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Identification and Quantification of Chemical Forms of Cu and Zn in MSWI Ashes Using XANES

Jenny Rissler,* Konstantin Klementiev, Jonas Dahl, Britt-Marie Steenari, and Mar Edo

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ABSTRACT: Incineration is in many countries a common treatment method for municipal solid waste, and utilization of the ash residues has attracted significant interest. The bottom ash is best suited as a secondary construction material, whereas the fly ash is being investigated as a secondary raw material for recovery of, for example, Zn, Cu, and salts. For both types of application, knowledge about the chemical speciation of Zn and Cu in the ashes is valuable. The present work focuses on identifying and quantifying the chemical species of Zn and Cu in 12 samples of fly ash and bottom ash from three waste-to-energy plants using X-ray absorption near edge structure (XANES). The XANES spectra of the ash samples showed similar distinctive features, and both in the bottom and fly ash samples, the same chemical forms were identified but in various ratios. Cu and Zn occurred in several chemical forms, with typically 5−7 forms present in the same sample. For Cu, the XANES spectra of the fly ash samples were nearly identical, indicating very similar chemical speciation (same chemical forms and similar ratios). Cu was found to exist in various oxide, hydroxide, chloride, silicate, and metallic forms. The most commonly occurring Zn compounds were the aluminate, ferrite, silicate, and oxide along with chloride, basic carbonate (hydrozincite), and occasionally metallic forms, probably alloyed with Cu in brass. Cu occurred in different oxidation states from zero to +II, with a higher prevalence of the lower oxidation states in bottom ash than in fly ash. Zn occurred mainly in oxidation state +II in all ashes analyzed. Finally, we showed that during outdoor storage of bottom ash, levels of Cu and Zn hydroxycarbonates were increased compared to fresh bottom ash. This carbonate formation aims to make Cu and Zn less leachable.

1. INTRODUCTION

Incineration is a common method to treat solid waste. The benefits include reduction of the waste volume by 80−90%, destruction of harmful waste components, and recovery of energy as heat and electricity. Solid waste incineration bottom ashes (BAs) typically consist of noncombustible materials (e.g., slag, concrete, stones, glass, brick, and metal pieces) and are typically stored for several months in contact with air in order to react with CO_2. This carbonation process aims at reducing the leachability of toxic metal compounds from the ash by the formation of minerals, such as aluminum hydroxides, iron hydroxides, and calcium carbonate, onto which the toxic metal ions are adsorbed and incorporated. Reactions during weathering and effects on metal leaching from municipal solid waste incineration (MSWI) BA have been studied extensively.[1−7]

The option of utilizing MSWI BAs as construction materials replacing virgin materials has been investigated and is in some regions applied. The most common use of BA is in road bases or as an aggregate replacement in concrete. However, the possibilities for utilizing BA depend on classification of the ash as nonhazardous waste. The ash classification depends on the content of ecotoxic compounds.[8] Therefore, there is an urgent need for methods to identify potentially toxic chemical forms of trace metals present in the ashes. Also, methods for analyzing the speciation of trace metals in ashes are important to understand ash formation processes and design methods to recover metals from fly ash (FA).[9−11]

Owing to the low concentration and high complexity of the ash matrix—containing many elements in various chemical forms—synchrotron-based X-ray absorption spectroscopy (XAS) is one of very few options available for identification of the chemical speciation of trace metals such as Cu and Zn.

Most of the previous studies applying XAS to investigate trace metal speciation in MSWI ashes focused on FA. There are very few publications where the speciation of trace metals in BA has been studied using XAS, and even fewer comparing BA and FA from the same facility. Because Cu species have been shown to act as catalysts in the formation of dioxins in MSWI combustion, there has been a special focus on the identification of Cu compounds in FA.[12] Some published results have indicated that Cu occurs mainly in oxidation state +II and as an oxide, hydroxide, chloride, and sulfate in various ratios. Hsiao and co-workers[13] determined the speciation of Cu in FA from MSWI and found mainly CuO and $Cu(OH)_2$, together with minor amounts of $CuCO_3$ and metallic Cu. Metallic Cu was also found in MSWI FA by Lassesson and co-workers.[10] In the latter study, FAs from a fluidized bed combustor and a grate fired combustor were compared,

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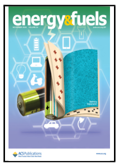

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showing that metallic Cu may be present in MSWI FA and that oxidation states zero, +I, and +II are possible, even though there is an oxidative environment in the entire flue gas channel. In the case of the fluidized bed combustor, the main forms of Cu were found to be $CuSO_4 \cdot 5H_2O$ (70%) and CuClOH (30%), compared to $Cu_3(PO_4)_2$ (55%), Cu metal, Cu_2S, and CuO (15% each) for the grate fired combustor. The reasons for the differences in Cu speciation between ashes from different MSWI units are not obvious, but part of the explanation probably lies in differences in air flow through the fuel beds and in the flue gas channels, temperature, time for reactions, the fuel composition, or other factors, such as quenching and weathering.[14]

Tuan and co-workers[15] studied the Cu distribution of both BA and FA from the same MSWI unit using XAS. Their results showed that Cu speciation in the BA was dominated by CuO (50%), followed by CuS, Cu_2O, $CuSO_4$, CuCl, and Cu metal (17% down to 4%). FA from the same unit was dominated by $CuSO_4$ (77%), followed by CuO, that is, higher oxidation states for Cu in FA than BA. Similar results were obtained in a study of ashes from a fluidized bed combustor,[16] where Cu in the BA was mainly in the form of copper metal, CuO, Cu_2O, and mixed metal oxides such as $CuCr_2O_4$ (up to 18%).

