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# Co-combustion of solid recovered fuel with coal in an entrained flow reactor and the effect of additives

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## Abstract

Co-combustion of a bituminous coal (COCERR) and a solid recovered fuel (SRF) was carried out in a 5KW entrained flow reactor, and the effects of different additives including NaCl, PVC, ammonium sulphate (AmSulf), and Kaolin on co-combustion were investigated. Different SRF shares, 7.9%, 14.8% and 25% (weight basis), were applied in the co-combustion experiments, and the effects of different additives on co-combustion were evaluated by maintaining the coal share at 85.2%. The experimental results showed that the both the NO and SO<sub>2</sub> emissions in co-combustion of coal and SRF decreased with increasing share of SRF. Most of the additives did not have significant impacts on the emissions of NO, except for the AmSulf which showed significant reduction effects on NO. For SO<sub>2</sub> emissions, it was found that all of the additives increased the retention of sulphur in the ashes. Analysis of the compositions of ashes from experiments showed that the majority of the S and Cl in the fuels was released to the gas phase during combustion, whereas the K and Na in the fuels were mainly retained in the ashes, with a slight enrichment in smaller particles. In co-combustion of coal and SRF, the majority of K and Na (~99%) in the fuels was present in a water insoluble form. The addition of NaCl, PVC, and AmSulf generally increased the overall vaporization of K and Na, resulting in increased formation of water soluble alkalis, whereas the addition of Kaolin showed a slight reduction effect on the formation of water soluble alkalis. During the experiments, ash deposits were formed on an air-cooled probe, with a flue gas temperature of 800 °C and a probe surface temperature of 550 °C. The results showed that the deposition propensity of the fly ashes in co-combustion generally decreased with increasing share of SRF. The addition of NaCl and PVC increased the ash deposition propensity, whereas the addition of AmSulf and Kaolin showed opposite effects. The Cl content in the deposits generally indicated a low corrosion potential, except for the cases with NaCl and PVC additions.

## 1. Introduction

Direct co-combustion of coal and secondary fuels in a pulverized coal-fired power plant is recognized as one of the most convenient and advantageous methods to replace part of coal consumption by more CO<sub>2</sub>-friendly fuels such as biomass and waste [1]. Besides the effect on the reduction of CO<sub>2</sub> emissions, co-combustion of coal and secondary fuels in an existing coal-fired boiler may influence the operations and performances of a boiler. To evaluate the possible influences of adding a secondary fuel on a pulverized coal-fired power plant and to optimize the technology, a number of co-combustion investigations have been carried out in full-scale boilers [2-5], pilot-scale reactors [6-10], and laboratory-scale instruments [11,12]. The secondary fuels which gained majority of the interests were straw [2,3,6,7,9], wood [4,5,7,10], sewage sludge [10,13,14], and waste derived fuels [10,15,16]. The main focuses of the studies were on the fuel burnout [3,7], SO<sub>2</sub> and NO emissions [4,7], ash deposition and corrosion [2,6,8,10], fly ash qualities [17], formation of fine particles [13,18], and the performances of SCR system in co-combustion [13].

Solid recovered fuel (SRF) derived from nonhazardous waste streams such as industrial waste and bulky waste is considered as an advantageous secondary fuel to be co-fired in pulverized coal-fired power stations [19]. Although waste is normally regarded as a highly heterogeneous fuel with low thermal value, the production technologies of SRF can significantly improve the combustion properties of waste. After processing steps such as screening, mechanical sorting and size reduction, the lower heating value of SRF could become approximately 20 MJ/kg (dry basis) [19,20], which is comparable to biomass such as straw and wood. Besides, SRF can be produced as a fluffy form which has the possibility to be blown into a pulverized coal-fired boiler directly, by using a similar injection method that has been applied for grinded straw particles [21]. Moreover, since SRF normally contains 40-80 wt% of biogenic components [19], co-combustion of coal and SRF could reduce the CO<sub>2</sub> emissions from a pulverized coal-fired power plant. Furthermore, it also has the potential to increase the efficiency of utilizing waste fuels, as the electrical efficiency of a pulverized coal-fired plant is usually 10-20% higher than that of a dedicated waste

incineration plant. If the SRF contains lower nitrogen and sulphur content than the coal, the emissions of NO<sub>x</sub> and SO<sub>x</sub> from the boiler may be decreased by co-firing the coal with the SRF.

Besides the potential advantages mentioned above, several problems may be associated with co-combustion of coal and SRF. In comparison with coals, SRF is usually characterized of higher chlorine content (0.3-0.8 wt%, dry basis [19,20,22]). When coal is co-fired with SRF, the high chlorine content in the SRF may lead to severe ash deposition and corrosion problems in the boiler, since the organically associated alkalis in the coal and SRF may react with the chlorine forming alkali chlorides which may enhance deposit formation and corrosion of superheaters. The contents of some trace element in SRF may be considerably higher (typically 1 order of magnitude) than those in coals [19,20,22]. Therefore, co-combustion of coal and SRF may significantly increase the trace element emissions from a pulverized coal-fired power plant, and generate fine particles which are potentially more harmful than those from dedicated coal combustion [16]. In addition, since SRF is a more heterogeneous fuel than coals, the variation of SRF properties may be significant in practical operations and may greatly influence the co-combustion behavior of coal and SRF. Moreover, co-combustion of coal and SRF may also influence the fly ash qualities, formation of fine particles, and the performance of SCR system in a pulverized coal-fired power plant.

To evaluate the feasibility of co-combustion of coal and SRF, it is desirable to study the combustion behavior of the fuel mixture in a condition similar to a real pulverized coal-fired plant. With this purpose, co-combustion behaviors of a bituminous coal (COCERR) and a SRF were studied in a 5KW entrained flow reactor (EFR). In this study, the effect of different SRF share (7.9 wt%, 14.8 wt%, and 25 wt%) was investigated. In order to further evaluate the potential influences of the variation of SRF properties on co-combustion, different additives (including NaCl, PVC, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (AmSulf), and Kaolin) were blended with the mixture of coal and SRF, and combusted in the EFR. The focuses of this study are on the influences of SRF and coal co-firing as well as the injection of additives on the emissions of NO and SO<sub>2</sub>, the ash deposition on an air-cooled probe, and the properties of the ashes and deposits from the experiments.

## 2. Experimental

### 2.1 Fuels and additives

A Columbian bituminous coal (COCERR) and a SRF mainly consists of waste paper, plastic and wood were chosen as the fuels in this study. The investigated additives included PVC, NaCl, AmSulf and Kaolin. The properties of the fuels and additives are given in Table 1. It can be seen that the SRF is of higher volatile, Cl and Ca contents than the COCERR coal, while the COCERR coal contains relatively higher ash, N, S, Si, Al and K contents than the SRF. The additives used in this study are mostly pure compounds, with chemical compositions shown in Table 1.

