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Experiment Report Form

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.

- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Heavy metal speciation on waste fly ashes: speciation, localisation and mechanisms	**Experiment number**: ME405
Beamline:	**Date of experiment**: from: 2002-06-07 to: 2002-06-11	**Date of report**: 2004-04-16
Shifts:	**Local contact(s)**: A. Somogyi, A. Simionovici	*Received at ESRF:*

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Report: Heavy metal speciation on waste fly ashes: speciation, localisation and mechanisms

Earlier studies on Cd in fly ash from combustion of MSW, including micro X-ray spectrometric measurements, have shown that the distribution of Cd in/on the particles is highly inhomogeneous with local “hot spots”, very high in Cd concentration. Other trace metals, such as Zn and Pb, showed similar, inhomogeneous distribution as Cd. Clear correlations between Cd and halogens were also noted (1,3).

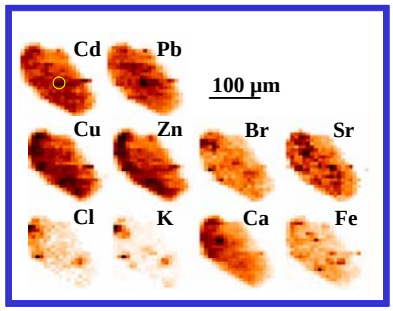

Figure showing the inhomogeneous distribution of Cd and other elements on a fly ash particle from combustion of MSW

In order to understand the chemical behaviour of cadmium in combustion and in the combustion residues, such as the fly ash, it is important that the chemical speciation of the metal is known (2). Due to the low concentrations of Cd in fly ash, conventional analytic methods have not given this information. Through the application of µ-XAS in local hot spots rich in Cd, it has been possible to investigate the oxidation state and the binding forms of Cd. µ-XAS spectra for pure Cd compounds were obtained at the same experimental set up as for the fly ash particles and used as references for the evaluation of experimental fly ash results.

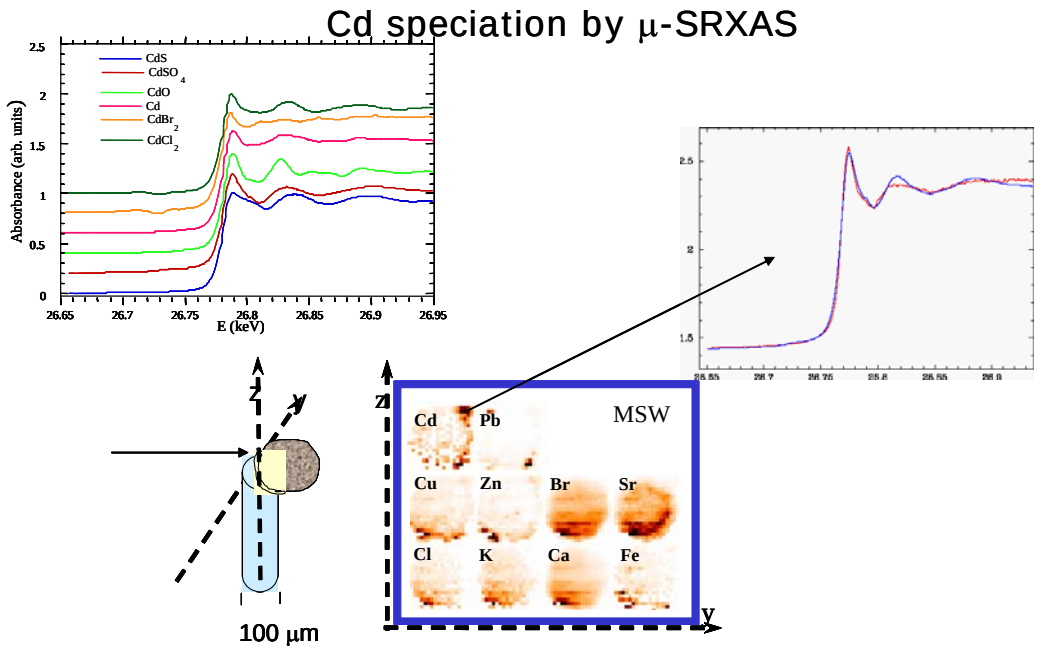

Figure showing the strategy for Cd speciation using µ-XRF and µ-XAS on sample and standards

By comparing Linear Combinations of XAS fit vectors using the data for the reference compounds, with the measured µ-XAS data for the Cd rich parts of fly ash particles it was concluded that Cd occurs in oxidation state +2. No other oxidation state was found in any particle, which shows that the MSW fly ash studied did not contain Cd in metallic form (1-6).