Zn has also attracted significant interest, mainly because of the regulation and classification of ash but also the potential for using FA as a secondary source of Zn.[9−11] Results published by Struis and co-workers[17] indicated that Zn in a MSWI FA was up to 60% in the form of oxides, mainly $Zn_5(OH)_6(CO_3)_2$, Zn_2SiO_4, and $ZnAl_2O_4$. They also reported indications of Zn−S bonds but no indications of zinc chlorides being present. Contrary to those results, Takaoka and co-workers found $ZnCl_2$ to dominate the Zn speciation in FA from a MSW combustion unit in Japan.[18] One study of the speciation of Zn in a MSWI BA in China showed that Zn was predominantly present as Zn_2SiO_4, $ZnFe_2O_4$, ZnO, and $ZnSO_4$ in fresh ash.[19]

In a recent study by Kitamura and co-workers,[20] EDX-data and correlation analysis were used to study the associations of Zn and Cu in FA from MSWI. The results indicated that Zn was associated with Cl, K, and Na in certain areas of the ash particles and with O, Si, Al, and Fe in other areas. This was interpreted as evidence of the presence of $ZnCl_2$ or ZnK_2Cl_4 and Zn_2SiO_4 in addition to $ZnAl_2O_4$ and $ZnFe_2O_4$. They further found that Cu correlated positively with Al, Cl, O, and Si, which was interpreted as Cu being present as chlorides and oxides enclosed in the aluminosilicate matrix of the ash. In addition, Cu correlated positively with Zn, indicating that brass could be a source of Cu in MSWI FA.

Although only a few earlier studies have focused on direct determination of Cu and Zn speciation in BA, numerous studies have been performed indirectly determining the form of toxic metals, such as Cu and Zn, and their transformation during, for example, ash treatment and storage. For example, Arickx and co-workers[4] studied Cu speciation in MSWI BA after a treatment process[21] and showed the presence of metallic Cu, CuO, Cu_2O, alloys with Zn or Sn (brass and bronze) and possibly compounds with Ca, Cl, and S. Bayuseno and Schmal[22] focused on the effect of BA aging on mineral composition and argued that during storage, the minerals were transformed from anhydrite and amorphous phases to stable crystalline compounds and the calcium minerals accommodated trace metals, thereby decreasing their release to the environment. Similar results have been published by Alam and co-workers,[23] who showed that trace metals, such as Cu, Zn, Ni, and Cr, were concentrated in a layer on BA particles, which mainly consisted of melilite minerals and amorphous material. Saffarzadeh and co-workers[24] studied the mineralogical transformations and effects on leaching properties of trace metals in BA deposited in landfills, suggesting that hydroxides of Fe and Al were most effective in incorporating trace metals, whereas $CaCO_3$ was not as effective.

In the present work, we investigated the chemical speciation of Cu and Zn in both BA and FA from three MSW waste-to-energy (WtE) plants using X-ray absorption near edge structure (XANES). A motivation for the work was that Cu and Zn are trace metals commonly occurring in MSWI ash which, depending on their chemical forms, are ecotoxic. To evaluate the possibility of utilizing MSW BA as a construction material, detailed knowledge of their chemical forms is needed. Furthermore, information about the chemical forms of Zn and Cu in FA is important when evaluating use of the ash as a secondary source of these metals. The study included investigation of the effect of BA storage according to the normal procedures used at the facilities on the speciation of Cu and Zn.

2. MATERIALS AND METHODS

In total, 12 FAs and BAs from three Swedish WtE plants were included in the present work.

Facility 1: a grate fired combustor burning MSW and CIW at 1100−1200 °C.

Facility 2*:* a rotary kiln combustor burning mainly hazardous waste at 1100−1400 °C.

Facility 3*:* a fluidized bed boiler burning MSW and CIW at 800−900 °C. Prior to combustion, the fuel was shredded, and ferrous metals were removed by magnetic separation.

2.1. Sample Description. Facilities 1 and 2 used water quenching, whereby BA was transported through a water filled trough for quenching while being conveyed for sorting by sieving and the magnetic removal of large pieces of metal. The ashes are then stored outdoors in piles to react with CO_2 from the air. At facility 3, BA was cooled in a dry system (not water quenched) and stored in closed containers.

Owing to the inherent heterogeneity of incineration ashes, careful sample selection methods were needed to select representative samples, especially for the BAs. Further details on the sample selection procedures are found in the Supporting Information. At facility 1, three samples were collected from the same pile of BA after 2, 3, and 4 months of outdoor storage (samples BA_1-1, BA_1-2, and BA_1-3, respectively). From facility 2, two samples were collected—one fresh sample (BA_2-1) collected from the top layer in the ash container and one aged sample (BA_2-2) collected from a pile after 3 months of outdoor storage. The BA sample from facility 3 (BA_3-1) was a homogenized sample composed of subsamples collected directly from the fresh top layer of the ash container at the plant.

The FA samples from facility 1 were collected from the electrostatic precipitator placed upstream of the scrubber. Sampling was repeated three times at about 2 month intervals, resulting in three samples (FA_1-1, FA_1-2, and FA_1-3). The FA samples from facilities 2 and 3 were taken from fabric filters placed after the alkaline scrubbers and the addition of activated carbon. At facility 2, two samples were collected (FA_2-1 and FA_2-2), whereas only one sample was collected from facility 3 (FA_3-1).

The final volume of all the FA and BA samples was about 10−15 L, while the original sample withdrawn was up to 10 tons and reduced according to standard procedures (see Supporting Information). After collection, the samples were stored dry in airtight containers until they were analyzed. An overview of the samples, flue gas treatment, and ash collection systems used is shown in Table 1.

2.2. Sample Preparation and Elemental Analysis. The size of ash samples collected at the WtE plants was reduced using standard

Table 1. Overview of Samples[a]

facility	sample name	combustion technique	FA separation	storage
1	BA_1-1	Grate		open air, 2 m
1	BA_1-2	Grate		open air, 3 m
1	BA_1-3	Grate		open air, 4 m
2	BA_2-1	Rot. Kiln		fresh/closed storage
2	BA_2-2	Rot. Kiln		open air, 3 m
3	BA_3-1	CFB		fresh/closed storage
1	FA_1-1	Grate	ESP	fresh/closed storage
1	FA_1-2	Grate	ESP	fresh/closed storage
1	FA_1-3	Grate	ESP	fresh/closed storage
2	FA_2-1	Rot. Kiln	fabric filter	fresh/closed storage
2	FA_2-2	Rot. Kiln	fabric filter	fresh/closed storage
3	FA_3-1	CFB	fabric filter	fresh/closed storage

[a]Abbreviations used: ESP = electrostatic precipitator, BA = bottom ash, FA = fly ash, CFB = circulating fluidized bed, m = month.

sample dividers prior to ICP-MS and XANES analyses to ensure a representative sample.

