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# Trace elements in co-combustion of solid recovered fuel and coal

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## ABSTRACT

Trace element partitioning in co-combustion of a bituminous coal and a solid recovered fuel (SRF) was studied in an entrained flow reactor. The experiments were carried out at conditions similar to pulverized coal combustion, with SRF shares of 7.9 wt.% (wet basis), 14.8 wt.% and 25.0 wt.%. In addition, the effect of additives such as NaCl, PVC, ammonium sulphate, and kaolinite on trace element partitioning was investigated. The trace elements studied were As, Cd, Cr, Pb, Sb and Zn, since these elements were significantly enriched in SRF as compared to coal. During the experiments, bottom ash was collected in a chamber, large fly ash particles were collected by a cyclone with a cut-off diameter of  $\sim 2.5 \,\mu m$ , and the remaining fly ash particles were gathered in a filter. It was found that when coal was co-fired with SRF, the As, Cd, Pb, Sb and Zn content in filter ash/cyclone ash increased almost linearly with their content in fuel ash. This linear tendency was affected when the fuels were mixed with additives. The volatility of trace elements during combustion was assessed by applying a relative enrichment (RE) factor, and TEM-EDS analysis was conducted to provide qualitative interpretations. The results indicated that As. Cd. Pb. Sb and Zn were highly volatile when co-firing coal and SRF, whereas the volatility of Cr was relatively low. Compared with coal combustion, co-firing of coal and SRF slightly enhanced the volatility of Cd, Pb and Zn, but reduced the volatility of Cr and Sb. The Cl-based additives increased the volatility of Cd, Pb and As, whereas addition of ammonium sulphate generally decreased the volatility of trace elements. Addition of kaolinite reduced the volatility of Pb, while the influence on other trace elements was insignificant. The results from the present work imply that trace element emission would be significantly increased when coal is co-fired with SRF, which may greatly enhance the toxicity of the dusts from coal-fired power plant. In order to minimize trace element emission in co-combustion, in addition to lowering the trace element content in SRF, utilizing SRF with low Cl content and coal with high S and aluminosilicates content would be desirable.

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#### 1. Introduction

Trace element emission is one of the major environmental concerns for pulverized coal-fired power stations. During pulverized coal combustion, the trace elements in the fuel usually undergo complicated chemical and physical transformations, and a fraction is eventually emitted to the atmosphere as dust or vapor [1-7]. Due to the adverse health effect [1], it is desirable to control the emission of trace elements from coal-fired power stations.

Co-combustion of coal and secondary fuel such as biomass and waste is recognized as a promising approach to reduce the  $CO_2$  emission from pulverized coal-fired power stations [8]. The typical secondary fuels are biomass such as straw [9,10] and wood [11], and waste derived fuels such as sewage sludge [4] and refuse derived fuels [12-15]. When biomass is used as the secondary fuel in

co-combustion, the emission of trace elements is usually not of great concern, since the trace element content in most biomass is much lower than that of coal. In contrast, waste derived fuels are often characterized by a significantly larger trace element concentration than coal [4,14]. Thus it is of importance to characterize the behavior of trace elements during co-combustion of coal and waste derived fuel.

The behavior of trace elements during pulverized fuel combustion is well-known to be influenced both by the fuel properties and combustion conditions. The trace elements present in the fuels can be 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 [1,2,6,16,17]. Similar investigations were also carried out on waste derived fuels such as sewage sludge [5] and refuse-derived char [18]. These studies generally suggest that the organically associated trace elements are more easily to vaporize during combustion than those associated with minerals [1]. On the

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other hand, the vaporization behavior of trace elements is also influenced by parameters such as combustion temperature, transport/ mixing phenomena, oxidizing/reducing condition, and the presence of gaseous species such as HCl and SO<sub>2</sub> [3]. In most cases, the presence of gaseous chlorine may shift the distribution of trace elements such as Pb and Cd towards more volatile chlorides, thus promoting the vaporization [1,3,19]. However, the presence of SO<sub>2</sub> may result in the formation of sulphates with relatively low vapor pressure [19].

After being vaporized from the fuel, the trace elements may undergo reactions both with the ash particles and the gaseous species in the flue gas [19,20]. The reactions between the vaporized trace elements and the ash particles constitute an important mechanism for the retention of trace elements in large fly ash particles that are easier to be captured by the air pollution control systems [1,2]. Typical examples are the reactions between trace elements such as Cd and Pb and aluminosilicates such as kaolinite [20]. Such reactions occur primarily on the particle external surface and may result in trace element concentration in the ash particle being proportional to  $1/d_{\rm p}$ (particle diameter) [1,21-23]. On the other hand, the vaporized trace elements may also react with other gaseous species in the flue gas, such as HCl and SO<sub>2</sub>. These reactions can alter the condensation behavior of the trace elements. In addition, they may influence the reactions between the vaporized trace elements and ash particles, since trace element in different gaseous forms (such as chlorides or hydroxides) may have different reaction rates with the ash particles [1].

