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Final Report – Co-Firing of Coal and RDF in Suspension

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COMBUSTION AEROSOLS FROM CO-FIRING OF COAL AND SOLID RECOVERED FUEL IN A 400 MW PF-FIRED POWER PLANT

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ABSTRACT

In this work, combustion aerosols (i.e. fine particles < 2.5 μm) formed in a 400 MW pulverized coal-fired power plant was sampled with a low-pressure impactor, and analysed by transmission and scanning electron microscopy. The power plant was operated at both dedicated coal combustion conditions and under conditions with co-firing of up to 10% (thermal basis) of solid recovered fuel (SRF). The SRFs were characterized by high contents of Cl, Ca, Na and trace metals, while the coal had relatively higher S, Al, Fe and K content.

The mass-based particle size distribution of the aerosols was found to be bi-modal, with an ultrafine (vaporization) mode centered around 0.1 μm , and a coarser (fine-fragmentation) mode above 2 μm . Co-firing of SRF tended to increase the formation of ultrafine particles as compared with dedicated coal combustion, while the coarse mode tended to decrease. The increased formation of ultrafine particles was probably caused by a relatively higher volatility (and subsequent enhanced homogeneous condensation) of Ca, P and K during co-firing of SRF. The influence of SRF type, thermal fraction, particle size and injection position was however not evident from our data, probably due to the inhomogeneous characteristics of SRF.

S was found to be a special case. While the concentration of S was decreased in the ultrafine particles from co-firing (in consistence with a low initial concentration in SRF), the concentration of S in the electrostatic precipitator ash was higher for co-firing as compared with dedicated coal combustion. This implies an increased capture of SO_2/SO_3 by reaction with CaO in the fly ash. It leads us to suggest that a reduced collection efficiency of the electrostatic precipitator observed during co-firing of SRF may be linked to SO_3 deficiency in the flue gas, as small amounts of SO_3 are needed for proper ESP performance.

Keywords: *combustion aerosols, pulverized coal combustion, co-firing, solid recovered fuel*

1. INTRODUCTION

Co-firing of coal and solid recovered fuel (SRF) derived from nonhazardous waste streams is recognized as an advantageous method to reduce the CO₂ emission from pulverized coal-fired power stations. However, compared with coals, SRF is usually characterized of higher chlorine, alkali and trace element contents, which may affect the mass concentrations and elemental compositions of the combustion aerosols (i.e. fine particles with an aerodynamic diameter below 2.5 μm), formed during combustion. This is a topic of concern, since emission of combustion aerosols from coal-fired power plants is an important source of fine particles in the atmosphere, and because such airborne particles may cause adverse health effects [1]. Although modern coal-fired power plants are usually equipped with efficient flue gas treatment devices such as electrostatic precipitators and wet flue gas desulphurization, which are extremely effective in decreasing the particulate content of the flue gas when considering the total mass, a considerable fraction of the submicron particles will still penetrate most cleaning devices to some extent [1,2].

While classical studies have reported that ash emitted from coal fired power stations typically presents a bi-modal mass size distribution, with a coarse (fragmentation) mode at around 20 μm (representing the majority of the mass), and an ultrafine (vaporization) mode centered around 0.1 μm, more recent studies have indicated the existence of an additional, central (fine-fragmentation) mode located around 2-3 μm [1,3-5].

The dominant formation mechanisms for the coarse mode (supermicron) particles from pulverized coal combustion are recognized as the fragmentation, melting and coalescence of coal inherent and excluded minerals [1,3,6]). This results in a composition of the supermicron particles that is dominated by refractory metals (such as Si, Al, Fe, Ca and Mg), and not significantly dependent on particle size [1-3,6-7]. The supermicron particles have been characterized as predominantly individual, almost spherical particles, with a rather smooth surface, sometimes with discrete submicron particles sintered into the surface [3,6,7].

The ultrafine (vaporization mode) particles below or around 0.1 μm, on the other hand, are believed to be formed predominantly by the vaporization, reaction, nucleation, coagulation and condensation of inorganic ash species in the coals [1,6-7]. This result in a composition and morphology that is significantly different from that of supermicron particles, e.g. the ultrafine particles contain notably smaller quantities of Si and Al than the supermicron particles [1]. The morphology of the ultrafine particles is dominated by agglomerates of tiny, not exactly spherical, partially fused particles, the size of the primary particles is in the nanometer range (10 – 60 nm) [1,7]. The inorganic elements of

importance for the formation of ultrafine particles in pulverized coal combustion can be categorized as refractory metals, alkali metals (such as K and Na), S, P and Cl [6]. The degree of vaporization of the different elements and their contribution to the formation of ultrafine particles are largely dependent on coal properties and combustion conditions [1,6-7].

