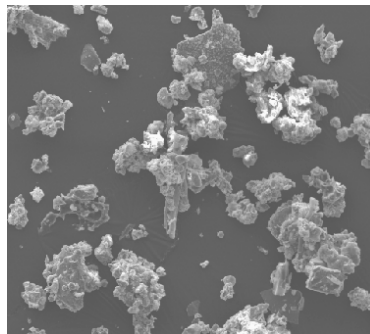


**Biofuels GS-2: Nordic course in analytical tools in  
combustion**

# **SEM/EDX Analysis of Deposit Rings and Cyclone Fly Ash**



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## 1 Introduction

The use of biomass in power plant boilers is an efficient method to reduce the net CO<sub>2</sub> amount produced. In annual biomass, Potassium (K) and Chlorine (Cl) are normally present in high concentrations and these will remain in ionic form and are not metabolized by the plant [3]. During biomass combustion, inorganic matter in the state of vapors, melts and solid particles are transported by the flue gas and is responsible for deposits on heat transfer surfaces. This process seriously inhibits the transfer of heat to the working fluid, resulting in the reduction of overall process efficiency. The mechanisms by which deposits are formed are: inertial impaction, thermophoresis and diffusion followed by condensation. Inertial impaction takes place when large particles with a large inertia do not follow the gas streamlines approaching heat transfer surface, e.g. cylindrical tube but instead impacts on the surface. Thermophoresis is related to the movement of particles in a thermal gradient from a high temperature toward a low temperature. This phenomenon is caused by the surrounding gas molecules which continuously collide with the particles from all directions. Condensation is the mechanism by which vapors are collected on surfaces cooler than the local gas. Biomass has the potential for producing large quantities of condensable material, and even smaller amounts of the condensable salts may considerably alter the deposit properties [5]. Deposits formed through condensation and thermophoresis covers the entire circumference of the tube and an ellipse-shaped deposit on the upstream side of the tube is formed due to inertial impaction. Nielsen [5] states that the main deposit on the upstream side of the probe for straw-firing consists of impacted fly ash particles and large amounts of condensable salts, forming a matrix that glues the fly ash particles together. The fly ash particles are dominated by K and K-Ca silicate. The K<sub>2</sub>SO<sub>4</sub> found in deposits on straw-fired boilers are believed to originate mainly from deposition of gaseous KCl followed by a subsequent slow sulfation of KCl in the solid phase. Jensen [8] after getting results from grate-firing of straw indicates that the composition of superheater deposits was found to be comparable to the fly ash composition with elements rich in Cl and alkali components. It is important to know how alkali is transported from the fuel to the surface where it deposits, in order to counteract the alkali-related problems. Several methods have been suggested to counteract the alkali related problems including removal of alkali from fuel and addition of additives to capture alkali.

In the present study, potassium, chlorine and sulphur chemistry, and the transport and the distribution of these species in Circulating Fluidized Bed (CFB) boiler is analyzed. The impact of ammonium sulphate as additive on fly ash composition and corresponding effect on ash deposition rate has been evaluated. The fly ash samples and the deposits obtained on deposit ring were analyzed by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray (EDX) technique.

## 2 Experiments

### 2.1 Fuels Analysis

The fuel used in the experiments is a combination of straw pellets and wood chips. The approximate value for fuel input was 0.979 t/h wood chips and 0.273 t/h straw pellets based on dry solids. The fuel flow corresponds to 4 kg/h ash flow from wood chips and 10kg/h ash flow from straw pellets. The approximate velocity in the boilers is 5.0 m/s. The fuel characterization results for both fuels are shown in Figure 1 and Figure 2. The most important difference between the wood chips and the straw pellets is that straw pellets have higher contents of ash and chlorine. Wood chips may not be very homogenous and the sample selected for analysis might not be representing the whole sample of wood chips. Overall, wood ash is rich in Ca, while K and Cl are in lower amounts. Compared to wood, the results are satisfactory for straw pellets case and the general contents of the inorganic element in straw are much higher. The high Cl and K contents indicate combustion of straw pellets may cause severe ash deposition and corrosion problems.

