



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

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;
- 1st September for experiments carried out up until January of the same year.

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.


Experiment title:

Heavy metal speciation in biomass and waste fly ashes: presence, localisation and mechanism

Experiment number:

ME-230

Beamline:

ID22

Date of experiment:

from: 22/March/2001 to: 27/March/2001

Date of report:

27/Feb/2002

Shifts:

15

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Report:

With the exp. ME-230, the concentrations of the major and minor components within each waste fly ash particle were determined from scanning μ -XRF experiments. Table 1 shows the total elemental compositions of the particles. Some variations in the concentration of the major and minor constituents can be observed from particle to particle, but the most dominant feature is the high Cl, K and Ca contents of most of the measured particles. The large amount of Ca in fly ashes is due to the presence of residues from the dry lime flue gas treatment used in the combustion plant. Other main components detected by μ -XRF were K, Zn and Cl. These values were in accordance with the element contents found in earlier studies [1,2] using AAS and ICP-MS. The presence of halogens in significant quantities indicates that the trace metals may be present in easily soluble salts. Such metal speciation would make the management of this filter ash problematic with respect to their possible leaching. The large differences between the average and maximum concentrations within individual particles indicate a considerable variation in concentrations with "hot-spots" containing about 10-100 times higher amount of a given element than the average. This finding supports the suggestion that the trace metals have special affinity to some ash minerals located at the particle surface.

Table 1: Average (Av) and Maximal (Max) element content of the MSW fly ash particles.

article no	Cd ppm		Pb ppm		Sr ppm		Mo ppm		Fe ppm		Cu ppm		Zn ppm		Br ppm		Cl % w/w		K % w/w		Ca % w/w	
	Av	Max	Av	Max	Av	Max	Av	Max	Av	Max	Av	Max	Av	Max	Av	Max	Av	Max	Av	Max	Av	Max
1	29	100	600	4700	100	300	12	200	700	4100	600	3600	1000	19100	400	2400	21.5	21.7	0.20	1.45	6.47	29.4
2	16	74	500	1100	100	400	10	58	300	13100	200	1300	400	7600	2100	4600	0.31	4.0	0.14	0.92	4.21	22.3
3	56	200	600	2200	28	100	7.4	29	600	4900	800	2300	2970	9900	88	500	0.57	7.2	0.25	5.43	1.16	5.1
4	43	150	500	3900	18	60	8.5	100	300	1600	500	1600	2600	7900	6.7	500	0.55	2.7	0.22	1.76	0.63	2.3
5	5.4	65	200	7600	73	400	1.1	46	82	1600	87	1200	100	2500	500	3100	0.49	10.3	0.13	2.11	8.17	84.3
6	13	38	300	3100	300	1700	6.4	56	200	1400	200	3100	200	4000	2500	8700	0.80	4.4	0.15	0.92	8.90	29.8
7	20	72	500	1400	100	400	11	96	200	800	400	1700	400	2200	1800	4200	0.06	1.4	0.02	0.49	1.48	11.4
8.1	4.2	42	200	11800	53	600	4.9	100	81	800	100	1100	96	900	500	2900	0.54	8.8	0.07	0.99	2.74	30.6
8.2	1.5	9.9	84	400	10	47	5.3	16	93	300	47	200	100	900	12	56	0	0	0.002	0.06	0.10	0.42
8.3	0	0	51	200	1.7	23	9.8	51	900	5300	63	400	65	200	0.4	18	0	0	0.01	0.19	0.02	0.17
9	10	33	300	2000	100	400	5.3	53	200	1300	200	700	100	800	1400	3000	0.62	4.7	0.16	1.04	7.44	29.0

The inhomogeneous distribution of heavy metals among and within individual particles is illustrated in Figure 1, where the spatial metal distributions of a fly ash particle are shown.

Inside each of those particles, the enrichment of Cu, Zn, Pb and Cd (up to 1100, 900, 11800 and 42 ppm level, respectively) in some well-defined hot-spots relative to the surrounding areas is clearly visible, suggesting that a part of these metals might be arranged in inorganic precipitates. In some of the maps, the corresponding anions (Cl⁻ and Br⁻) are visible, featuring the formation of CdCl₂, ZnCl₂ and PbBr₂ salts. The results obtained here are in agreement with the thermodynamical equilibrium results reported by Verhulst et al. [3] showing that, at standard conditions for waste incineration, Cd, Pb and Zn volatilise as the corresponding halogens.

