Structure analysis with relevance for complex materials – an outlook to X-ray absorption spectroscopy on phosphorus

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1. Introduction and Short Description:

Several challenges in thermal energy conversion of biomass are directly linked to so-called ash transformation reactions. These reactions are responsible for interactions between fuel ash and bed material, issues arising from melt formation, fouling and deposit formation. The current strategy to understand these complex reactions are mainly related to methods such as scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM—EDS), chemical fractionation, or powder X-ray diffraction (XRD).

These methods, respectively, have advantages and draw-backs. SEM-EDS provides spatial information concerning elements but is limited by penetration depth and sample morphology. Chemical fractionation on the other hand may alter the chemical composition of the sample during analysis due to changes induced by using a solvent that may cause new compounds to form and precipitate or dissolve. XRD can provide information concerning which compounds has actually formed but is limited to crystalline compounds only and depends on a relevant reference library.

Ash and material interactions in thermochemical processes has been successfully studied through these methods but several questions remain. For instance, the chemical composition in phosphorus-rich ash fractions that could be suitable for recovery. If these contain significant amounts of amorphous material the cat-ions surrounding the phosphate anions cannot be accurately described. This has severe implications for the recycling of nutrients from ashes which should be a part of a circular bioeconomy.

This lack of analytical information could be addressed using synchrotron-based X-ray absorption spectroscopy (XAS), which directly probes the average chemical environment of a selected element. This is made possible by fine-tuning the incoming X-ray beam energy and scanning the absorption with fine resolution. Further, if coupled X-ray fluorescence, it is possible to not only produce an elemental map similar to that from SEM-EDS, but also determine the chemical environment of selected elements in specific points.

The aim of the present work is to show some examples from on-going work on phosphate structures in ash particles from beamline 10.3.2 at the synchrotron Advanced Light Source, Lawrence Berkeley National Laboratory, USA. Importantly, it is demonstrated that ashes from biomass combustion are valid sample types for this analysis technique.

2. Methodology, Results and Discussion

Measurements with X-ray absorption spectroscopy at the phosphorus K-edge were performed at beamline 10.3.2 at the synchrotron Advanced Light Source, Lawrence Berkeley National Laboratory, USA. A library of reference phosphate compounds was prepared based on compounds previously identified in literatyre. Emphasis was placed on the anionic state when prioritizing samples as orthosphosphates were found to be most common. Additionally, phosphorus-rich ash particles from bubbling fluidized bed combustion of rapeseed cake were analysed.

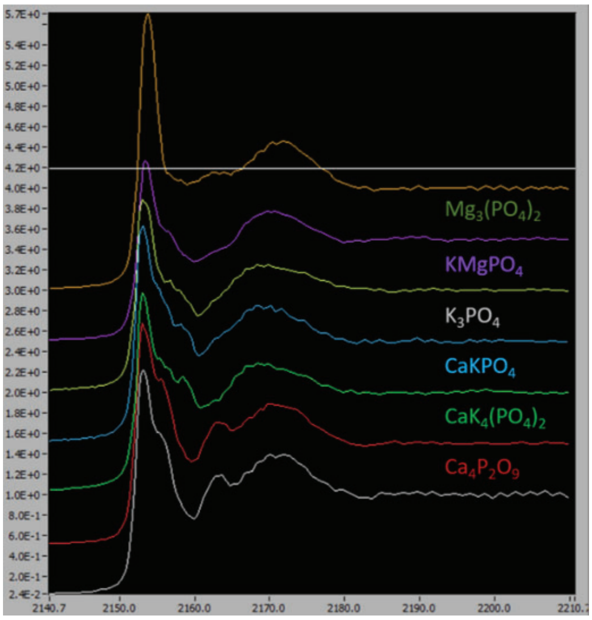

Fig. 1 X-ray absorption spectroscopy from phosphates standards plotted as a function of energy vs detector counts.

The results obtained display that the local structure surrounding cations are different enough to allow linear combination fitting even in amorphous samples. Further, the biomass ash did yield a spectra proving the feasibility of analyzing biomass ash types with synchrotron-based XAS. This also show that such materials could be used with other elements in focus which opens up new possibilities.

3. Conclusion and Outlook

The full paper will contain initial results from measurements on phosphate references and a phosphorus-rich biomass ash sample. This high-lights the potential of this advanced analytical method for application in the field of energy technology, where analytical challenges such as material interactions and oxidation state of interesting elements could be analysed in detail.

4. Acknowledgements

This research was funded by Swedish Research Council (Grant No. 2017-05331) and FORMAS (Grant No. 2017-01613), and used the resources of the Advanced Light Source (ALS), at Lawrence Berkeley National Laboratory, Berkeley, California, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231 (ALS08232 T.A.L.). ALS Beamline 10.3.2 is acknowledged and I thank research scientist Dr Sirine Fakra for valuable assistance with the analyses at ALS.