

RESEARCH REPORT NO D4.4-7 & D4.4-8 HELSINKI 2016

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Thermodynamic modeling of ash formation in combustion of solid recovered fuels (SRF) and the influence of chlorine and sulfur on the ash chemistry

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CLIC INNOVATION OY ETELÄRANTA 10 P.O. BOX 10 FI-00131 HELSINKI, FINLAND CLICINNOVATION.FI

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ISBN 978-952-5947-95-3 ISSN XXXX-XXXX



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Thermodynamic modeling of ash formation in thermal conversion of solid recovered fuels (SRF) and the influence of chlorine and sulfur on the ash chemistry

ARVI Deliverable 4.4-7 and 4.4-8





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Key words: Thermodynamic modeling, volatilization, ash formation, solid recovered fuel

Summary

In the present study, the speciation and volatilization of Co, Cu, and Sb in thermal conversion of SRF at various temperatures and air/fuel ratios were studied using thermodynamic equilibrium modeling. The main goal was to study if there are conditions in the combustion unit where these elements are feasible to separate and enrich from other ash-forming matter. Based on the predicted results, cobalt occurs mainly in the condensed phases and is not feasible for enrichment in fly ash or filter ash. Copper is enriched in the gas phase at especially oxidizing conditons if chlorine levels in the fuel is high. Controlled conditions in relation to local temperature of the flue gas and air staging are possible methods to form fly ash or filter ash enriched in copper compounds. In general, concentration of copper is considerably higher than antimony and cobalt in waste-derived fuels. Antimony is predicted to be mainly in the flue has except at oxidizing conditions below 600 °C, and it is therefore possible to enrich antimony in filter ash if a hot cyclone is utilized to separate condensed fly ash particles from the flue gas stream that contains the volatilized ash forming elements. The effect of sulfur and chlorine on the ash chemistry was not very pronounced in the present study. Higher chlorine levels increased volatility of alkali species, Pb, Zn, and Co, but Cu and Sb were not affected to any large extent. Increase of sulfur levels had only minor effects. Complete removal of sulfur and chlorine decreased the volatility of Pb and the alkali metals at lower temperatures. Results suggest that Cu and Sb concentrations in filter ash condensates are considerably higher than the levels in the bulk fuel. However, uncertainties in the calculations stemming from missing or uncertain thermodynamic data, or applicability of the thermodynamic equilibrium assumption for the predictions, are issues that need to be studied, and the predicted results need to be verified with experimental data.



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1. Introduction

Different types of ash fractions and various types of APC (air pollution control) residues are formed in thermal conversion of the waste-derived fuels. The solid residues from WtE plants may contain harmful components, such as toxic metal compounds and organic micropollutants, which may lead to problems in the utilization or safe disposal of the material. Various treatment methods and processes can be used to to reduce the leachability of harmful residue constituents, destroy toxic organic compounds (organic micropollutants), reduce residue volume, and produce material suitable for utilization.

Van der Sloot et al. [1], Sabbas et al. [2], Quina et al. [3], Whiticar and Ralph [4], and Zacco et al. [5] have recently reviewed different approaches in the management of the ash and solid APC residues from waste combustion. The two main approaches are safe disposal and recycling or reuse of the ash. In order to safely dispose of or reuse/recycle the ash, separate treatment processes are often required.

The main treatment methods for ash and APC residues can be divided into three groups: 1) separation process (physical or chemical); 2) stabilization and solidification; 3) thermal treatment. Table 1 gives an overview of the principles and methods for treatment of MSW ash, based on the reviews of the International Ash Working Group [6], van der Sloot et al. [1], Sabbas et al. [2], and Whiticar and Ralph [4].

Lindberg et al. [7] recently reviewed different thermal treatment methods of MSW ash residues. The main categories for thermal treatment are vitrification, fusion/melting, and sintering. The thermal methods are mainly differentiated based on the characteristics of the process product, rather than the process itself. In vitrification, a glassy phase is produced, whereas in fusion processes, a crystalline or heterogeneous product is formed by melting the ash or residue. In sintering, the residues are heated to achieve a reconfiguration of solid materials.

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In addition, thermal separation processes may also be combined with the abovementioned processes to vaporize harmful trace elements from the bulk material. Thermal treatment processes are among the best methods to destroy harmful organic compounds, such as dioxins and furans, present in the solid residues.



