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Critical review of thermodynamic data for heavy metals in aqueous solutions and thermodynamic calculations of solubility of heavy metal compounds in ash

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Key words: Ash leaching, thermodynamic modeling, solubility calculations

Summary

Thermodynamic properties and the solubility of Co, Cu, and Sb compounds occurring in MSW ash has been studied to assess if the elements can be separated and enriched from the ash.

Thermodynamic predictions of the speciation of Co, Cu, and Sb in MSW ash show that the elements mainly occur as different oxides, such as Co_3O4, CuO, Sb_2O_5. Experimentally determined speciation of Cu and Sb suggest similar results. Additional Cu compounds were also observed, such as $CuSO_4$ and $Cu_3(PO_4)_2$. Firing MSW fuels containing high concentrations of halogens may lead to formation of metal halides.

The solubility of the oxides of Co, Cu, and Sb in water is generally low based on previously reported solubility data. The continuous leaching tests corroborate these results, where Co, Cu, and Sb were more or less insoluble when treated in water. However, the calculated solubility of the oxides is increased in acidic solutions, which was also observed in the leaching experiments. Complex forming agents, such as EDTA, can also act as mobilizing agents for Co, Cu, and Sb.

Based on the calculated and measured results on the speciation of Co, Cu, and Sb in MSW ashes, the compounds are most likely in low soluble forms in the ash. Treatment of the ash with water to mobilize Co, Cu, and Sb is therefore not a feasible method to extract the metals from the ash. However, acid leaching or treatment with chelating agents can be used to mobilize Co, Cu, and Sb. Thermodynamic predictions on both speciation and on the solubility of Co, Cu, and Sb and water and in acidic solutions agree with experimental leaching tests of MSW ashes

Helsinki, september 2015

Contents

1. Introduction

The water solubility of different ash fractions and APC residues is an important property, as it strongly influences the options available for treatment, disposal or possible utilization of the residues. Generally, APC residues, such as filter ash, contain a high proportion of soluble components than fly ash and especially bottom ash due to the high fraction of inorganic salts, such as various halides, sulfates and carbonates. In a review by Yli-Laine et al. (Arvi deliverable 4.4-1, 2014) on valuable elements in MSW ashes, it was identified that cobalt, copper, and antimony are elements that occur in elevated and can be of interest for recovery from ashes.

In the present study, the focus is on the aqueous chemistry and solubility of Co, Cu, and Sb from ashes with special emphasis on the behavior of these elements from the ash leaching tests done

2. Characterization of ash and APC residues

The ash is the non-combustible residue that remains after combustion or gasification of a fuel. *Bottom ash* is typically the ash found on the grate or that is collected from the bottom of the furnace. It tends to consist of inert ash-forming matter, such as silicates and oxides, and is depleted of volatile components such as alkali and trace metal compounds, especially halides, chlorine and sulfur. *Fly ash* can be defined as particulate matter carried over from the combustion chamber and removed from the flue gas stream prior to addition of any type of sorbent material (IAWG, 1997). Fly ash is typically collected in different types of cyclones or filters, and therefore the term *filter ash* is used for part of the fly ash collected in filters in the flue gas channels. In addition, various APC residues may include part of the fly ash. Quina et al. (2008), in a review of the treatment methods of APC residues from MSW incineration, categorized the solid wastes that are carried over by the flue gases from the combustion chamber, into six main groups:

- **Heat recovery system ash, or fly ash**
- **Electrostatic precipitator ash**
- **Fabric filter or baghouse ash**
- **Dry, semi-dry, or wet scrubbing residues**
- **Cyclone ash**
- **APC residues.**

Solid residues that are thermally treated may therefore originate from both the fuel and from various chemical additives used in the WtE plant.

In solid fuels, such as wood, peat, straw or coal, the ash-forming matter is mainly present as minerals and salts, bound to the organic matter, or dissolved in moisture and fluids (Zevenhoven et al., 2010). The form of the ash-forming matter in waste-derived fuels is more complicated. The origin of the ash-forming matter is strongly dependent of the type of waste (municipal solid waste, recovered waste wood, etc.) and the different waste fractions present in the waste (e.g. paper, plastics, food-derived waste, scrap metal). For example, food-derived waste can contain considerable amounts of NaCl, whereas paper fractions may contain high amounts of filler materials, such as lime and kaolin.

Several studies have measured or collected data on the chemical composition of bottom ash, fly ash and APC residues. The major elements are Si, Al, Fe, Ca, Mg, K, Na, S, P, and Cl and are found in the residues as oxides, silicates, phosphates, chlorides and sulfates. Important trace elements are As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, due to their toxicity and/or high concentrations in the residues. Trace quantities of very toxic organic compounds are usually present in the residues. These organic micropollutants are polycyclic hydrocarbons (PAH), chlorobenzenes (CB), polychlorinated biphenyls (PCB), and polychlorinated dibenzo-*p*-dioxins (PCDD) and furans (PCDF).