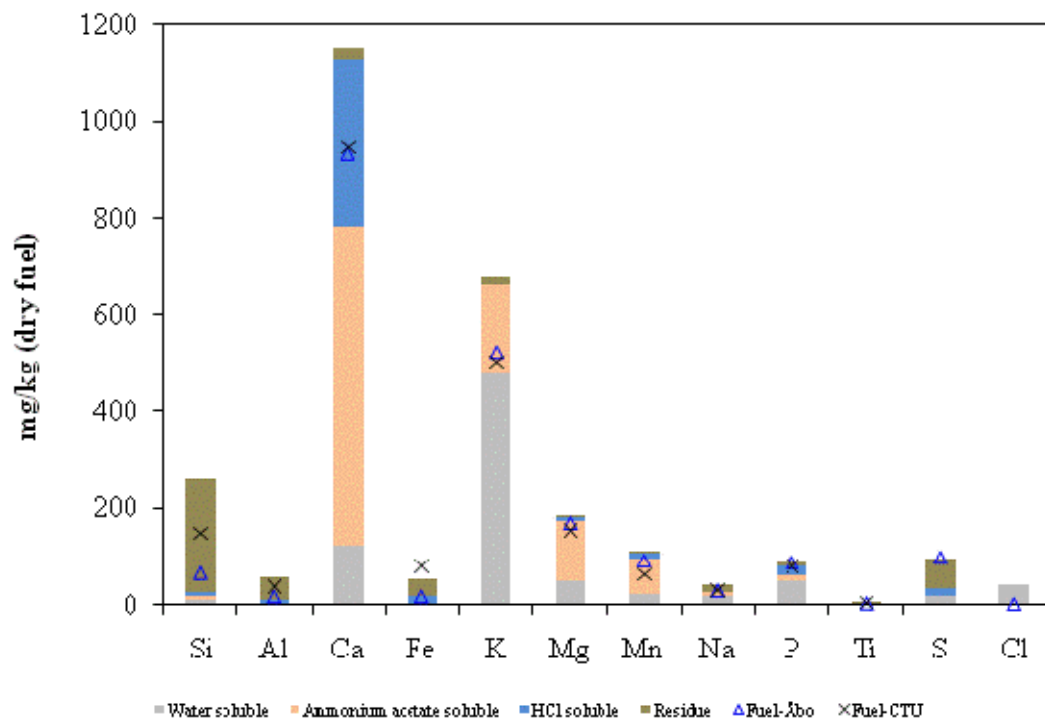
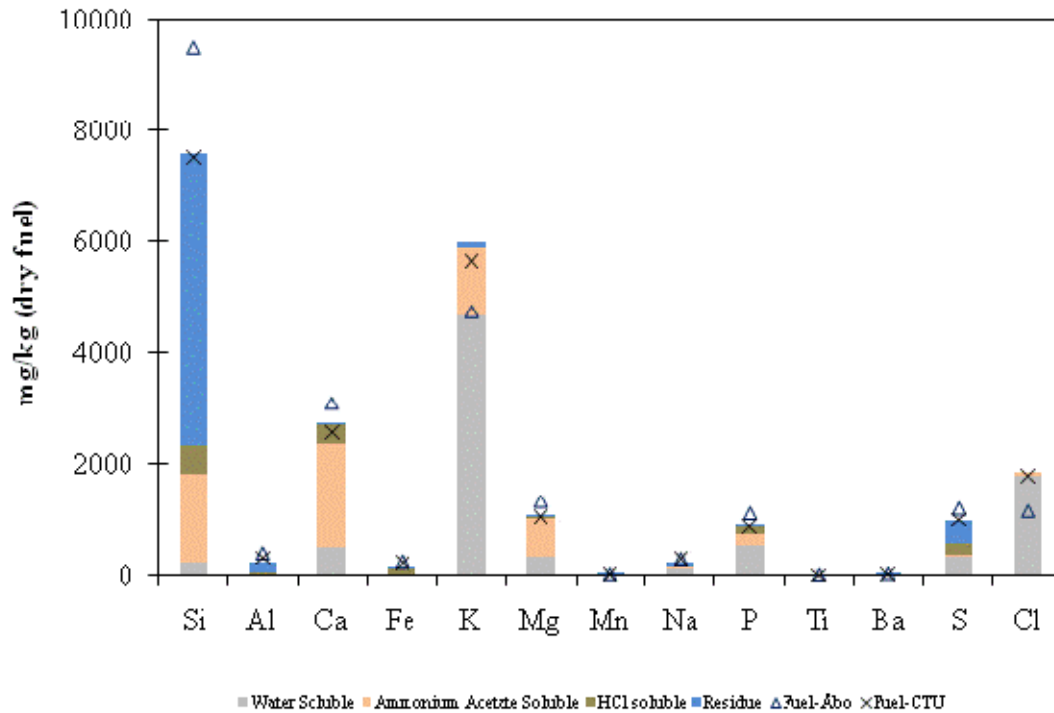


Figure 1: Wood chips characterization results.



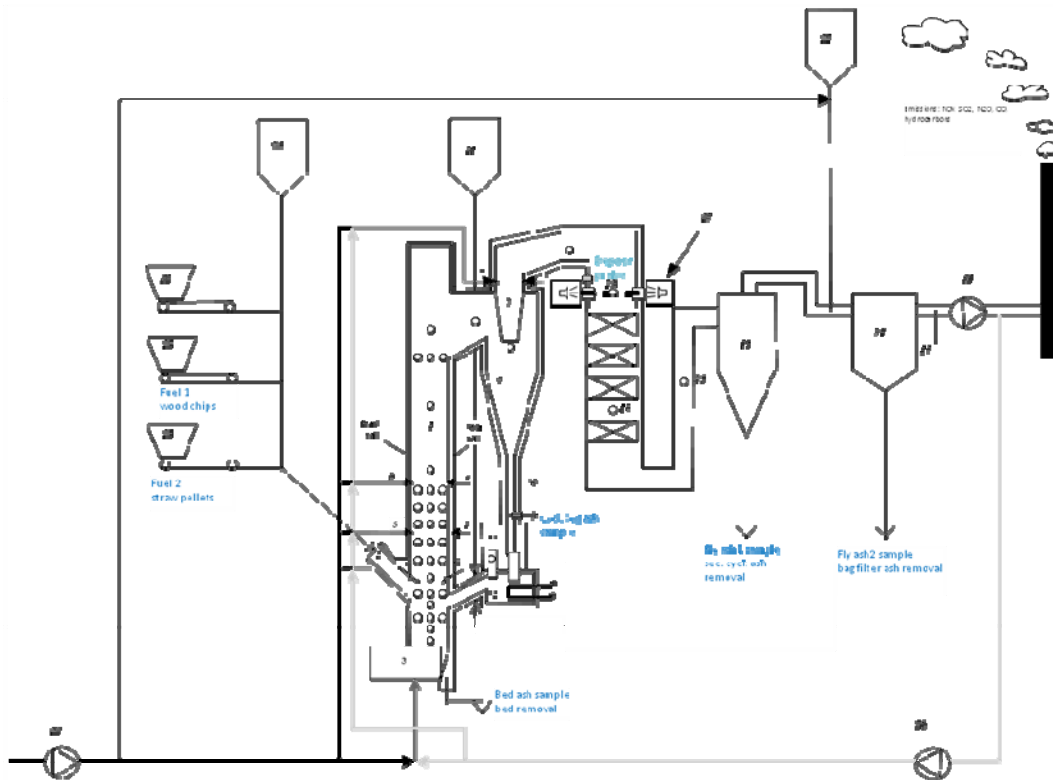
**Figure 2: Straw pellets characterization results.**

