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# Behaviors of trace element in co-combustion of solid recovered fuel and coal in an entrained flow reactor

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## ABSTRACT

Trace element behaviors in co-combustion of a bituminous coal and a solid recovered fuel (SRF) have been studied in an entrained flow reactor. The experiments were carried out both at dedicated coal combustion condition and different SRF share conditions (7.9wt%, 14.8wt% and 25.0wt%). The effects of some additives (including NaCl, PVC, ammonium sulphate, and Kaolin) on trace element behaviors were also investigated. The trace elements studied were As, Cd, Cr, Pb, Sb and Zn. The ashes from the experiments were collected as bottom ash, cyclone ash and filter ash, and were analyzed by ICP-OES. When coal was co-fired with SRF, the As, Cd, Pb, Sb and Zn contents in the filter ashes/cyclone ashes were found to increase almost linearly with their contents in the fuel ashes. This linear tendency was affected to some extent when the fuels were mixed with the additives. The volatilities of trace elements at different experiments were assessed by using a relative enrichment (RE) factor. The results indicated that the volatilities of As, Cd, Pb, Sb and Zn were high in co-combustion of coal and SRF, whereas the volatility of Cr was relatively low. Compared with dedicated coal combustion, co-combustion of coal and SRF slightly enhanced the volatilities of Cd, Pb and Zn, but reduced the volatilities of Cr and Sb. The chlorine based additives mostly increased the volatilities of Cd, Pb and As, whereas the addition of ammonium sulphate generally decreased the volatilities of trace elements. The addition of Kaolin showed a reduction effect on the volatility of Pb, while the influences on other elements were not evident. The results from this study imply that the emission of trace elements might become a significant concern in co-combustion of coal and SRF, primarily due to the high trace element contents in the SRF. The chlorine content in the SRF as well as the sulphur and aluminosilicates contents in the coal are important parameters to control the emission of trace elements.

**Keywords:** *co-combustion, pulverized coal combustion, solid recovered fuel, trace element, additive*

## 1. INTRODUCTION

Trace element emission is one of the major environmental concerns for pulverized coal-fired power stations. In pulverized coal combustion, the trace elements in the fuels usually undergo complicated chemical and physical transformations, and a fraction is eventually emitted to the atmosphere as dusts or vapors [1,2]. Due to the adverse health effects of the emitted trace elements [1], it is desirable to reduce the emission of trace elements from coal-fired power stations.

Co-combustion of coal and secondary fuels such as biomass and waste is recognized as one of the most promising approaches to reduce the CO<sub>2</sub> emissions from pulverized coal-fired power stations [3]. The typical secondary fuels for co-firing with coal are biomass fuels such as straw [4] and wood [5], and waste fuels such as sewage sludge [6] and refuse derived fuels [7,8]. When biomass fuels are used as the secondary fuels in co-combustion, the emission of trace elements is usually not a great concern as compared with dedicated coal combustion, since the trace element contents in most of the biomass fuels are lower than that of coal. In contrast, waste fuels are often characterized by significantly higher trace element contents than the coals [6,7]. To explore the feasibility of co-firing coal and waste fuels, it is important to study the behavior of trace elements in co-combustion.

In a pulverized fuel combustion system, the behavior of trace elements is influenced both by the fuel properties and the combustion conditions. The trace elements present in the fuels can be generally categorized as organic association (elements that are organically bounded, ionically bounded, or water soluble) and mineral association (elements that are present as included or excluded minerals) [2]. Extensive studies on the association of trace elements in different coals have been performed [9,10], with part of them summarized in [1,2]. Similar investigations were also carried out on some waste fuels such as sewage sludge [11] and refuse-derived char [12]. The associations of trace elements play an important role on the vaporization of these elements. The organically associated trace elements are usually more likely to be vaporized during the combustion than those associated with minerals [1]. On the other hand, the vaporization behavior of trace elements from the fuels would be influenced by combustion conditions such as the temperature, oxidizing/reducing condition, and the presence of different gaseous species (such as HCl and SO<sub>2</sub>) [13]. It is generally found that the presence of gaseous HCl may shift the distribution of some trace elements (such as Pd and Cd) towards more volatile chlorides, thus increasing their vaporization degrees [1,13,14]. However, the presence of SO<sub>2</sub> sometimes has the opposite effect, due to the formation of sulphates which may have low vapor pressure [14].

After being vaporized from the fuels, trace elements may undergo reactions both with the ashes and the gaseous species in the flue gas [14,15]. The reactions between the vaporized trace elements and the ashes constitute an important mechanism for retaining the trace elements in large fly ash particles that are more easily to be captured by the flue gas treatment systems [1,2]. Typical examples are the reactions between some trace elements (such as Cd and Pb) and aluminosilicates (such as Kaolin) [15]. These reactions

would primarily occur on the particle surfaces and result in trace element concentrations proportional to  $1/d_p$  (particle diameter) [1,16-18]. The reactions between the vaporized trace elements and the gaseous species in the flue gas may affect the condensation of the trace elements in the flue gas by varying the dew points of the trace element compounds. It may also influence the reactions between vaporized trace element and ashes in the flue gas, since trace element in different gaseous forms (such as chlorides or oxides) may have different reaction rates with the fly ash particles [1].

When the flue gas temperature becomes lower than the dew point of the relevant trace element, condensation will occur on the surfaces of existing ash particles. For ash particles in the continuum regime (larger than  $0.5\text{-}1\mu\text{m}$ ) condensation would lead to trace element concentrations proportional to  $1/d_p^2$ , while for particles in the free molecular regime (smaller than  $0.5\text{-}1\mu\text{m}$ ) the concentration of the condensed trace element would be proportional to  $1/d_p$  [16-18].

All of the mechanisms mentioned above would influence the emission of trace elements, and the significance of the mechanisms may vary for different trace element and different conditions. In a real combustion system, the partitioning of trace elements involves complex chemical and physical processes (such as vaporization, reaction, nucleation, condensation and coagulation). These processes would become more complicated when a secondary fuel is introduced to the system, as the secondary fuel may have significantly different fuel properties and combustion behaviors as compared with the primary fuel. To evaluate the behavior of trace elements during co-combustion in a pulverized coal-fired plant, performing experiments at fuel and combustion conditions that are similar to a real plant is an advantageous approach.