Table 1. Overview of principles and methods of treatment of ash residues from WtE plants [1, 2, 4, 6].

Treatment Principle	Processes/methods and Unit	
	Operations	
Chemical and physical separation	Washing	
	Chemical precipitation	
	Crystallization/evaporation	
	lon exchange	
	Density and particle size based separation	
	Distillation	
	Electrolysis	
	Electrokinetic separation	
	Magnetic separation	
	Eddy-current separation	
	Chemical extraction/mobilization	
	Adsorption	
Stabilization and/or solidification	Solidification/stabilization with hydraulic binders and pore-filling additives	
	Chemical stabilisation	
	Ageing/weathering	
Thermal treatment	Sintering	
	Vitrification	
	Melting	
	Vaporization/condensation	



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Most of the thermal methods are processes separated from the thermal conversion of the fuel. One exception is the gasification-melting process or the direct melting process [8-10]. MSW is gasified in a fluidized bed reactor and the syngas is used as the heat source for the ash melting. The gasification-melting process may lead to better separation of different elements compared to traditional MSW incineration, with elements distributed between a silicate slag, the fly ash in the process and a metallic phase [10]. Pb, Zn, and Cl tend to form fly ash, whereas Fe and Cu form a metallic phase. Other common ash-forming elements are distributed in both fly ash and the silicate slag.

Another in-situ process for elemental separation into different fractions is the use of hot cyclones in the combustion unit.

During combustion or gasification, heavy metals such as Cd and Pb volatilize. The volatilized metals condense when the gas is cooled and will be found in the fly ash or filter ash. The use of a hot cyclone prior to the heat exchanger could make it possible to separate the heavy metals from the fly ash. In a hot cyclone separation concept, the fly ash is collected in a hot cyclone, where volatilized heavy metals continue with the flue gas stream and is collected as filter ash. In an ideal case, the cyclone ash is heavy metal free, and can be used directly as a product, while the filter ash is highly enriched in heavy metals and may be more easily handled due to lower volumes of hazardous ash (Figure 1).



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Figure 1 Schematic picture of the hot cyclone separation process used by Ljung and Nordin [11].



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Ljung and Nordin [11] studied the fate of different elements during combustion of a fast-growing energy tree (Salix spp.) and hot cyclone separation in theory using chemical equilibrium model calculations. The calculations were done with CHEMSAGE 3.0. Air to fuel ratio was set as 1.3 as an average of normal fluidized bed conditions. Pressure was set to 1 atm and temperature from 100 to 1600°C. Four different levels (0, 1, 10 and 100%) of S and CI were considered during the calculations.

When no S and CI was available Cd formed condensed $CdCO_3(s)$ and CdO(c) at lower temperatures and gaseous Cd at 700-750°C. When 50-100% of S and Cl in the fuel were available for reactions with Cd vaporized $CdCI_2(g)$ was formed at 600-800°C. At higher temperatures Cd(g) was formed. The distribution of Cd at different temperatures can be seen in Figure 2.



a) Distribution of Cd, no S or Cl available

Figure 2 Distribution of Cd a) no S or Cd available, b) 100% S and Cd available [11].



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Pb was highly influenced by the amount of CI and S available just like Cd. Pb formed stable carbonate and oxide at lower temperatures. PbO(g) started to volatilize at about 550°C. For higher amounts of CI and S gaseous chloride was formed already at temperatures below 100°C possibly depending on inaccuracies in thermochemical data of PbCl(g). For CI and S concentrations higher than 10% PbCl₄(g) was formed around 700°C.

Zn started to volatilize at temperatures above 1170°C. The Cl content had no significant effect on Zn or Arsenic. $As_4O_6(g)$ volatilizes at 550°C and AsO(g) at temperatures higher than 850°C. When the thermochemical data for $Ca_3(AsO_4)_2(c)$ was added the volatilization temperature became 1050°C. The distribution of Pb and Zn are shown in Figure 3.

Calculation results indicated that hot cyclone separation might be possible for Cd, Pb and Cu due to their relatively low volatilization temperatures. According to the calculations Ni, Zn and V would be difficult to separate with the hot cyclone due to their high volatilization temperatures. The calculations were in good agreement with results from previous field studies.



Figure 3. Distribution of a) Pb and b) Zn [11].