The International Ash Working Group (1997) divided the elements in bottom ash and fly ash/APC residues in three different categories based on the elemental concentration: Major elements (>10,000 mg/kg) , minor elements (1,000-10,000 mg/kg), and trace elements (<1000 mg/kg).

Table 1 shows the major, minor, and trace elements in bottom ash and fly ash/APC residues and typical inorganic phases based on the analysis made by the International Ash Working Group (1997).

In the review of Quina et al. (2008), the variation of the elemental composition and concentration of organic pollutants in fly ash and various APC residues is given based on previous compilations. Table 2 gives the range of elemental concentrations and organic micropollutants concentrations in the review of Quina et al. (2008). The range of elemental concentrations of bottom ash is also given in table 2, taken from the International Ash Working Group (1997). For detailed information from the original sources, refer to the following papers (Eighmy et al., 1995; Hjelmar, 1996; IAWG, 1997; Le Forestier and Libourel, 1998; Quina et al., 2008; Song et al., 2004). Si, Fe, Al, and Ca typically are the most common elements in bottom ash (excluding O and C), whereas Ca, Cl, K, Na, and Si are the most common elements in fly ash and APC residues. Part of the calcium may originate from lime based additives/sorbents instead of from the MSW fuel.

Table 1. Major, minor, and trace elements and examples of major phases in bottom ash and fly ash/APC residues based on the classification of the International Ash Working Group (1997)

Bottom ash

Major matrix elements	Minor matrix elements	Other minor elements	Other trace elements (a: oxyanionic elements; b: metals; c: non-metals))
>10,000 mg/kg	1,000-10,000 mg/kg	1,000-10,000 mg/kg	<1,000 mg/kg
O, Si, Fe, Ca, Al, Na, K, C	Mg, Ti, S, P, Cl, Mn, Ba	Zn, Cu, Pb, Cr	a) Sn, Sb, V, Mo, As, Se b) Sr, Ni, Co, Cd, Ag, Hg c) B, Br, F, I

Major Phases
SiO_2, Fe_3O_4, Fe_2O_3, $KAlSi_3O_8$, $NaAlSi_3O_8$, $CaAl_2Si_2O_8$, $CaMgSi_2O_7$, CaO, $CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$, NaCl, KCl,

Fly ash/APC residues

Major elements	Minor elements	Trace elements
>10,000 mg/kg	1,000-10,000 mg/kg	<1,000 mg/kg
O, Cl, Ca, Si, Mg, Fe, Al, K, Zn, S, Pb	Ti, Mn, Ba, Sn, Cu	Hg, Cd, Sb, Cr, Sr, Ni, As, V, Ag, Co, Mo, Se

Major Phases
K_2ZnCl_4, KCl, NaCl, $CaSO_4$, $PbSO_4$, $KAlSi_3O_8$, $CaAl_2Si_2O_8$

Table 2. Chemical composition range of bottom ash and fly ash/APC residues from MSW incineration based on literature (Eighmy et al., 1995; Hjelmar, 1996; IAWG (International Ash Working Group), 1997; Le Forestier and Libourel, 1998; Quina et al., 2008; Song et al., 2004).

		Bottom ash		Fly ash/APC residues	
Element	Unit	Min	Max	Min	Max
Si	g/kg	91	308	36	190
Al	g/kg	21.9	72.8	6.4	93
Fe	g/kg	4.12	150	0.76	71
Ca	g/kg	0.37	123	46	361
Mg	g/kg	0.4	26	1.1	19
K	g/kg	0.75	16	17	109
Na	g/kg	2.87	42	6.2	84
Ti	g/kg	2.6	9.5	0.7	12
S	g/kg	1	5	1.4	32
Cl	g/kg	0.8	4.19	45	380
P	g/kg	1.4	6.4	1.7	9.6
Mn	g/kg	0.083	2.4	0.2	1.7
Ag	mg/kg	0.28	36.9	0.9	192
As	mg/kg	0.12	189	18	960
Ba	mg/kg	400	3000	34	14000
Cd	mg/kg	0.3	70.5	16	1660
Co	mg/kg	6	350	1.9	300
Cr	mg/kg	23	3170	72	570
Cu	mg/kg	190	8240	16	2220
Hg	mg/kg	0.02	7.75	0.1	51
Mo	mg/kg	2.5	276	9.3	49
Ni	mg/kg	7	4280	19	710
Pb	mg/kg	98	13700	254	27000
Se	mg/kg	0.05	10	0.7	31
Sn	mg/kg	2	380	367	5900
Sr	mg/kg	85	1000	<80	500
V	mg/kg	20	122	4	150
Zn	mg/kg	613	7770	4308	41000
PAH	µg/kg	n.a.	n.a.	18	5600
CB	µg/kg	n.a.	n.a.	0.03	890
PCB	µg/kg	n.a.	n.a.	<40	
PCDD	µg/kg	n.a.	n.a.	0.7	1000
PCDF	µg/kg	n.a.	n.a.	1.4	370
TCDD	eqv	n.a.	n.a.	0.8	2.5
TOC	g/kg	n.a.	n.a.	4.9	17
LOI	g/kg	n.a.	n.a.	11	120

3. Speciation of Cu, Co, Sb in ash

The speciation of Cu, Co, and Sb can be determined with various experimental methods, such as X-ray diffraction based on crystallographic structure or SEM/EDXA based on the chemical composition. However, due to the low concentrations of Cu, Co, and Sb in the ash, it is often difficult to identify phases containing these elements. Cu typically occurs in higher concentrations compared to Co and Sb, and is therefore the most likely to identify in a phase.