The investigations of the speciation of Cd in fly ash from MSW and biomass were continued during experiment ME 405. Fly ash from combustion of Salix was chosen as an example of biomass ash with relatively high content of Cd. A large number of particles were analysed using µ-fluorescence as well as µ-XAS techniques. The µ-XAS measurements were also extended into the µ-EXAFS region and additional EXAFS data was collected for fly ash particles from combustion of MSW (same as in experiment ME230). The results showed that the cadmium distribution was more even on the biomass ash particles than on the MSW fly ash particles, but sections with higher concentration occurred here as well. The oxidation state of Cd was +2, similar to what was observed for the MSW ash. No metallic cadmium was found. In both types of fly ash, Cd was present in water soluble

compounds ($CdSO_4$ and $CdCl_2$) as well as in compounds with low solubility (CdO). The quantity of water soluble Cd-species was significantly higher in fly ash from MSW than from Salix.

During experiment ME 405 it was possible to perform micro-X-ray fluorescence tomography on some fly ash particles as well. The measurements were carried out using pink beam and 27 keV energy. In all cases, Al compound refractive lense (CRL) of 100 lenses were used for focusing of the beam. The spot size on the particle was 3x5 μm^2. Individual fly ash particles mounted on capillaries were moved by a step-by-step system for horizontal translation and rotation around a vertical axis. The measurement of the transmission intensity gave the possibility to register the absorption tomogram of the chosen slices of the particles at the same time as that of the fluorescent one. The modified simultaneous algebraic reconstruction technique was used for the retrieval of quantitative self-absorption corrected 2D elemental specific fluorescence and transmission signals.

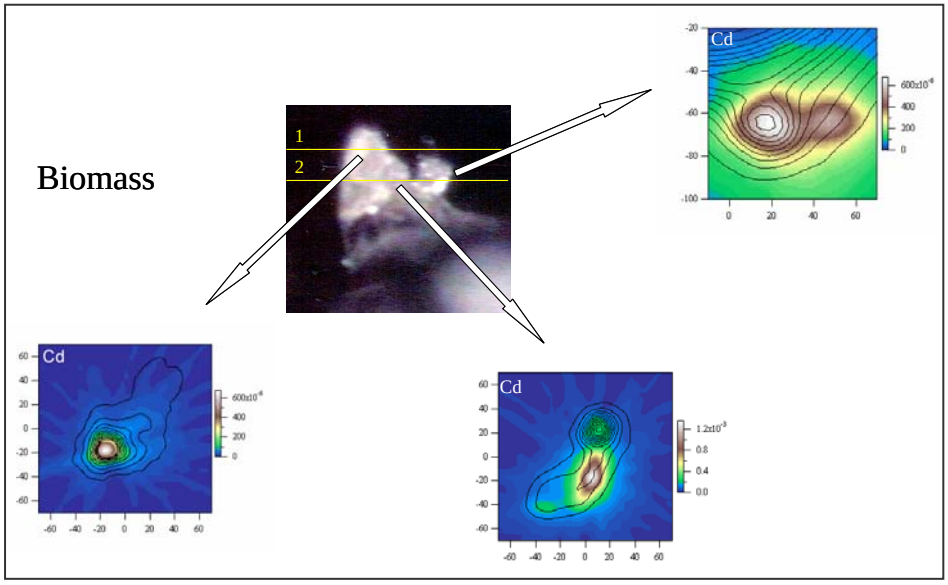

Figure showing tomography results for three slices of a biomass fly ash particle. Cadmium concentrated in the particle interior.

The tomography results showed that Cd as well as other trace metals was concentrated in the interior of the ash particles rather than on the surface. Again, as in earlier studies, Cd was found to be segregated to calcium bearing phases together with halogens. These findings explained the contradiction in the earlier results that indicated that Cd would preferably be present in easily soluble forms, whereas leaching tests showed that only a minor part of the Cd present was released to a water phase. The conclusions drawn were that Cd is present mainly as chloride and sulphate in fly ash from MSW and biomass, that Cd is segregated to Ca-compounds (indicating solid solution) and that Cd species are concentrated in the particle interior. Thus, Cd is not so easily leached out from the ash particles as would be expected from the speciation.

References

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