Studying the speciation of zinc and copper compounds in thermal treatment residues to inform waste classification

Commonly the concentration of zinc in thermal treatment residues is such that it is necessary to take into account the speciation of zinc compounds to assess ecotoxicity. The Water Research Centre Limited (WRc) has worked on an in-depth characterization of incineration bottom ash (IBA) and aggregates made from them (IBAA), studying the speciation of zinc and copper compounds to inform an appropriate waste classification. Accurate waste characterisation supports waste recovery, avoids landfill disposal and protects the environment.

THE CHALLENGE

Zinc has emerged as a priority contaminant in incineration residues for waste characterisation. Its concentration in ash residues is too low for many analytical techniques, and its reactive nature makes it impossible for wet chemical extraction tests to be able to differentiate different zinc compounds. Thus, to identify the presence and give a quantification of potentially hazardous zinc compounds, in the last couple of years WRc has been testing ash samples with X-ray absorption spectroscopy (XAS) performing several measuring sessions in different European synchrotron light sources facilities. Based on an extensive knowledge of the mineralogy, total composition and origins of the material, WRc has been building an extensive library of standard zinc compound references and also refined its sample preparation methodology, working towards improving the quality of the readings and data analysis.

METHOD

The XAS measurements were taken at the PETRA III beamline P65 at DESY in Hamburg. In these measurements Extended X-Ray Absorption Fine Structure (EXAFS) data around the Zn K-energy in a range of circa 9,500 eV to 10,500 eV on IBA samples and zinc standard compounds were acquired. The zinc standards were measured in transmission while the ash samples were measured in fluorescence. The samples were prepared making sure that the material was ground down to particle size below 150 µm. Subsamples were carefully prepared making sure that they were thoroughly mixed to optimize their representativeness and homogeneity. 15 scans were acquired for each ash sample and between 4 and 5 for each of the references. Given the total concentration of zinc in the ash samples, the sample pellets were made entirely with the ash with no need for dilution, using kapton tape on both side of the pellet helped avoiding the pellet to break. The standard pellets were prepared diluting with dry cellulose to aim an overall zinc content of 4%. Some of the reference material were hydrophilic so the preparation of the pellet required to be carried out in a glove box. The samples were measured in vacuum at room temperature.

SOLUTION

Part of this study aimed to test the repeatability of the measurements carried out at different synchrotron light sources replicating the same experimental conditions. This would allow an industrial client such as WRc to have the flexibility to work with different scientific partners. The feasibility study gave a very positive outcome. The X-ray absorption near edge structure (XANES) was compared with those that had been tested previously in another beamline lab facility and a very good repeatability was confirmed by the PETRA readings. These readings had actually increased the definition of the data collected on those samples.
It was therefore possible to acquire the spectra from the measurements carried out on the new zinc standards. This way WRc was able to improve and expand the library of zinc compounds available to perform linear combination fittings. The updated library was applied to the large pool of data collected on several IBA and IBAA samples in the last few months. The quality of the fittings has constantly been improved allowing a more defined and reliable quantification of the zinc compounds present in the ash samples.
In Figure 1 a comparison of three sample spectra measured at PETRA III and SOLEIL is shown.

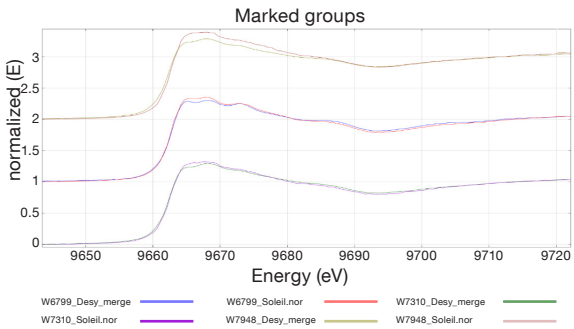

Figure 1 | Comparison of three sample spectra measured at PETRA III and SOLEIL

BENEFITS

Giving the needs of an industrial clients and the difficulties in planning a work with many months in advance, it was very important for a private technical consultant such as WRc to be able to access through the mail-in service the PETRA III facility to perform XAS measurements. One of the major outcomes of the feasibility study was the confirmation of the comparability of the measurements carried out at different beamlines laboratories in Europe. Under the rigorous guide of the beamline scientist and the careful data analysis of the specialized technical consultant, this would enable an industrial client to use this service more often and with more flexibility. What can still be seen mostly as an academic resource, this way has acquired greater accessibility to the private sector raising the standards and the quality of the analytical methodologies available on the market. From a scientific point of view WRc was able to upgrade the library of zinc standards compounds at its disposal to perform more accurate linear combinations fittings and produce a more scientifically sound speciation study of zinc in IBA and IBAA. In the last couple of years of work in this field WRc has found out that one of the most challenging aspects was represented by the constant research and difficulties in finding the minerals or making the most appropriate compounds of interest to build good libraries. Once proven that the measurements carried out under the same experimental conditions at different beamlines can be compared, it would be extremely useful if a shared collection/data-bank of EXAFS spectra around the K-energy of key elements of interest would be made available also to the private sector. This would represent a major scientific upgrade and commercial opportunity at the same time.

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