



	Experiment title: Speciation of Cu/Zn/Pb in bottom and fly ash upon different steam washing condition	Experiment number: EV-467
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Report:

Municipal solid waste incineration (MSWI) is a widespread technology for MSW treatment, but one of its drawbacks is the production of solid residues: bottom ash (BA) and fly ash (FA). In latest years, our group has widely studied and characterized both BA and FA, providing a significant background of information about their bulk composition, which has pointed out promising characteristics for secondary raw materials (SRM), due to high content of Si, Al, Ca, as well as detrimental aspects such as relevant release of chlorides and heavy metals. A more in-depth analysis on the heavy metals' speciation distribution has demonstrated the fundamental role of how heavy metals are bonded in the matrix, as well as eluent pH, in the leaching process. Therefore, we aimed to exploit XAS, especially in the XANES region, to get insight into BA/FA selected heavy metals coordination, namely Cu/Zn/Pb, using suitable reference minerals. In addition, the final objective was to provide more information on the mechanism of action of a novel pre-treatment, i.e. steam washing, which has been proven to be effective in reducing the release of these metals.

The samples were selected between the pristine ash, namely BA and FA, and steam washing treated BA, since this treatment has been successfully tested only on BA, while FA application is still underway. In addition, an effort has been made to take into account the effect of BA particle size. BA represents the residual unburned fraction that remains at the bottom of the combustion chamber after the municipal solid waste incineration, therefore it is characterized by a large particle size (s) distribution, spanning from few millimetres to tens of microns. Previous investigations have shown that the BA treatment can be better optimized if it is preceded by a sieving process, in order to separate the material in subclasses that shares a trend in terms of pollutant release (usually, it increases with the reduction of particle size). In particular, the steam washing treatment has been applied with success on the coarser BA fraction, i.e. $s > 1$ mm. Therefore, we selected this fraction for the measurements, together with a set of treated samples by employing different time of exposure and steam/air ratio.

All samples were finely ground, and 13 mm-diameter pellets were prepared with similar weight (around 150 mg), for measurements in fluorescence mode. In fact, although the selected heavy metal content (between 0.05-1 wt%) can be considered a problem from the environmental perspective, preliminary evaluation has shown that the absorption step would not be enough to acquire spectra with satisfactory signal-to-noise ratio in transmission

mode, even more so considering the highly absorbent matrix (i.e., iron 9 wt%). On the other hand, the reference minerals samples were all collected in transmission mode, by calculating the optimal mass for an absorption jump around 1 and mixing the amount with BN to reach 100 mg for the pelletization. For each BA samples, a number of scan between 3-5 was employed, while 1-2 was used for reference minerals. After an initial evaluation of the quality of the samples spectra, which required long acquisition time related to the low signal-to-noise ratio, and after the discussion with the local contact we decided to not measure Pb L₃-edge and rather focus on Zn and especially Cu K-edge, since the latter represents the heavy metal with the highest leaching in our BA.

The pristine BA Cu K-edge XANES showed features from both Cu⁺ and Cu²⁺ oxidation states, indicating the non-homogenous oxidizing conditions of the combustion chamber. The profile was satisfactorily modelled using LCF contribution mainly from tenorite (CuO), followed by cuprite (Cu₂O) and chalcocite (Cu₂S), together with malachite (Cu₂(OH)₂CO₃), this latter probably formed during the water quenching used in the plant to cool down the material. By considering the k-space and Fourier transformed EXAFS spectra it was possible to evidence many similarities between tenorite and pristine BA, suggesting that in this sample the Cu environment can be approximate to a bulk CuO domain. When the treated samples are considered, a marked reduction of CuO is observed, while the other contributions increase. Due to the nature of the treatment, which has been defined as mild dissolution and mechanical removal of fine dust on the BA grains, it is unlikely that these differences are the result of chemical redox transformations. A possible interpretation can be found assuming that the steam washing has removed the CuO particles on the BA larger grains, thus changing the overall average Cu speciation distribution and the resulting leaching profile, as tenorite has been proposed as one of the main solubility controlling minerals in BA. This seems to be in accordance with EXAFS analysis, where the treated BA spectra seems more dampened in intensity and without the higher coordination shells of CuO bulk. The differences in the other contributions between the treated BA are probably related to the relevant heterogeneity of this material with respect to the scale of XAS beam size, as the treatments are performed on tens of grams of coarse grains (4<S<1 mm) since the leaching tests require large quantities to be significant. To tackle this limitation, three spectra on different pellets of pristine BA were collected, confirming CuO as the main speciation contribution. This, coupled with measurements on pellets of independently treated samples, which have shown a similar trend with respect to CuO, seems to support the hypothesis derived above. The main results are shown in Figure 1.