The ICP-MS analysis was performed by ALS Scandinavia AB according to ASTM standards and EPA methods. The samples were dissolved using two dissolution methods: (i) melting with lithium borate ($LiBO_2$) and dissolving the melt in HNO_3 and (ii) digesting the samples with HF, HNO_3, and HCl in a microwave oven.[25−27] The uncertainties in the analytical results due to the sample preparation in the laboratory and ICP measurement are indicated in Table 3.

For the XANES analyses, the ash samples were ground, mixed with boron nitride, and pressed into 13 mm diameter tablets.

2.3. Reference Substances Used for XANES Data Evaluation.

Cu and Zn reference compounds were purchased as pure chemicals (>99%) when available. Natural minerals were also used as reference substances because they are often formed by chemical alterations of other minerals due to the influence of air and water, and similar alterations can be expected to occur with metal compounds in MSWI ashes. X-ray powder diffraction (XRD) analyses were carried out to ensure that the ashes did not contain additional compounds of the two target metals Cu and Zn. A few reference compounds not available for purchasing were synthesized and characterized by XRD.

Reference compounds for Cu were as follows: CuCl, $CuCl_2$, Cu_2O, CuO, CuS, Cu_2S, $CuSO_4{\cdot}5H_2O$, $CuFe_2O_4$, $Cu_3(PO_4)_2$, $Cu(OH)_2$, $CuCO_3{\cdot}Cu(OH)_2$, and $CuSiO_3{\cdot}H_2O$. Reference compounds for Zn were as follows: ZnO, $Zn(OH)_2$, $ZnCO_3$, $Zn_5(CO_3)_2(OH)_6$, $ZnCl_2$, $ZnSO_4{\cdot}H_2O$, ZnS, $Zn_3(PO_4)_2{\cdot}4H_2O$, $ZnFe_2O_4$, $ZnAl_2O_4$, $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, Zn_2SiO_4, and $Ca_2ZnSi_2O_7$. The last two Zn minerals (Zn_2SiO_4 and $Ca_2ZnSi_2O_7$) were provided by Prof. Ellery Ingall (details about those minerals have been given elsewhere[28]). The reference compounds were mixed with boron nitride to achieve an optical thickness of ~2.5 and pressed into 13 mm diameter tablets.

2.4. XANES Measurements, Data Collection, and Analysis.

XANES data collection was carried out at the XAS beamline Balder placed at the 3 GeV ring at MAX IV, Lund, Sweden.[29] The storage ring was operated at 3.0 GeV and ~250 mA. Monochromatization was achieved with a pair of Si111 crystals, and the beam was focused down to ~100 × 100 μm^2. The XANES spectra of reference substances were recorded in transmission mode at the K-edges of Cu (8979 eV) and Zn (9659 eV). Prior to all measurements, the energy axis was calibrated to the K-edge of a reference foil of Cu and Zn, respectively. Data for the ash samples were collected in the fluorescence mode with a seven-element silicon drift detector. At least ten repeat scans were acquired for the subsequent summation, shifting the sample position by 0.2 mm between scans to mitigate possible radiation damage. Based on the elemental content, the attenuation length was modeled to around 20−30 μm, and thus the data collected in both the transmission and fluorescence modes were bulk-sensitive.

XANES ash sample data were pre-processed (summation, background subtraction, normalization, and interpolation onto a common energy grid) using the software "Viper" and "XANES dactyloscope"[30] and further analyzed using the ATHENA software package.[31] To determine the presence of different species of Zn and Cu and their relative contribution, a method of linear combination fitting (LCF) was used.

Prior to the LCF, a blind test was performed by preparing four mixtures of three different reference compounds of each element (Cu and Zn) and analyzing them using the same procedures as used for the ash samples. The conclusion was that any fitted content of the reference compounds below 3−4% was questionable. Therefore, the fitting procedure was made iterative by removing the species with the lowest content until all species included in the fit represented a content of 5% or higher.

Table 2. Chemical Composition of Ash Samples

	BA_1-1	BA_1-2	BA_1-3	BA_2-1	BA_2-2	BA_3-1	FA_1-1	FA_1-2	FA_1-3	FA_2-1	FA_2-2	FA_3-1	M.U.[a] (~%)
Si	23.4[d]	18.6	23.4	16.8	18.8	31.1	11.3	8.98	8.79	0.96	0.91	8.84	20
Al	5.23	4.68	4.93	5.72	4.94	4.50	3.80	3.65	3.41	0.31	0.30	9.16	20
Ca	12.6	9.65	12.0	4.44	4.67	6.04	17.8	15.4	15.9	17.2	17.8	21.2	20
Fe	8.11	8.18	9.09	9.65	8.25	2.67	1.66	1.62	1.68	0.55	0.57	3.13	20
K	1.09	1.03	1.14	1.15	1.42	1.75	4.26	4.32	3.93	3.40	2.19	1.69	20
Mg	1.41	1.13	1.34	1.63	1.54	0.81	1.60	1.56	1.49	0.39	0.39	1.92	20
Mn	0.11	0.13	0.13	0.24	0.21	0.07	0.08	0.09	0.08	0.02	0.02	0.14	20
Na	3.18	2.62	2.94	3.02	3.32	3.20	5.58	5.77	5.56	6.66	7.26	2.41	20
P	0.31	0.31	0.37	0.27	0.21	0.11	0.47	0.66	0.66	0.49	0.69	0.62	20
Ti	0.79	0.68	0.92	2.12	2.58	0.31	1.30	1.50	1.44	0.23	0.15	1.36	20
S	0.70	0.63	0.66	0.78	0.41	0.66	5.28	5.78	6.27	2.96	3.27	2.89	20
Cl	0.20	0.22	0.13	0.29	0.15	0.05	8.56	10.9	7.46	18.0	18.4	9.46	25
Cu	0.17	0.25	0.28	1.38	0.71	0.34	0.14	0.14	0.14	0.13	0.14	0.59	25
Zn	0.35	0.31	0.41	0.95	0.54	0.48	2.64	2.52	2.65	4.77	4.85	0.82	20
MC[b]	15.6	15.9	17.9	16.8	28.3	0	0	0	0	25.8	24.7	0.5	2
LOI[c]	4.4	3.2	4.3	7.4	2.8	0.2	5	4.8	4	25.2	25.3	8.6	5

[a]Measurement uncertainty (M.U.). [b]Moisture content. [c]LOI at 1000 °C. [d]All values in wt % (on dry basis).