The principal objective of this paper is to study the behavior of trace elements in co-combustion of coal and solid recovered fuel (SRF) at a combustion condition similar to a pulverized coal-fired plant. This is achieved by performing co-combustion experiments in an entrained flow reactor, and by investigating the trace element partitioning in different ash fractions (bottom ash, cyclone ash and filter ash). The experiments are carried out at both dedicated coal combustion and different SRF share conditions (7.9 wt%, 14.8 wt%, and 25.0 wt%). In addition, the effects of some additives (including NaCl, PVC, ammonium sulphate, and Kaolin) on the behavior of trace elements in co-combustion of coal and SRF are evaluated. These additives are selected since they may have notable effects on the partitioning of trace element during combustion [14,15]. Thus the results may provide suggestions for fuel selection and/or trace element emission control in co-combustion of coal and SRF. The trace elements studied in this paper are As, Cd, Cr, Pb, Sb and Zn.

## **2. EXPERIMENTAL**

### **2.1 Fuels and additives**

A Columbian bituminous coal, and a SRF mainly consisting of waste paper, plastic and wood, are selected as the fuels in the experiments. The investigated additives include PVC, NaCl,  $(\text{NH}_4)_2\text{SO}_4$  (denoted as AmSulf in the following) and Kaolin. The main

properties of the fuels are given in Table 1. It can be seen that the SRF is characterized of higher volatile, Cl and Ca contents than the coal, while the coal has higher ash, N, S, Si, Al and K contents than the SRF. The trace element contents of the two fuels are significantly different. The contents of As, Cd and Cr in the SRF are 5-10 times higher than those in the coal. For Pb, Sb and Zn, the contents in the SRF are even 30-150 times higher. The additives used in this study are all pure compounds purchased from chemical companies. The trace element contents in the additives can be neglected compared with that in the SRF.

**Table 1: Major properties of fuels and additives**

Properties	Coal	SRF	Properties	Coal	SRF
LHV (MJ/kg wet)	26.53	20.86	Mg(wt% dry)	0.15	0.09
Moisture (wt% wet)	5.25	5.20	P (wt% dry)	0.02	0.02
Volatiles (wt% wet)	34.11	72.05	Ca (wt% dry)	0.18	0.67
Ash (wt% wet)	10.42	5.69	Na (wt% dry)	0.07	0.11
C (wt% dry)	71.00	58.00	K (wt% dry)	0.21	0.09
H (wt% dry)	4.90	6.60	As (ppm dry)	3.71	18.9
N (wt% dry)	1.50	1.00	Cd (ppm dry)	0.20	1.07
S (wt% dry)	0.70	0.42	Cr (ppm dry)	15.2	178.0
Cl (wt% dry)	0.03	0.28	Pb (ppm dry)	7.35	206.1
Si (wt% dry)	3.06	1.08	Sb (ppm dry)	1.0	51.5
Al (wt% dry)	1.21	0.21	Zn (ppm dry)	25.2	3500

The particle size distribution of the fuels and additives is analyzed by the laser diffraction method (Malvern Mastersizer 2000 particle size analyzer). The  $d_{50}$  (meaning that 50 vol% of the particles are below this size) of the SRF is approximately 164 $\mu$ m, whereas the  $d_{50}$  of the coal is about 19 $\mu$ m, which is much smaller than that of SRF. The  $d_{50}$  of PVC, NaCl, AmSulf, and Kaolin is approximately 104 $\mu$ m, 259 $\mu$ m, 222 $\mu$ m, and 8 $\mu$ m respectively. It should be noted that the SRF particles have a higher tendency to form agglomerates than the coal particles. Thus, the actual particle size of SRF during the experiments may be larger than that obtained by the particle size analyzer.

## 2.2 Setup

The experiments are 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 two meters long vertical reactor which is electrically heated by 7 heating elements, a bottom chamber, a particle and gas extraction system, and an ash deposition system which is used to simulate deposit formation on the superheater tubes of a boiler. More detailed description of the reactor can be found in [4].

To perform co-combustion experiments, the fuels as well as the additives are premixed and injected into the reactor with primary air. The feeding rate of the fuel particles is controlled by a gravimetric screw feeder, and is adjusted for different experiments to control the overall excess air ratio at approximately 1.43. The injected fuel particles are mixed with the preheated secondary air at the inlet of the vertical reactor, and

consequently combusted in the reactor. The flow rate of the primary air and secondary air is maintained at 13 Nl/min and 82 Nl/min respectively during the experiments. The temperature of the heating element in the preheater is set to be 900°C, and the wall temperature of the vertical reactor is set to be 1000-1300°C for all of the experiments, to simulate a high temperature environment comparable to a pulverized coal-fired plant.

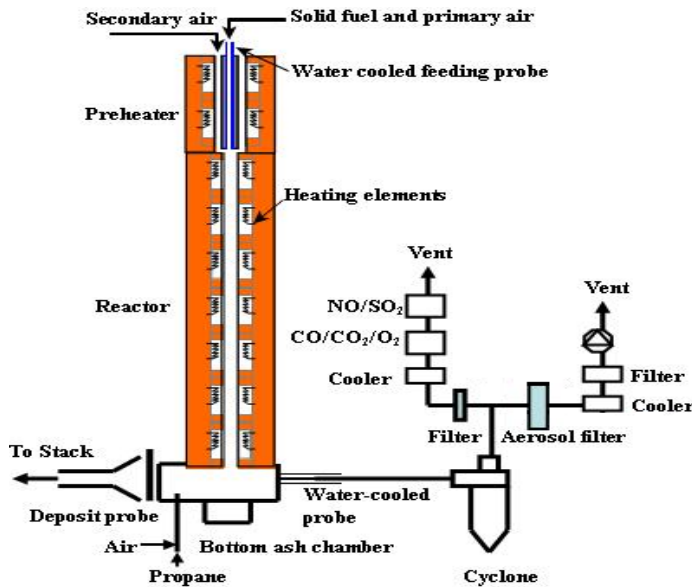


Figure 1: Schematic draw of the CHEC entrained flow reactor.

During the experiments, the bottom ashes are collected in the bottom chamber. The flue gases together with the fly ash particles from combustion are separated as 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. The large fly ash particles are collected by a cyclone with a cut-off diameter of 2.5  $\mu\text{m}$ , and the fly ashes passing through the cyclone are gathered in a total filter with a pore size of 0.1  $\mu\text{m}$ . Apart from the flue gas that is drawn by the extraction system, the remaining part of the flue gas from the combustion is directed towards a deposition probe which simulates the superheater tube in a real boiler. The probe surface temperature is controlled to be 550°C and the flue gas temperature is adjusted to 800°C during the experiments.