Table 1 Properties of fuels and additives

Properties	COCERR coal	SRF	PVC*	NaCl	AmSulf	Kaolin
LHV (MJ/kg wet)	26.53	20.86	19.88	-	-	-
Moisture (wt% wet)	5.25	5.20	1.10	0.04	0.08	0.98
Volatiles (wt% wet)	34.11	72.05	98.90	-	99.92	-
Ash (wt% wet)	10.42	5.69	-	99.96	-	85.20
C (wt% dry)	71.00	58.00	38.40	-	-	-
H (wt% dry)	4.90	6.60	4.80	-	5.33	1.55
N (wt% dry)	1.50	1.00	-	-	30.67	-
S (wt% dry)	0.70	0.42	-	-	21.33	-
Cl (wt% dry)	0.03	0.28	56.80	60.68	-	-
Si (wt% dry)	3.06	1.08	-	-	-	22.75
Al (wt% dry)	1.21	0.21	-	-	-	20.05
Mg (wt% dry)	0.15	0.09	-	-	-	0.17
P (wt% dry)	0.02	0.02	-	-	-	-
Ca (wt% dry)	0.18	0.67	-	-	-	0.03
Na (wt% dry)	0.07	0.11	-	39.32	-	0.58
K (wt% dry)	0.21	0.09	-	-	-	1.32

\* The heating value of PVC is estimated from [23].

To be able to feed into the reactor, both of the COCERR Coal and SRF were pulverized by an Alpine<sup>®</sup> pin mill. The particle size distributions of the fuels and additives are determined by an analyzer using laser diffraction method (Malvern Mastersizer 2000 particle size analyzer). It is found that the d<sub>50</sub> (meaning that 50 vol% of the particles are below this size) of SRF is approximately 164μm, while the d<sub>50</sub> of COCERR coal is about 19μm, which is significantly smaller than that of SRF. The d<sub>50</sub> of PVC, NaCl, AmSulf, and Kaolin is approximately 104μm, 259μm,

222 $\mu\text{m}$ , and 8 $\mu\text{m}$  respectively. In addition to the differences on particle size, it should be noted that the SRF particles do more easily form agglomerates compared to the coal particles. Thus, the actual particle size of SRF in the experiments may be larger than that obtained by the particle size analyzer.

## 2.2 Setup

The experiments were carried out in the CHEC entrained flow reactor which is designed to simulate the combustion environment of a suspension fired boiler. A schematic drawing of the setup is shown in Figure 1. The setup consists of a gas supplying system, a fuel feeding system, a gas preheater, a vertical reactor which is electrically heated by 7 heating elements, a bottom chamber, a particle and gas extraction system, and a deposition system which is designed to simulate deposit formation on the superheater tubes of a boiler. More detailed description of the reactor can be found in [6].

In co-combustion experiments, the fuel particles are injected into the reactor together with primary air. To have a comparable residence time ( $\sim 1\text{s}$ ) for different experiments, the flow rate of the primary air and total air is maintained at 13 NI/min and 95 NI/min respectively. The feeding rate of the fuel particles is controlled by a gravimetric screw feeder, and is adjusted for different experiments in order to control the excess air ratio to be approximately 1.43. The injected fuel particles are mixed with preheated secondary air at the inlet of the vertical reactor, and consequently the combustion of the particles takes place in the reactor. The temperature of the heating element in the preheater is set to be 900 $^{\circ}\text{C}$ , and the wall temperature of the vertical reactor is set to be 1000-1300  $^{\circ}\text{C}$  for all of the experiments.

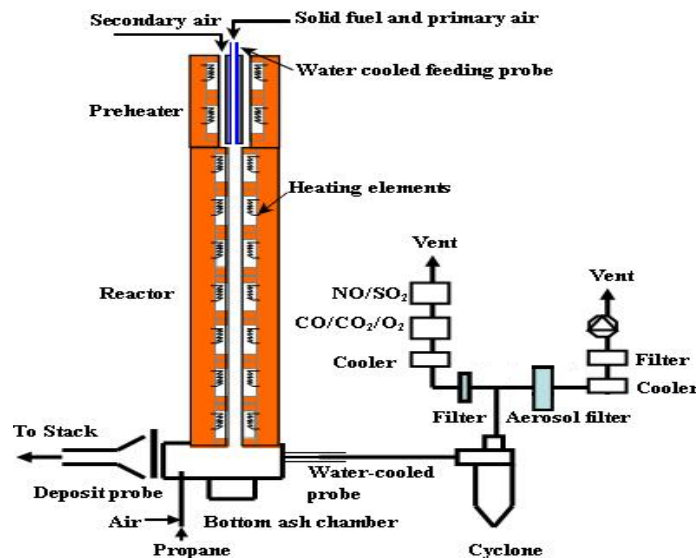


Figure 1 Schematic draw of the CHEC entrained flow reactor (modified from [6]).

During combustion experiments, the bottom ashes are collected in a metal collector placed at the bottom chamber. The flue gases from combustion are separated to two directions. As shown in Figure 1, a minor part of the flue gas is drawn to an extraction system through a water-cooled probe. In the extraction system, large fly ash particles are collected by a cyclone with a cut diameter of 2.5  $\mu\text{m}$ , and fine fly ash particles going through the cyclone are gathered in an aerosol filter using a polycarbonate membrane with a pore size of 0.1 $\mu\text{m}$ . Concentrations of CO, CO<sub>2</sub>, O<sub>2</sub>, NO and SO<sub>2</sub> are measured in the extraction system by two gas analyzers. Apart from the flue gas that is drawn by the extraction system, the major part of the flue gas from the combustion is directed toward a deposit probe which is designed to simulate the superheater tubes in a real boiler. In front of the deposition probe, a propane burner is mounted to control the flue gas temperature to be 800  $^{\circ}\text{C}$ . The air-cooled deposit probe used in this study is made of stainless steel, with an outer diameter of 1 cm and a length of 10 cm. During the experiment, the deposit probe is placed in front of the exit slit of bottom chamber which has a size of 4\*8 cm. By adjusting the temperature of the air preheater and the heating tape connected to the probe, the surface temperature of the deposit probe is controlled to be 550  $^{\circ}\text{C}$  during the experiments.

The duration of an experiment is 1.5 hours. To achieve a stable combustion condition, the reactor is preheated to operational temperatures and kept over-night, and the fuel injection begins 40 minutes prior to the start of an

experiment. After the experiment, the deposits on the probe, the ashes from extraction tubes, cyclone, aerosol filter, and bottom chamber are collected, weighted and preserved for chemical analysis. With the purpose of minimizing the influences of the deposit built-up inside the reactor on the experimental results, the reactor is heated to 1400 °C for 20 hours after every experiment, to perform high temperature cleaning.