The central, or “fine-fragmentation”, mode has a composition that is similar to that of the larger (coarse fragmentation mode) particles. However, the fine-fragmentation mode has been found to display a significant number of rounded (irregularly shaped) particles, in addition to spherical particles. The nature of the rounded particles, of which many appear to be deformed oblates with softened and rounded surfaces and edges, indicate that these particles have not been entirely melted [1,3]. Different dominant formation mechanisms have been proposed for the fine-fragmentation mode, such as the ejection of molten ash particles from rapidly rotating char particles [4], particle inflation [3] and the fragmentation of thin-walled, cenospherical char particles [6].

In the present study, combustion aerosols (here defined as PM_{2.5}, i.e. fine particles with an aerodynamic diameter below 2.5 μm) formed in a 400 MW pulverized coal-fired power plant was sampled and characterized. The power plant was operated at both dedicated coal combustion conditions and under conditions with co-firing of up to 10% (thermal basis) of solid recovered fuel (SRF).

This paper is related with a previous publication [8], in which a fraction of data from the current aerosol measuring campaign is presented. The present paper aims at further interpreting the influence of SRF co-firing, including the effects of SRF type, size, thermal fraction, and injection position, on the formation of combustion aerosols. We also discuss the results in relation to the overall performance of the power plant (such as stack emissions). We may also draw the reader’s attention to a related publication in these proceedings [9], which presents results from co-firing experiments with the same coal and SRF in a laboratory scale entrained flow reactor, with special focus on trace elements behaviour.

2. MATERIALS AND METHODS

The coal boiler at Esbjerg power station has a production capacity of 378 MW_{el} and 460 MJ/s district heating. The steam data are: 304 kg/s at 251 bar and 560 °C. The combustion chamber is equipped with 24 coal burners, placed in tangential formation in the four corners, to ensure optimal turbulence and combustion. The coal burners are placed in 6 burner levels (named 10, 20, 30, 40, 50 and 60). Oil burners are placed between level 10 and 20, and in levels 30, 40, 50, 60. The coal burners each consists of two “sub-burners”, one “rich” and one “lean”. The coal is distributed from the coal mills to the (sub) burners (together with the primary air) through an “enricher”, in a ratio of app. 80/20 %. The coal consumption at 100 % load is 120 t/h. The plant is equipped with an SCR for NO_x reduction, electrostatic precipitators (ESP) and wet flue gas desulphurization (FGD).

The fuels used during the present measurements comprised a high-volatile bituminous coal from South America, and two types of SRF obtained from different suppliers. The SRF was co-fired with the coal in shares up to 10 % (thermal basis). The SRF, which had a fluffy morphology, was injected through special tubes, into the “lean” part of the existing coal burners, at either burner level 20 or 30. The influence of SRF particle size (10 mm or 20 mm average particle size) was also investigated. The composition of the fuels is given in Table 1.

It is seen from Table 1 that the SRF fractions are characterized by high Cl and Ca contents, and also a relatively high content of Na and the trace metals Pb and Zn, while the coal has relatively higher S, Al, Fe and K contents. The main difference between the two SRF fractions is a significantly higher content of Cl in SRF A as compared to SRF B.

The combustion aerosols were measured using a 10-stage Berner LPI (low-pressure cascade impactor) with an aerodynamic diameter range of 0.03 – 12.7 μm , and a gas ejector-diluter sampling system. The ejector capillary, which is the inlet of the flue gas, performs as a pre-filter with a cut-off diameter of $\sim 3 \mu\text{m}$. The extracted flue gas is diluted and quenched by dry, filtered air in the ejector probe before directed to the LPI. The dilution ratio is determined by measuring the CO_2 concentration in the raw flue gas and in the diluted gas. The system is described in detail elsewhere [8,10]. During the present measurements, the dilution ratio was between 15 and 25, and the duration of one experiment was around 30 minutes.

Table 1: Fuel composition (wt % or mg/kg, dry fuel basis).

	Coal	SRF A	SRF B		Coal	SRF A	SRF B
Ash (wt %)	12.8	12.9	15.8	Ca (wt %)	0.32	2.4	2.3
C (wt %)	72	53	53	Fe (wt %)	0.64	0.27	0.28
H (wt %)	4.7	6.6	6.9	K (wt %)	0.24	0.12	0.17
N (wt %)	1.5	1.1	1.3	Mg (wt %)	0.20	0.23	0.28
S (wt %)	0.69	0.31	0.28	Na (wt %)	0.08	0.23	0.23
Cl (wt %)	0.07	1.02	0.41	P (wt %)	0.02	0.03	0.04
Al (wt %)	1.5	0.70	1.1	Pb (mg/kg)	6.4	274	240
Si (wt %)	2.9	2.3	3.2	Zn (mg/kg)	22	751	426

The measuring point was downstream of the SCR unit of the plant, at a flue gas temperature around 380°C . The aerosols were collected on Al-foils coated with a thin film of Apiezon H grease. The foils were weighted before and after sampling to find the mass-based particle size distributions. The morphology and chemical composition of the collected aerosols was studied by means of Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), both equipped with Energy Dispersive Spectroscopy (EDS) for elements quantification. The particles for TEM analysis were transferred from the Al-foils to TEM grids by touching the TEM grid to the surface of the deposits on the Al-foils.