The duration of an experiment is kept at 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, total filter, and bottom chamber are collected and weighted. 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 co-combustion experiments of coal and SRF, the weight 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 weight share of coal is maintained at 85.2 wt%, and the weight share of the secondary fuels (SRF + additives) is kept at 14.8 wt%. With fixed weight share of coal, the addition of additives can be considered as a significant variation of the SRF properties. The addition of NaCl

(1 wt% and 2 wt%) simulates a SRF with considerable alkali chloride contents, while the addition of PVC (2 wt% and 4 wt%) gives the SRF significantly higher chlorine content. For the addition of AmSulf or Kaolin, the main objective is to study the co-combustion behavior of SRF with a coal that is rich in sulphur or aluminosilicates contents. To ensure all of the experiments to be carried out at similar combustion condition, 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**

Experimental number	Fuel composition wt%						Feeding rate (kg/h)	Excess air ratio
	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

## 2.4 Fuel/ash analysis

The chemical compositions of the fuel/ash samples from the experiments are analyzed at Enstedværket Laboratory, DONG Energy A/S. The contents of the major and trace elements in the fuels, bottom ashes, cyclone ashes, and filter ashes are determined by ICP-OES or IC.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Mass balances

The mass balances for different experiments have been calculated based on the fuel feeding rate, the amount of the collected ashes, and the composition of the fuels and ashes. Figure 2 shows the mass balances of ash, Si, and trace elements in different experiments. It can be seen that the ash balance for most of the experiments is between 80% and 90%. All of the ash balance is lower than 100%, primarily due to the deposition of some ashes in the reactor tube. Moreover, although the collection of ashes is carried out carefully during the experiments, some fly ashes are remaining in the sampling system after collection, which would further lower the ash balance. Considering the influences of the reactor and the sampling system, the ash balances obtained in this study are believed to be satisfactory, which indicates that all of the experiments are performed at relatively consistent conditions. The mass balances for the major inorganic elements are mostly between 70% and 90%, which are quite similar to the ash balances, further confirming the reliability of the experiments. To provide an example, the mass balances of Si are shown in Figure 2.

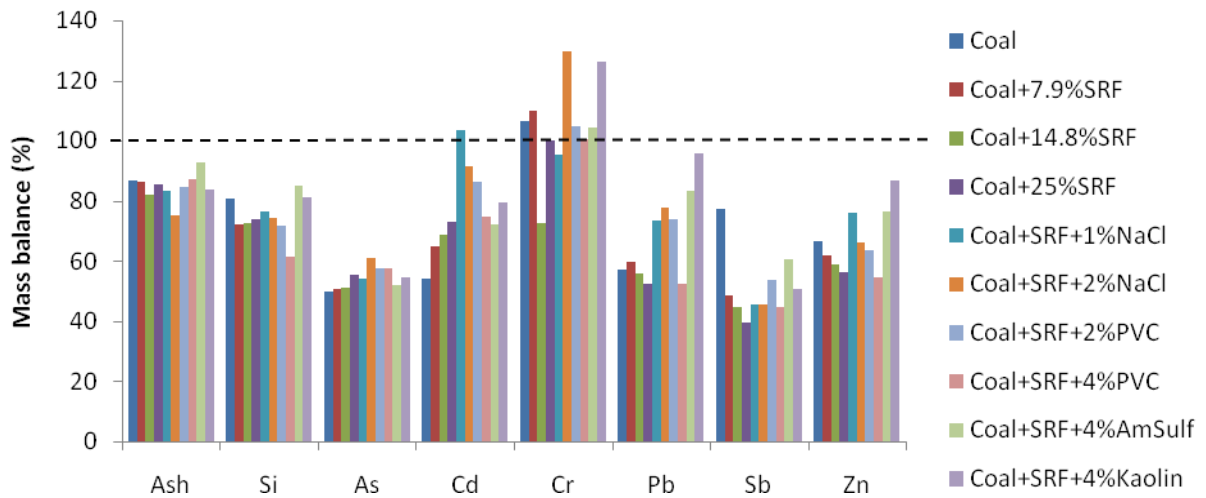


Figure 2: Calculated mass balances for different experiments.

In comparison with the major inorganic elements, the mass balances of the trace elements are generally less satisfactory. This is most likely related with the analysis uncertainties of the fuels and ashes, particularly for the SRF which is a more heterogeneous fuel than the coal. It is well-known that the contents of trace elements in different waste fractions can vary significantly [19]. Although the SRF used in this study has been homogenized through the production and the grinding processes, it may still be difficult to select a representative sample for analyzing the trace element contents. Moreover, the collection efficiency of different ash fractions may also influence the mass balances, since the distributions of trace elements in different ash fractions are much more uneven compared with the major inorganic elements. Due to the uncertainties mentioned above, it is suggested to focus on the tendencies shown by the results in this study, rather than the detailed values.

### 3.2 Trace element contents in the cyclone ashes and filter ashes

To assess the influences of co-combustion on the trace element contents in fly ashes, the trace element contents in the filter ashes and cyclone ashes collected from the experiments are plotted versus their contents in the fuel ashes, as shown in Figure 3 and Figure 4. The trace element contents in the fuel ashes are calculated from the fuel properties, i.e. the contents of ash and trace element in the fuel/fuel mixture. From the two figures, it can be seen that when coal is co-combusted with SRF (i.e. without additive), the contents of As, Cd, Pb, Sb and Zn in the filter ashes/cyclone ashes increase almost linearly with their contents in the fuel ashes. Compared with the contents in the fuel ashes, the As, Cd, Pb, Sb and Zn contents in the filter ashes are typically 2-5 times higher, whereas the contents in the cyclone ashes are usually 40-60% lower. The observed enrichment of As, Cd, Pb, Sb and Zn elements in filter ashes is in agreement with literature, where these elements are classified as volatile trace elements in pulverized coal combustion [2]. The depletion of these trace elements in the cyclone ashes may be primarily related with two reasons. For elements such as As and Sb, the mass balances



shown in Figure 2 are mostly around 50%. It is likely that the As and Sb contents in the fuel ashes are over-estimated, resulting in the trace element contents in the cyclone ashes 40-60% lower than those in the fuel ashes. In addition, for elements such as Cd, Pb, Sb and Zn, the contents in the bottom ashes collected from co-combustion experiments are notably higher than these in the fuel ashes. This would adversely affect the partitioning of trace elements to the cyclone ashes, thus lower the trace element contents in the cyclone ashes. The high trace element contents found in the bottom ashes from co-combustion experiments may be related with the physical properties of the SRF particles. The SRF particles used in the study are much larger than the coal particles, and tend to form agglomerates during injection. As a result, the burnout degree of the SRF particles may be lower than the coal particles in the reactor, and part of the unburnt SRF particles may end up as bottom ashes with relatively high trace element contents. This explanation is supported by the fact that the total amount of the bottom ashes collected during co-combustion experiments is increased with increasing share of SRF.