## 2.2 Additive

The additive used in the current experiments is ammonium sulphate. The addition of ammonium sulphate (concept developed and patented by Vattenfall AB) is effective for Cl capture and may be one of the most attractive methods for different combustion technologies [48]. The reason is that additive is added in the flue gas in certain temperature window. In the current study, an aqueous solution of ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$  is sprayed into the combustion zone at temperatures around 800-900°C upstream of the superheaters. During the experiments, ammonium sulphate was added in the inlet of the primary cyclone.

## 2.3 Boiler

The measurements were performed during the period 21-22 October 2008, in 12MWth CFB boiler at Chalmers University of Technology. The schematic representation of boiler is shown in Figure 3. The boiler was running at load of 6MWth during the experiments.

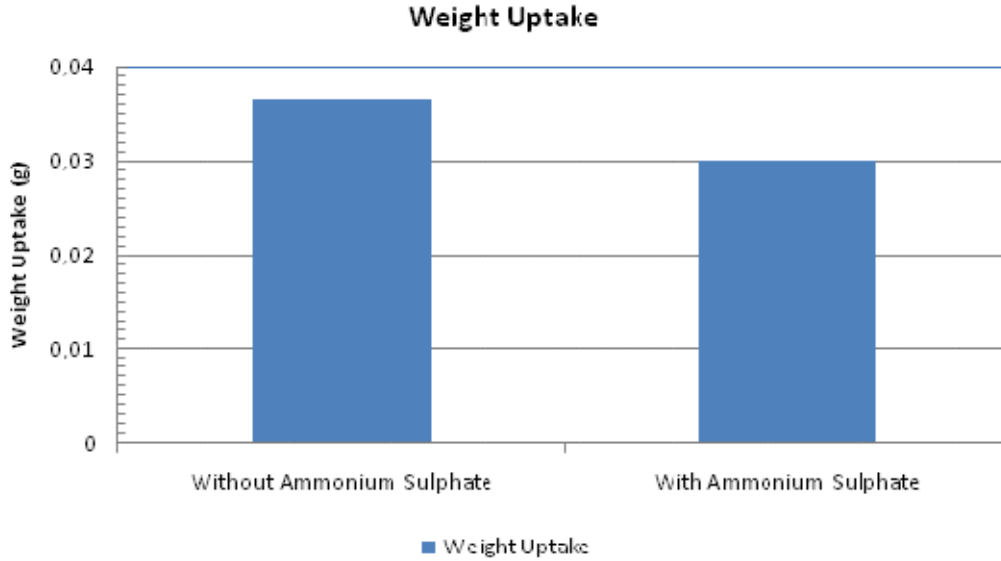


**Figure 3: The 12-MWth CFB boiler at Chalmers University of Technology: (1) combustion chamber; (2) fuel feed chute; (3) primary air to plenum; (4) secondary air inlet at 2.1m; (5) bottom ash removal; (6) hot primary cyclone; (7) particle return leg; (8) particle seal; (9) heat exchanger; (10) cold secondary cyclone; (11) secondary cyclone as removal; (12) bag filters; (13) filter ash removal; (14) flue gas fan; (15) sand bin; (16) lime bin; (17) fuel bunkers; (18) air fan; (19) flue gas recirculation fan [8,9].**

### 3 Results and Discussion

#### 3.1 Weight Uptake

The weight uptake on the deposit ring placed in the superheater region is shown in Figure . It is clear that for approximately similar exposure time and available surface area for the deposit ring, the deposit formed has been reduced by about 35% with the addition of the aqueous solution of ammonium sulphate as an additive. According to Nielsen [5], potassium components play a significant role in the deposit formation. Potassium acts as glue bonding the individual fly ash particles together. Since the melting point of KCl is much lower compared to  $K_2SO_4$ , 774°C and 1059 °C respectively, it can be concluded that at the boiler operating temperature, there is a strong tendency for KCl to melt compared to  $K_2SO_4$ . The reduction of the deposit weight is mainly due to this fact whereby the formation of KCl is reduced while  $K_2SO_4$  is formed with the addition of ammonium sulphate. The presence of  $K_2SO_4$  reduces the uptake of the fly ash particles on the deposit ring.