Obernberger and Biedermann [12] compared a combustion plant (Lofer) and a plant with integrated fractionated heavy metal separation (Straßwalchen). The temperature in the combustion zones was varied to check the influence on the heavy metal concentrations. A high-temperature cyclone was placed behind the furnace in Straßwalchen. The temperature in the cyclone varied between 950 and 1050°C. Figure 4 shows a schematic picture of the Straßwalchen plant.





<u>Explanations</u>: The temperatures shown are average measurement data from the test runs. <u>Abbreviations</u>: $T_{precip.}$ - precipitation temperature.

Figure 4. Straβwalchen combustion plant with high-temperature cyclone [12].

The Cd concentrations in the bottom ashes were about 20 times lower in the new plant compared to the old. Cd levels in combustion zone fly ash and fly ash from the high-temperature cyclone were also lower for the new plant. Cd concentrations in hot-precipitated fly ash showed clear temperature dependence. The Cd concentrations decreased with increasing temperature of ash precipitation. Figure 5 shows Cd concentrations in hot-precipitated fly ash at different temperatures.



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Figure 5. Temperature dependence of Cd concentrations in hot-precipitated fly ash [12].

Zn concentrations in the bottom ash were 5 times lower in the ash from the new plant compared to the old. Zn concentration in the combustion zone fly ash were lower than in hot-precipitated fly ashes produced in the old plant but considerably higher in the fly ash precipitated in the high-temperature cyclone. Zn showed no temperature dependence in the investigated range in either plant. The amounts of fly ashes produced were lower in the new plant and the amount of condensation sludge higher. The average distribution of Cd and Zn in different ash fractions are shown in Figure 6.



Figure 6. Average distributions of Cd and Zn in different ash fractions [12].



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Coarse fly ash particles could be separated from in the combustion zone at high temperatures with a hot cyclone catching the large scale particles between the furnace and the boiler of the plant. The temperature in the hot cyclone has to be above 900°C to be efficient for heavy metal fractionation.

Bajamundi et al. [13] studied the concentration of seven heavy metals in fly ash as a function of cyclone temperature. Refuse derived fuel (RDF), bark and impregnated wood were combusted in a bubbling bed reactor. Figure 7 shows a schematic picture of the experimental set-up and temperatures of the experimental runs. The investigated elements could be divided into two categories, elements with and elements without clear temperature dependence. Elements with clear dependence were Cr, Cu, Zn, Sb and Pb. The concentration of Pb decreased up to 720°C but after this a reverse trend was found. Elements without a clear dependence were As and Ni. Figure 8 shows the trace element concentrations at different temperatures.









Figure 8. Trace element concentrations in cyclone fly ash at different temperatures [13].

According to calculations Cd, Pb and Cu could be removed by hot cyclone separation from the fly ash [11]. Due to higher volatilization temperatures Ni and Zn would be difficult to separate from the fly ash. According to Obernberger et al. [12, 14] the cyclone temperature has to be over 900°C for efficient separation.

2. Objective and approach

Objective of the study is to investigate the ash chemistry in combustion of wastederived fuels (SRF) with emphasis on the separation of ash-forming elements in different ash streams during the thermal conversion of the fuel. The main division between different ash element streams is between elements that stay in a condensed form during the main conversion process and elements that form volatile species at temperatures prevailing at the conversion temperatures and air/fuel ratios. Predictons of this separation is done by using thermodynamic modeling based on Gibbs Energy Minimization. Thermodynamic modeling predicts the amount and composition of stable phases and components at chemical equilibrium at a specified temperature, total pressure and overall elemental composition. The approach does not require any prior knowledge of specific chemical reactions or intial speciation of elements. However, in the general approach, chemical kinetics cannot be considered. However, Kangas et al. [15, 16] have utilized a so-called constrained Gibbs Free Energy Method, where kinetic limitations can be considered for certain reactions. This is however



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not included in the present study. An overview of the approach is shown in Figure 9.



Figure 9. Schematic picture of global equilibrium modeling approach for predicting ash chemistry.