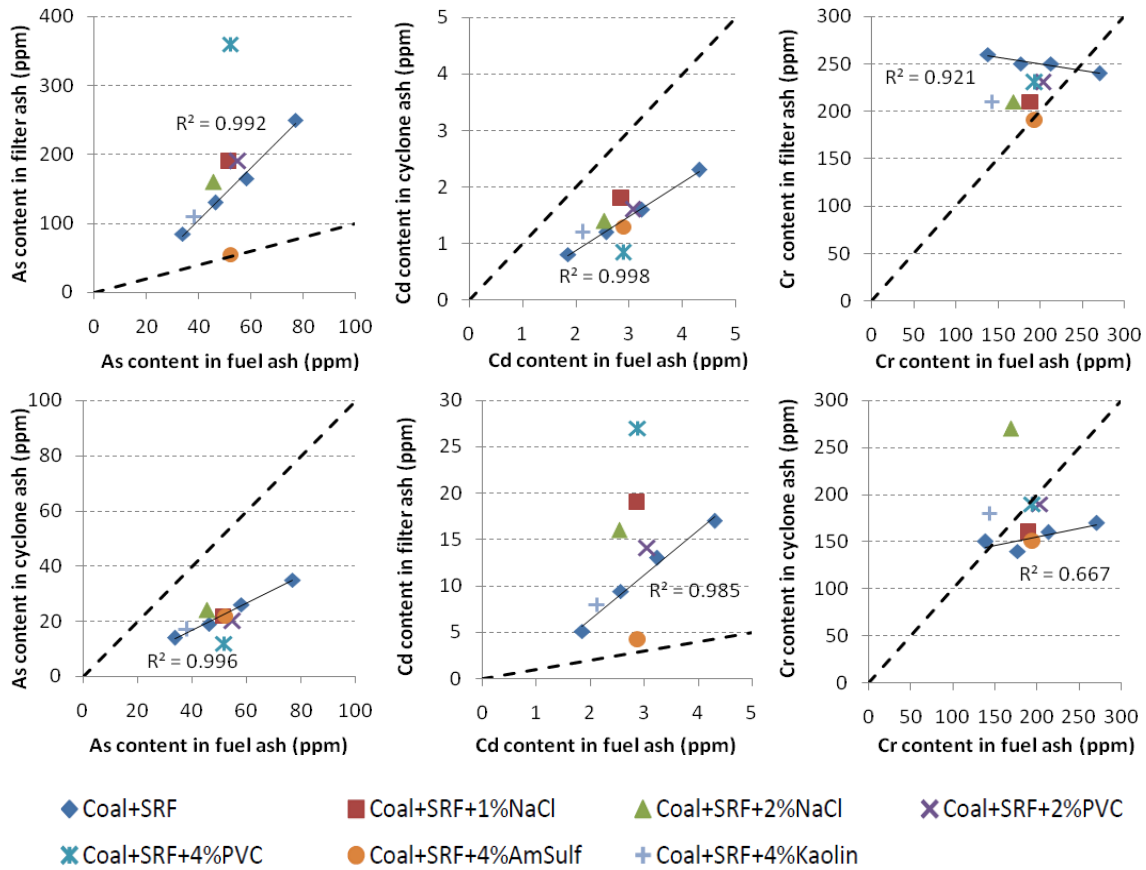


Figure 3: The contents of As, Cd and Cr in the filter ashes and cyclone ashes collected from different experiments versus their contents in the fuel ashes

Compared with the elements mentioned above, the behavior of Cr shown in Figure 3 is quite different. During co-combustion of coal and SRF, the Cr contents in the filter ashes decrease slightly with increasing Cr contents in the fuel ashes, whereas the Cr contents in the cyclone ashes increase a little with increasing Cr contents in the fuel ashes. In comparison with other trace elements, the contents of Cr in the cyclone ashes seem to be

much closer to their contents in the fuel ashes. It is probably linked the relatively high mass balance of Cr, which is close to or even higher than 100%, as shown in Figure 2. The Cr contents in the bottom ashes from co-combustion of coal and SRF are found to be higher than the contents in the fuel ashes. This may be one explanation for the slightly Cr contents in the cyclone ashes, with respect to the fuel ashes.