Talonen [2008] studied the speciation of several trace elements in MSW combustion and gasification by using thermodynamic modeling to predict the phase equilibrium and the composition of the condensed phases and the gas phase at temperatures varying between 200 °C and 1600 °C. The study emphasized the differences when using different thermodynamic databases.

Cobalt was predicted to occur mainly as solid $CoSO_4$, Co_3O_4, or CoO and gaseous $CoCl_2$ and $Co(OH)_2$ at oxidizing conditions, whereas different cobalt sulfides or metallic Co are the stable solid phases at reducing conditions.

Copper was predicted to occur mainly as solid $CuSO_4$, CuO or $CuO{\cdot}CuSO_4$ phas and gaseous CuCl as well as minor amounts of other gaseous copper halides at oxidizing conditions. At reducing conditions, solid Cu_2S or metallic Cu is predicted to be the main stable phases.

Antimony was predicted to be stable mainly as solid Sb_2O_5 at lower temperatures and as various gaseous Sb-O compounds at higher temperatures (SbO, Sb_4O_6) at oxidizing conditions. At reducing conditions, solid Sb_2S_3 is stable upt to around 400 °C, with gaseous Sb, SbCl or SbO are the main stable compounds at higher temperatures.

Lassesson & Steenari (2013) have analyzed the speciation of copper in bottom ash, cyclone ash and filter ash from a MSW-fired BFB boiler using synchrotron based X-ray absorption spectrometry. They concluded that the most common copper compounds in the bed ash were metallic copper, Cu_2O, CuO, and mixed oxides, such as $CuCr_2O_4$. The cyclone ash contained a mix of metallic copper, Cu_2O, CuCl, $Cu(OH)_2$, $CuSO_4{\cdot}5H_2O$, and possibly CuO. Copper sulfate was the major species in the filter ash together with hydroxides and chlorides. Lasseson et al. (2014) analyzed the speciation of Cu in two different MSWI fly ashes, one rich in Ca and Cl with a Cu-concentration at 5.4 g / kg dry ash (Ash A), and the second fly ash with high levels of Ca, K, Na, S, Si, and Cl, containing 2.5 g Cu / kg dry ash (Ash B). The copper speciation in Ash A was mainly $CuSO_4{\cdot}5H_2O$, with minor amounts of CuClOH, whereas Ash B contained a mainly $Cu_3(PO_4)_2$ and minor amounts of metallic Cu, Cu_2S, and CuO.

Miravet et al. (2006) determined that most of the soluble antimony in coal fly ash was in the form of Sb(V), with only minor amounts of Sb(III) occurring in the leachate.

In this study, thermodynamic predictions of the speciation of ash-forming elements have therefore been made to estimate in which form Cu, Co, and Sb can be found in the ash. The predictions were made with the thermodynamic software package Factsage [Bale et al., 2009] version 6.4 using the FactPS database for thermodynamic data of the phases and compounds that may form. The estimations were made based on the ash composition of the BFB and CFB ashes given in Fig 2, 6, and 11 in Deliverable 2.5-2 (Vainio et al.). The calculations give the stable phases at 25 °C, for both dry ash and for ash with 10 wt% H_2O, simulating slightly hydrated ash. The predicted phase composition is given in table 3.

Table 3. Predicted ash phases for the three different ashes at 25 °C.