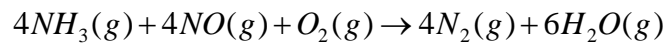
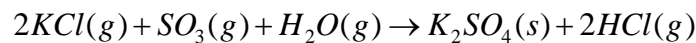


This is one of the possibilities for reduction in deposit weight because

**Figure 4: Weight uptake on the deposit ring with and without deposit.**

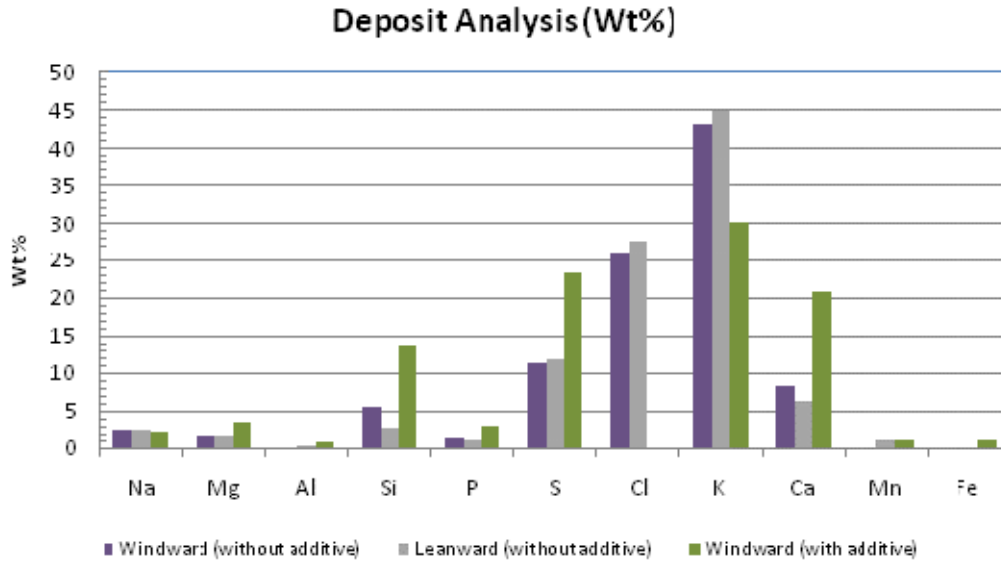
### 3.2 Deposits Analysis

The deposits obtained on deposit ring were analyzed by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray (EDX) technique. It is obvious from Figure the amount of S has been increased with the presence of ammonium sulphate as additive. The additive has effectively converted alkali chlorides i.e KCl into alkali sulphates i.e  $K_2SO_4$ . These sulphates are much less corrosive, having higher melting points than the potassium chlorides and therefore the overall corrosion rate will be reduced [14]. The spraying of ammonium sulphate can also reduce the  $NO_x$  formation [14]. The main reactions [14] involved with the additives are as following;



In the above reactions,  $(NH_4)_2SO_4$  probably decomposes faster than the other sulphates, which then produces  $SO_3$  over a longer furnace zone [14]. The most important point seen from the figures is that there has been no presence of Cl in the deposits when ammonium sulphate is added. This is due to the fact that HCl is formed according to the aforementioned reaction mechanism and escapes in the flue gas. The relative amounts of Si, S and Ca are increased with the addition of additive.

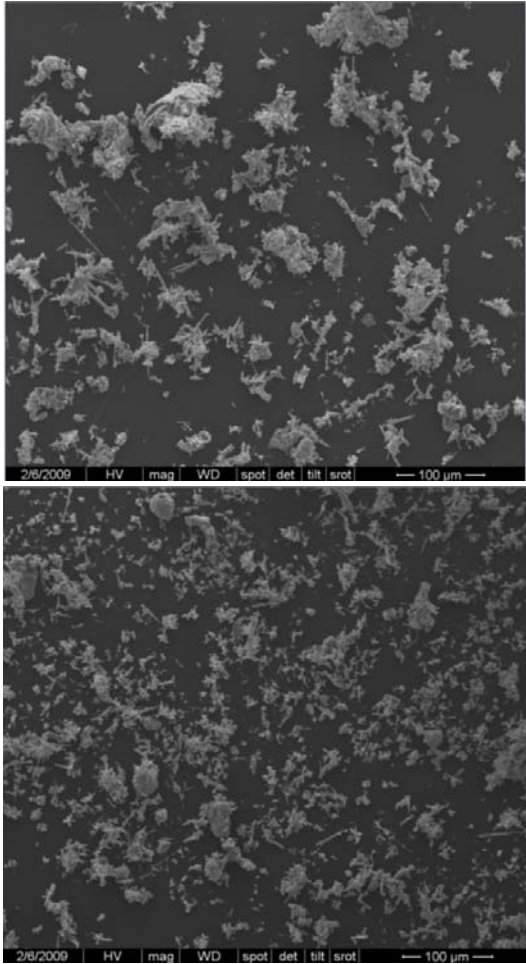




**Figure 5: Elemental composition of the deposits without and with addition of additive a) Windward direction (without additive) b) Lean ward direction (without additive) c) Deposits in the windward direction (with additive).**

When lean ward and windward composition of the deposits are compared (only possible to take lean ward deposits for no additive addition, as the quantity attached to deposit ring was much less to be analyzed), the amount of Si and K is higher in the windward direction. This is due to the fact that Si particles have been attached to the windward direction of the deposit ring through inertial impaction. Cl and S present in about the same amount both in the lean ward and windward direction. The SEM/EDX analysis shows that the deposit samples with and without additives are composed of sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl), potassium (K), calcium (Ca), manganese (Mn) and iron (Fe). Si, S, K, Cl and Ca are the main components and small quantities of Na, Mg, Al, P, Cl, Mn and Fe.