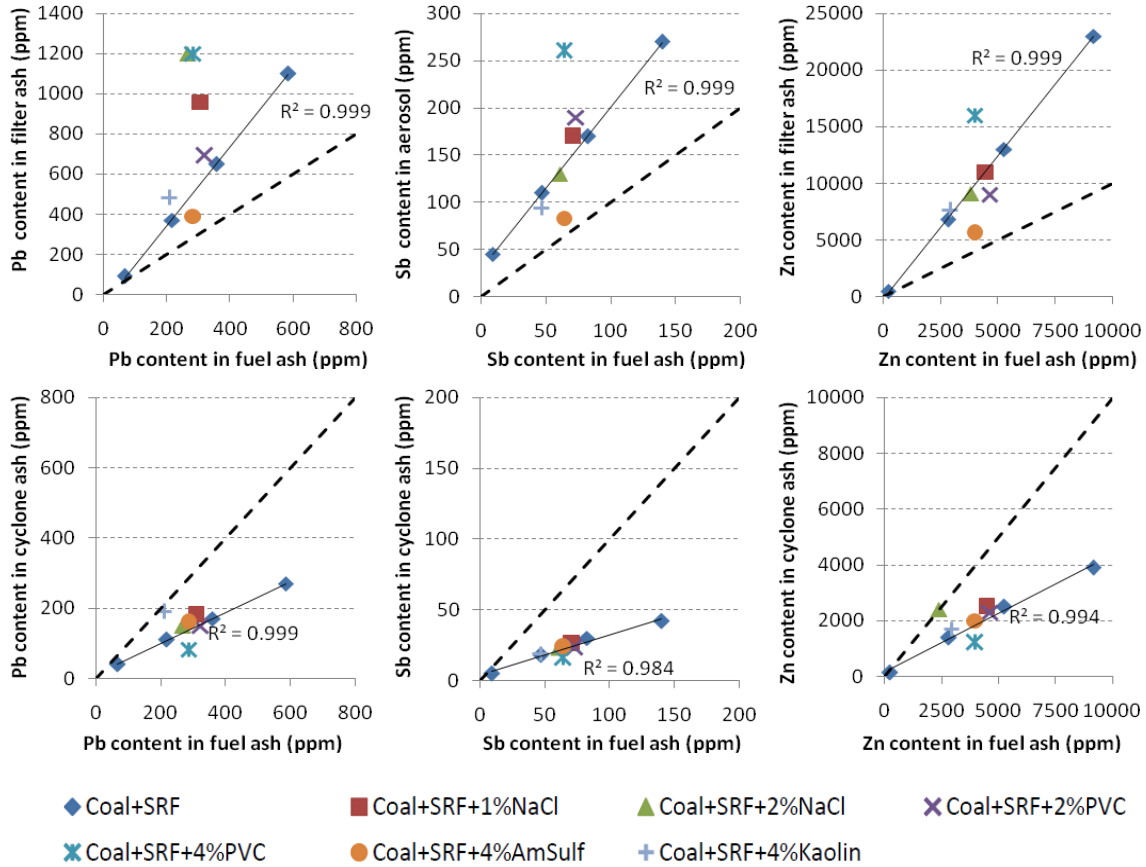


Figure 4: The contents of Pb, Sb and Zn in the filter ashes and cyclone ashes collected from different experiments versus their contents in the fuel ashes

The effects of additives on the trace element contents in the cyclone and filter ashes are also illustrated in Figure 3 and Figure 4. The main tendency is that the chlorine based additives (NaCl and PVC) generally enrich the contents of As, Cd, Pb and Sb in the filter ashes. This effect is particularly pronounced with the addition of 4 wt% PVC. However, the influences of chlorine based additives on Zn and Cr are somewhat different. For Zn, most of the chlorine based additives do not have a significant effect on the Zn contents in the filter ashes, except for the addition of 4 wt% PVC which shows an obvious enhancing effect. For Cr, the chlorine based additives appear to have a reduction effect on their contents in the filter ashes. In comparison with the influences on filter ashes, the effects of the chlorine based additives on the cyclone ashes are generally less significant. One notable impact is that the As, Cd, Pb, Sb and Zn contents in the cyclone ashes are depleted to some extent by the addition of 4 wt% PVC. Besides, the addition of NaCl seems to slightly enrich some trace element contents (such as Cd and Zn) in the cyclone

ashes. For Cr, it is found that most of the chlorine based additives increase the Cr contents in the cyclone ashes.

Compared with chlorine based additives, the effects of Kaolin are not significant on the contents of As, Cd, Sb and Zn in the cyclone ashes and filter ashes. For Pb, it seems that the addition of Kaolin significantly enriches the Pb contents in the cyclone ashes and slightly enriches the contents in the filter ashes. For Cr, the addition of Kaolin shows a reduction effect on the contents in filter ashes and an enhancing effect on the contents in the cyclone ashes.

The addition of 4 wt% AmSulf generally depletes the contents of different trace elements in the filter ashes. However, the impacts of AmSulf on the trace element contents in the cyclone ashes are almost negligible. The results present in Figure 3 and Figure 4 demonstrate the influences of the additives on the trace element contents in the cyclone ashes and filter ashes. However, further discussions on the effects of the additives on the partitioning of trace elements and the underlying mechanisms will be carried out in Section 3.3.

### 3.3 Volatility of the trace elements

To assess the relative volatility of trace elements in pulverized coal combustion, a widely applied method is the enrichment of trace elements in different ash fractions with respect to the fuel ashes [6,16]. However, the results and discussions performed in Section 3.2 reveal that such enrichment in this study would be interfered by the mass balances of trace elements which are considerably lower than 100% (as indicated by Figure 2) and the unreacted trace elements in the SRF. To minimize those influences, the following relative enrichment (RE) factor is applied in this study to evaluate the volatility of trace elements during different experiments:

$$RE\ factor = \frac{C_i\ in\ filter\ ash / C_{Al}\ in\ filter\ ash}{C_i\ in\ cyclone\ ash / C_{Al}\ in\ cyclone\ ash} \quad (1)$$

where  $C_i$  is the content of element  $i$  and  $C_{Al}$  is the content of Al.

Similar as the relative enrichment factor used in [20,21], the equation above uses Al as a reference element, as Al is usually considered as an abundant and nonvolatile element with relative even distribution at different particle sizes. The RE factor of an element indicates whether the element is enriched (RE factor > 1) or depleted (RE factor < 1) in the filter ashes, with respect to the content in the cyclone ashes.

It should be noted that the filter ashes and cyclone ashes collected in this study are separated by a cut-off diameter of 2.5  $\mu\text{m}$ . The cyclone ashes particles mostly consist of spherical particles formed by included/excluded minerals, whereas the filter ashes would contain both spherical particles formed by minerals and nucleates formed from the nucleation and coagulation of the vaporized major inorganic elements [22]. The vaporized trace elements would partition to the cyclone ashes and filter ashes through the condensation and/or gas-solid reactions. Both mechanisms would favor the enrichment of

trace elements in filter ashes [1,16-18], and the RE factor would increase with increasing vaporization degree of trace elements. However, if the vaporization degree of a trace element is constant, a shift from gas-solid reaction mechanism to condensation mechanism may also result in a higher RE factor. This is primarily due to that the gas-solid reaction mechanism would lead to trace element concentration proportional to  $1/d_p$ , whereas the condensation mechanism would cause the trace element concentration proportional to  $1/d_p^2$  in continuum regime (larger than  $0.5-1\mu\text{m}$ )[16-18]. Therefore, the condensation mechanism would lead to a higher enrichment of trace element in small particles (around  $0.5-2.5\mu\text{m}$ ), compared with the reaction mechanism. In addition, there are probably more particles available for condensation than for gas-solid reaction, which would further promote the enrichment of trace elements in small particles when the condensation mechanism is important. As a consequence, an increased RE factor of a trace element can be read as a higher vaporization degree of the trace element and/or a shift from reaction to condensation mechanism. Both influences need to be considered in interpreting the results of RE factor.