3. RESULTS

3.1. Mass-based particle size distribution

The experimental conditions included in the present study are summarized in Table 2, together with the corresponding results for the total aerosol mass load ($PM_{2.5}$), as measured by LPI. The mass-based particle size distributions are depicted in Fig. 1 for the experiments with co-firing of SRF A, and in Fig. 2, for the experiments with co-firing of SRF B.

Table 2: Experimental matrix for the present experiments and the resulting $PM_{2.5}$ (as measured by LPI). High and low injection position corresponds to burner level 30 and 20, respectively.

	Coal	SRF A				SRF B		
Particle size (mm)	-	10	10	10	20	20	20	20
Injection position	-	High	High	Low	High	High	High	High
Thermal fraction (%)	-	7	10	10	3	5	7	10
$PM_{2.5}$ (mg/m^3)	362 ± 36	304 ± 11	253 ± 16	222 ± 21	268 ± 50	351 ± 72	246 ± 7.6	$376 \pm -$

As noticed in Section 2, the cut-off diameter for particles extracted by the ejector is approximately $3 \mu m$, meaning that the results for the mass-based size distribution are not accurate above this size. However, our results may indicate the existence of two distinct particle modes, in consistency with recent literature findings for pulverized coal combustion [1,3]: an ultrafine (vaporization) mode at approximately $0.1 \mu m$, and an additional, supermicron (fine-fragmentation) mode around $2-3 \mu m$. The total aerosol mass load ($PM_{2.5}$) is quite stable when no SRF is introduced ($PM_{2.5}$: $362 \pm 36 mg/m^3$).

It is seen from Fig. 1 and Fig. 2 that the size of the ultrafine particle mode (at $0.1 \mu m$) tends to increase when co-firing SRF, while the coarse mode above $2 \mu m$ tends to decrease. This trend is quite evident for SRF type A (Fig. 1), although the influence of thermal fraction, particle size and injection position is not clear from our results. $PM_{2.5}$ is decreased slightly when co-firing SRF A (range: $222 - 351 mg/m^3$).

For SRF type B (Fig. 2) the fluctuations between the individual measurements are very large (the error bars depict the standard deviation), making interpretation of the results very difficult. The $0.1 \mu m$ peak appears to be less distinct, and partly merged with the left flank of the coarse mode, however the results are not quite evident. $PM_{2.5}$ is decreased in some experiments with SRF B, and increased in others (range: $245 - 376 mg/m^3$). It is not clear whether the fluctuations are caused by the larger particle size ($20 mm$ vs. $10 mm$), or if it is because SRF B is more inhomogeneous as compared to SRF A. Referring to Table 1 it is seen that the most important difference between SRF A and B, in terms of fuel composition, is the content of Cl, which is significantly higher in SRF A as compared to SRF B. A further interpretation of the results regarding the influence of thermal fraction, particle size, SRF type and injection position, is difficult, due to the inconsistency in the results.

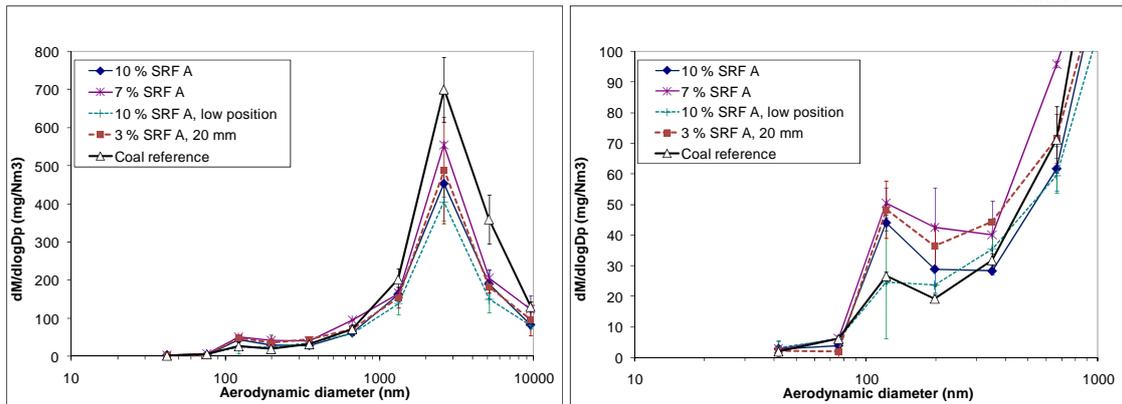


Figure 1: Mass based particle size distribution of aerosols from various co-firing experiments with SRF A. Left: Total overview of the distribution. Right: Magnification of the 0.1 µm peak. The curves are the average of two or three measurements. The error bars depict the standard deviations.