BFB1_dry		BFB1_10% H2O		BFB2_dry		BFB2_10% H2O		CFB ESP_dry		CFB ESP_10% H2O	
Al_2SiO_5	21.7	$KAl_3Si_3O_{10}(OH)_2$	25.1	$Ca_3Al_2Si_3O_{12}$	22.5	$Na_2Ca_3Si_6O_{16}$	16.4	$Ca_3Fe_2Si_3O_{12}$	21.7	$Ca_3Fe_2Si_3O_{12}$	22.3
$Na_2Ca_3Si_6O_{16}$	18.8	$Na_2Ca_3Si_6O_{16}$	18.6	$CaSO_4$	19.3	$CaSO_4(H_2O)_2$	14.7	Ca_2SiO_4	19.7	$Ca(OH)_2$	18.1
$KAlSi_3O_8$	17.3	$CaAl_2Si_2O_7(OH)_2(H_2O)$	18.0	$CaMgSiO_4$	10.0	$Ca_3Al_2Si_3O_{12}$	13.6	$Ca_3MgSi_2O_8$	16.9	$Na_2Ca_3Si_6O_{16}$	14.0
$CaMgSi_2O_6$	10.9	H_4SiO_4	15.3	$Ca_3Fe_2Si_3O_{12}$	9.7	$Ca_3Fe_2Si_3O_{12}$	8.8	$CaSO_4$	11.3	$CaSO_4(H_2O)_2$	10.0
Fe_2O_3	8.1	Fe_2O_3	8.0	$Na_2Ca_2Si_3O_9$	7.4	$CaCl_2(H_2O)_6$	8.4	$CaTiO_3$	7.5	$CaTiO_3$	6.8
$Ca_3(PO_4)_2$	7.6	$Mg_5Al_2Si_3O_{10}(OH)_8$	5.6	$KCaCl_3$	7.3	$Mg_5Al_2Si_3O_{10}(OH)_8$	6.5	$CaMg_2Al_{16}O_{27}$	6.6	$Mg_5Al_2Si_3O_{10}(OH)_8$	6.6
SiO_2	7.3	SiO_2	3.1	$CaTiO_3$	7.1	$CaTiO_3$	6.4	$ZnAl_2O_4$	3.0	$CaCl_2(H_2O)_6$	3.8
$CaSiTiO_5$	2.2	$CaSO_4$	2.0	$ZnAl_2O_4$	6.4	$CaSO_4$	5.9	KCl	2.8	$Al_2O_3(H_2O)$	3.7
$CaSO_4$	2.1	$Ca_{10}(PO_4)_6F_2$	1.2	$Na_2Ca_3Si_6O_{16}$	4.5	$ZnAl_2O_4$	5.8	$Na_2Ca_2Si_3O_9$	2.6	$Ca_3Al_2Si_3O_{12}$	3.3
$Ca_{10}(PO_4)_6F_2$	1.3	Others	2.9	$Ca_{10}(PO_4)_6F_2$	1.8	$Ca(OH)_2$	5.6	NaCl	2.2	$ZnAl_2O_4$	2.7
Others	2.6			Others	3.6	KCl	3.4	$Ca_{10}(PO_4)_6F_2$	1.2	KCl	2.5
						$Ca_{10}(PO_4)_6F_2$	1.6	$(CaO)_2(PbO_2)$	1.2	$CaSO_4$	2.3
						Others	2.7	Fe_2O_3	1.0	$Ca_{10}(PO_4)_6F_2$	1.1
								Others	2.2	Others	2.7
CuO	0.06	$Cu(OH)_2$	0.07	CuO	0.3	$Cu(OH)_2$	0.3	CuO	0.19	$Cu(OH)_2$	0.21
Sb_2O_5	0.004	Sb_2O_5	0.004	Sb_2O_5	0.02	Sb_2O_5	0.02	Sb_2O_5	0.02	Sb_2O_5	0.02
Co_3O_4	0.003	Co_3O_4	0.003	Co_3O_4	0.004	Co_3O_4	0.004	Co_3O_4	0.004	Co_3O_4	0.004

The predictions of the main phases show that various Ca-Al-Fe silicates, as well as $CaSO_4$ and gypsum, are the dominating phases. The main highly soluble phases are KCl, NaCl, $CaCl_2(H_2O)_6$, and $KCaCl_3$.

The predicted speciation of Cu is CuO in completely dry ash, and $Cu(OH)_2$ in humid ash, whereas Sb occurs as Sb_2O_5 in all cases and Cu occurs as Co_3O_4 in all cases.

Similar predictions for the ash speciation at 500 °C give similar results for the bulk ash composition (Table 4). The difference between dry ash and humid ash is minimal due to the instability of hydrated species at these temperatures. The predicted speciation of Cu, Co, and Sb is slightly different compared to the low-temperature case. Sb occurs as Sb_2O_5, whereas Cu is predicted to form either CuO or $CuO{\cdot}Fe_2O_3$ (or $CuFe_2O_4$, cuprospinel), and Co is predicted to form Co_3O_4 or $CoO{\cdot}Cr_2O_3$ (or $CoCr_2O_4$).

Table 4. Predicted ash phases for the three different ashes at 500 °C.

