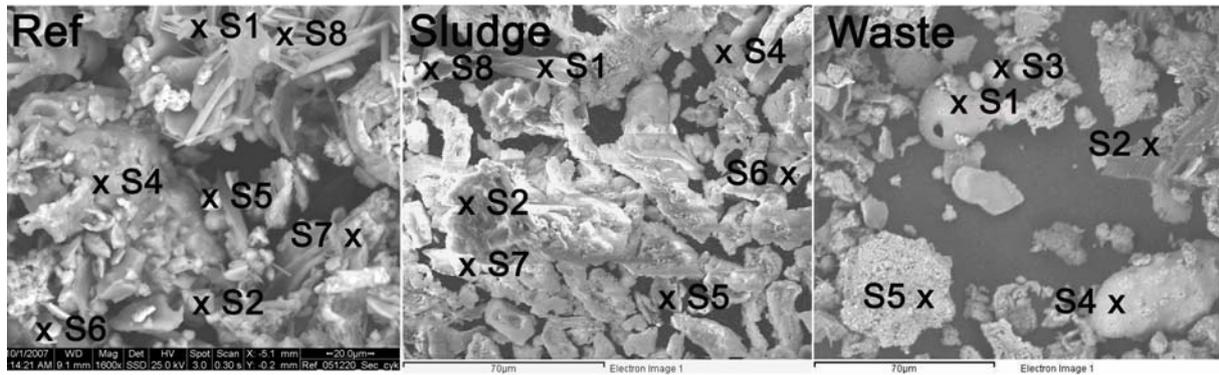


Figure S14: SEM-EDX spot analyses on the sec. cyclone ashes from the Ref, Sludge and Waste case corresponding to Table 7. The x marks the location of the spot and S1 corresponds to Spot 1.

Table S1: Results from the spot analyses. The spots were chosen within the same areas as the mapping results in Figure S11 and S12 and the same sample as Figure S13.

wt-%	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	SO ₃	Cl
Ref											
Spot 1	-	2	2	39	1	28	26	-	3	34	-
Spot 2	7	-	18	69	-	6	1	-	-	-	1
Spot 4	1	4	-	86	2	2	4	-	1	-	-
Spot 5	-	-	-	74	-	11	15	-	-	57	-
Spot 6	-	-	-	47	15	15	23	-	-	-	-
Spot 7	1	6	-	41	5	7	39	-	2	3	1
Spot 8	-	1	-	25	2	35	31	-	5	48	1
Sludge											
Spot 1	2	3	16	28	16	9	12	1	14	6	5
Spot 2	-	2	18	23	17	2	8	1	29	-	-
Spot 4	1	1	29	31	14	3	7	-	15	1	-
Spot 5	1	2	19	33	20	4	7	1	14	-	-
Spot 6	-	1	11	22	18	9	8	1	31	-	-
Spot 7	-	-	2	62	4	5	10	-	17	4	3
Spot 8	-	-	17	65	2	14	1	-	1	-	-
Waste											
Spot 1	4	3	2	76	-	2	10	-	3	1	-
Spot 2	5	3	17	19	6	8	21	3	19	8	4
Spot 3	2	2	11	11	11	2	7	1	55	-	-
Spot 4	-	1	9	11	18	4	53	2	3	-	-
Spot 5	1	2	5	7	8	1	7	1	68	-	-

- Below detection limit