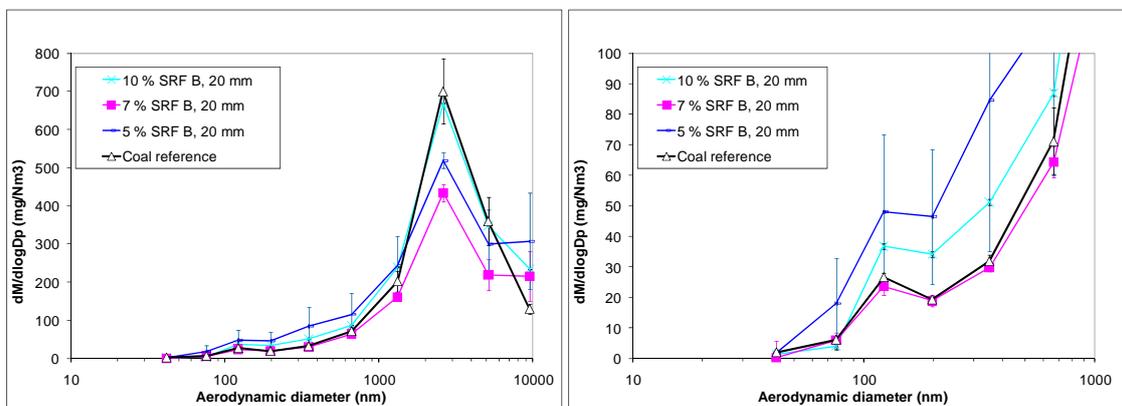


Figure 2: Mass based particle size distribution of aerosols from various co-firing experiments with SRF B. Left: Total overview of the distribution. Right: Magnification of the 0.1 µm peak. The curves are the average of two or three measurements (except for “10 % SRF B, 20 mm”, which is only one measurement). The error bars depict the standard deviations.

3.2. Particle morphology and chemical composition (TEM/EDS)

The particle morphology, as characterized by high resolution TEM, is illustrated in Figure 3. The shown results are from dedicated coal combustion, but the figure is representative for all experiments as no obvious difference between the morphology of the particles from co-firing and dedicated coal combustion were found.

Figure 3 clearly shows that two distinct types of particles are present: i) Agglomerates of small nucleates (Fig. 3(a) and 3(b)). The primary particles seem to be as small as 10-20 nm, although the agglomerates have much larger characteristic diameters (Fig 3(b)). This type of particles, which are probably formed from the vapour phase by nucleation and coagulation of volatilized ash species, dominates the ultrafine ash mode below 0.2 µm. ii) Individual, rounded or spherical particles (Fig. 3(a), 3(c) and 3(d)). These particles are generally larger than approximately 0.2 µm and are thought to be formed primarily due to fine-fragmentation mechanisms, as discussed by [1,3]. This particle type is dominating

the coarser particle fractions above 0.5 - 1 μm . Some of the rounded/spherical particles have small nucleates attached to, or sintered into, the surface (Fig. 3(d)).