BFB1_dry		BFB1_10% H2O		BFB2_dry		BFB2_10% H2O		CFB ESP_dry		CFB ESP_10% H2O	
$CaAl_2Si_2O_8$	29.1	$CaAl_2Si_2O_8$	30.2	$Ca_3Al_2Si_3O_{12}$	22.3	$Ca_3Al_2Si_3O_{12}$	22.4	$Ca_3MgSi_2O_8$	21.5	$Ca_3MgSi_2O_8$	21.5
$KAlSi_3O_8$	17.0	$KAlSi_3O_8$	19.3	$CaSO_4$	19.3	$CaSO_4$	19.3	$Ca_2Al_2SiO_7$	18.7	$Ca_2Al_2SiO_7$	18.7
$NaAlSi_3O_8$	16.7	$NaAlSi_3O_8$	18.2	$CaSiO_3$	11.6	$CaSiO_3$	11.6	$Ca_3Si_2O_7$	13.2	$Ca_3Fe_2Si_3O_{12}$	13.2
$CaMgSi_2O_6$	10.5	$CaMgSi_2O_6$	10.8	$Ca_3Fe_2Si_3O_{12}$	9.7	$Ca_3Fe_2Si_3O_{12}$	9.7	$Ca_3Fe_2Si_3O_{12}$	13.1	$Ca_3Si_2O_7$	13.0
Fe_2O_3	8.0	Fe_2O_3	8.7	$CaMgSiO_4$	8.5	$CaMgSiO_4$	8.5	$CaSO_4$	10.3	$CaSO_4$	10.3
$Ca_3(PO_4)_2$	7.6	SiO_2	3.6	$CaTiO_3$	7.1	$CaTiO_3$	7.1	$CaTiO_3$	7.5	$CaTiO_3$	7.5
SiO_2	3.2	$CaSiTiO_5$	2.4	$ZnAl_2O_4$	6.4	$ZnAl_2O_4$	6.4	$ZnFe_2O_4$	3.9	$ZnFe_2O_4$	3.9
$CaSiTiO_5$	2.2	$CaSO_4$	2.1	NaCl	3.6	NaCl	3.6	NaCl	2.9	NaCl	2.9
$CaSO_4$	2.0	$Mg_2Al_4Si_5O_{18}$	1.4	KCl	3.0	KCl	3.1	KCl	1.9	KCl	1.9
$Ca_{10}(PO_4)_6F_2$	1.3	$Ca_{10}(PO_4)_6F_2$	1.4	$CaMgSi_2O_6$	2.2	$CaMgSi_2O_6$	2.1	$Ca_{10}(PO_4)_6F_2$	1.2	$Ca_{10}(PO_4)_6F_2$	1.2
Others	2.2	Others	1.6	$Ca_{10}(PO_4)_6F_2$	1.8	$Ca_{10}(PO_4)_6F_2$	1.8	$(PbO)(Al_2O_3)$	1.1	$(PbO)(Al_2O_3)$	1.1
				$KCaCl_3$	1.5	$KCaCl_3$	1.4	Others	4.1	Others	4.0
				K_2PbCl_4	1.0	K_2PbCl_4	1.0				
				Others	1.6	Others	1.6				
$(CuO)(Fe_2O_3)$	0.17	$(CuO)(Fe_2O_3)$	0.16	CuO	0.29	CuO	0.3	$(CuO)(Fe_2O_3)$	0.6	$(CuO)(Fe_2O_3)$	0.6
Sb_2O_5	0.004	$(CoO)(Cr_2O_3)$	0.01	Sb_2O_5	0.02	Sb_2O_5	0.02	Sb_2O_5	0.02	Sb_2O_5	0.02
Co_3O_4	0.003	Sb_2O_5	0.004	Co_3O_4	0.004	Co_3O_4	0.004	Co_3O_4	0.004	Co_3O_4	0.004

As a summary, Cu, Co, and Sb are predicted to form oxide phases in the studied ashes, or possibly $Cu(OH)_2$ if the ash is hydrated. None of the metals were predicted to form silicates, sulfates or halides.

4. Solubility of Cu, Co, and Sb compounds

The speciation of these metals strongly affects to leachability of them. In the following section, an overview of the aqueous chemistry of Cu, Co, and Sb is made.The solubility of various Cu, Co, and Sb compounds are given in Table 5.

Table 5. Solubility of Co, Cu, and Sb compounds and their hydrates in water, given as grams of dehydrated form per 100 g H_2O. Qualitative solubility is given for compounds with no available quantitative data. Quantitative data are for T=20 °C or T=25 °C. Data are taken from Handbook of Chemsitry and Physics unless marked by *.

Compound	Solubility g / 100 g H_2O	T (°C)
$CoBr_2$	113.2	20
$CoCO_3$	0.00014	20
$CoCl_2$	56.2	25
CoF_2	1.4	25
$Co(NO_3)_2$	103	25
CoO	Insoluble	
Co_3O_4	Insoluble	
Co_2O_3	Insoluble	
$Co(OH)_2$*	0.00018	
$Co(OH)_3$*	0.00032	
$CoSO_4$	38.3	20
CuBr	0.0012	20
CuCl	0.0047	20
CuOH**	$8.1\cdot10^{-7}$	20
Cu_2O	Insoluble	
$CuBr_2$	126	25
$CuCO_3$**	$1.5\cdot10^{-4}$	
$CuCl_2$	75.7	25
CuF_2	0.075	25
$Cu(NO_3)_2$	145	25
Cu		
CuO	Insoluble	
$Cu(OH)_2$	$1.7\cdot10^{-6}$	
$CuSO_4$	22	25
$SbCl_3$	987	25
SbF_3	492	25
Sb_2O_3	Slightly soluble	
$Sb_2(SO4)_3$	Soluble	
Sb_2O_5	0.3	20

It can be seen that Co(II) , Cu(II), and Sb(III) halides (especially bromides and chlorides are highly soluble in water, whereas the different oxides or hydroxides are practically insoluble or have very low solubility in water. The sulfates are soluble but have comparatively lower solubility than the corresponding chlorides or bromides.