SEM pictures shown in Figure 6 indicate that in the lean ward direction of the deposit ring, particles are of smaller diameter and the particles are approximately evenly distributed. In the windward direction, the particles are of larger size and are widely spaced. The possible reason for these may be because the particles on the lean ward direction are formed through diffusion/condensation and thermophoresis, while in the windward direction the particle attachment is primarily through inertial impaction.



a)

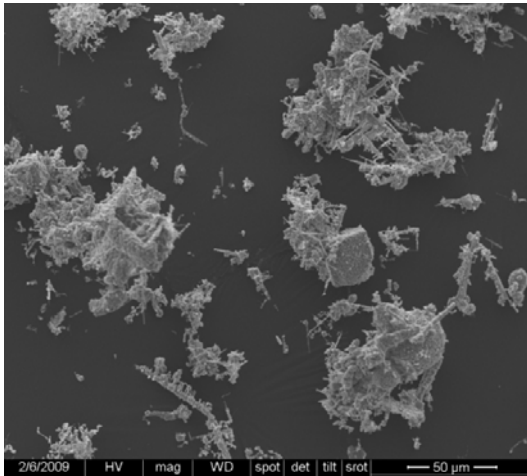
b)

**Figure 6: SEM pictures of deposits without addition of additives a) Windward direction b) Lean ward direction.**

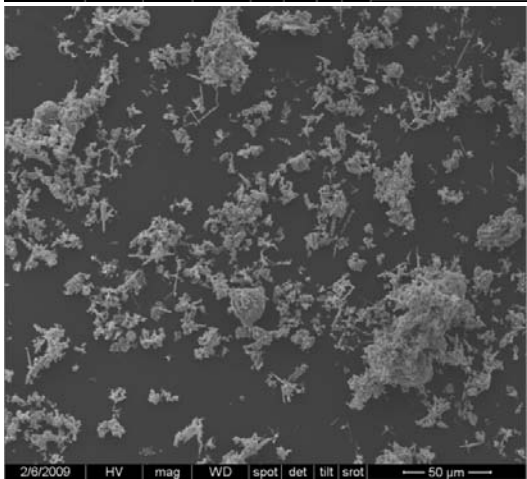
Figure indicates the comparison of spot analysis for 50 micrometers. It is clearly observed from the figure that the addition of ammonium sulphate caused the deposits to appear more spherical and whitish. Further comparison with the windward direction deposits for both with and without the addition of additive shows clearly that the particle size is reduced with the presence of the ammonium sulphate. This is possible as KCl which is stickier as compared to  $K_2SO_4$  has been reduced to  $K_2SO_4$ .

The comparison of lean ward and windward deposits without the addition of ammonium sulphate shows that the particles are hollow and widely spaced. This is also clear from Figure which indicates the hollow particle in the windward direction. The figure indicates that main particle is hollow (sponge shaped) but glued with other particles. This gives clear indication that particles in the windward direction are attached primarily because of inertial impaction. The deposit analysis indicates that Si oxide is present primarily in the windward direction, meaning that silica oxide particle

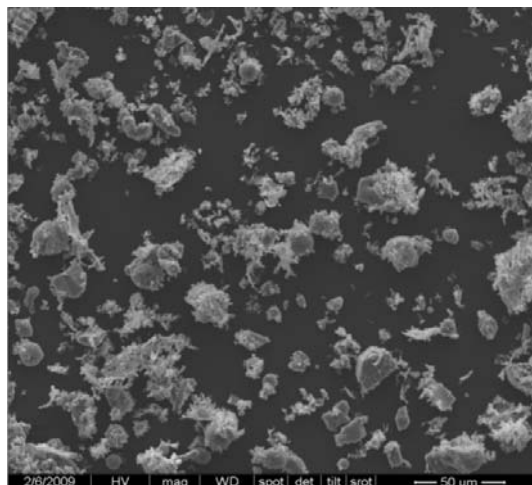
larger than 10 micrometer had attached to the deposit ring in the direction of the flue gas.



a)

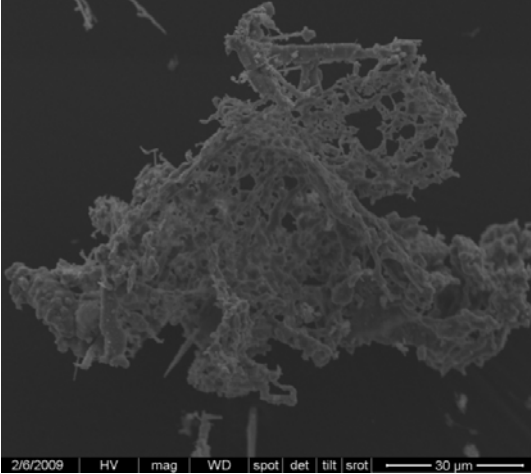


b)