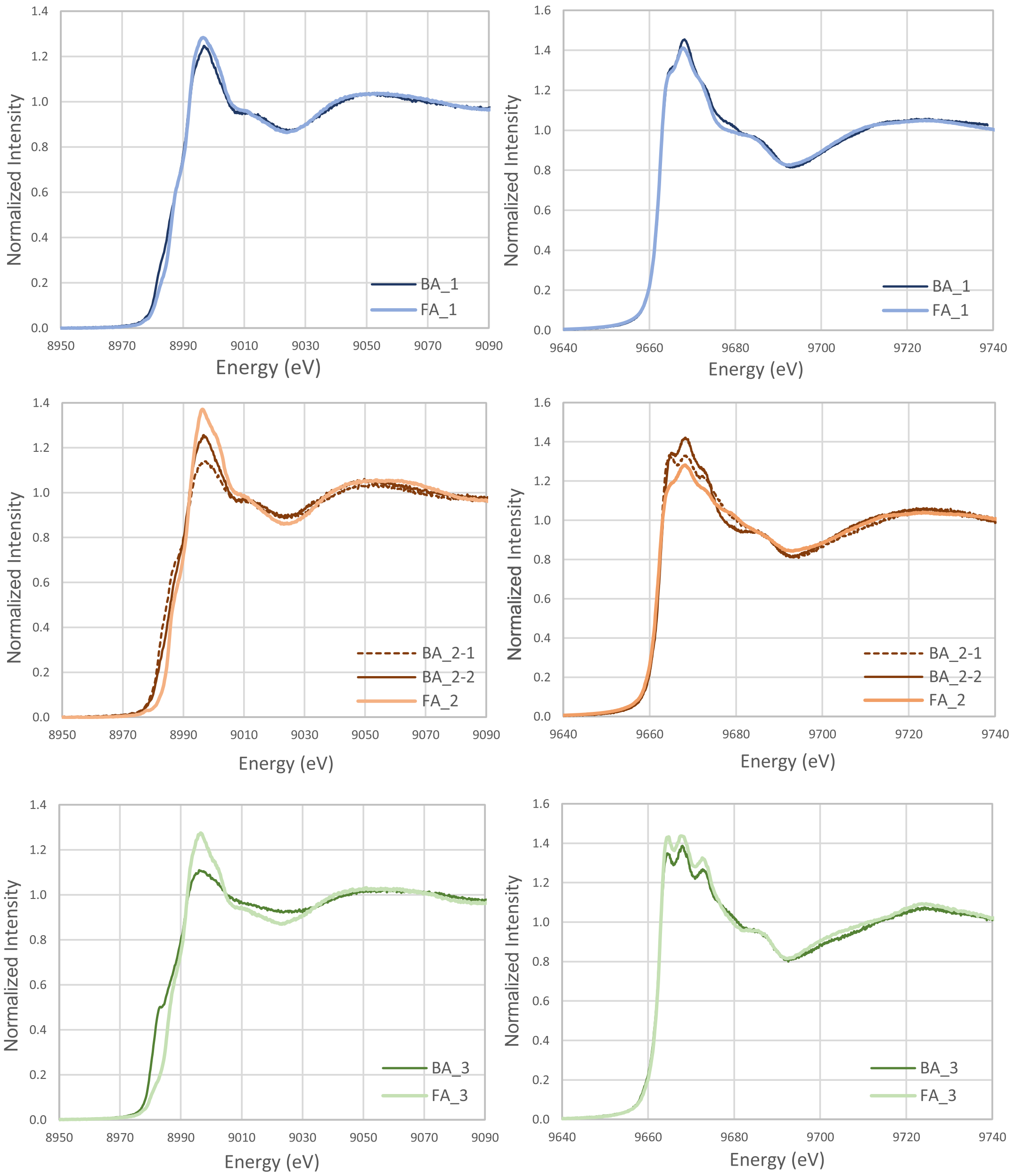

Figure 1. XANES spectra of FA and BA from different facilities. If several samples were of the same type from a facility, the average of the XANES spectra is shown. XANES spectra of fresh and aged BA ash from facility 2 are both shown due to the pronounced differences. Left panels: Cu; right panels: Zn.

3. RESULTS AND DISCUSSION

3.1. Chemical Composition of the Ashes Analyzed.

The concentrations of the major elements as well as Cu and Zn are summarized in Table 2 together with other relevant parameters, such as mass loss on ignition (LOI) and moisture content (MC), for the 12 ash samples included in the study. The concentrations of the trace metals Cu and Zn differed significantly between the facilities and type of ash (FA or BA). The BAs from the grate fired combustor (facility 1) and rotary kiln (facility 2) had a higher Cu content than the respective FAs, whereas the CFB (facility 3) produced a FA that had a slightly higher Cu content than the BA. Zn was more abundant in the FAs than in the BAs, in line with earlier investigations of MSWI ashes.[32,33] One reason for the higher concentration of Zn in the FAs may be the formation of volatile zinc compounds, such as $ZnCl_2$, in the combustion.

3.2. XANES Analyses of Cu and Zn in BA and FA.

The final XANES spectra of the ash samples comprised the sum of at least 10 individual XANES scans, for which the sample position was moved by 0.2 mm between each scan. Analysis of the variation in the edge step (reflecting the elemental Cu/Zn content) between these individual XANES scans showed that the BAs were more heterogeneous than the FAs with respect to Zn/Cu concentration. For the BAs, the elemental content often varied by >50% between measurement positions, whereas for the FAs, the variation was less than ~15%. Despite differences in the height of the edge step, the individual scans were mostly similar, indicating a similar chemical speciation at each measurement position. The XANES spectra of the BA samples had a higher noise level than those of the FA samples, resulting in longer measurements for the BA samples, especially for those with low Cu/Zn

Table 3. Results of Cu Speciation from LCF of Reference Spectra to XANES Spectra of Ash Samples