Pöykiö et al. (2014) performed sequential leaching of biomass-based bottom ash and fly ash using water, ammonium acetate, and hydrochloric acid as leaching agents. For cobalt, leaching was not observed when using water or ammonium acetate, but about 90% was leached from the bottom ash and about 35% was leached from the fly ash when using HCl. For copper, about 40% was leached with ammonium acetate and 60% leached with HCl from the bottom ash, and 10% was leached with ammonium acetate and 50% leached with HCl from the fly ash. Water did not leach any of the copper from the ash fractions. Leaching of antimony was not observed in any of the leaching agents, but the levels of antimony in the ash fractions were very low.

Karlfeldt Fedje et al. (2010) studied the leaching of hazardous metals from MSW fly ash rich in Ca and Cl (same as Ash A refered to by Lassesson et al (2014)) using different leaching agents. It was observed that mineral acids and EDTA mobilized many elements, especially Cu, Zn, and Pb, whereas organic acids generally were not as effective as leaching agents for metals. The use of ammonium nitrate (NH_4NO_3) was especially effective for the release of Cu. Lassesson et al. (2014) studied the leaching behavior of Ash A and B mentioned earlier in 3 mol / liter HNO_3 at pH = 2 and 3 mol / liter NH_4NO_3 at pH=9. Leaching tests were made at L/S = 5 for 24 h. For Ash A containing mainly $CuSO_4{\cdot}5H_2O$, with minor amounts of CuClOH, almost 100% was leached using both methods. For Ash B containing mainly $Cu_3(PO_4)_2$ and minor amounts of metallic Cu, Cu_2S, and CuO, about 60% of the copper was released using both methods. The main reason for the lower solubility of copper in Ash B was the Cu speciation, with the occurrence of low soluble copper compounds.

Kida et al. (1997) studied the leaching behavior of bottom ash and fly ash form MSW incinerators using both acidic and alkaline leaching agents. At acidic conditions, about 10% of Cu was leached from the bottom ash, and about 40% was leached from the fly ash. About 30% of Co was leached from the fly ash (no results for bottom ash).

Hong et al. (2000) studied the extraction of Cr, Cu, Pb, and Zn from five different MSW fly ashes by treating them with HCl, nitrilotriacetic acid (NTA), ethylendiaminetetraacetate (EDTA), or diethylenetriaminepentaacetate (DTPA) in a batch process in the pH range 2.5–10. The extraction levels of Cu using the chelating agents was independent of pH and reached around 60-90 % of Cu. NTA gave slightly lower extaction levels for some of the ashes. The extraction of Cu using HCl was shown to be strongly dependent on the final pH of the solution, with increased extraction levels at pH<6. Figure 1 shows the extraction levels of Cu for the different leaching agents.

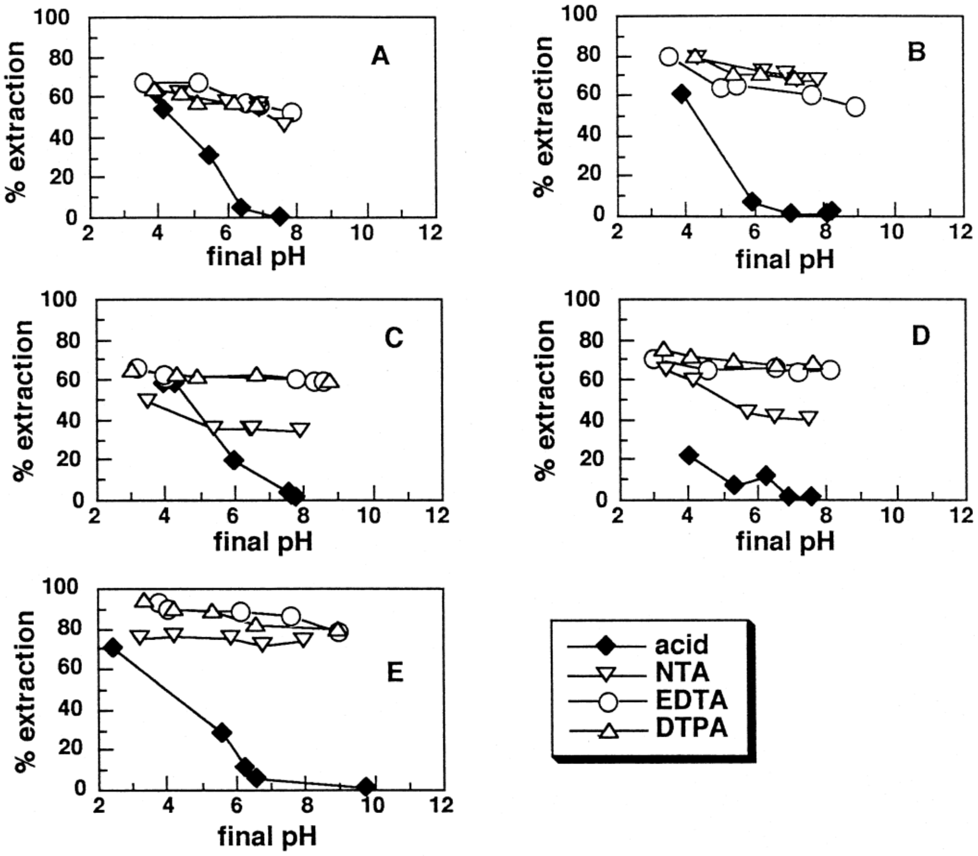

Figure 1. Extaction of Cu from fly ashes (acid = HCl, concentration chelating agents = 3 wt%). From Hong et al. (2000).