### 3.3.1 Behaviors of Si and Cr

The RE factors of Si and Cr in different experiments are present in Figure 5. It can be seen that the RE factors of Si are rather consistent in the experiments, with values mostly between 0.7 and 0.8. The results are in line with a number of studies, showing that Si is an element with low volatility in pulverized coal combustion and the content of Si in the submicron particles are slightly lower than that in the larger fly ash particles [22,23].

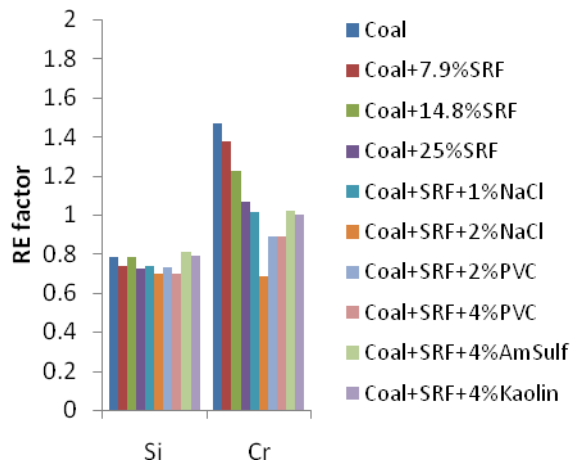


Figure 5: RE factors of Si and Cr in different experiments

For Cr, it can be seen the RE factor of Cr in coal combustion is about 1.5, indicating that the volatility of Cr is slightly higher than that of Al or Si. Similar behaviors of Cr have been observed in some other studies [17,21]. When coal is co-fired with SRF, it is found that RE factor of Cr decreases with increasing share of SRF. Similar reduction effect on the volatility of Cr has been observed during co-combustion of coal with sewage sludge [6] or RDF [7]. The reduced volatility of Cr was attributed to the lower flame temperature in co-combustion [6]. For co-

combustion of coal and SRF, it is most likely that the flame temperature would also decrease with increasing share of SRF, as the flame temperature of a similar waste derived fuel (RDF) is found to be  $200-300^{\circ}\text{C}$  lower than that of a coal flame with same excess air ratio [24]. The sensitivity of Cr vaporization on temperature has been demonstrated by thermodynamic calculations [6,25]. Besides, the associations of Cr may also be different in the coal and SRF, which may be responsible for the reduction of RE

factors. However, the study of trace element associations in coal and SRF is outside the scope of this work.

For different additives, it is shown that the RE factors of Cr are reduced to some extent with the addition of chlorine based additives, especially for case with 2 wt% NaCl. The addition of 4 wt% AmSulf or 4 wt% Kaolin also appears to have a reduction effect on the RE factor of Cr, but not as significant as that of chlorine based additives. For the addition of NaCl, AmSulf and Kaolin, it may be the case that the flame temperature in those experiments is further lower than that in co-combustion of coal and SRF, since vaporization of NaCl as well as the decomposition of AmSulf and Kaolin are all endothermic processes. For the addition of PVC, some thermodynamic calculations predict that the vaporization of Cr could be significantly enhanced with a large increase of HCl concentration in the flue gas, due to the formation of  $\text{CrO}_2\text{Cl}_2$  [1]. However, such an effect is not observed in this study. Overall, the results shown in Figure 5 reveal that Cr does not have a high volatility in co-combustion of coal and SRF. The volatility of Cr decreases with increasing share of SRF, and are further reduced by the additives used in this study.

### 3.3.2 Behaviors of Cd and Pb

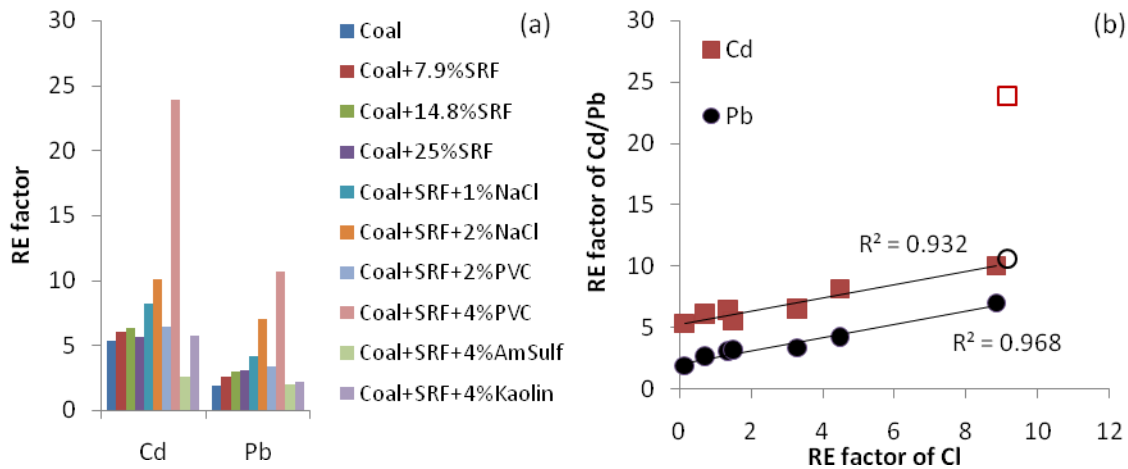


Figure 6: (a) The RE factors of Cd and Pb in different experiments; (b) Comparison of the RE factors of Cd and Pb versus the RE factor of Cl in different experiments (the open symbols denote the results from the addition of 4 wt% PVC).