### 2.3 Experimental matrix

The experimental matrix and the excess air ratios of different experiment are shown in Table 2. In the experiments at which COCERR and SRF are co-combusted, the mass share of SRF is chosen as 7.9 wt%, 14.8 wt% and 25.0 wt%, which corresponds to a thermal share of 6.3 th%, 12.0 th% and 20.8 th% respectively. In the experiments with additives, the mass share of COCERR coal is maintained at 85.2 wt%, and the mass share of secondary fuels (SRF + additives) is kept at 14.8 wt%. With fixed mass share of COCERR coal, the addition of additives can be regarded as a significant variation of the SRF properties. The addition of NaCl (1 wt% and 2 wt%) is aimed to simulate a SRF with considerable high alkali chloride contents, while the addition of PVC (2 wt% and 4 wt%) gives the SRF a significant high chlorine content. For the addition of AmSulf and Kaolin, the main objective is to study the co-combustion behavior of SRF with a coal that is rich in S or aluminosilicates contents. To ensure all of the experiments to be carried out at similar combustion conditions, the excess air ratio for different experiments was controlled at around 1.43, as shown in Table 2.

Table 2 Experimental matrix and excess air ratios

Experiment	Fuel composition wt%						Feeding rate (kg/h)	Excess air ratio
	COCERR Coal	SRF	NaCl	PVC	AmSulf	Kaolin		
1*	100	-	-	-	-	-	0.582	1.44
2*	92.1	7.9	-	-	-	-	0.594	1.43
3*	85.2	14.8	-	-	-	-	0.607	1.42
4*	75	25.0	-	-	-	-	0.629	1.39
5*	85.2	13.8	1.0	-	-	-	0.623	1.42
6	85.2	12.8	2.0	-	-	-	0.615	1.42
7*	85.2	12.8	-	2.0	-	-	0.604	1.43
8	85.2	10.8	-	4.0	-	-	0.604	1.43
9	85.2	10.8	-	-	4.0	-	0.618	1.42
10	85.2	10.8	-	-	-	4.0	0.631	1.42

\*Repetition experiments have been performed.

### 2.4 Ash/deposit analysis

The ash/deposit samples from the experiments were analyzed at Enstedværket Laboratory, DONG Energy A/S. The contents of Al, Ca, Fe, K, Mg, Na, P, Si, Ti, S, and Cl in the bottom ashes, cyclone ashes, and aerosols were analyzed by ICP-OES (inductively coupled plasma optical emission spectrometry). Furthermore, the water soluble K, Na, Cl and S contents in the cyclone ashes and deposits were analyzed by ICP-OES. During the analysis of water soluble elemental contents, the ash/deposit sample is dissolved in ultra-pure water at 120 °C for 1 hour, and then the solution is filtered and analyzed by ICP-OES. Two different liquid/solid ratios (80 and 40) were used in determining the water soluble elements in cyclone ashes and the obtained results were in good agreement.

## 3. Results and discussion

### 3.1 NO emission

The NO emissions (ppmv, dry, 6 % O<sub>2</sub>) from different experiments are shown in Figure 2a. It is seen that the emission of NO from co-combustion of coal and SRF decreases with increasing share of SRF, which is in agreement with the fact that the SRF used in the experiments has lower nitrogen content than the coal. The addition of NaCl, PVC or Kaolin generally does not affect the NO emission, whereas the addition of AmSulf reduces the NO emission significantly. The reduction effect is likely caused by the NH<sub>3</sub> yielded by the thermal decomposition of AmSulf, which occurs at temperature higher than 257 °C [24] and the final products are NH<sub>3</sub>, SO<sub>3</sub> and H<sub>2</sub>O [25]. The released NH<sub>3</sub> may go through two major pathways, i.e. either reacting with O<sub>2</sub> to form NO, or reacting with NO to form N<sub>2</sub> [26]. For the AmSulf particles used in the experiments which result in reduced NO emission, the reaction between NO and NH<sub>3</sub> is probably the dominant pathway. To further investigate the behavior of AmSulf particles in the experiments, it is necessary to know the decomposition rate of AmSulf particles at different temperature as well as the temperature profile of the particles in the reactor, which are outside the scope of this study.

To neglect the dilution effect caused by fuel nitrogen content, the percentage of fuel nitrogen that is converted to NO has been calculated for different experiments, by assuming all the NO in the flue gas is formed from fuel nitrogen. From Figure 2b, it can be seen that with increasing share of SRF, the conversion of fuel nitrogen NO decreases. This is in agreement with the results from co-combustion of coal and straw/wood, which showed decreased fuel nitrogen conversion to NO with increasing share of straw/wood [27]. The reduced conversion of fuel nitrogen to NO in co-combustion of coal and SRF is likely related with the high volatile content of SRF, with which a reduction zone with lower excess air ratio may be generated near the burner, when part of the coal is replaced by the SRF. The lower oxygen concentration in the reduction zone may inhibit the conversion of fuel nitrogen to NO, resulting in reduced NO formation [27]. In addition, since the formation of thermal NO is not negligible in the EFR experiments, it may be the case that co-combustion of coal and SRF would result in a lower flame temperature than that in dedicated coal combustion, thus leading to reduced formation of thermal NO. This hypothesis is possible as the flame temperature of a refuse derived fuel (RDF) is found to be 200-300 °C lower than the coal flame, at same excess ratio condition [28].

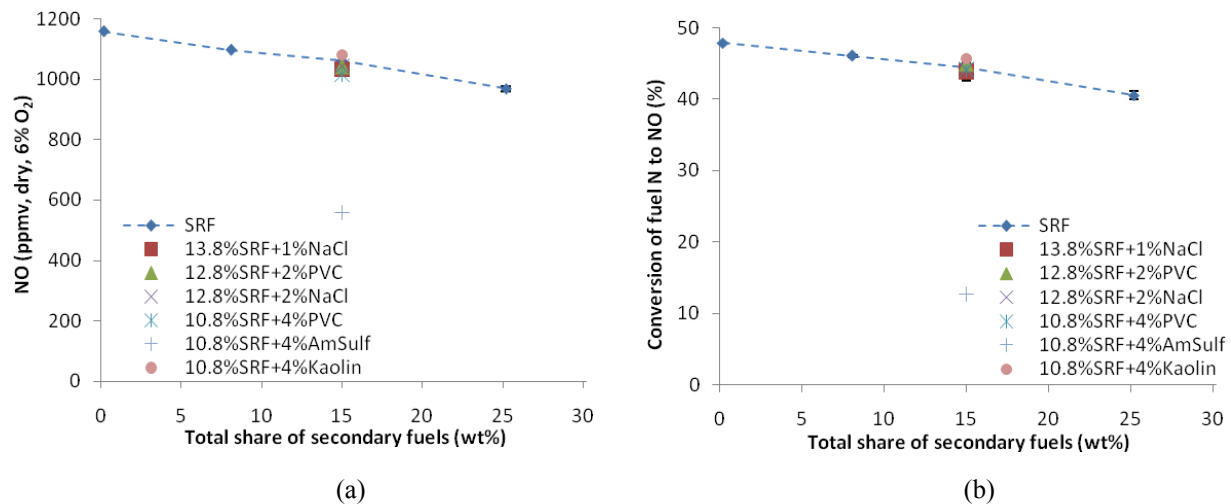


Figure 2 (a) NO emissions (ppmv, dry, 6 % O<sub>2</sub>) from EFR experiments with different shares and types of secondary fuels, (b) Conversion of fuel nitrogen to NO (%) in EFR experiments with different shares and types of secondary fuels, by assuming the NO generated during combustion is totally from fuel nitrogen