Miravet et al. (2006) showed that around 20-40% of Sb was readily soluble from coal fly ash when using citrate at pH=5 as a leaching agent, and that most of Sb is bound to the matrix in the ash and can be considered “not mobile”. The leached antimony was shown to occur mainly as Sb(V), with only minor amounts of extracted Sb(III).

Calculations of solubility of Cu and Co compounds

The solubility of CuO, $CuSO_4$, $CuCl_2$, CoO, $CoSO_4$, $CoCl_2$ in water and in nitric acid was calculated using the Factsage software and the FactPS database for aqueous species. Calculations were made for 1 mol of the Cu- or Co-compound and 1000 g H_2O and varying amounts of HNO_3 (0-5 mol HNO_3) at 25 °C. A complete set of thermodynamic data for solubility of Sb-compounds is not available in the FactPS database, and therefore Sb was omitted from these calculations.

The calculations are not directly comparable to the actual leaching tests but the comparative solubility of the different compounds from neutral to very acidic conditions can be investigated. The concentrated HNO_3 in the leaching tests corresponding to the 5 mol HNO_3 / 1000 g H_2O in the calculations.

The speciation of Co and Cu for the different compounds is shown in Figure 2.

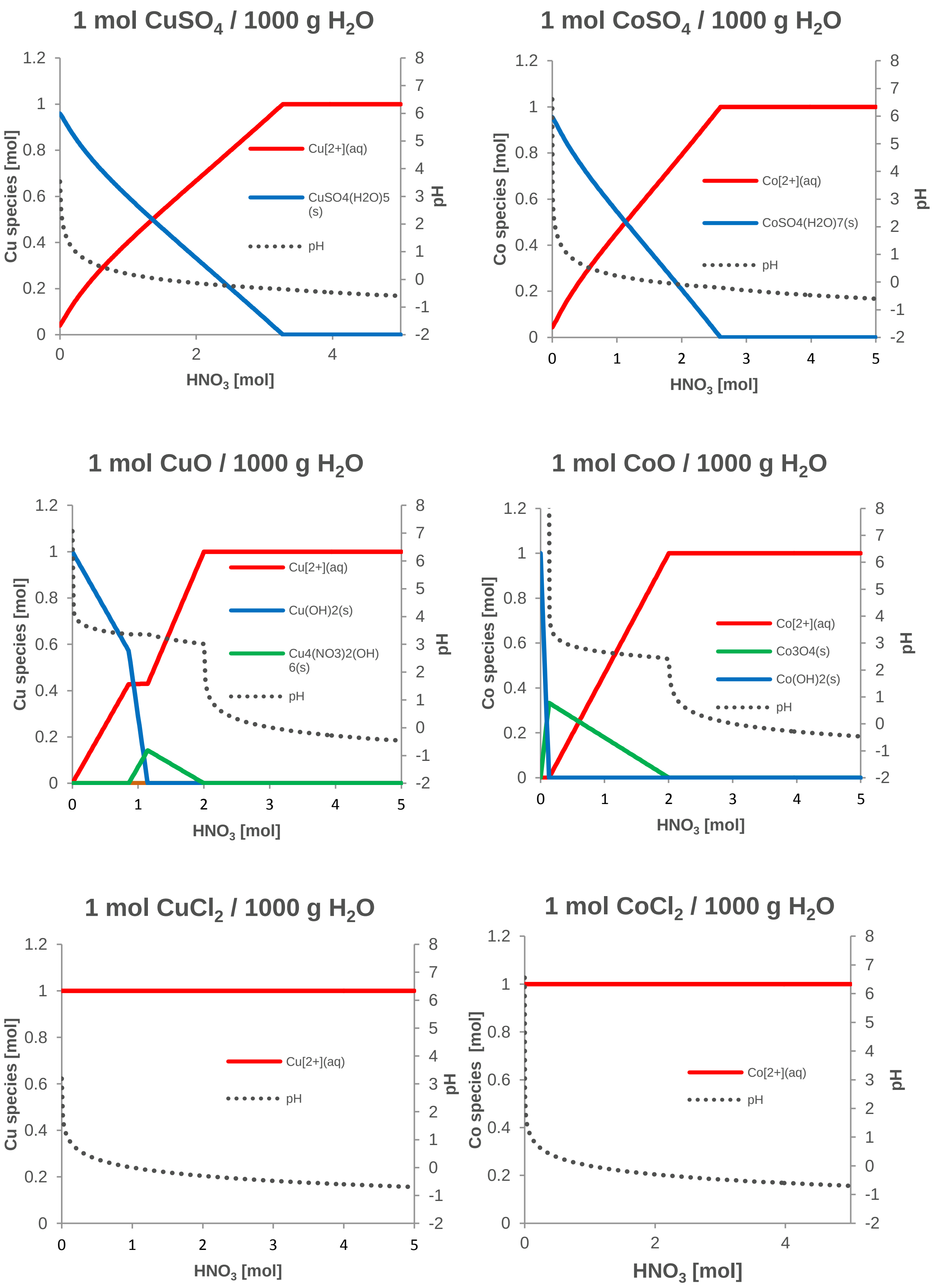

Figure 2. Calculated speciation of Cu and Co for 1 mol/kg H_2O solutions of $CuSO_4$, CuO, $CuCl_2$, $CoSO_4$, CoO, and $CoCl_2$ at 25 °C and as a function of added HNO_3.

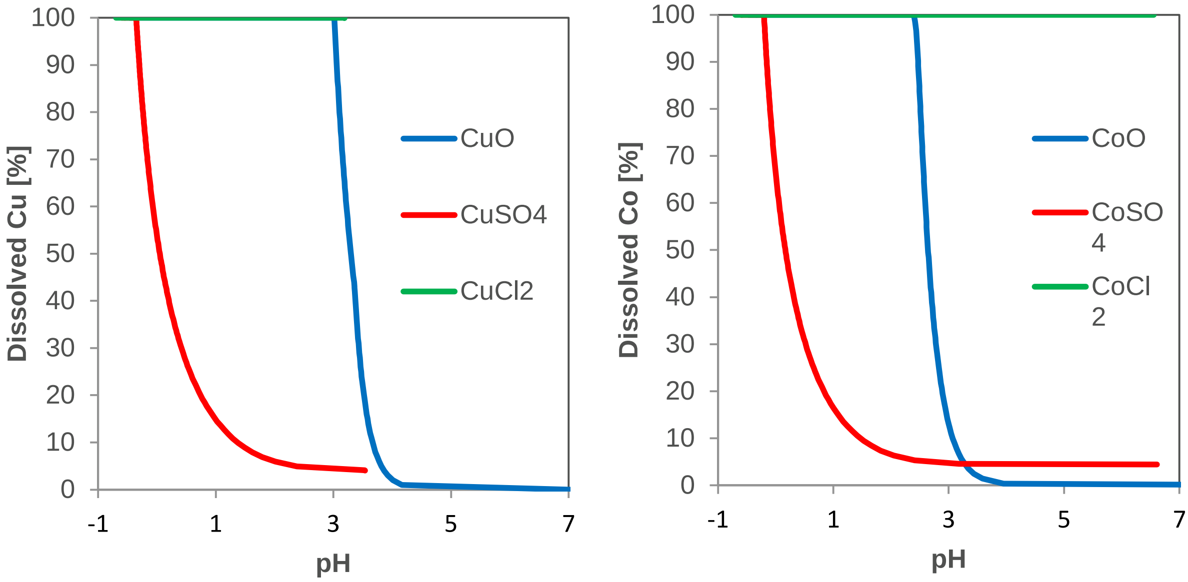

Figure 3. Fraction of dissolved Cu and Co as a function of pH.

