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ESRF

Experiment Report Form

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Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- 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:** **Fate of cadmium in biomass and waste fly ashes: origin, distribution and speciation**	**Experiment number**: ME489
Beamline:	Date of experiment**:** from: 2003-02-06 to: 2003-02-11	**Date of report**: 2004-04-16 *Received at ESRF:*
Shifts:	**Local contact(s)**: A. Somogyi, A. Simionovici	
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Report:

Fate of cadmium in biomass and waste fly ashes: origin, distribution and speciation

There is growing environmental concern regarding the management of landfills for municipal waste. Among the various disposal methods, combustion processes provide a convenient way to reuse the waste. Although the combustion process can effectively reduce the volume of the waste, the disposal of fly ashes generated during waste combustion may pose a significant risk to the environment due to possible leaching of hazardous substances, such as Cd and other toxic metals.

Cd is a toxic heavy metal without any known positive biological effects, e.g. it is one of the heavy metals causing forest damage. The risks posed to living organisms by the presence of Cd in our environment are determined by its availability and solubility together with its concentration. As a consequence, knowledge of the total Cd concentration in fly ashes provides only limited information, as this does not show how strongly this metal is bound to the particle matrix. Thus, Cd quantitative speciation as well as its variation with time is a prerequisite for long term risk assessments.

A detailed definition of speciation includes the following components: (1) identity of the contaminant of interest; (2) oxidation state of the contaminant; (3) associations and complexes to solids and dissolved species (surface complexes, metal-ligand bonds, surface precipitates); and (4) the molecular geometry and coordination environment of the metal. The more of these parameters that can be identified, the better one can predict the potential risk of toxicity to organisms by the contaminant.

In a series of detailed studies into the chemistry of Cd in combustion of MSW and biomass, cadmium speciation in fly ash has been investigated using synchrotron based micro-X-ray spectroscopy techniques (1-8). The following methods have been applied:

- μ-X-ray Fluorescence (μ-XRF)
- μ-X-ray Absorption Spectroscopy (μ-XAS)
- μ-X-ray Extended Absorption Spectroscopy (μ-EXAFS)
- μ-X-ray Fluorescence Tomography (μ-XRFT)
- μ-X-ray Diffraction (μ-XRD)

By employing these methods it has been shown that Cd is inhomogeneously distributed in/on fly ash particles from combustion of MSW and biomass (Salix). Large differences between the average and the maximal Cd concentrations were found for MSW fly ash, whereas Cd was more evenly distributed on biomass ash particles. Furthermore, the ashes studied showed no correlations between Cd-concentration and particle size as has been reported earlier in the literature.

The experimental results obtained in experiments ME230 and ME405 along with other data have indicated that Cd preferably follows halogens and Ca-matrices. Theoretical calculations based on density functional theory in the solid state were employed to test a hypothesis that Cd is able to replace Ca in various ionic compounds, due to the similarity in ionic radii of the two elements. Only minor structural effects were observed for a number of different host matrices. These observations and model calculations together with the absence of particle size dependence in the Cd concentration and inhomogeneous Cd distribution suggest that the Cd species present in a combustion flue gas have special affinity to certain ash matrix minerals.

In order to verify this suggestion, extended micro-X-ray absorption spectroscopy was applied on a number of sample materials and standards during experiment ME489. The set of standards included all chemical species of Cd that could be suspected to be present: Cd, CdO, $CdSO_4$, $CdCl_2$, $CdBr_2$, $CdCO_3$, $CdSiO_3$, $Cd_2P_2O_7$. Sample materials were prepared by reacting Cd chloride vapour with various ash matrix minerals such as Ca compounds, kaolin and other silicates. In addition fly ash particles were analysed with the same method.

A new quantification procedure was developed for the evaluation of the micro-EXAFS data sets based on Reverse Monte Carlo simulation. Evidence has been presented for the existence of cadmium silicate and cadmium chloride, with the cadmium silicate being the dominant form in MSW fly ash.

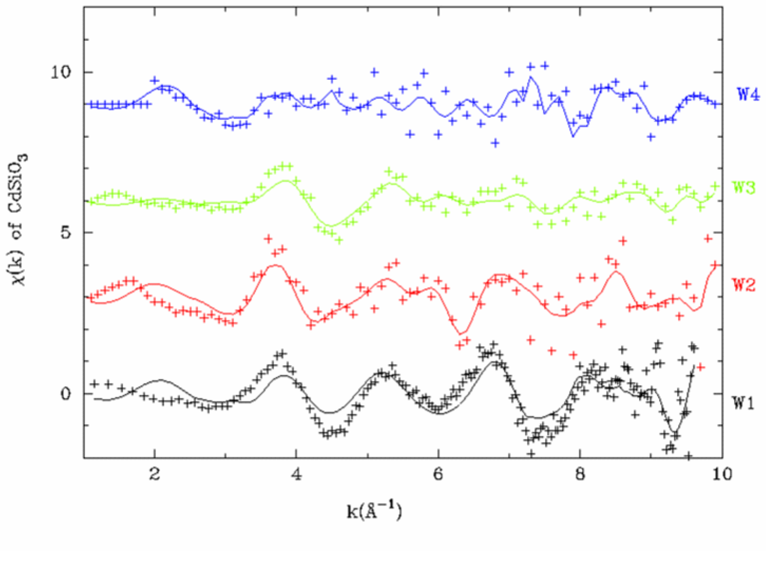

Figure illustrating the modelling results (line) and measured data (+).

It was also demonstrated that the Cd in MSW fly ash exists in both crystalline and amorphous forms (9). The results imply that the crystals of Cd compounds are very small, <5 μm^3, and heading towards the nano-crystalline scale. This indicates that the crystallisation process had been very fast.

Furthermore, the results verified the indications that Cd is concentrated to calcium matrix compounds, a mechanism for this behaviour has been proposed in a thesis (10).

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