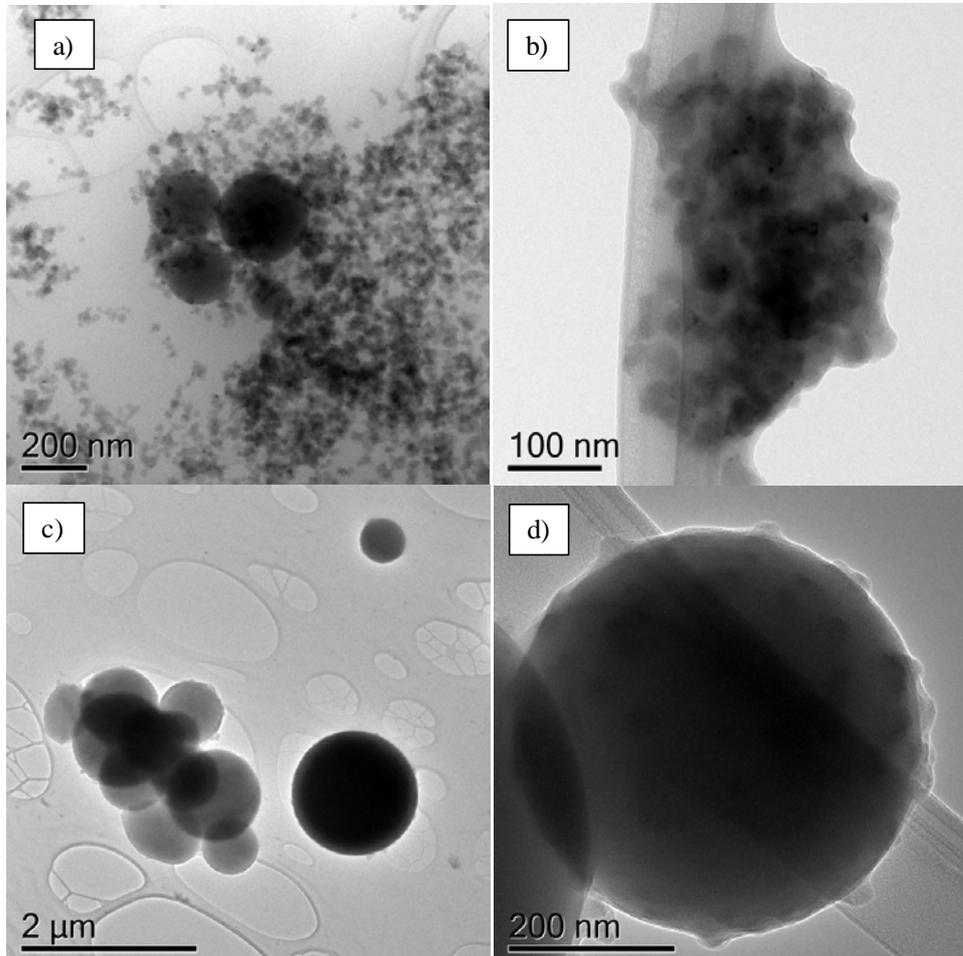


Figure 3: TEM micrographs of aerosol particles collected from dedicated coal combustion. (a) and (b) are from LPI stage 3, representing the ultrafine/vaporization mode (mean $d_{ac} = 0.12 \mu\text{m}$), and (c) and (d) are from LPI stage 7, representing the supermicron/fine-fragmentation mode (mean $d_{ac} = 1.32 \mu\text{m}$). Agglomerates of small nucleates at stage 3, while stage 7 is dominated by individual, rounded or spherical particles, some of them with submicron particles attached to, or sintered into, the surface.

The two distinct types of particles (agglomerates of small nucleates, and coarse, rounded or spherical particles, respectively) were analysed separately for inorganic composition by EDS (in the TEM). Figure 4 depicts the results from EDS analysis of ultrafine particles (from impactor stage 3) and coarser (spherical) particles (from impactor stage 7), from dedicated coal combustion and from co-firing of coal and 10 % SRF A, respectively. Element concentrations below 1-2 % are not considered accurate (as they are below the accuracy limits for EDS).

The TEM/EDS results reveal significant differences in the chemical composition of the two types of particles. The ultrafine particles agglomerates are enriched significantly in

Ca, S and P, whereas the coarse (spherical) particles are high in Al, Si and K. Fe is slightly enriched in the ultrafine particles as compared to the coarse particles fraction.

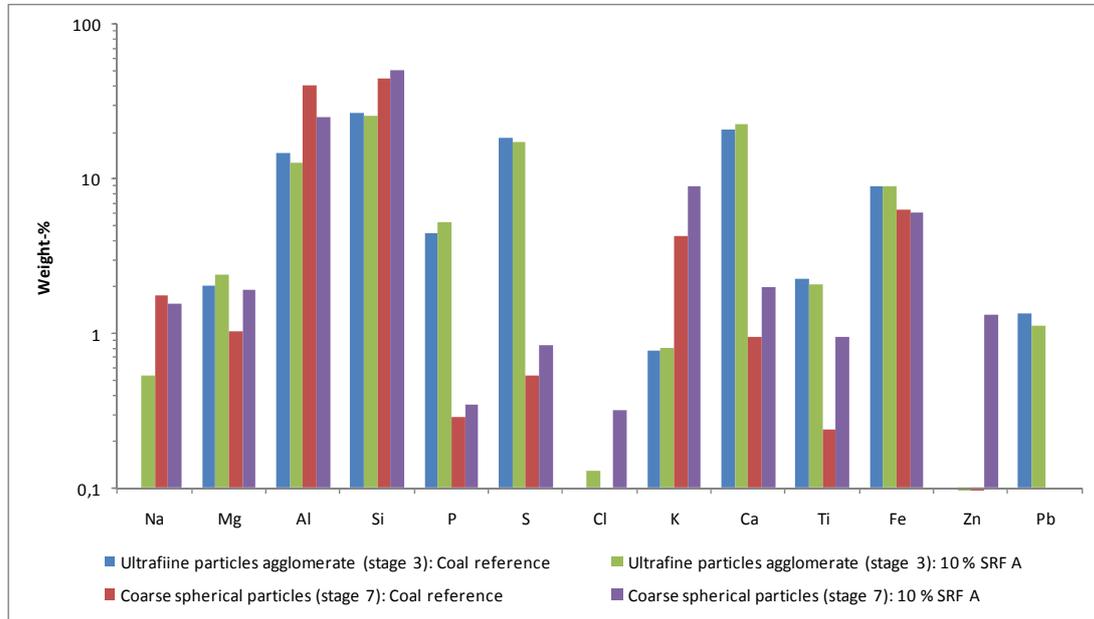


Figure 4: Comparison of the inorganic composition of ultrafine particles agglomerate (from impactor stage 3), and coarse spherical particles (from impactor stage 7), as determined by TEM/EDS. Results are shown for dedicated coal combustion, and for co-firing of coal with 10 % SRF A, respectively.