	BA_1-1	BA_1-2	BA_1-3	BA_2-1	BA_2-2	BA_3-1	FA_1-1	FA_1-2	FA_1-3	FA_2-1	FA_2-2	FA_3-1
Cu (metal)	10%[a]	16%	9%	14%	12%	26%	17%	8%	9%			18%
CuCl	15%	14%	13%	26%	20%	17%	13%	9%	13%	5%	5%	8%
Cu_2O	7%	5%	9%			26%						
Cu_2S												
$CuCl_2$												6%
CuO	27%	23%	21%	15%	17%	23%				23%	10%	
CuS				12%								
$CuSO_4 \cdot 5H_2O$						8%	7%	9%	5%			
$Cu(OH)_2$	16%	24%	17%	14%	11%		41%	49%	42%	52%	59%	38%
$CuCO_3 \cdot Cu(OH)_2$	8%		9%		12%							
$CuSiO_3 \cdot H_2O$	6%	9%	5%	20%	18%		22%	24%	25%	19%	26%	19%
$CuFe_2O_4$	11%	9%	16%		9%				6%			10%
R-factor	0.00020	0.00047	0.00039	0.00020	0.00012	0.00067	0.00054	0.00112	0.00058	0.00270	0.00340	0.00064
χ-square	0.022	0.039	0.033	0.017	0.006	0.063	0.024	0.110	0.065	0.130	0.340	0.067

[a] The percentages given in the table show in which chemical form Cu atoms occurred (according to the LCF).

content. The high noise level for the BA samples may be due to several factors, such as the powder heterogeneity in the Cu/Zn elemental content, particle size (as compared to the beam size), sample porosities, and possible diffraction caused by crystalline matrix compounds.

The XANES spectra of the three BA samples from facility 1, collected from the same ash pile after 2, 3, and 4 months of outdoor open-air storage, indicated that even if present, chemical transformations of Cu and Zn occurring after 2 months of outdoor storage were minor. However, the XANES spectra of the fresh ash and 2 month-aged BA samples collected at facility 2 showed clear differences, as discussed in detail in later subsections. In the XANES spectra for the BAs collected at different facilities, clear differences were observed at both the Zn and Cu edges. In Figure 1a−f, XANES spectra recorded at the Cu edge (left panels) and Zn edge (right panels) for the BAs and FAs are shown for each facility.

The XANES spectra of the three FA samples collected at facility 1, each representing one day of production, were very similar at both the Cu and Zn edges. The same was true for the two FAs collected at facility 2. Thus, variation in the ash speciation of Cu and Zn seems to have been minor at both facilities. The XANES spectra at the Cu edge of the FA samples collected at the different facilities were also similar, whereas the Zn edge showed more pronounced differences, indicating a larger variation in the chemical speciation of Zn than Cu between facilities (Figure 1). These observations are discussed in Sections 3.2.1 and 3.2.2.

The similarities between the XANES spectra of the multiple samples collected of the same type of ash from the same facility indicate that the procedure for ash withdrawal was sufficiently robust.

3.2.1. Chemical State of Copper.

XANES spectra recorded at the Cu edge are shown in the left panels of Figures 1 and S1−S3 in the Supporting Information. Figures in the Supporting Information also show spectra resulting from the LCF. The chemical speciation of Cu in the ash samples, as obtained by the LCF, is presented in Table 3.

Features that appeared in most of the XANES Cu spectra of the ashes analyzed included one distinct but relatively broad peak at 8997 eV and a relatively weak structure at around +15 eV. Furthermore, a few samples showed a pronounced shoulder in the lower energy part of the absorption edge, meaning that less oxidized forms of copper were present. The described features are indicated by vertical gray dashed lines in Figure 2, where three selected examples of XANES spectra for ashes are shown together with spectra for all reference compounds included in the LCF.

The results from the LCF showed that Cu was present in the form of metallic Cu, CuCl, and CuO in all BA samples. Other chemical Cu forms commonly present in the BAs were $Cu(OH)_2$, $CuSiO_3 \cdot H_2O$, $CuCO_3 \cdot Cu(OH)_2$, and $CuFe_2O_4$. The Cu speciation of the MSWI ashes showed that Cu was present in different oxidation states (0, +I, and +II). For BA, this seems reasonable because the fuel bed has zones with different access to oxygen. The presence of Cu in the oxidation state I in the FAs may be due to the reduction of Cu(II) to Cu(I) occurring at 1030 °C even in oxygen-rich regions.[14] Another observation, made already from the appearance of the XANES spectra in Figure 1, was that Cu in the BAs was slightly less oxidized than Cu in the FAs (the XANES absorption edge was shifted toward lower energies for the BAs compared to the FAs). This is in-line with results from previous studies.[15,16] The largest difference in oxidation state between BA and FA was observed for facility 3 (fluidized bed combustor).

CuCl was found in both FA and BA samples. CuCl can be formed by a reaction between metallic Cu and Cl_2 gas at 450−900 °C.[34] Based on the results, CuCl was stable in the ashes even after wetting of the ash and open-air storage. One reason may be that soluble salts get physically trapped in the melt from incineration.[35] Most of the BAs contained copper ferrite, $CuFe_3O_4$, which indicates reactions between Cu compounds and iron compounds in the combustion.

The chemical speciation of the BA is a result of combustion, quenching, and weathering. All BAs that had been water-quenched and stored in open air contained $Cu(OH)_2$ and basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$, whereas the non-aged BA from the facility with dry quenching (facility 3) did not contain these compounds. The water quenched fresh BA from facility 2 (rotary kiln) contained $Cu(OH)_2$ but no $CuCO_3 \cdot Cu(OH)_2$. This could indicate that (i) $Cu(OH)_2$ is formed during wet quenching and (ii) that the open-air stock piling of BA leads to the formation of $CuCO_3 \cdot Cu(OH)_2$. However, there was no trend of increasing levels of $CuCO_3 \cdot Cu(OH)_2$ for the BA from facility 1 after the first 2 months of open-air storage. This is in line with observations of rapid initial aging during weathered storage.[5] $CuSiO_3 \cdot H_2O$ was present in all BAs except that from facility 3.