Thermodynamic equilibrium calculations

Thermodynamic equilibrium calculations were made to predict the speciation of the ash-forming elements as a function of temperature for) at both oxidizing and reducing conditions. The advanced thermodynamic modeling was performed using the software package Factsage, version 6.4[17]. A tailor-made thermodynamic database was used for the calculations. The data for the gas phase and the stoichiometric solid phases of the elements C-H-O-N-S-CI-Na-K-Zn-Pb-Ca-Mg-Fe-Al-Si-P-Ti-Co-Cr-Cu-Mn-Sb-Sn were taken from the FACT Pure substancedatabase in the Factsage software. It was assumed that N₂ was the only stable nitrogen compound as the formation of NO_x compounds in biomass combustion is strongly dependent on kinetics and N-speciation in the fuel. A multicomponent molten salt phase including NaCI- $KCI-Na_2SO_4-K_2SO_4-Na_2CO_3-K_2CO_3$ was also included together with corresponding solid solutions [18]. A molten silicate/slag phase is available in the thermodynamic databases in Factsage but was excluded due to calculational limitations. All condensed silicate phases are therefore considered as stoichiometric phases in the current calculations.

The main fuel studied in the present report is SRF (solid recovered fuel). The chemical composition of the fuel is given in table 2. It was based on the chemical



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composition of a SRF fuel that has been burned in an BFB plant in Anjalankoski operated by Stora Enso.

Table 2. Fuel composition of SRF used as input for the calculations.

FUEL: SRF					
Proximate analysis	moisture	wt-%	49.36		
	volatiles	wt-% (d.s.)			
	fixed carbon	wt-% (d.s.)			
	ash (815 °C)	wt-% (d.s.)			
	ash (550°C)	wt-% (d.s.)			
Ultimate analysis (dry solids)	C	wt-% (d.s.)	51.0		
	Н	wt-% (d.s.)	6.5		
	S	wt-% (d.s.)	0.2		
	0	wt-% (d.s.)	37.4		
	Ν	wt-% (d.s.)	0.7		
	Cl	wt-% (d.s.)	0.258		
	F	wt-% (d.s.)	0.003		
	Br	wt-% (d.s.)	0.001		
Element concentrations in the dry					
substance	AI	g/kg	3.324		
	Si	g/kg	8.936		
	Ti	g/kg	1.067		
	Na	g/kg	1.772		
	Mg	g/kg	1.421		
	К	g/kg	1.612		
	Са	g/kg	17.884		
	Fe	g/kg	1.596		
	Р	g/kg	0.559		
Heavy metals concentrations in the dry					
substance	Sb	mg/kg	3.58		
	As	mg/kg	0.73		
	Cd	mg/kg	0.24		
	Cr	mg/kg	50.16		
	Co	mg/kg	0.44		
	Cu	mg/kg	24.44		
	Pb	mg/kg	42.63		
	Mn	mg/kg	378.38		
	Hg	mg/kg	0.09		
	Ni	mg/kg	9.91		
	ТІ	mg/kg	0.50		
	Sn	mg/kg	15.91		
	V	mg/kg	3.30		
	Zn	mg/kg	159.44		

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The fuel compositions taken from table 2 were used as input for the calculations. Four different cases were considered: a) base case; b) base case with 2 x Cl; c) base case with 2 x S; d) base case with no S & Cl. The calculations were made as a function of temperature and air-to-fuel ratio (λ). The air-to-fuel ratio was varied between 0.4 and 1.2 with steps of 0.01 and the temperature was varied between 400 and 1300 °C with steps of 10 °C.

3. Results

The predicted main ash phases, the main gas components, and the minor gas components of ash forming elements (>1 ppm) are shown in in Figure 10 and 11 as a function of temperature for reducing and oxidizing conditions (λ =0.7 and λ =1.2). Ca-AI- and Ca-Mg-silicates dominate the condensed phases, whereas HCI, KCI, and SO₂ (oxidizing conditions) or H₂S (reducing conditions) are the main alkali, sulfur or chlorine species.

The elements Co, Cu, and Sb are of special interest in the present study for assessing the viability to recycle these elements from the ash [19-21]. It was concluded that these elements often occur in the waste ashes at levels higher compared to other sources, and therefore may have a potential to be recovered from the ash. In the present study, where solid recovered fuel was studied, Cu has the highest concentration in the fuel and Co has the lowest. It is of intereset to predict if these elements can be enriched in the flue gas so that they may be captured in filter ash instead of fly ash or bottom ash.