### 3.2 SO<sub>2</sub> emission

Figure 3a shows the emissions of SO<sub>2</sub> (ppmv, dry, 6 % O<sub>2</sub>) from different EFR experiments. It can be seen that the emission of SO<sub>2</sub> decreases slightly with increasing share of SRF. This is consistent with the fuel properties, i.e. the SRF contains less sulphur than the COCERR coal. With the same share of secondary fuels, the addition of NaCl, PVC or Kaolin does not largely affect the emission of SO<sub>2</sub>. However, the addition of 4 wt% AmSulf significantly increases the SO<sub>2</sub> emission, probably because a certain fraction of SO<sub>3</sub> released from the decomposition of AmSulf has been converted to SO<sub>2</sub> during the experiment.

To further investigate the influences of co-combustion on the behavior of sulphur in combustion, the percentage of sulphur that is retained in ashes is calculated for different experiments, based on the input of the fuel sulphur and the composition and amount of the collected bottom ashes, cyclone ashes and aerosols. As shown in Figure 3b, it can be seen that the retention of sulphur generally increases with increasing share of SRF. A primary reason for this is that the SRF contains more calcium than the COCERR coal, which would promote the formation of calcium sulphate and retain more sulphur in ashes. Similar retention effects have been found when coal is co-fired with wood that has high calcium content [7]. The additives also show some effects on the retention of sulphur in the ashes. For the addition of NaCl, it can be seen that higher percentage of sulphur is retained in the ashes, in comparison with that of co-combustion of coal and SRF. The observed increase of sulphur retention in ashes is probably related with the sulphation reaction between gaseous sulphur and the added NaCl. Similar effects have been seen in straw and coal co-combustion, where the retention of sulphur was found increased in co-combustion due to the high potassium content in straw [27]. With the addition of AmSulf, a significant increase of the retention of sulphur in ashes is observed in Figure 3b. The higher extent of sulphation reactions between gaseous sulphur and alkalis is probably an important reason for the higher sulphur retention in ashes during AmSulf addition. In addition, it is likely that part of

gaseous sulphur may form  $H_2SO_4$  in the presence of water in the hot combustion products and condenses on the surface of ash particles when the flue gas is cooled to about  $120^\circ C$  [29]. Since the cyclone ashes and aerosols from the EFR experiments are collected by maintaining the flue gas temperature at  $100^\circ C$ , condensation of  $H_2SO_4$  may occur on the surfaces of cyclone ashes and aerosols. Therefore, it is likely that the enhanced formation and condensation of  $H_2SO_4$  on the surfaces of ashes is another important reason for the significant increased sulphur retention during AmSulf addition.

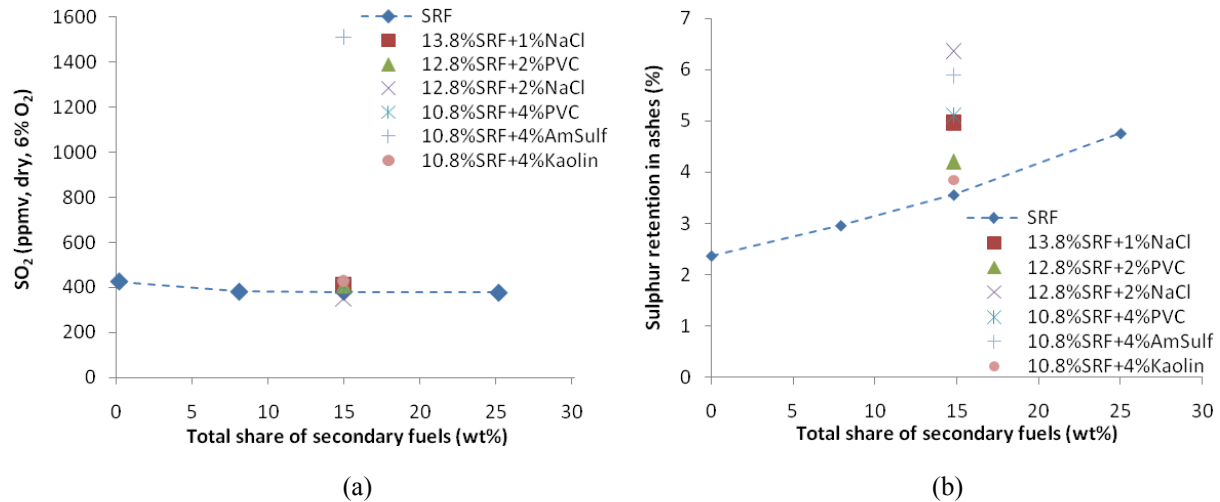


Figure 3 (a)  $SO_2$  emissions (ppmv, dry, 6 %  $O_2$ ) from EFR experiments with different shares and types of secondary fuels, (b) the percentage of sulphur retained in ashes in EFR experiments with different shares and types of secondary fuels

When PVC is added to the mixture of coal and SRF, it is seen that the retention of sulphur in ashes is slightly increased, and the effect becomes more pronounced with increasing share of PVC. A possible explanation is that the overall vaporization degree of the fuel alkalis may be enhanced by the addition of PVC, as more gaseous alkalis released from the fuels may initially form alkali chlorides. However, those alkali chlorides may further react with the  $SO_2/SO_3$  in the flue gas and form alkali sulphates. As a result, more alkali sulphates may be formed, leading to more pronounced sulphur retention in ashes. For the addition of 4 wt% Kaolin, it is also seen a slight increase of sulphur retention in the ashes compared to the estimations. In this case, the fraction of fuel sulphur that resulting in sulphates is probably less than that in co-combustion of coal and SRF, due to the competing reactions of the added Kaolin. However, the added fine Kaolin particles would significant increase the amount of ashes from combustion as well as their total surface area. It may be the case that a significant increase of the total surface area of the ashes would result in a larger extent of  $H_2SO_4$  condensation on the ashes, thus enhances the overall retention of sulphur in the ashes.