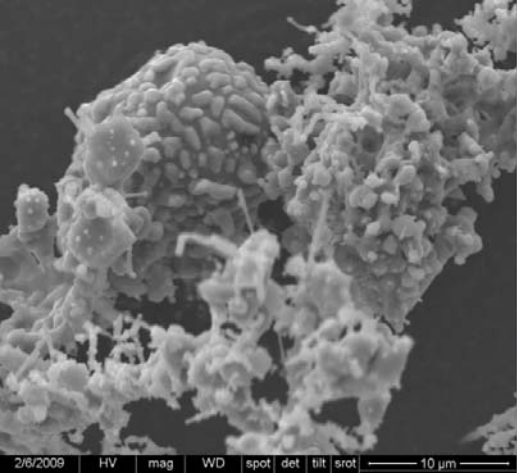
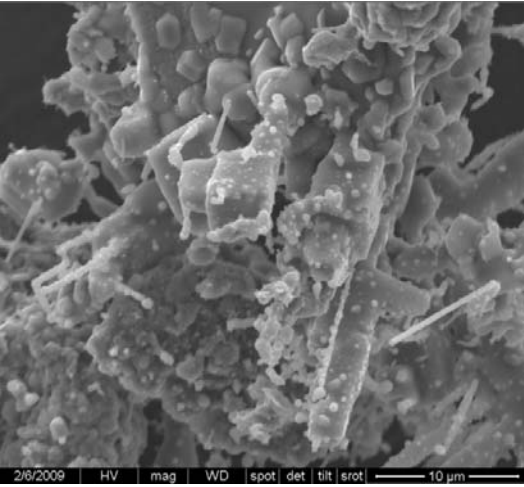


c)

**Figure7: SEM pictures of deposits without and with addition of additives a) Windward direction (without additive) b) Lean ward direction (without additive) c) Deposits in the windward direction (with additive).**



**Figure 8: SEM spot analysis of deposits without addition of additive a) Windward direction.**



a)

b)

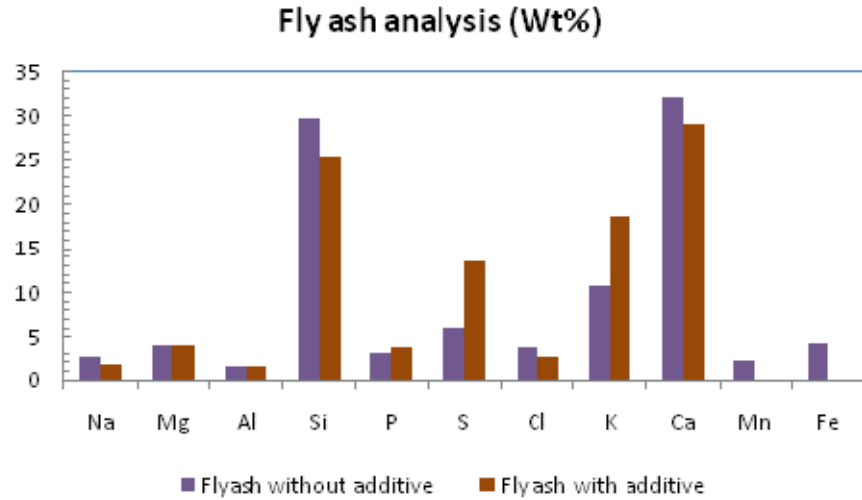
**Figure 9: SEM pictures of deposits without addition of additive a) Windward direction b) Lean ward direction.**

Figure 9 indicates the comparison of particles both in the lean ward and windward direction without the addition of additive for spot SEM analysis of 10 micrometer. The figure clearly illustrates that the particles in the windward direction are larger and hollow in structure, while particles in the lean ward direction are almost spherical in nature, smaller in size and more homogeneous as compared to particles in the windward direction. Whitish color of deposits collected indicates that more  $K_2SO_4$  is attached in the lean ward direction compared to windward direction on deposit quantitative ratio. It is also clear that outer part predominantly formed from K, Si and Ca in the windward direction.

### 3.3 Fly ash Analysis

The SEM/EDX analysis shows that the fly ash samples with and without additives from the secondary cyclone are composed of sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl), potassium (K), calcium (Ca), manganese (Mn) and iron (Fe). Si, S, K and Ca are the main components and small quantities of Na, Mg, Al, P, Cl, Mn and Fe.

It is shown in **Error! Reference source not found.**, Na, Si, Cl and Ca have been successfully reduced with the presence of ammonium sulphate. Ammonium sulphate plays a major role in the formation of  $Na_2O$ ,  $SiO_2$ ,  $KCaSO_4$  and HCl. On the other hand, the weight percent of P, S and K elements have been increased with the addition of ammonium sulphate. The increment of S by almost double the content before the addition of additives can be contributed by the sulphur element present in the ammonium sulphate. P increased only by 17%. P could be reduced by formation of  $P_2O_5$ . 100% reduction of manganese and iron are due to the oxides formations namely  $MnO_2$  and  $Fe_2O_3$ . It should be noted that the oxygen (O) contents detected by SEM are neglected in the results shown in this study in order to focus on the major inorganic elements.



**Figure 10: Elemental composition of fly ash with and without the addition of ammonium sulphate.**

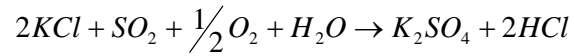
The overall elemental composition and distribution of elements in terms of molar ratios is presented in the following Table 1.