Cobalt is predicted to be present as Co(s, g), $Co_9S_8(s)$, $CoCl_2(g)$ at reducing conditions and $Co_3O_4(s)$, $CoCr_2O_4(s)$, $CoCl_2(g)$ at oxidizing conditions. Copper is predicted to present as Cu (s,l,g), Cu₂S(s), Cu₅FeS₄(s), CuCl(g) at reducing conditions, and CuO(s), CuFeO₂(s), CuCl(g) at oxidizing conditons. Antimony is predicted to be present as SbO(g), and Sb₂S₃(g) at reducing conditions and SbO(g), and Sb₂O₅(s) at oxidizing conditons. At reducing conditons, no condensed antimony compounds were predicted to be stable at temperatures above 400 °C.

The fraction of volatile Co, Cu, and Sb as a function temperature and air-to-fuel ratio is shown in Figures 12-15. In addition, the volatile fraction of the important ash-forming elements Pb, Zn, K, and Na, as well as Sn, are shown. It can be



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seen that Co is volatilized mainly at reducing conditions and at temperatures above 1100 °C for the normal case, sulfur case, and sulfur/chlorine-free case (Fig 12, 14, 15). In the case with higher chlorine content in the fuel (Fig 13), the volatilization of cobalt becomes considerable at temperatures above 700 °C. Copper is volatilized at 600-700 °C at oxidizing conditions (Fig 12-14) except for the sulfur/chlorine-free case (Fig 15), where temperatures above 1100 °C are needed for copper to volatilize. At reducing conditions, copper is volatilized at temperatures above 1000 °C. Antimony is predicted to be in a condensed phase only at temperatures below 500 °C and only at oxidizing conditions. Sn and Zn are mainly in the condensed phase at oxidizing conditions up to 1000 °C, whereas Pb is volatilized at oxidizing conditions even down to around 500 °C. K is the main volatilized alkali element, occurring as KCI(g), KOH(g) or KOH(g), and Na occurs as condensed NaAlSiO₄(s) up to high temperatures.









Figure 10. Predicted condensed phases (top graph), major (middle graph) and minor (bottom graph) gas components as a function of temperature for SRF conversion at λ =1.2.













Figure 12. Fraction of Co, Cu, Sb, Sn, Pb, Zn, K, and Na in the gas phase as a function of temperature and air-to-fuel ratio (lambda) for the normal case (a).



Figure 13. Fraction of Co, Cu, Sb, Sn, Pb, Zn, K, and Na in the gas phase as a function of temperature and air-to-fuel ratio (lambda) for the chlorine case (b = double amount of Cl).

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Figure 14. Fraction of Co, Cu, Sb, Sn, Pb, Zn, K, and Na in the gas phase as a function of temperature and air-to-fuel ratio (lambda) for the sulfur case (c = double amount of sulfur).

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Figure 15. Fraction of Co, Cu, Sb, Sn, Pb, Zn, K, and Na in the gas phase as a function of temperature and air-to-fuel ratio (lambda) for the sulfur- and chlorine-free case (d = no sulfur/chlorine).



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Enrichment of Co, Cu, Sb in gas phase

The enrichment of Co, Cu, and Sb in relation to the other ash-forming elements were calculated for the four different compositional input conditions. The enrichment was calculated as follows:

Enrichment factor of element i in $gas = \frac{m(i, gas)/m(total metals, gas)}{m(i, fuel)/m(total metals, fuel)}$

In addition to the metals, phosphorus was also included, whereas the halogens and sulfur were excluded. Two examples of the calculated enrichment factors for Co, Cu, and Sb are shown in Figure 16 at air/fuel ratios of 0.7 and 1.2 for the base case fuel. An enrichment factor <1 means that the element is preferentially stable in the condensed phases, whereas values >1 means an enrichment in the gas phase. It can be seen that cobalt is depleted in the gas phase except for high temperatures at reducing conditions and at around 600 °C at oxidizing conditions. Copper becomes enriched in the gas phase above 900 °C at reducing conditions and above 600 °C at oxidizing conditions. Antimony is predicted to be strongly enriched in the gas phase, especially at lower temperatures. There is a thousandfold enrichment of Sb at both reducing and oxidizing conditions below 600 °C. At higher temperatures, the level of volatilized ash-forming elements, such as K, Na, Pb, start to become significant. The enrichment factors as a function of both temperature and air/fuel ratio are shown in Figs 17-19.



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Figure 16. Enrichment factors of Co, Cu, and Sb as a function of temperature for air/fuel ratios of 0.7 (left) and 1.2 (right) for the base case.

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Figure 17. Gaseous fraction of cobalt (left) and enrichment factor of cobalt in the gas phase (right) for the base case (a), double chlorine case (b), double sulfur case (c), and the sulfur/chlorine-free case (d).