### 3.3 Ash compositions

To study the general behavior of K, Na, S and Cl in co-combustion of coal and SRF as well as in the cases of additives injection, the contents of K, Na, S and Cl in the bottom ashes, cyclone ashes, and aerosols collected from different experiments are plotted against the contents of those elements in fuel ash in Figure 4. It is seen that the K content in the ashes from experiments generally increases in an order of bottom ashes, cyclone ashes, and aerosols. The enrichment of K in the smaller particles, especially aerosols, indicates that the vaporization degree of K is higher than other major ash forming elements such as Al, Si, Fe and Ca. The result is in line with a number of laboratory- or pilot-scale studies on pulverized coal combustion, which showed that the finer ash particles were of higher alkali content than the coarser ash particles due to the relative high vaporization degree of alkali [30-33]. The gaseous K from combustion, such as  $K_2SO_4$  and KCl, may either generate aerosols through nucleation or condense on the surfaces of existing ash particles during the cooling of flue gas. Both mechanisms would lead to higher content of K in finer ash particles, as the nucleated aerosols are usually in submicron region and the specific surface area for condensation is generally larger for smaller particles. In addition to the concentration difference in the different ash fractions, it is also shown in Figure 4 that the K content in the fuel ash is quite close to the K content in different ash fractions, implying that majority of K in the fuel is recovered as solids. For different experiments, mass balance calculations have been performed for ashes and other major inorganic elements, showing that the mass

balances for ash and major inorganic are mostly about 80%. It indicates that approximately 20% of the ashes or inorganic elements are not collected in the experiments. A primary reason for this is that part of the ashes/major inorganic elements forms deposits in the reactor tube during the experiments, thus cannot be collected. In addition, although the ashes in the sampling systems are carefully collected, it would be possible that part of the ashes in the sample systems has not been collected, which would lower the mass balances.

Compared to K, it is more difficult to identify the differences of the Na content in different ashes from Figure 4, as the Na content is generally low in the fuels. However, by directly comparing the Na contents in different ash fractions, it can be found the Na content in the ashes mostly increases in an order of bottom ashes, cyclone ashes, and aerosols, excepting for the two cases with NaCl addition which shows considerable higher Na content in the bottom ashes. The observed general enrichment of Na in smaller particles is probably due to its relative higher volatility compared to other major ash forming elements, which has been demonstrated in lab- and pilot-scale experiments on pulverized fuel combustion [30-33]. However, for the two cases with NaCl addition, it is most likely that some of the large NaCl particles were not fully vaporized during combustion and collected as bottom ashes. Even though, it is still found that the Na content in aerosols is much higher than it in cyclone ashes during the addition of NaCl, highlighting the general high vaporization degree of Na.

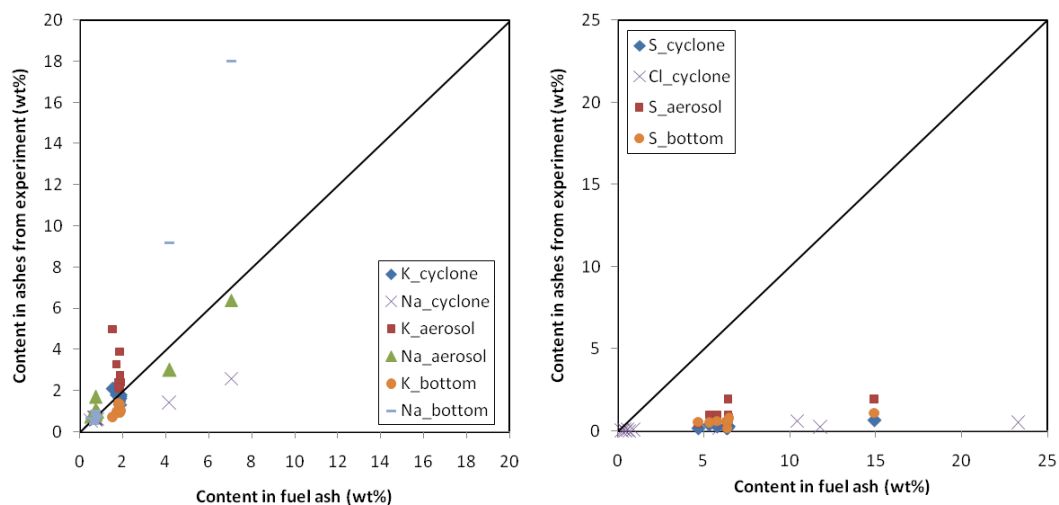


Figure 4 Comparison of the elemental compositions of the ashes from experiments (including bottom ashes, cyclone ashes and aerosols) and the fuel ash compositions

The contents of S and Cl in the ashes collected from experiments are also shown in Figure 4. It should be noted that the Cl contents in bottom ashes and aerosols are generally below the analysis limitation, thus are not shown in the figure. The chlorine content of cyclone ashes is obtained from the content of water soluble chlorine. From Figure 4, it is seen both the S and Cl contents in the ashes collected from experiments are significantly lower than those in the fuel ash, indicating that the majority of S and Cl in the fuels would be released to gas phase (mainly as  $\text{SO}_2$  and  $\text{HCl}$ ) during combustion. Furthermore, it can be seen that the content of S mostly increases in order of cyclone ashes, bottom ashes, and aerosols. The highest concentration of S in aerosols is consistent with some laboratory or pilot-scale experiments which show that S is significantly enriched in fine ash particles due to the nucleation or condensation of sulphates during flue gas cooling [31-38]. However, for the higher content of S in the bottom ashes than in the cyclone ashes, it is likely because that the bottom ashes from the experiments generally show considerable higher Ca content than the cyclone ashes. Therefore, more sulphur would be retained in the bottom ash through the formation of calcium sulphate. The high Ca content in the bottom ashes may be because that some of the SRF particles are not fully combusted due to their large particle size and agglomeration behavior and would appear as bottom ashes. It may also be the case that part of the ashes from SRF is of higher density than the coal ashes, which may have a higher probability to be collected as bottom ashes than the ashes from coal.

In co-combustion of coal and SRF, the alkalis in the fuels can be converted into two categories i.e. water soluble alkalis and water insoluble alkalis. The water soluble alkalis would mainly consist of alkali chlorides and sulphates, while the water insoluble alkalis would be dominated by alkali silicates or aluminosilicates. From operational point of view, it is more desirable to convert the alkalis to a water insoluble form, as the water soluble alkalis may



introduce operation problems such as severe deposition and corrosion in the boiler and deactivation of the SCR units [6]. Figure 5a shows the percentage of water soluble alkali/total alkali in the cyclone ashes collected from different experiments. Although this parameter cannot provide the exact percentage of fuel alkalis that appears as water soluble form after combustion, it would be able to reflect the tendency of the percentage of fuel alkalis that are converted to water soluble alkalis during the combustion. From Figure 5a, it can be seen that for co-combustion of coal and SRF, less than 1 wt% of alkalis would appear as water soluble form in the cyclone ashes. It implies that majority of fuel alkalis in co-combustion of coal and SRF would present as insoluble form such as alkali silicates or aluminosilicates. With increasing share of SRF, the change of the percentage of water soluble alkali/total alkali in the cyclone ashes is not significant.