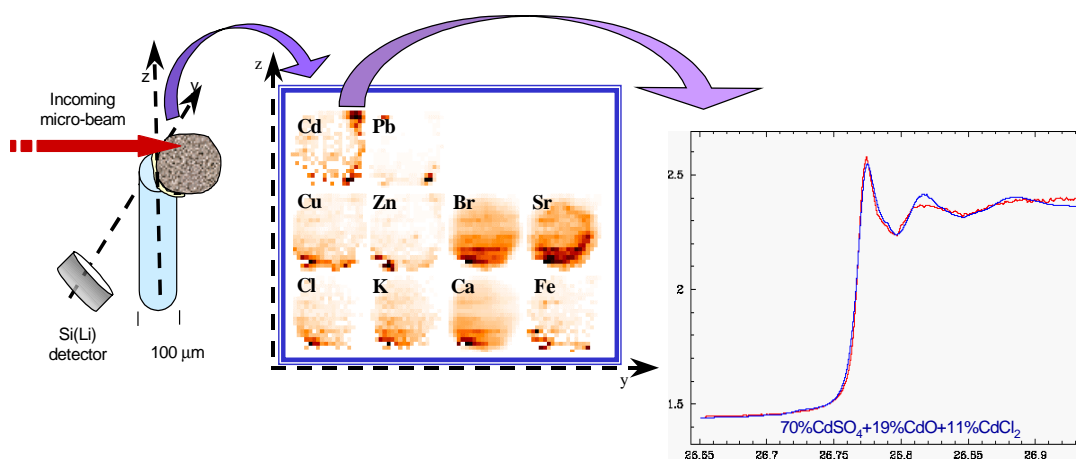


Figure 1: μ -XRF maps of various elements obtained from a waste fly ash particle (diameter ca. 160 μm). Light tones indicate lower concentrations. μ -XAS in the 26.65-26.95 keV range was performed on a (HxV) $3 \times 12 \mu\text{m}^2$ micro-area containing the highest concentration of Cd.

The use of μ -XRF gives the possibility to avoid the systematic errors that may be introduced by the contribution of close areas in cases where methods with lower spatial resolution are employed [4]. On the other hand, the maps shown in Figure 1 also demonstrate a limitation of 2D-mapping with highly penetrating photon beams for trace level microanalysis of heavy elements: since the penetration and sampling depths of the high energetic primary and characteristic photons are in the few hundred μm range, the elemental signals originating from the whole excited depth of the particle are detected simultaneously. This causes the μ -XRF maps such as those shown in Figure 1 to become two-dimensional (2D) projections of the three-dimensional (3D) distribution of these trace elements throughout the fly ash particles. So, from the μ -XRF maps alone, it is not possible to judge whether the spots of accumulation of the heavy metals are situated on the surface of the sample (i.e. most prone to leaching) or are present at some depth within the particle (where they might be more shielded from chemical attack by water). Other types of analytical X-rays methods, such as μ -tomography, might also be applicable together with XRF and thus would give more detailed information of the microchemistry of individual fly-ash particles.

To further understand the speciation of Cd in single fly ash particles, the oxidation state, bond distance, and coordination number of Cd were studied by μ -XAS in the areas of the particles showing a higher Cd concentration. μ -XAS spectra of pure Cd compounds such as Cd, CdO, CdSO₄, CdS, CdCl₂, CdBr₂ pellets were measured prior to the single particle analysis and reported in Figure 2. The μ -XAS spectra of a typical “hot-spot” within a waste fly ash particle is shown in Figure 1.

The μ -XAS spectra of the hot-spots of the particles were also expressed mathematically as a Linear Combination (LC) of XAS fit vectors, using the measured absorption data of the Cd reference compounds [5]. Comparisons of XAS spectra for fly ashes and for reference compounds show that in the particles studied Cd is present in oxidation state +2 instead of metallic form.

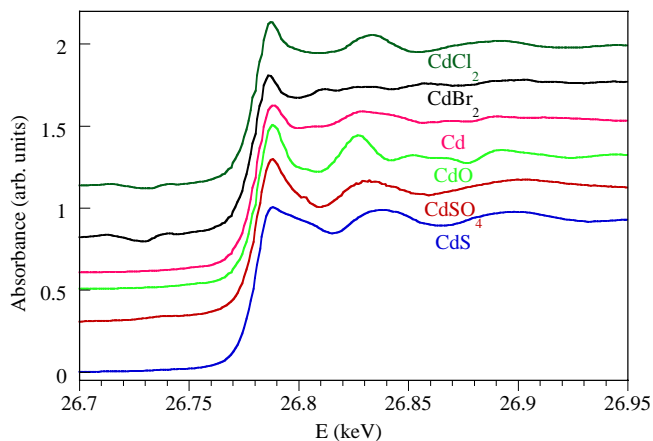


Figure 2: Absorption spectra of the measured pure Cd compounds. The spectra are shifted along the y axis in order to compare them.

The comparison between the linear combinations of the standard spectra and the measured XAS-spectra of the Cd hot-spots allow to estimate the concentrations of the possible Cd compounds in those spots, e.g. in the case of particle 6, Cd is present as an admixture of CdSO₄ (70%) CdO (19%) and CdCl₂ (11%) with over 90 % confidence in the fitting process.

These results confirm what was found by μ -XRF mapping and agree with earlier studies [2,7] which show that Cd in MSW fly ashes is strongly present in water soluble species, mainly as CdCl₂ and CdSO₄. On the other hand this is not a conclusive identification because the spectra of other Cd sulphates and some other possibly significant compounds, like Cd silicates, were not examined due to the lack of standard materials. These investigations are planned during future work.

REFERENCES

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