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Figure 18. Gaseous fraction of copper (left) and enrichment factor of copper in the gas phase (right) for the base case (a), double chlorine case (b), double sulfur case (c), and the sulfur/chlorine-free case (d).

а

b

С

d



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Figure 19. Gaseous fraction of antimony (left) and enrichment factor of antimony in the gas phase (right) for the base case (a), double chlorine case (b), double sulfur case (c), and the sulfur/chlorine-free case (d).



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It can be seen in Fig 17 that enrichment of cobalt in the gas phase is only at increased levels for the calculated case with double chlorine (b). In the other cases, cobalt is mainly depleted from the gas phase and is therefore expected to be found in the bottom ash of different combustion units. The bottom ash fraction is typically considerably higher than fly ash or filter ash fractions, which makes it unlikely of finding high levels of cobalt in any ash fraction.

Copper enrichment in the gas phase is predicted to be the highest at oxidizing conditions at around 600-900 °C (Fig 18) for all cases except the sulfur/chlorine-free case. Antimony is predicted to exist mainly for the studied conditions, with the exception of low temperatures at oxidizing conditions. The highest enrichment is predicted to be mainly at temperatures below 600 °C at reducing conditions (Fig 19). For the sulfur/chlorine-free case, low-temperature oxidizing conditions also show considerable enrichment

4. Discussion and conclusions

In a previous report [20], thermodynamic predictions of the speciation of Co, Cu, and Sb in MSW ash showed that the elements mainly occur as different oxides, such as Co_3O_4 , CuO, Sb₂O₅. Experimentally determined speciation of Cu and Sb suggest similar results. Additional Cu compounds were also observed, such as CuSO₄ and Cu₃(PO₄)₂. Firing MSW fuels containing high concentrations of halogens may lead to formation of metal halides.

In the present study, the speciation and volatilization of Co, Cu, and Sb in thermal conversion of SRF at various temperatures and air/fuel ratios were studied using thermodynamic equilibrium modeling. The main goal was to study if there are conditions in the combustion unit where these elements are feasible to separate and enrich from other ash-forming matter. Based on the predicted results, cobalt occurs mainly in the condensed phases and is not feasible for enrichment in fly ash or filter ash. Copper is enriched in the gas phase at especially oxidizing conditons if chlorine levels in the fuel is high. Controlled conditions in relation to local temperature of the flue gas and air staging are possible methods to form fly ash or filter ash enriched in copper compounds. In general, concentration of copper is considerably higher than antimony and cobalt in waste-derived fuels. Antimony is predicted to be mainly in the flue has except at oxidizing conditions below 600 °C, and it is therefore possible to enrich antimony in filter ash if a hot cyclone is utilized to separate condensed fly ash

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particles from the flue gas stream that contains the volatilized ash forming elements.

The effect of sulfur and chlorine on the ash chemistry was not very pronounced in the present study. Higher chlorine levels increased volatility of alkali species, Pb, Zn, and Co, but Cu and Sb were not affected to any large extent. Increase of sulfur levels had only minor effects. Complete removal of sulfur and chlorine decreased the volatility of Pb and the alkali metals at lower temperatures.

As a final example to study the possible overall chemistry of ash phases and flue gas in SRF combustion, a case where the condensed fly ash/bottom ash composition as well as the possible compounds condensating from the flue gas was calculated. The calculated condensed phases at 900 °C show that Cu and Sb are predicted to be in the gas phase, whereas the Co concentration in the condensed phases (bottom ash/condensed fly ash) is only 3 ppm. If the corresponding flue gas is cooled to around 200 °C or lower, the Co concentration in the condensate is only 1 ppm, but the Sb concentration is 1630 ppm and the Cu concentration is 11130 ppm (Fig 20).



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Fig 20. Upper graph shows the predicted stable condensed phases at air/fuel ratio=1.2 and 900 °C; lower graph shows predicted stable condensed phases that will form if the flue gas is cooled from 900°C to 200 °C.

This suggests that Cu and Sb concentrations in filter ash condensates are considerably higher than the levels in the bulk fuel. However, uncertainties in the calculations stemming from missing or uncertain thermodynamic data, or applicability of the thermodynamic equilibrium assumption for the predictions, are issues that need to be studied, and the predicted results need to be verified with experimental data.

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