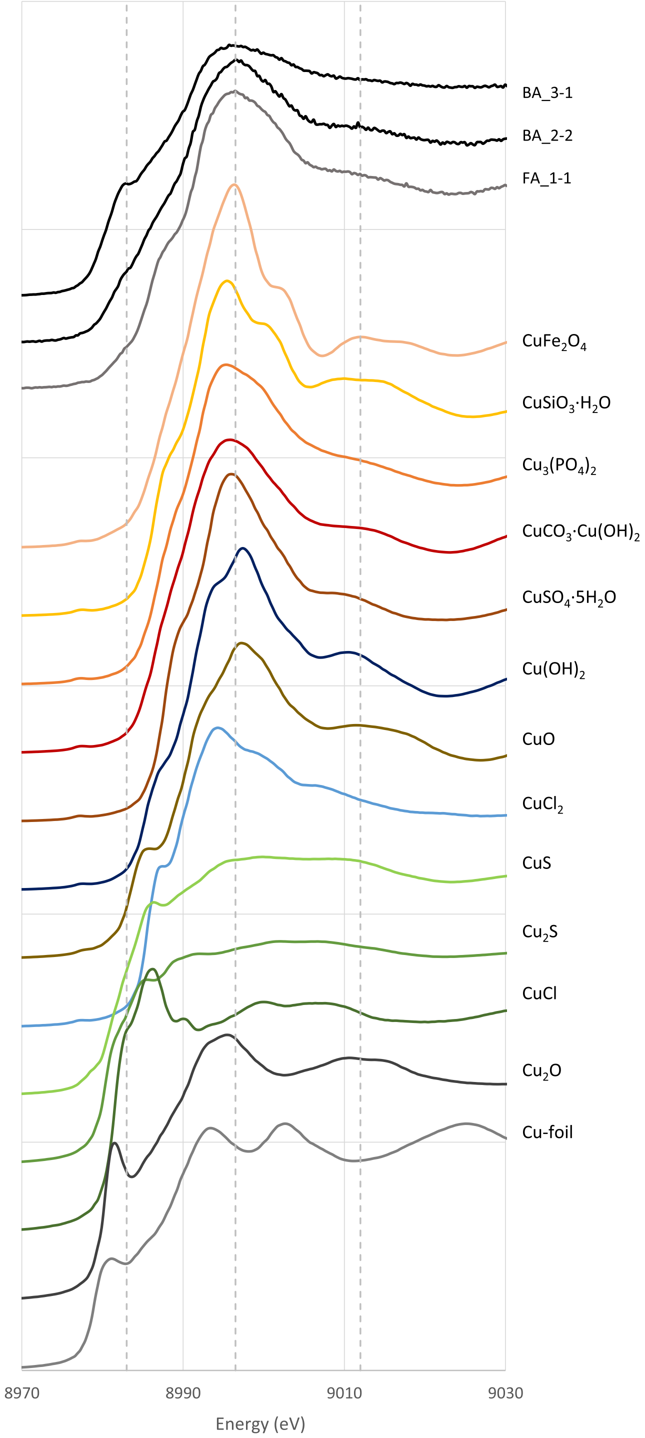

Figure 2. Copper K-edge XANES spectra of Cu references and selected characteristic examples of BA and FA. All individual ash spectra, including the fitted spectra, are presented in the Supporting Information (Figures S1−S3).

All FAs studied contained CuCl, $Cu(OH)_2$, and $CuSiO_3·H_2O$. In addition, the FAs from facilities 1 and 3 contained copper in metal form. This suggests that metal pieces were transported through the combustion chamber and flue gas cleaning without being oxidized. This has in fact been frequently observed even for metallic aluminium.[36] Because the scrubber liquids contained sulfate ions, it was first expected to find $CuSO_4·5H_2O$ in the FA collected after the flue gas scrubbers, that is, in facilities 2 and 3. Instead, this compound was only found in low concentrations in the FA samples from facility 1, where the FA was taken out before the scrubber. This indicates that SO_2 and water vapor in the flue gas can react with Cu in the FA particles. The presence of copper silicate, in this work represented by $CuSiO_3·H_2O$, was found in all FAs and most BAs.

It was noted in a recent study by Kitamura and co-authors[20] that Cu may occur together with Zn in ash from waste incineration, interpreted as the alloy brass. Brass was not included in the library of references in our study. However, an old XANES spectrum collected at the beamline I811 at MAX III, Lund, was available. Comparison of the spectra for Cu foil and brass at the Cu edge showed that they were very similar, both in shape and energy, consistent with previous reports.[37] The resolution in energy at Balder is different from that of I811. Nevertheless, we attempted to perform LCF including the spectrum of brass. When both Cu metal and brass were included as references, Cu metal gave the best fit. When excluding the reference spectrum of the Cu foil in the LCF, the brass was instead included as a component in a similar amount as the Cu foil, and with sufficient quality of the fit. We conclude that both metallic copper and brass may be possible forms of Cu in both BA and FA from MSWI units.

Lassesson and co-workers[10] found $Cu_3(PO_4)_2$ in samples of FA from waste incineration. In this study, we chose not to include this compound in the references because it was not likely to be present in ashes based on chemical considerations (according to the PubChem database[38]), as it decomposes upon heating.

3.2.2. Chemical State of Zinc.

XANES spectra of the ash at the Zn edge typically showed three characteristic peaks with varying relative ratios. These peaks were also present in the spectra of the Zn references (Figure 3). Two of the characteristic peaks in the ash XANES spectra matched those found in the XANES spectra of $ZnFe_2O_4$ and partly those of $ZnAl_2O_4$. Furthermore, a broad peak at around 9690 eV was observed which was also seen in the spectra of some reference compounds. The XANES spectra of ZnO and $Zn(OH_2)$ were identical, and thus these two forms could not be distinguished. This was also noted earlier by others.[39] Therefore, the speciation determined by LCF presented in Table 4 includes the label "ZnO and/or $Zn(OH)_2$". XANES spectra for each ash are presented in the Supporting Information (Figures S1−S3) together with the XANES spectra resulting from LCF.

As expected, the XANES spectra showed that Zn mainly occurred in oxidation state +II, and no clear differences in oxidation state between the FAs and BAs were observed. Even if differences were observed in the XANES spectra of the 12 ashes, the same chemical forms of Zn were predicted by the LCF but in varying ratios for both the BA and FA samples. The results are presented in Table 4. Generally, the LCF fitting of the XANES spectra resulted in better fits for the BAs than FAs for both Cu and Zn (Figures S1−S3 of the Supporting Information). In the case of the FA samples from facility 2, the fit of the Zn XANES spectra indicated that a relevant reference was missing (Figure S3d).