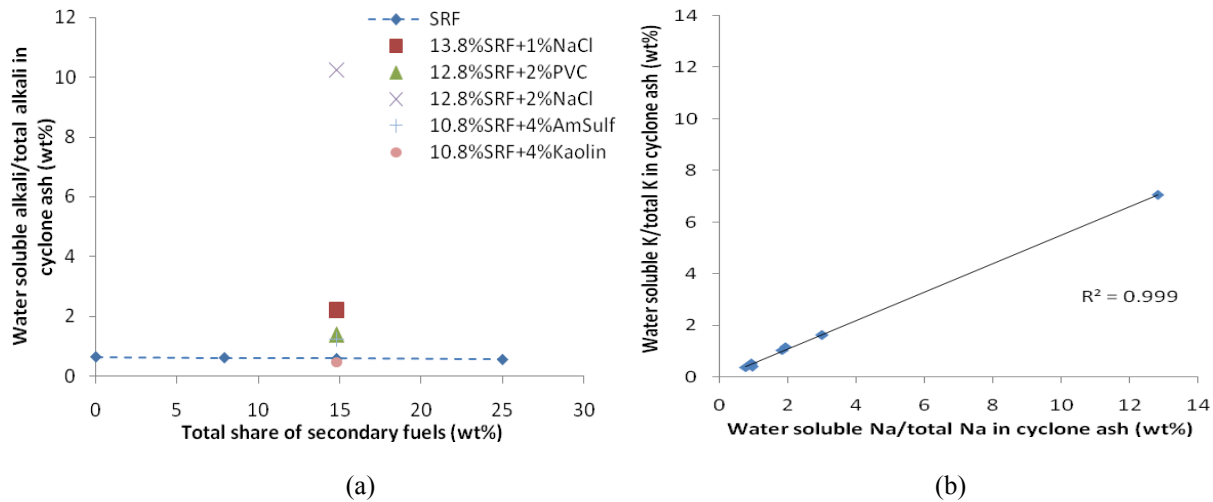


Figure 5 (a) percentage of water soluble alkali in the total alkali of the cyclone ashes from EFR experiments with different share and type of secondary fuels, (b) comparison of the percentage of water soluble K/total K and the percentage of water soluble Na/total Na in the cyclone ashes

The effects of additives on the percentage of water soluble alkali/total alkali are also shown in Figure 5a. With the addition of 1 wt% NaCl, it is seen that the percentage of water soluble alkali/total alkali in cyclone ashes increases to approximately 2 wt%. By increasing the addition amount of NaCl to 2 wt%, the percentage of water soluble alkali/total alkali in cyclone ashes is increased further to about 10 wt%. This indicates that addition of NaCl would result in increased percentage of alkali being present in a water soluble form. Furthermore, it seems that the increase of the percentage of water soluble alkali is not linear with the added amount of NaCl, since the percentage of water soluble alkali/total alkali in cyclone ashes becomes approximately 5 times higher when the addition of NaCl is increased from 1 wt% to 2 wt%. To explain this, both the release and conversion of alkalis during pulverized fuel combustion need to be considered. When NaCl is added to the mixture of coal and SRF, it would significantly increase the primary release of sodium to gas phase. A certain fraction of the primarily released gaseous alkalis would react with the minerals in the fuels and result in water insoluble alkalis, while the remaining gaseous alkalis would either stay un-reacted or react with the gaseous sulphur and chlorine and finally forms water soluble alkalis. With the addition of 1 wt% NaCl, although the percentage of the primarily released alkalis is increased significantly, the minerals in the fuels may still be able to react with the majority of the released alkalis, resulting in the percentage of water soluble alkali/total alkali in cyclone ashes to be around 2 wt%. However, when 2 wt% NaCl is added to the fuel mixture, the fraction of the primary released gaseous alkali that are converted to insoluble alkali may be significantly reduced, due to the limited amount of the reactive minerals in the fuels. Therefore, a much larger percentage of water soluble alkali/total alkali (~10 wt%) in cyclone ashes is obtained.

As shown in Figure 5a, the addition of 2 wt% PVC slightly increases the percentage of water soluble alkali/total alkali in the cyclone ashes. With the addition of PVC, since no additional alkali is added to the fuel mixture, it is considered the primary release of alkali would not be largely affected. However, the gaseous chlorine generated from PVC combustion would compete with the fuel minerals, for reacting with the primarily released gaseous alkali. With increased gaseous chlorine concentration, the formation of alkali chlorides would become more pronounced, leading to a higher percentage of water soluble alkali/total alkali in the cyclone ashes. In Figure 5a, it is also shown that the addition of 4 wt% AmSulf increases the percentage of water soluble alkali/total alkali in the cyclone ashes.

Similar as the PVC case, the increased concentration of gaseous sulphur would compete with the reaction between gaseous alkali and fuel minerals, resulting in increase formation of water soluble alkalis. With the addition of 4 wt% Kaolin, a slightly decrease of the percentage of water soluble alkali/total alkali in the cyclone ashes is seen. It is likely because that the addition of Kaolin increases the availability of minerals for reacting with the primarily released alkalis. However, the effect of Kaolin addition is not significant, implying the minerals in the fuels are almost sufficient for reacting with the majority of the released gaseous alkalis.

To study the behavior of Na and K separately rather than the total alkalis, the percentage of water soluble Na/total Na in the cyclone ashes is plotted against the same parameter of K in Figure 5b. A good linearity is seen between the two parameters, including the cases with NaCl addition. The percentage of fuel Na that results in a water soluble form after combustion would provide an indication on the overall vaporization degree of Na during combustion. The results shown in Figure 5b imply that the addition of NaCl does not only increase the overall vaporization degree of Na, but also enhances the overall vaporization of degree K in the fuel mixture. The overall vaporization degree of alkali metals would be influenced both by the primary release of alkalis and consequent reactions of those alkalis. It may be the case that the addition of NaCl has promoted the reaction between the primarily released gaseous Na and fuel minerals, resulting in less reactive minerals available for the primarily released gaseous K. Therefore the overall vaporization degree of K is increased due to the depletion of reactive minerals. Furthermore, in Figure 5b it is seen that the percentage of water soluble Na/total Na in the cyclone ashes is always slightly higher than that of K. It may indicate that reaction rate of gaseous K and fuel minerals may be greater that of Na. Another possibility is that a lower percentage of K is released to the gas phase compared to Na.