When the flue gas temperature becomes lower than the dew point of a trace element species, condensation may occur on the surface of the existing ash particles. For ash particles in the continuum regime (supermicron particles with Kn<<1) condensation may lead to the trace element concentration in the ash particles being proportional to  $1/d_p^2$ , while for particles in the free molecular regime (ultrafine particles with Kn>>1) the concentration of the condensed trace element may be proportional to  $1/d_p$  [21-23]. One should be aware that the correlations mentioned earlier are based on several assumptions which may deviate from practical situations, such as perfect spherical and nonporous particles [23]. Therefore care must be taken in applying these theoretical correlations in practice.

All of the mechanisms mentioned earlier can influence the partitioning of trace elements in combustion. For a practical combustion system, the partitioning of trace elements involves complex processes such as vaporization, reaction, nucleation, condensation and coagulation. These processes become more complicated when a secondary fuel is introduced to the system, since it may have different fuel properties and combustion behavior as compared with the primary fuel. In order to evaluate the behavior of trace elements during co-combustion in a pulverized coal-fired plant, performing controlled experiments at combustion conditions similar to a practical plant is an advantageous approach.

The objective of the present work was to study the partitioning of trace elements in co-combustion of coal and solid recovered fuel (SRF) at conditions similar to a pulverized coal-fired plant. This was achieved by performing experiments in an entrained flow reactor, and by investigating the trace element partitioning in different ash fractions (bottom ash, cyclone ash and filter ash). It should be noted that the conditions in the entrained flow reactor are not fully representative of a pulverized coal-fired plant, with respect to particle residence time, temperature profile and fluid flow. Therefore the results from the present work may not fully represent the practical situation. The trace elements studied were As, Cd, Cr, Pb, Sb and Zn. These elements were emphasized since their content in the SRF was significantly (~5-150 times) larger than that of coal. The experiments were carried out at coal combustion with different SRF share conditions (7.9 wt.%, 14.8 wt.% and 25.0 wt.%, wet basis). In addition, the effect of additives such as NaCl, PVC, ammonium sulphate, and kaolinite on the behavior of trace elements was investigated. These additives were selected since they may have notable effect on the partitioning of trace elements [19,20]. Therefore the results from the present work could provide suggestions for trace element emission control in co-combustion of coal and SRF, through a systematic assessment of the behavior of trace elements at different fuel conditions.

#### 2. Experimental

#### 2.1. Fuels and additives

The fuels used in the experiments were a Columbian bituminous coal and a SRF mainly comprised of waste paper, plastics and wood. The selected additives were PVC, NaCl,  $(NH_4)_2SO_4$  (denoted as AmSulf) and kaolinite, which are all pure compounds purchased from chemical companies. The properties of the fuels are listed in Table 1. It can be seen that the SRF has relatively larger volatile, Cl and Ca content than the coal, while it is lower in S, Si, Al and K. The trace element content in the two fuels is significantly different. The content of As, Cd and Cr in the SRF is 5–10 times larger compared to the coal. For Pb, Sb and Zn, the content in the SRF is 30–150 times larger than that of coal.

The SRF used in the present work has been pulverized by an Alpine® pin mill. Although SRF is normally regarded as a heterogeneous fuel, the grinding process has significantly improved the homogeneity of the SRF. For confirmation, the Si and Al content in the SRF have been analyzed 3 times and the average deviations were found to be 9% and 13%, respectively. This indicates that the SRF is quite homogeneous. In addition, the homogeneity of the SRF has been further evaluated by performing repeating co-combustion experiments, showing a good reproducibility of the NO and SO<sub>2</sub> emission during co-combustion of coal and SRF (average deviation <2%).

The particle size distribution of the fuels and additives was analyzed by a 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. The  $d_{50}$  of PVC, NaCl, AmSulf, and kaolinite is about 104  $\mu$ m, 259  $\mu$ m, 222  $\mu$ m, and 8  $\mu$ m, respectively. It should be noted that the SRF particles used in the present work tend to form clusters, whereas the other fuel/additive particles do not have such behavior.

## 2.2. Setup

The co-combustion experiments are carried out in an entrained flow reactor shown schematically in Fig. 1. The setup consists of a gas supplying system, a fuel feeding system, a gas preheater, a vertical reactor electrically heated by 7 heating elements, a bottom chamber, a particle and gas extraction system, and an ash deposition system simulating deposit formation on the superheater tubes of a boiler. The

Tabl	e 1	
Fuel	properties	

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

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