The enrichment of Ca in the ultrafine particles implies that the volatility of Ca is much higher than other refractory metals and alkali metals, which moves the distribution of Ca towards ultrafine particles [8]. Similar results have been reported by others, and the vaporization of Ca is probably favoured by high combustion temperatures and local reducing conditions in the char particles, as discussed in detail in [8]. The enrichment of P likely reflects that a certain fraction of the P in coal is present in a form that can be vaporized at combustion temperatures, in consistence with previous findings [2,8]. The importance of sulphur to the formation of ultrafine particles is probably related with sulphation reactions between vaporized metal species and SO₂/SO₃ in the flue gas, early in the boiler [2,8]. Another possibility is that sulphuric acid formed during the cooling of the flue gas may condense on the surface of the fine particles, or form nucleates [2,8].

Figure 4 also reveals that the ultrafine particles from co-firing of coal with SRF tend to have higher contents of Ca and P, and lower content of S and Al, as compared to the ultrafine particles from dedicated coal combustion. The coarse particles from co-firing of SRF are enriched significantly in K content.

Regarding trace elements, the concentrations are generally very low (and below the accuracy limit of 1-2 % for EDS). Fig. 4, however, indicates enrichment of Pb in the ultrafine particles from both dedicated coal combustion and co-firing of SRF. Traces of Zn is seen in the coarse fraction from co-firing of SRF. The content of Cl is insignificant (< 1 %) in all cases.

The observed trends are in good consistency with the findings from the SEM/EDS analysis previously reported by Wu et al. [8] and confirm the different formation mechanisms for submicron and supermicron particles described previously. Fig. 5 depicts the elemental composition of the aerosols as a function of particle size, as determined by SEM/EDS, for dedicated coal combustions and co-firing of coal with 7 % SRF A, respectively. (Only elements present in concentrations above ~2 % are included).

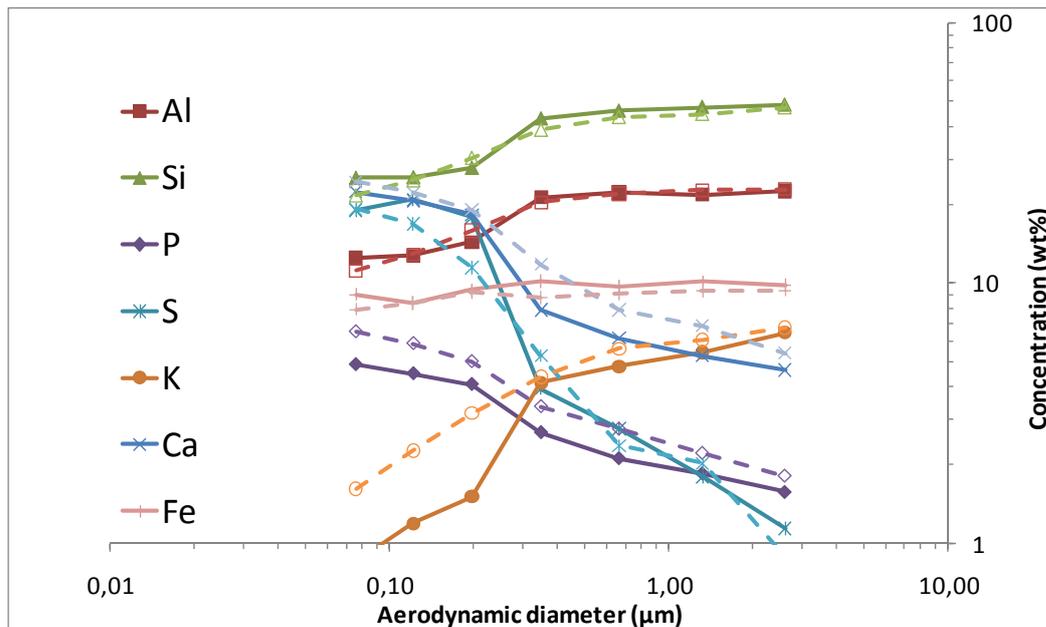


Figure 5: Comparison of the particle elemental compositions from co-firing of coal with 7 % SRF A (dashed lines and open symbols) and dedicated coal combustion (solid lines and solid symbols).

As seen from in Fig. 5, and previously reported by Wu et al. [8], the concentration of Ca, S and P is increasing progressively with decreasing particle size, and the aerosol particles from co-firing of coal with SRF is found to have generally higher contents of Ca, P and K, as compared to the aerosol particles from dedicated coal combustion.

For ultrafine particles, the content of S is lower in the particles from co-firing, while the content in the larger particles is comparable in the two cases. The distribution of S is likely related with the relative low S content and high Ca content in the SRF, as discussed in detail below.