### 3.4 Deposits

To evaluate the influences of coal and SRF co-firing as well as different additives on the formation of deposits in the convective part of a boiler, deposits are collected during the EFR experiments by using an air-cooled probe. The average deposition flux obtained from different experiments is shown in Figure 6a. It can be seen that when the COCERR coal is co-fired with SRF, the deposition flux generally decreases with increasing share of SRF. By fixing the total share of secondary fuels to 14.8 wt%, it is seen that the addition of NaCl/PVC has enhanced the deposition flux and the effects are more pronounced with higher share of NaCl/PVC. It is also seen that addition of 4 wt% Kaolin to the mixture of coal and SRF has increased the deposition flux considerably. However, with the addition of 4 wt% AmSulf, the obtained deposition flux is quite similar to that of co-combustion of coal and SRF.

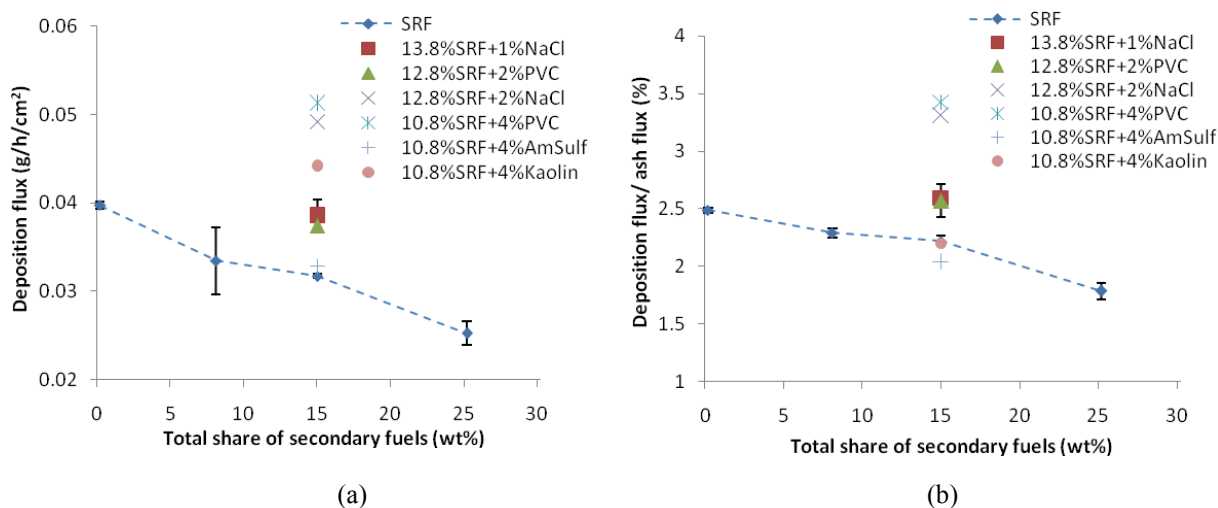


Figure 6 (a) Deposition fluxes ( $\text{g/h/cm}^2$ ) from EFR experiments with different shares and types of secondary fuels, (b) The values of deposition flux/ash flux (%) from experiments with different shares and types of secondary fuels

The deposition fluxes shown in Figure 6a would be primarily affected by two factors i.e. the ash fluxes to the probe and the deposition propensity of the ashes. For different experiments, the ash fluxes to the probe would vary due to the variations in the fuel ash contents. To neglect the effects of the ash fluxes, the obtained deposition fluxes are divided by the calculated ash fluxes that are directed to the probe. The obtained deposition flux/ash flux (%) is a parameter that gives implications about the deposition propensity of the fly ashes. Figure 6b shows the values of deposition flux/ash flux from different experiments. It is seen that when the COCERR coal is co-fired with SRF, the

obtained deposition flux/ash flux decreases with increasing share of SRF. It implies that co-combustion of coal and SRF may reduce the deposition propensity of the fly ashes, compared to dedicated coal combustion. The reduced ash deposition propensity may be related with the relatively high calcium content in the ashes of the SRF, which may generate calcium species with high melting temperature and decrease the fouling tendency of fly ashes.

With the addition of NaCl/PVC, it can be seen in Figure 6b that the obtained deposition flux/ash flux is higher than that of co-combustion of coal and SRF, and the effects are more pronounced with increasing share of NaCl/PVC. However, with the addition of AmSulf/Kaolin, the obtained deposition flux/ash flux is slightly lower than that of co-combustion of coal and SRF. To further investigate the possible reasons for the increased or decreased deposition propensity of fly ashes, the deposition flux/ash flux obtained from the EFR experiments carried out at 14.8 wt% secondary fuels is plotted against the Cl content of the cyclone ashes. As shown in Figure 7a, a positive correlation is found between the deposition flux/ash flux and the Cl content in the collected cyclone ashes. It indicates the increased deposition flux/ash flux during the addition of NaCl/PVC is likely related with the increased concentration of chlorides in the fly ashes and flue gases. It is well-known that alkali chlorides generally have low melting temperatures, thus can significant increase the stickiness of the deposits and fly ash particles [8,39]. However, when the Cl content in the cyclone ashes is lower than 0.1 wt%, it is seen that the deposition flux/ash flux decreases slight with increasing Cl content in cyclone ashes. With a considerable low Cl content in the cyclone ashes, it is likely that the influences of other factors (such as the physical characteristics of the fly ashes, ect.) may become more significant for the deposition propensity of fly ashes.