Figure 3 shows the fraction of Cu and Co in the aqueous phase as a function of pH. The calculations show that the chlorides are soluble independent of pH whereas the oxides dissolve at pH<3, whereas the sulfates dissolve at very acidic conditions at pH<1.

5. Discussion and conclusions

Thermodynamic predictions of the speciation of Co, Cu, and Sb in MSW ash show that the elements mainly occur as different oxides, such as Co_3O_4, CuO, Sb_2O_5. Experimentally determined speciation of Cu and Sb suggest similar results. Additional Cu compounds were also observed, such as $CuSO_4$ and $Cu_3(PO_4)_2$. Firing MSW fuels containing high concentrations of halogens may lead to formation of metal halides.

The solubility of the oxides of Co, Cu, and Sb in water is generally low based on previously reported solubility data. The continuous leaching tests corroborate these results, where Co, Cu, and Sb were more or less insoluble when treated in water. However, the calculated solubility of the oxides is increased in acidic solutions, which was also observed in the leaching experiments. Complex forming agents, such as EDTA, can also act as mobilizing agents for Co, Cu, and Sb.

Based on the calculated and measured results on the speciation of Co, Cu, and Sb in MSW ashes, the compounds are most likely in low soluble forms in the ash. Treatment of the ash with water to mobilize Co, Cu, and Sb is therefore not a feasible method to extract the metals from the ash. However, acid leaching or treatment with chelating agents can be used to mobilize Co, Cu, and Sb. Thermodynamic predictions on both speciation and on the solubility of Co, Cu, and Sb and water and in acidic solutions agree with experimental leaching tests of MSW ashes.

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