Table 3 compares the composition of the fly ashes from the electrostatic precipitator during dedicated coal combustion, and co-firing of SRF A and B, respectively. It is noticed that the concentration of S tends to be increased in the fly ashes from co-firing, as compared to the coal reference case, in spite of a lower initial concentration in SRF (Table 1). Thereby, the overall picture seems to indicate that for co-firing of coal with SRF, a relatively larger fraction of the S is “captured”, primarily in the coarser particles, as compared to dedicated coal combustion. This may be a consequence of the increased

Ca concentration in the fly ashes from SRF co-firing (Table 3). CaO can readily react with SO₂/SO₃ in the gas phase, forming CaSO₄ [2, 11,12]. This, in turn, may decrease the concentration of SO₂/SO₃ in the flue gas, while increasing the concentration of S in the fly ash [12]. Such effects have previously been observed by others for co-combustion of Ca-rich fuels such as SRF and biomass [11,12]. Wu et al. [11] studied co-firing of coal with SRF in a laboratory-scale entrained flow reactor, and found that the retention of S in the ashes increased with increasing share of SRF, and with increasing Ca-content in the ash (bottom ash > cyclone ash). Spliethoff and Hein [12] studied effects of co-combustion of biomass in pulverized fuel furnaces and found that since biomass in most cases contained considerable less sulphur than coal, an increasing biomass share made the SO₂ emissions decrease proportionally. In addition, biomass co-combustion enhanced the content of S in the ash, due to capture by CaO and MgO in the biomass ash [12].

Unfortunately, no data for the SO₂/SO₃ concentrations in the flue gas during the present SRF co-firing campaign are available.

Table 3: Comparison of the ESP fly ash compositions from dedicated coal combustion, and from co-firing of coal with SRF. Analysis method: Wet chemical (acid digestion and ICP-OES).

Concentration in ESP ash (wt-%)	Coal reference	Co-firing SRF A [range]	Co-firing SRF B [range]
Ca	1.61	2.16 – 3.65	2.72 – 4.35
S	0.32	0.36 – 0.52	0.39 – 0.46
P	0.12	0.20 – 0.45	0.31 – 0.43
K	1.74	1.83 – 2.17	1.98 – 2.01

3.3. Link to overall plant performance: Increased dust emissions

During the present co-firing campaign, it was observed that the dust concentration in the stack (after ESP and wet FGD) increased significantly. The dust emissions were increased by a factor of up to 8 as compared to “normal levels” (which is approximately 5 mg/Nm³) for the power plant. Consequently the emission of several particle-born trace elements (such as Zn) was also increased. There was no obvious explanation for this increase, and the emissions decreased to the normal levels again at the end of the campaign.

We have analyzed the plant’s emission data during the co-firing campaign and looked for possible explanations for the increased dust emissions. While we have found no significant correlations between the dust emissions and the amounts of aerosols formed, there may be a link between the increased dust emissions and the behaviour and fate of Ca and S in the boiler:

It has been reported in the literature that replacement of high-sulphur coals with low-sulphur coals has led to decreased efficiencies of the electrostatic precipitators, and this has been explained by the lower concentrations of SO₂/SO₃ in the flue gas while firing low-sulphur coals [13]. Small amounts of SO₃ are needed for proper electrostatic precipitator performance, as SO₃ reacts with moisture and forms a conductive film of sulfuric acid on the fly ash when the flue gas cools. Without this conductive layer, ash

resistivity increases, limiting the transfer of particle charge over the particle surface to the grounded collection plates. As a result, the collected ash forms a charged layer on the collection plates, repelling other charged particles [13].

Hence, the presence and fate of SO_3 , in particular, seems to be a “key parameter” for efficient ESP performance. The formation of SO_3 is determined by the oxidation of SO_2 to SO_3 , and this step is most evidently kinetically limited [14]. During pulverized coal combustion, the majority of the fuel-sulphur is converted into SO_2 , with only a few % converted into SO_3 [14,15]. This results in quite low SO_3 concentrations in the flue gas, approximately ten ppm by volume for coal containing 0.5 – 5 wt % sulphur [15].

Cao et al. [15] studied the fate of SO_3 in different coal-fired boilers, burning high-sulphur (> 3.5 % S) bituminous coal and low sulphur (~0.4 % S) sub-bituminous coal, respectively. They reported that different interaction mechanism between SO_3 and fly ash applies for the different-rank coals, as temperature change: Under higher temperature ranges (> ~300 °C), alkali earth metal (Ca + Mg) constituents in fly ash are active on capturing SO_3 through chemical reactions, to form sulphate salt. Sub-bituminous coal generally has higher alkali earth metals in their fly ash, which allows the SO_3 in their flue gas to be captured effectively in the higher temperature zone (> 300 – 350 °C) prior to the air pre-heater (APH). Under lower temperature ranges, on the other hand (below the dew-point of SO_3 which is ~150 °C), the carbon residue in the fly ash functions as major adsorption sites for SO_3 condensation. Bituminous coal generally has high carbon-residue content in fly ash but lower occurrence of alkali earth metal constituents, which allows the SO_3 to be captured effectively through condensation, in the lower temperature zone after the APH.