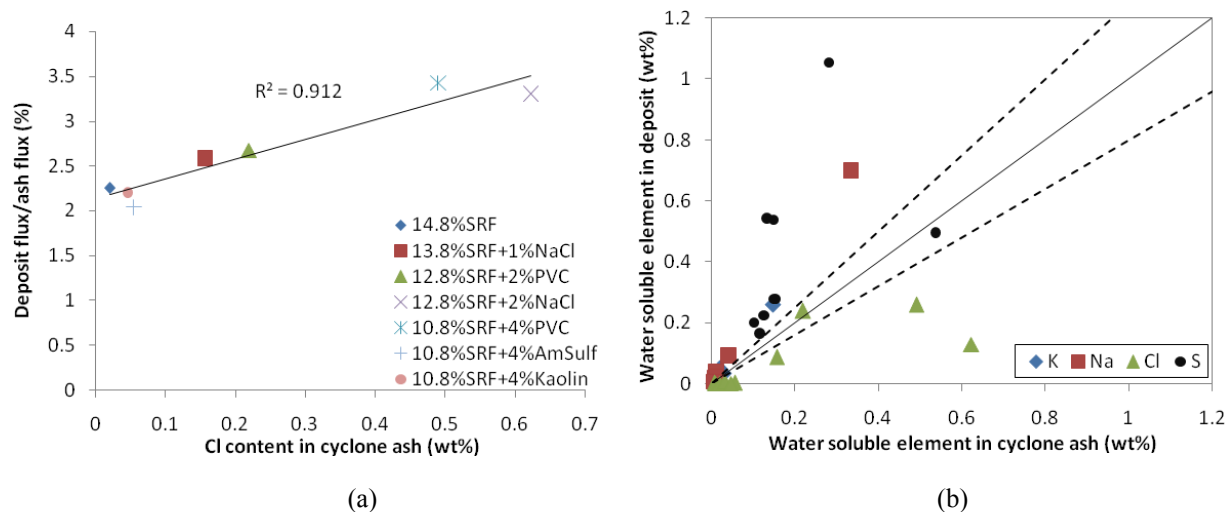


Figure 7 (a) A comparison of the deposition flux/ash flux (%) from different EFR experiments and the Cl content of the cyclone ashes obtained in the experiments. The results shown in the figure are carried out with the same total share of secondary fuels (14.8 wt%) but different additives, (b) Contents of the water soluble elements in the deposits and cyclone ashes from different EFR experiments, the two dash lines indicate a deviation of  $\pm 20\%$

The deposition rates obtained in this study are based on an experimental period of 1.5 hours, which are quite different from the deposit build-up time scale in a real boiler. However, it is still considered that the results shown in Figure 6 would provide information about the deposition propensity of the fly ashes from co-combustion of coal and SRF as well as the possible influences of additives. In addition to the deposition rate/propensity of the fly ashes, the composition of the deposits is also of high importance, since it is closely related with the corrosion potential of the superheaters [25]. In Figure 7b, the contents of the water-soluble elements in the cyclone ashes are plotted against the contents of water-soluble elements in the deposits collected in the experiments. It can be seen that the content of water-soluble chlorine is generally lower than 0.1 wt% in the coal and SRF co-combustion tests, indicating a low potential for corrosion [25]. However, with the addition of NaCl/PVC, the water-soluble Cl in the deposits becomes higher than 0.1 wt%, implying a high potential for chlorine corrosion.

In Figure 7b, it can be seen that the contents of water-soluble K and Na in deposits are mostly more than 20% higher than those in the cyclone ashes. There are several reasons that may contribute to the enrichment of water-soluble alkali in the deposits. Firstly, although the cyclone ashes are the major source for the formation of deposits on the probe, the aerosols from combustion would still have some contribution to the deposit formation, mainly through thermophoresis. The contents of water-soluble alkali in the aerosols would be higher than those in the cyclone ashes,

due to the condensation/nucleation of gaseous alkali chlorides/sulphates. Thus it can be expected that the water soluble alkali contents in the deposits would be higher than that in the cyclone ashes, due to the contribution of aerosols. In addition to the aerosols, gaseous alkali chlorides may also contribute to the formation of deposits, as the flue gas and probe surface temperature used in the experiments would allow direct condensation of gaseous alkali to be a deposit formation mechanism.

The water soluble sulphur is also found to be enriched in the deposits compared to that in the cyclone ashes. The relatively higher water soluble sulphur contents in the deposits may be explained by the same reasons that have been attributed to the enrichment of water soluble alkalis, since a large fraction of water soluble alkalis would exist as alkali sulphates. In addition, a further possible mechanism for the enrichment of sulphur is that condensed phase sulphation reaction may occur on the deposits, which could convert a fraction of chlorides in the deposits to sulphates. Such reactions could be significant at temperature higher than 750 °C [40]. An exceptional case shown in Figure 7b is that when AmSulf is added to the fuel mixture, the content of water soluble sulphur in the cyclone ashes becomes similar to that in the deposits, which is about 0.5 wt%. In this situation, due to the high gaseous sulphur concentration, it is likely that condensation of H<sub>2</sub>SO<sub>4</sub> could occur on the surfaces of the collected cyclone ash particles and increase the content of water soluble sulphur, whereas the condensation of H<sub>2</sub>SO<sub>4</sub> cannot occur on the deposits due to the high gaseous/surface temperature. This may lead to the content of water soluble S in the cyclone ashes being similar to that in the deposits.

Different from sulphur and alkalis, the content of water soluble Cl is mostly depleted in the deposits, in comparison with that in the cyclone ashes. Due to the fact that the collected aerosols would contain more water soluble Cl than the cyclone ashes and the condensation of gaseous alkali chlorides is a possible deposit formation mechanism, the initially formed deposits would probably contain more water soluble Cl than the cyclone ashes. Therefore, there is a strong indication that the depletion of water soluble Cl in the deposits is mainly caused by the reaction between the initially deposited chlorides and gaseous sulphur, which has been discussed previously.

#### **4. Conclusion**

Co-combustion of coal and SRF as well as the effects of different additives including NaCl, PVC, AmSulf and Kaolin were studied in an entrained flow reactor. It was found that the NO emissions in co-combustion of coal and SRF decreased with increasing share of SRF, because of the relatively low nitrogen content of the SRF and the positive interactions between the coal and SRF. The additives generally did not affect the NO emissions, except for the AmSulf which showed significant reduction effects on NO emissions. Similarly, the SO<sub>2</sub> emissions in co-combustion of coal and SRF also decreased with increasing share of SRF. Furthermore, it was found that the retention of sulphur in the ashes increased with increasing share of SRF, possibly because of the high calcium content in the SRF. All of the additives increased the retention of sulphur in the ashes, either through chemical reactions or physical absorptions. Analyses of the ash compositions from experiments showed that a majority of the S and Cl in the fuels were released to the gas phase during the combustion, while the K and Na in the fuels were mainly retained in the ashes, with a slight enrichment in smaller particles. In co-combustion of coal and SRF, the majority of K and Na (~99%) in the fuels appeared in the fly ashes in a water insoluble form. The addition of NaCl, PVC, and AmSulf generally increased the overall vaporization of K and Na, resulting in increased formation of water soluble alkalis, whereas the addition of Kaolin showed a slight reduction effect on the formation of water soluble alkalis. Furthermore, it was found that the overall vaporization degree of Na and K were closely related and would have a positive correlation between each other. During the experiments, ash deposits were formed on an air-cooled probe. The results showed that ash deposition rate as well as the deposition propensity of the fly ashes in co-combustion generally decreased with increasing share of SRF. The addition of NaCl and PVC slightly increased the ash deposition propensity, and showed a positive correlation between ash deposition propensity and Cl content in the cyclone ashes. However, the addition of AmSulf and Kaolin showed opposite effects. The Cl content in the deposits generally indicated low corrosion potential, except for the cases with NaCl and PVC additions. It was found that the water soluble alkali were generally higher in the deposits than in the cyclone ashes. Higher water soluble sulphur content and lower water soluble chlorine content were also seen in the deposits than in the cyclone ashes, which may be partly caused by condensed phase sulphation of the deposits.

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