Regarding Zn K-edge, the pristine BA presents a Zn mainly associate with aluminosilicates, such as hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O), willemite (Zn₂SiO₄) and Zn-aluminate (ZnAl₂O₄), together with hydrozincite (Zn₅(OH)₆(CO₃)₂), as weathering product. Similar compositions were found in treated BA, without a significant trend in terms of semiquantitative LCF analysis.

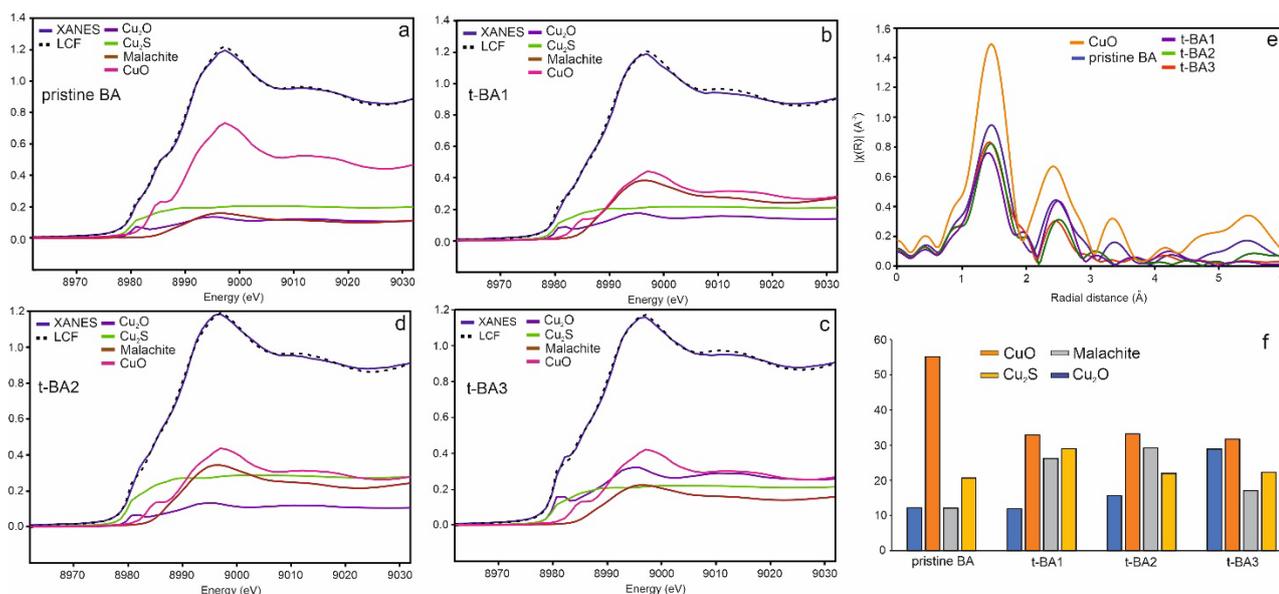


Figure 1. BA Cu K-edge XANES profile with LCF of a) pristine BA, b) t-BA1 c) t-BA2, d) t-BA3. e) Fourier Transformed EXAFS spectra of BA samples and CuO. f) Results of LCF quantifications.