The RE factors of Cd and Pb in different experiments are shown in Figure 6a. When coal is co-fired with the SRF, the RE factors of Cd are in a range of 5-7, and tend to increase slightly with increasing share of SRF. The effects of the chlorine based additives are obvious. With the addition of 1 wt% and 2 wt% NaCl, the RE factors of Cd are increased to 8.2 and 10 respectively. With the addition of 2 wt% and 4 wt% PVC, the RE factors of Cd become 6.4 and 23.4 respectively. To further illustrate the impacts of chlorine on the volatility of Cd, the RE factors of Cd from different experiments are plotted versus the RE factors of Cl in Figure 6b (the experiments with AmSulf and Kaolin are excluded due to chlorine contents in the ashes from these experiments are under the detection limit). A

general positive correlation is found between the RE factor of Cd and the RE factors of Cl, indicating that the partitioning of Cd is closely related with that of Cl. If the experiment with 4 wt% PVC is excluded, such correlation is almost linear. However, in the case with 4 wt% PVC addition, a remarkably higher RE factor of Cd is obtained. The influences of chlorine based additives may be primarily related with the formation of  $\text{CdCl}_2$ , which is a volatile and thermodynamically favorable compound when chlorine is present in the flue gas [13,14]. Although most of the thermodynamic calculations predict that Cd would be totally volatilized at combustion temperature [13,14], retention of Cd at high temperature is observed [14], possibly related with the association forms of Cd in the fuels and the limitations on the reaction time or mixing level in a combustor. For the experiments in this study, it may be the case that the injected chlorine based additives would react with some of the relatively stable Cd species in the fuels and increase the overall vaporization degree of Cd.

With the addition of 4 wt% AmSulf, it is seen that the RE factor of Cd is decreased notably, indicating a reduced vaporization degree of Cd at this condition. The reduction may be both related with the possible lower flame temperature caused by the decomposition of AmSulf (as discussed in Section 3.3.1) and the chemical reactions between AmSulf and the Cd in the fuels, such as the reaction between  $\text{SO}_3$  and Cd which forms  $\text{CdSO}_4$  [13]. However, to further illustrate the possible chemical effects of AmSulf, it is desirable to perform thermodynamic calculations at this extreme high sulphur condition, which is not yet performed in this paper. The addition of 4 wt% Kaolin also shows a reduction effect on the RE factor of Cd. It is most likely that part of the vaporized Cd has been reacted with the injected Kaolin particles. The mechanisms of such reactions have been well described in [15].

As shown in Figure 6a, the RE factor of Pb is in a range of 2-3 during co-combustion of coal and SRF, and it increases slightly with increasing share of SRF. The addition of chlorine based additives generally enhance the RE factors of Pb, particularly for the addition of 4 wt% PVC. Similar as Cd, the RE factors of Pb are plotted versus the RE factors of Cl in Figure 6b. It can be seen that positive corrections generally exist between these two factors. If the result of 4 wt% PVC addition is not considered, it can be seen that the RE factor of Pb increases almost linearly with the RE factor of Cl. However, for the case with 4 wt% PVC addition, the RE factor of Pb is higher than that predicted from the tendency of other experiments. According to thermodynamic calculations [13,14], the presence of chlorine in the combustion would favor the formation of  $\text{PbCl}_2$ , which is a volatile compound at flue gas temperature higher than  $700^\circ\text{C}$ . Therefore, it could be the case that the injection of chlorine based additives would promote the vaporization of Pb through the formation of  $\text{PbCl}_2$ . Furthermore, with the addition of chlorine based additives, the distribution of the vaporized Pb compounds may be shift from  $\text{PbO}$  to  $\text{PbCl}_2$ . This transition may inhibit the reactions between vaporized Pb and coal minerals such as Kaolin [1,15], and cause a shift of the reaction mechanism to the condensation mechanism, which would also increase the RE factor of Pb.

Different from the chlorine based additives, the addition of AmSulf and Kaolin both have reduction effects on the RE factor of Pb. For the addition of AmSulf similar explanations

that have been used for Cd may be applied here, i.e. lower flame temperature and chemical effects caused by the  $\text{SO}_3$  from AmSulf decomposition. The lower Pb volatility during Kaolin addition is probably related with the reaction between the vaporized Pb species and Kaolin [15]. In comparison with Cd, the reduction effect of Kaolin is more significant for Pb, which is consistent with the different capture efficiency/rate found for these two elements and Kaolin [1,15].

### 3.3.3 Behaviors of As, Sb and Zn

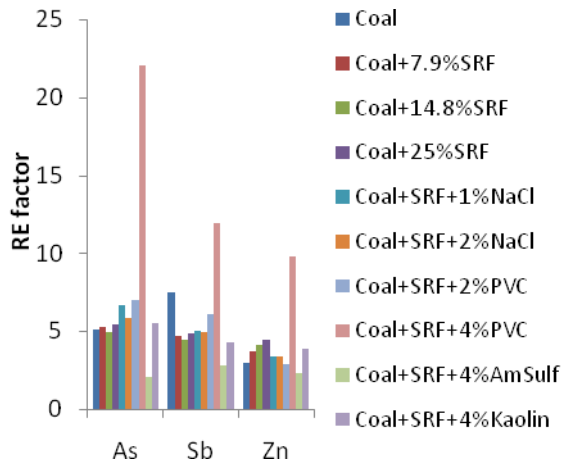


Figure 7: RE factors of As, Sb and Zn in different experiments

Figure 7 shows the RE factors of As, Sb and Zn in the experiments. It can be seen that the RE factor of As is around 5 when coal is co-fired with SRF. Although the RE factor of As varies slightly, no obvious difference is seen with different share of SRF. However, for the addition of chlorine based additives, the RE factor of As is generally increased. This effect is particularly pronounced with the addition of 4 wt% PVC, in which the RE factor of As becomes about 22. The increased RE factor of As during the injection of chlorine based additives is in line with other studies which found that the injection of HCl enhanced the condensation of As on small fly ashes [14]. This may be related with the formation of  $\text{AsCl}_3$ , which is a volatile compound at combustion temperature and could increase the vaporization degree of As [26]. Thermodynamic calculations indicate that the presence of other major inorganic elements such as Na and K may decrease the concentration of gaseous chlorine available for reacting with As [26]. This may explain the high volatility of As found in the injection of 4 wt% PVC, since the major inorganic elements probably do not play an important role in this experiment and a large amount of gaseous chlorine would be available for reacting with As. For the addition of 4 wt% AmSulf, it can be seen that the RE factor of As is reduced significantly. This result is in agreement with a study showing that the injection of  $\text{SO}_2$  increased the retention of As in ash by 30% [14]. Since the sulphur retention effect was not predicted by thermodynamic calculation [14], it was suggested there may be some As compounds which has not been taken into account in thermodynamic calculations. These compounds may have high condensation temperature and would decrease the vaporization degree of As. The addition of 4 wt% Kaolin does not show a noticeable effect on the RE factor of As.