The compounds hemimorphite ($Zn_4Si_2O_7(OH)_2·H_2O$) and zinc ferrite ($ZnFe_2O_4$) were both found in all ash samples studied. The zinc aluminate, $ZnAl_2O_4$, which exhibits XANES spectra similar to those of zinc ferrite, was also found in most ashes (except for the FAs from facility 2), but in relatively low amounts (5−18%). ZnO and/or $Zn(OH_2)$, hydrozincite

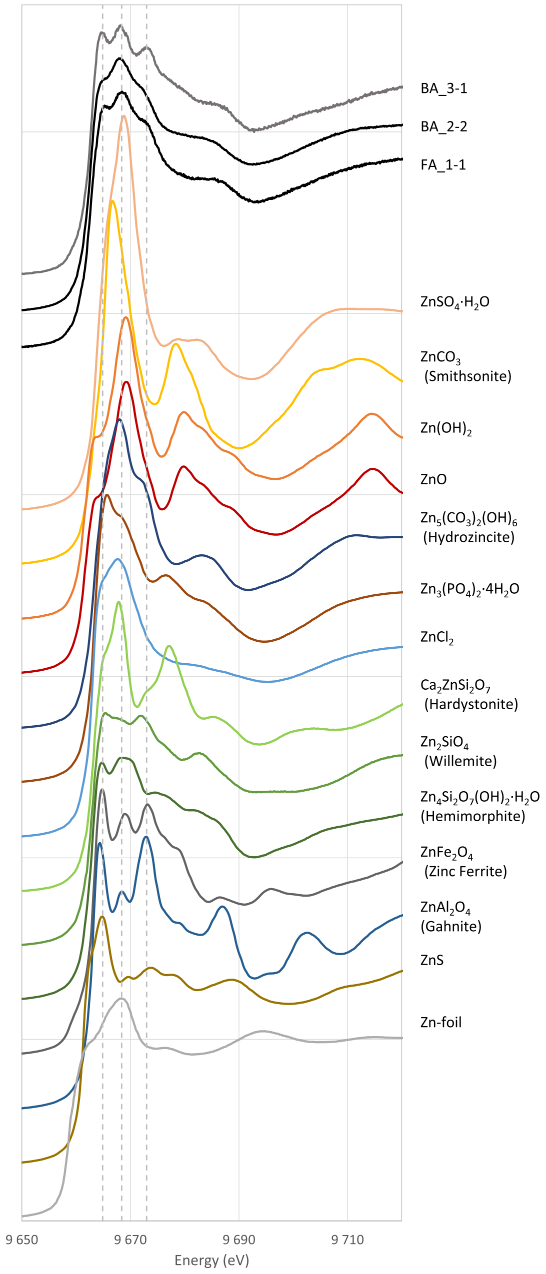

Figure 3. Zn XANES spectra of reference materials and three selected examples of typical XANES spectra of ash samples. All individual ash spectra, including the fitted spectra, are presented in the Supporting Information (Figures S1−S3).

($Zn_5(CO_3)_2(OH)_6$), and $ZnCl_2$ were also commonly found in both BA and FA. Apart from the presence of $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ (and absence of willemite), the Zn forms detected in FA were similar to those reported by Cai and co-workers[40] in FA from the incineration of municipal waste in China. There were also similarities with the Zn speciation reported by Takaoka and co-authors,[18] with the exception of ZnS, which is unlikely to be stable in FA (see later discussion). Regarding Cu, the linear combination fits of the BA Zn speciation were better than those of the FA, especially for the FAs from facility 2 (rotary kiln) (Figure S3), indicating that some relevant reference may have been missing.

A high content of $ZnCl_2$ has been reported in several previous studies of FA from waste incineration.[18,20,40]

Table 4. Results of Zn Speciation from LCF of Reference Spectra to XANES Spectra of Ash Samples

	BA_1-1	BA_1-2	BA_1-3	BA_2-1	BA_2-2	BA_3-1	FA_1-1	FA_1-2	FA_1-3	FA_2-1	FA_2-2	FA_3-1
Zn (metal)	9%[a]			6%	7%		9%	6%	5%	15%	9%	
$ZnFe_2O_4$ (zinc ferrite)	9%	19%	16%	21%	15%	26%	5%	6%	6%	12%	14%	32%
$Zn_4Si_2O_7(OH)_2 \cdot H_2O$ (hemimorphite)	32%	32%	27%	42%	9%	32%	30%	24%	23%	35%	30%	7%
$Zn_3(PO_4)_2 \cdot 4H_2O$												
$ZnSO_4 \cdot H_2O$												
$ZnAl_2O_4$ (gahnite)	8%	5%	5%	11%	16%	13%	10%	13%	13%			18%
ZnO and/or Zn(OH)2	11%	11%	17%		5%	5%	11%	9%	9%	11%	19%	
$ZnCO_3$ (smithsonite)												
Zn_5(CO3)2(OH)6 (hydrozincite)	16%	16%	23%		29%		15%	16%	19%			16%
$ZnCl_2$	16%	16%	11%	20%	18%	22%	19%	25%	23%			27%
Zn_2SiO_4 (willemite)										26%	28%	
$Ca_2ZnSi_2O_7$ (hardystonite)												
R-factor	0.00056	0.00061	0.00046	0.00130	0.00093	0.00094	0.00070	0.00065	0.00041	0.00160	0.00120	0.00062
χ-square	0.030	0.079	0.063	0.167	0.122	0.119	0.037	0.085	0.053	0.189	0.140	0.035

[a] The interval fitted was −20 to 30 eV, where 0 eV corresponded to the absorption edge. The percentages given in the table show in which chemical form Zn atoms occurred (according to the LCF).

Kitamura and co-authors[20] interpreted the co-location of Zn and Cl in FA as either $ZnCl_2$ or K_2ZnCl_4 adsorbed to the particle surfaces. In the Supporting Information, modeled XANES spectra of $ZnCl_2$ and K_2ZnCl_4 are presented, showing clear resemblances. In our study, K_2ZnCl_4 was not included in the reference library. In BA, the presence of $ZnCl_2$ can be explained by the encapsulation of chloride within sintered BA particles.

The presence of hemimorphite has rarely been reported in the literature but occurred in all ashes in this study. Hemimorphite has been found as one of several reaction products between zinc ions in a water phase and the silica rich ash in biochar.[41] It has also been reported as a reaction product in slag from the combustion of tyres.[42] Most of the earlier published studies using XANES for Zn speciation did not include hemimorphite as a reference compound for LCF. Instead, willemite (Zn_2SiO_4) has often been included to represent Zn bound in silicates. In the present study, hemimorphite, willemite, and hardystonite ($Ca_2ZnSi_2O_7$) were included as reference compounds. Apart from hemimorphite, willemite appeared as a probable component only in FA from facility 2 (rotary kiln), while hardystonite was not found in any ash samples.