**Table 1: Change in elemental composition and molar ratios during addition of ammonium sulphate as additive.**

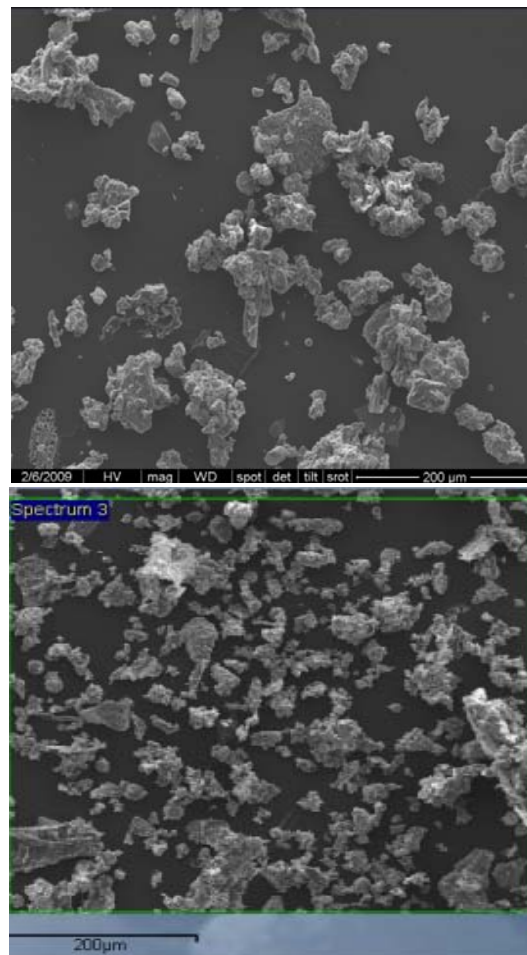
Sample	Deposit		Deposit	Fly ash	
Position	Windward	Leanward	Windward	Sec. Cyclone	Sec. Cyclone
Additive Use	Without additive	Without additive	With additive	Without additive	With Additive
Elements	wt%	wt%	wt%	wt%	wt%
Na	2,553	2,560	2,238	2,701	1,688
Mg	1,711	1,681	3,639	4,105	3,859
Al	0,000	0,376	0,732	1,431	1,592
Si	5,442	2,685	13,595	29,841	25,470
P	1,515	0,954	3,117	3,106	3,618
S	11,417	11,895	23,321	6,022	13,507
Cl	25,891	27,629	0,000	3,565	2,508
K	43,086	44,969	29,973	10,802	18,717
Ca	8,387	6,248	20,874	32,028	29,040
Mn	0,000	1,004	1,255	2,079	0,000
Fe	0,000	0,000	1,255	4,321	0,000
<b>Molar Ratios</b>					
K/(2S+Cl)	0,764	0,756	0,527	0,580	0,524
Cl/K	0,663	0,678	0,000	0,364	0,148

2S/K	0,646	0,645	1,898	1,360	1,760
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The presence of excessive sulphur content reduces the formation of KCl in the flue gas by the following reaction [1].



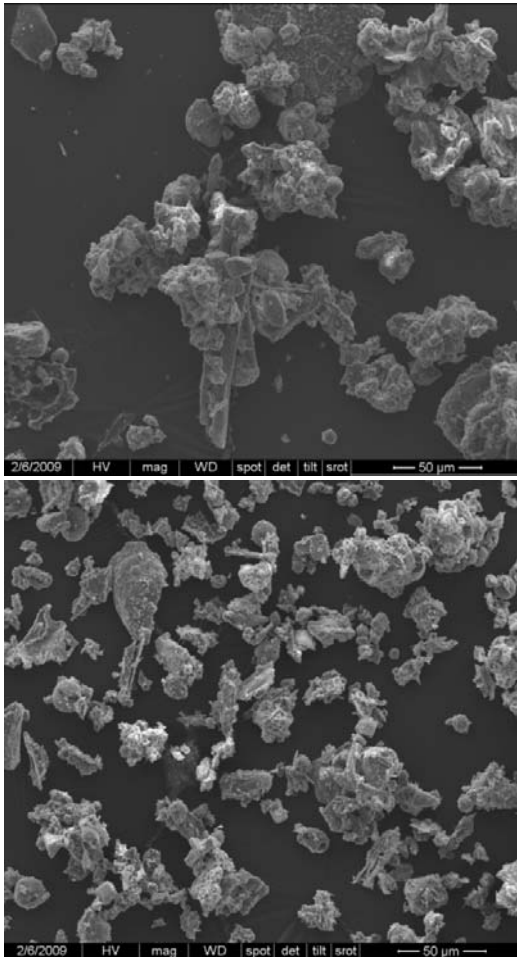
The additive, ammonium sulphate decomposes to SO<sub>3</sub>. SO<sub>3</sub> reacts directly with K to form K<sub>2</sub>SO<sub>4</sub>. This explains the increase of potassium by 72% with addition of ammonium sulphate. The main contributors to potassium increase are the presence of KCl and K<sub>2</sub>SO<sub>4</sub>. Calcium reduction can be due to the formation of potassium calcium sulphates. Since potassium has higher affinity towards chlorine and sulphates, calcium is only reduced by 10%. Cl is reduced by 30% with the formation of HCl.



a)

b)