For Sb, it is found that its RE factor in dedicated coal combustion is about 7.5, which is significantly higher than those in co-combustion of coal and SRF. The significant difference may be related with the association form of Sb in the two fuels. It has been found that the Sb in coals may be primarily associated with pyrite or organically bounded, which would be easy to vaporize during combustion [16]. For the SRF, the Sb

may be inorganically bounded with more stable species. However, this explanation needs to be confirmed by performing association analysis of the trace element in the two fuels, which is outside the scope of this work. According to Figure 7, the addition of NaCl does not have obvious effects on the RE factor of Sb, whereas the addition of PVC appears to increase the RE factor of Sb. Since the addition of PVC would largely increase the HCl concentration, it seems that the vaporization of Sb can be enhanced with the presence of a large amount of HCl, although such effects are not predicted from thermodynamic calculations [27]. For the addition of AmSulf, it can be seen that the RE factor of Sb is reduced slightly. However, the addition of Kaolin does not show an evident influence on the RE factor of Sb.

The RE factor of Zn is found to increase slightly with increasing share of SRF, when the coal is co-fired with SRF. This observation is in line with the results from co-combustion of coal with sewage sludge [6]. It may be related with the associations of Zn in the SRF and coal. It has been found that Zn in municipal waste can be associated as pigments for waste wood or stabilizers for plastic [19], which would be easier to vaporize than the silicates associated Zn in some coals [16]. For the addition of NaCl or 2 wt% PVC, the RE factor of Zn is slightly decreased compared with the experiment without additives. For NaCl, this may be partly related with the lower flame temperature at this experiment, which would adversely affect the vaporization of Zn. During the addition of 4 wt% PVC, the RE factor of Zn is considerably increased. In this experiment, the HCl concentration in the flue gas would be very high, which may shift the distribution of Zn from relative stable ZnO to more volatile ZnCl<sub>2</sub> [28]. For other additives, the addition of Kaolin shows an insignificant effect on the RE factor of Zn, However, the addition of AmSulf gives a reduction effect, which is likely related with the possible low flame temperature at this condition, since the chemical effect of SO<sub>2</sub>/SO<sub>3</sub> would probably not be significant for the vaporization of Zn, both confirmed by experiments and thermodynamics [14].

## 4. CONCLUSIONS

The behaviors of As, Cd, Cr, Pb, Sb and Zn in co-combustion of coal and SRF are studied in an entrained flow reactor, and the influences of NaCl, PVC, ammonium sulphate (AmSulf) and Kaolin on the partitioning of these trace elements are investigated. During the experiments, the ashes from combustion are separated into bottom ashes, cyclone ashes and filter ashes. By analyzing the ashes from different co-combustion experiments, it is found that the As, Cd, Pb, Sb and Zn contents in the filter ashes/cyclone ashes are almost proportional to their contents in the fuel ashes, and the contents in the filter ashes are significantly higher than those in the cyclone ashes. The partitioning of trace elements is influenced by the additives. In general, the chlorine based additives (NaCl and PVC) enrich the contents of As, Cd, Pb and Sb in the filter ashes, and reduce the Cr content in the filter ashes. The addition of AmSulf shows a general reduction effect on all of the trace elements in the filter ashes. Most of the additives do not have significant impacts the trace element contents in the cyclone ashes, whereas the addition of Kaolin enriches the Pb content in the cyclone ashes.



To evaluate the volatility of trace elements in different experiments, a relative enrichment (RE) factor, which compares the trace element content in the filters with that in the cyclone ashes, has been introduced. The results reveal that the volatility of Cr is low compared with other studied trace elements. The volatilities of As, Cd, Pb, Sb and Zn are generally found to be high in the experiments, suggesting a large fraction of those elements are vaporized during combustion. The detailed behaviors of those elements in co-combustion of coal and SRF, and the effects of different additives are summarized here:

- The RE factor of Cr is found to decrease with increasing share of SRF, and all of the additives show a reduction effect on its RE factor.
- For Cd and Pb, their RE factors increase slightly with increasing share of SRF, and can be further enhanced by the chlorine based additives, The positive correlation between the RE factor of Cd/Pb and the RE factor of Cl indicates that the partitioning of Cd/Pb is closely related with that of Cl. The addition of AmSulf reduces both the RE factor of Cd and Pb. The addition of Kaolin shows an evident reduction effect on the RE factor of Pb which is linked with the reactions between kaolin and the vaporized Pb.
- The influences of different SRF share and Kaolin are not significant on the RE factor of As. The chlorine based additives generally show an enhancing effect on the RE factor of As, while the addition of AmSulf has an opposite effect.
- For Sb, it is found that its RE factor is significantly lower in co-combustion of coal and SRF, compared with that in dedicated coal combustion. The addition of NaCl and Kaolin does not have an obvious influence on the RE factor of Sb. The addition of PVC enhances the RE factor of Sb, while the addition of AmSulf shows a reduction impact.
- The RE factor of Zn increases slightly with increasing share of SRF during co-combustion, which may be related with the different associations of Zn in the coal and SRF. The addition of chlorine based additives generally adversely affect the RE factor of Zn, expecting for the addition of 4 wt% PVC which remarkably enhances its RE factor. The addition of AmSulf reduces the RE factor of Zn, while the addition of Kaolin does not have an obvious influences.

The results from this study imply that co-combustion of coal and SRF in a coal-fired power plant may increase the contents of trace elements in the large and fine fly ash particles significantly, primarily due to the higher trace element contents in the SRF compared to coal. Compared with dedicated coal combustion, the volatility of trace elements may also be affected when coal is co-fired with SRF. For Cd, Pb and Zn, their volatilities in co-combustion of coal and SRF seem to be slightly higher than those in the dedicated coal combustion, which may further increase the emission of these trace elements. The chlorine content in the SRF is found to be an important parameter that may enhance the volatilities of some trace elements such as Cd, Pb and As. Besides, the sulphur and aluminosilicates content in the coal may reduce the volatilization of typical trace elements such as Pb. These properties would be important for controlling the emission of trace elements during co-combustion of coal and SRF.

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