If these effects also apply to co-firing of coal with SRF (as in our case), this means that SO_3 could be effectively captured by reaction with Ca in the fly ash, at relatively high temperatures, to form CaSO_4 . This, in turn, would suppress the condensation of sulphuric acid on the surface of the fly ash particles at lower temperatures, especially if the rate of oxidation of SO_2 to SO_3 is much slower than the reaction between SO_3 and CaO, which is very likely. This may lead us to suggest that the increased dust emission observed during the present SRF co-firing campaign is linked to a deficiency of SO_3 in the flue gas, due to enhanced capture by CaO in the fly ash.

4. CONCLUSIONS

The formation of combustion aerosols (i.e. particles with an aerodynamic diameter below 2.5 μm) during co-firing of coal and solid recovered fuel (SRF) was studied through direct sampling in a 400 MW pulverized coal-fired power plant. During the measurement campaign, the plant was operated at both dedicated coal combustion conditions and under conditions with co-firing of up to 10 % (thermal basis) of SRF. The influence of SRF type, size, and injection position was also investigated. The SRF was characterized by high contents of Cl, Ca, Na and trace metals, while the coal (a bituminous coal from South America) had relatively higher S, Al, Fe and K contents.

The mass-based particle size distribution of the aerosols was found to be bi-modal, with an ultrafine (vaporization) peak centered around $0.1 \mu\text{m}$, and a supermicron (fine-fragmentation) peak at $2\text{-}3 \mu\text{m}$. The total aerosol mass load was quite stable when no SRF was introduced ($\text{PM}_{2.5}$: $362 \pm 36 \text{ mg/m}^3$). Co-firing of SRF tended to increase the ultrafine peak, while decreasing the coarse peak as well as the total mass load ($\text{PM}_{2.5}$). The influence of SRF thermal fraction, type, size, and injection position was not evident from our data, probably due to the inhomogeneous characteristics of SRF.

Morphology investigations by TEM and SEM revealed that two distinct types of particles were present: a) agglomerates of ultrafine particles; the size of the primary particles being as small as $10 - 20 \text{ nm}$, and, b) individual, rounded or spherical particles with characteristic sizes above $\sim 0.2 \mu\text{m}$. The chemical composition of the different particle types was analysed by EDS. The ultrafine particles were enriched significantly in Ca, S and P, whereas the coarser (rounded/spherical) particles were high in Si, Al and K, reflecting the different formation mechanisms of the ultrafine versus the coarser particles.

The aerosol particles from co-firing of SRF had generally higher contents of Ca, P and K, especially in the ultrafine particles, as compared to the aerosols from dedicated coal combustion. This lead us to conclude that the increased formation of ultrafine particles when co-firing SRF was probably caused by a relatively higher volatility, and subsequent enhanced homogeneous condensation, of Ca, P and K.

S was found to be a special case. While the concentration of S was decreased in the ultrafine particles from co-firing as compared to dedicated coal combustion (in accordance with a relatively low initial concentration in SRF), the concentration in the coarser aerosol particles was comparable for the two cases, and in the ESP ash, the concentration of S was higher when co-firing SRF as compared to dedicated coal combustion. This was probably due to enhanced capture of sulphur by CaO in the fly ash.

A reduced collection efficiency of the electrostatic precipitator was observed during co-firing of SRF. Based on our results, we suggest that the increased dust emission while co-firing SRF is linked to a deficiency of SO_3 in the flue gas. A relatively high content of Ca in the fly ashes from SRF co-firing promotes effective capture of SO_3 at relatively high temperatures ($> 300 \text{ }^\circ\text{C}$) through chemical reactions, to form CaSO_4 . Consequently, SO_3 is exhausted from the flue gas, and subsequent condensation of sulphuric acid on the surface of the fly ash particles is suppressed. Small amounts of SO_3 are needed for proper electrostatic precipitator performance, as SO_3 condenses as a conductive layer of sulphuric acid on the ash during cooling of the flue gas.

In conclusion, we have found that the formation of aerosols is to some extent influenced by co-firing of coal with SRF, both with respect to amount and chemical composition. However, further investigations are needed in order to evaluate the effects of parameters such as SRF type, share, size, and injection position. Laboratory investigations on char reactivity and burn-out may serve to clarify the ash formation mechanisms during co-firing of coal with SRF, as well as the effects of initial particle size distribution and injection position of the SRF. This will be a topic for our future research. The trace

elements is another topic that deserves further attention; for co-firing of coal with waste fuels such as SRF the concerns on the aerosol emission are aggravated, due to significantly higher trace element contents in the waste fuels with respect to coals. Most of the trace elements would concentrate on aerosols during combustion and pose severe health threat. This topic (trace elements in co-combustion of solid recovered fuel and coal) is dealt with in a related publication, to which we may refer [9].

At this point we have identified no serious technical obstacles for co-firing of coal with SRF at the investigated conditions. Potential dust emission problems may probably be solved by using a coal with higher sulphur content, or alternatively by injection of a fly ash conditioning agent, as e.g. SO₃, upstream of the ESP.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

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