**Figure 11: SEM pictures of fly ash a) without and b) with the addition of additives for 200 μm.**



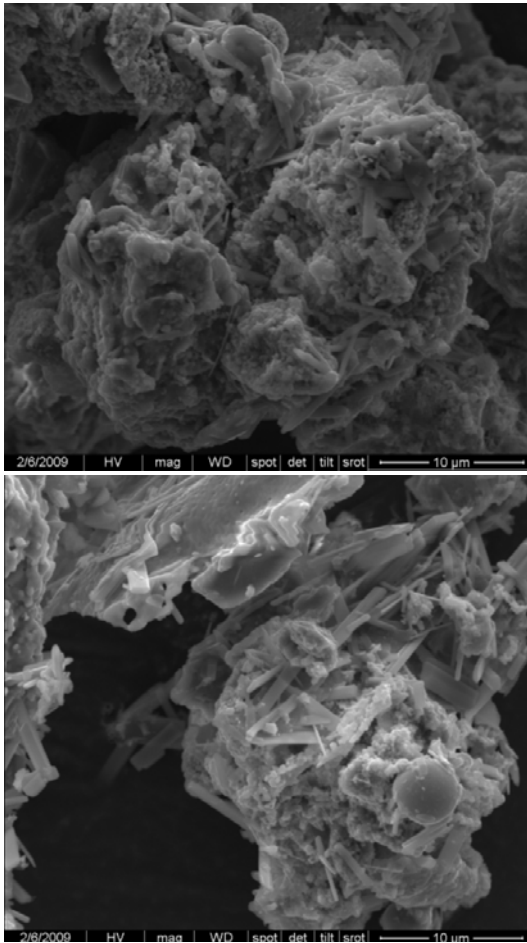
a)

b)

**Figure 12: SEM pictures of fly ash a) without and b) with the addition of additives for 50µm.** Figure 11 shows that with the addition of ammonium sulphate the fly ash particles forms smaller and more spherical particles compared to the sample without ammonium sulphate. Furthermore it is also obvious that with addition of ammonium sulphate produces some whitish compounds in the fly ash. This can be mainly due to the formation of  $K_2SO_4$ . It is clear from Figure 11 that the particle size distribution is more even than the one without the addition of ammonium sulphate.

By comparing the particle size of 50 µm for both cases as shown in Figure, particles with the addition of ammonium sulphate appears denser than the one without ammonium sulphate. This can be probably due to the presence of KCl in the fly ash without ammonium sulphate while due to the presence of  $K_2SO_4$  in the case of addition of ammonium sulphate.





a)

b)

**Figure 13: SEM pictures of fly ash a) without and b) with the addition of additives for 10 µm.**

Figure 1 shows that the particle size of 10 µm both cases. In the case of without ammonium sulphate the particles appears more lumpy than the case with ammonium sulphate.

## 4 Conclusions

The addition of ammonium sulphate as an additive in the combustion zone of a boiler has shown a positive effect. The addition of the additive has successfully reduced the amount of deposits formed by reducing the formation of KCl. The SEM/EDX analysis of the deposits formed shows that the addition of the additive plays a vital role in converting the alkali chlorides to alkali sulphates. The most favorable reduction is of Cl. The formation of Cl in the deposit has been totally eliminated via the formation of  $K_2SO_4$ . This reaction has also favored in the reduction of the KCl formation. The SEM/EDX analysis of the fly ash samples from the secondary cyclones shows that the amount of S has increased almost by 50% with the addition of additives. This can be contributed by the S element present in the ammonium sulphate. A major conclusion can be drawn by stating that the addition of the ammonium sulphate has reduced the formation of deposits which is one of the most important factors in the boiler.

## 5 References

- [1] Anna-Lena Elled; Co-combustion of Biomass and Waste Fuels in a Fluidized Bed Boiler, Phd Thesis, Chalmers University of Technology, 2008.
- [2] A. Zbogar, F. J. Frandsen, P. A. Jensen and P. Glarborg, (2006), Literature Study: Shedding of Ash Deposits. PSO Project 4106, CHEC Research Center, Technical University of Denmark.
- [3] L. Hindiyarti, (2007), Gas Phase Sulfur, Chlorine, and Alkali Metal Chemistry in Biomass Combustion. PhD Thesis, Technical University of Denmark.
- [4] F. J. Frandsen, (2005), *Fuel*. (84) 1277-1294.
- [5] H. P. Nielsen, (1998), Deposition and High Temperature Corrosion in Biomass-Fired Boilers. PhD Thesis, Technical University of Denmark.
- [6] C. Yin, L. A. Rosendahl and S. K. Kær., (2008), *Prog Energy Combust Sci*, (35), 725-754.
- [7] B.M. Jenkins, L.L. Baxter, T.R. Miles (J) and T.R. Miles (1998), *Fuel Processing Technology*, (54) 17-46.
- [8] P. A. Jensen, M. Stenholm and P. Hald, (1997), *Energy and Fuels*. (11) 1048-1055.
- [9] K. O. Davidsson, L. -E. Åmand and B. Leckner, (2007), *Energy and Fuels*. (21) 71-81.
- [10] K. O. Davidsson, L. -E. Åmand, B. -M. Steenari, A. -L. Elled, D. Eskilson and B. Leckner, (2008), *Chemical Engineering Science*. (63) 5314-5329.
- [11] L. S. Johansson, B. Leckner, C. Tullin, K. O. Davidsson and L. -E. Åmand, (2008), *Energy and Fuels*. (22) 3005-3015.
- [12] K. H. Andersen, (1998), Deposition Formation during Coal Straw Co-Combustion in a Utility Pf-Boiler. PhD Thesis, Technical University of Denmark.
- [13] L. L. Baxter, (1993), *Biomass and Bioenergy*, (2) 85-102.
- [14] ChlorOut. European Patent EP 1354167. (2002) International Patent Application: PCT/SE 02/00129.