The XANES spectra for the three BA samples from facility 1 (grate fired) showed a weak trend of increasing hydrozincite levels with aging time, from 16 to 23% during 2−4 months of aging in open-air stock piling. Consistently, neither of the two BA samples regarded as fresh (no outdoor open-air storage) contained hydrozincite (BA_2-1 and BA_3-1), whereas the aged samples from facility 2 (BA_2-2) did. This indicates a reaction between carbon dioxide in the air and the zinc compounds in the ashes during storage, probably as a result of a reaction between CO_2 and Zn ions dissolved in the pore liquid in ash particles, as suggested by Zhang.[11] These carbonate formation reactions are often assumed to make Cu and Zn less leachable, but observations showing the converse have also been reported.[6] Another very weak trend in the composition in BA from facility 1 with storage time was decreasing levels of $ZnCl_2$. However, the observed 4% decrease was within the expected uncertainty of the LCF method.

As discussed in the section on Cu speciation, it is possible that Zn and Cu in the ash were also present in the form of the copper−zinc alloy brass. XANES spectra of Zn as a metal and as brass nanoparticles were reported in a study by Jeon and co-authors,[37] showing that the two spectra had clear resemblances. As brass was not included as a reference in the present study, it can only be hypothesized that the fraction of Zn presented in Table 4 as Zn in the metal form may, at least partly, be in the form of brass.

ZnS was first included in the references used in the LCF. However, results from earlier studies on the oxidation of ZnS in a similar process, that is, roasting of ZnS, have shown that it is highly unlikely that ZnS would stay unoxidized in FA because there is oxygen present in the flue gas.[43] Because of this and the fact that LCF predicted a relatively high content of ZnS (up to 22%), we present the LCF excluding ZnS in the main results shown in Table 3. LCF results including ZnS are presented in Table S1 in the Supporting Information.

3.3. Values of Metal Speciation Data.

BA from MSWI facilities investigated for a possible technical utilization, such as a construction material for road bases, is evaluated based on whether it is classified as non-hazardous or hazardous. For EC countries, the directive for the classification of waste materials is described in the Waste Framework Directive,[44] which contains definitions of all properties that can make waste hazardous, basic principles, and basic obligations when handling waste. The Waste Framework Directive, amended by Commission Regulation (EU) No 1357/2014,[44] specifies 15 hazard properties (HPs) and defines limits for the maximum concentrations of substances in the waste with respect to these properties. Klymko and co-authors[45] found that since Council Regulation (EU) 2017/997[46] came into force, the criteria for HP 14 (Ecotoxic) may lead to the classification of many MSWI BAs as hazardous.

Assessment of HP 14 can be done using bioavailability tests and/or using a summation (calculation) method.[46,47] However, to date, no harmonized standard has been defined at the EU level for carrying out these bio-tests, and for some elements, the summation method requires knowledge of the actual speciation. Thus, scenarios must be used where the entire concentration of these elements is assumed to be in a plausible reference form, such as Zn as ZnO and Cu as CuO. This assumption means that most MSWI BAs would be considered as ecotoxic.[47] Therefore, data on the metal speciation in MSWI ashes, such as those presented in this work, are important to allow better determination of the possible ecotoxicity risks of using the ash.

LCF of XANES spectra has been proposed as a method that can provide such results with reasonable certainty, for example, unquestionably showing that not all Zn occurs in the ecotoxic reference form ZnO. However, even though in the present study we showed that LCF yielded reasonable fitted speciation, there were still significant uncertainties hampering the indisputable identification and determination of levels of some compounds. Thus, classification of MSWI ash should not be done based on XAS data alone but in combination with leaching tests and toxicity tests.

Another situation where metal speciation data in MSWI ash are valuable is in the development of methods to recover metals from the ash. Metal recovery methods often include a leaching step that can be adjusted based on the chemical characteristics and solubilities of the metal compounds in the ash.

4. CONCLUSIONS

The speciation of Zn and Cu in MSWI ash collected at three WtE plants was determined using XANES. A method of LCF was applied to provide the best representation of the measured spectrum by a selected subset of relevant reference compounds.

Cu occurred in different oxidation states, from zero to +II, with a higher occurrence of the lower oxidation states in BA than in FA. In contrast, Zn occurred mainly in oxidation state +II. Cu and Zn typically occurred in several chemical forms, with up to eight forms identified in the same ash. The most commonly occurring forms were metallic Cu, CuCl and CuO, $Cu(OH)_2$, $CuSiO_3{\cdot}H_2O$, $CuCO_3{\cdot}Cu(OH)_2$, $CuFe_2O_4$, hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$), zinc ferrite ($ZnFe_2O_4$), $ZnAl_2O_4$, ZnO and/or $Zn(OH_2)$, hydrozincite ($Zn_5(CO_3)_2(OH)_6$), and $ZnCl_2$. The same chemical forms were identified in samples of BA and FA but typically in different ratios.

During the outdoor storage of BA, the relative levels of Cu and Zn hydroxycarbonates increased as compared to fresh BA. This carbonation of Cu and Zn has been suggested before, but, to the best of our knowledge, not previously shown.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c02226.

Description of Samples Withdrawal Procedures; XANES Spectra: Measured and Fitted; and LCF Results including ZnS (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jenny Rissler − *RISE Research Institutes of Sweden, SE-223 60 Lund, Sweden; Ergonomics and Aerosol Technology, Design Sciences, Lund University, E-221 00 Lund, Sweden;* orcid.org/0000-0001-8650-4741; Email: jenny.rissler@ri.se

Authors

Konstantin Klementiev − *MAX IV Laboratory, Lund University, SE-221 00 Lund, Sweden*

Jonas Dahl − *RISE Research Institutes of Sweden, SE-504 62 Borås, Sweden*

Britt-Marie Steenari − *Department of Chemistry and Chemical Engineering, Energy and Materials, Chalmers University of Technology, SE-41296 Gothenburg, Sweden*

Mar Edo − *RISE Research Institutes of Sweden, SE-504 62 Borås, Sweden*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.energyfuels.0c02226

Notes

The authors declare no competing financial interest.

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