

**Experiment title:**

Erudition of Zn evaporation mechanisms from filter ash:
An EXAFS study

Experiment**number:**

1-01-253

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REPORT:

Fly ash is normally deposited in landfills, as it contains high concentrations of toxic heavy metals, such as Zn, Pb, Cd and Cu, among other elements, like Na, K, Ca, Cl, S, Al, Si, and O. The Laboratory for Energy and Materials Cycles (LEM) at PSI studies means to detoxify materials like fly ash by thermal treatment under various gas atmospheres (inert, reducing, or oxidising) and/or by adding solid additives to the ash (such as carbon), with the ultimate goal to produce secondary raw materials suited for reprocessing industry.

1 INTRODUCTION

Heating up a sample of fly ash under an Argon flow leads to 3 distinct peaks for the rate of evaporation of Zn species (see Figure 1), as revealed by our on-line detection of heavy metal species with an Inductively Coupled Plasma-Optical Emission Spectrometer [1].

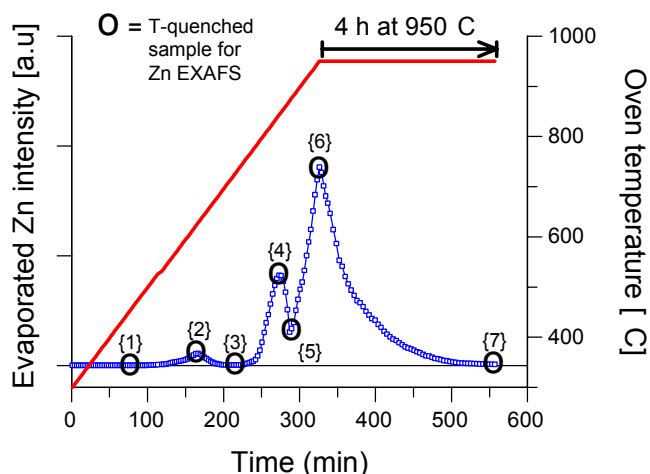


Fig. 1: Zinc evaporation rate during thermal treatment of fly ash under inert flowing conditions.

While it is plausible to infer from thermo-dynamical data [2] that peak {2} is due to evaporation of “indigenous” ZnCl_2 and peak {6} to evaporation of Zn^0 (metallic zinc), it was not clear what Zn species would evaporate at position {4}. Therefore, we prepared several fly ash samples by temperature quenching at the respective positions {1} to {7}. These and reference samples were analysed using EXAFS to determine the atomic species neighbouring zinc within the respective samples.

2 EXPERIMENTAL

The spectra of the fly ash and reference spectra were recorded at the beam line BM1b (Swiss-Norwegian Beam Lines, SNBL) of the European Synchrotron Radiation Facility at Grenoble, using a Si(111) channel-cut monochromator. Beam energy was calibrated by assigning the first

inflection point in the K absorption edge of a Zn metal foil to an energy of 9.659 keV. All spectra were obtained at room temperature. The spectra of the fly ash samples were collected in fluorescence mode using a Stern-Heald-type detector (Lytle detector, The EXAFS Co.). The spectra of the reference samples (ZnCl_2 , ZnO , ZnS , Zn_2SiO_4 , ZnAl_2O_4) were collected in transmission mode using ionisation chambers purged with appropriate inert fill gases. A typical raw spectrum with fly ash sample {1} is shown in Figure 2.

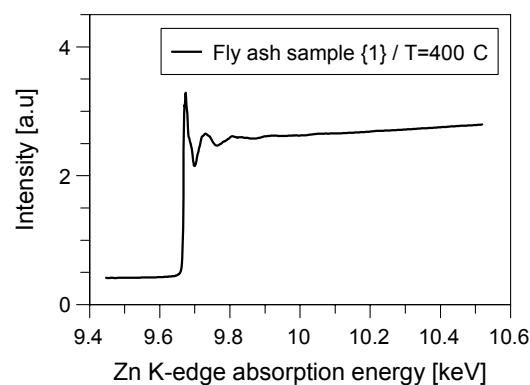


Fig. 2: Raw Zn K-edge absorption spectrum.

Data reduction was performed using WINXAS vs. 2.0, following standard procedures [3]. The resulting χ functions as a function of wavelength k (not shown here) were weighted by k^3 to account for dampening of oscillations with increasing k and Fourier Transformed to achieve radial structure functions (RSF). A Bessel window with a smoothing parameter of 4 was used to suppress artefacts due to finite Fourier filtering range between $k = 3.7\text{-}12.5 \text{ \AA}^{-1}$.

3 RESULTS

Fourier transformation of the spectra yields a RSF, which aids the identification of characteristic frequencies resulting from backscattering atoms coordinated with the absorbing Zn atoms. The RSFs shown in Figure 3 reveal that ZnO , Zn_2SiO_4 and ZnAl_2O_4 are all marked by oxygen as first neighbouring atom at a typical (phase uncorrected) radial distance around 1.5 \AA . With ZnS , sulphur is positioned around 1.9 \AA and with zinc metal foil, the neighbouring zinc lays at around 2.3 \AA . We note that the respective curves also differ substantially at higher interatomic distances, indicating differences in the higher coordination shells as well. From the EXAFS analysis of the fly ash (see Figure 4) and the reference samples (Figure 3), it became evident that sulphur (contained in the fly ash) competes with “indigenous” chloride to react with ZnO to form solid ZnS , instead of volatile ZnCl_2 .

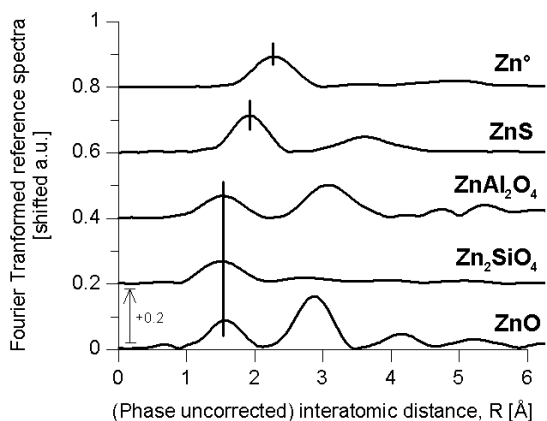


Fig. 3: Radial structure functions (RSF) derived from Zn EXAFS spectra with reference compounds.

We note that ZnCl_2 itself was not detected, likely due to its high volatility under the given temperature conditions. The formation of Zn-S on the cost of Zn-O is well illustrated by the rise in the EXAFS intensity for the samples {1} to {4} (viz., $T = 400 \rightarrow 865^\circ\text{C}$) at the typical (phase uncorrected) Zn-S distance around 2 Å.

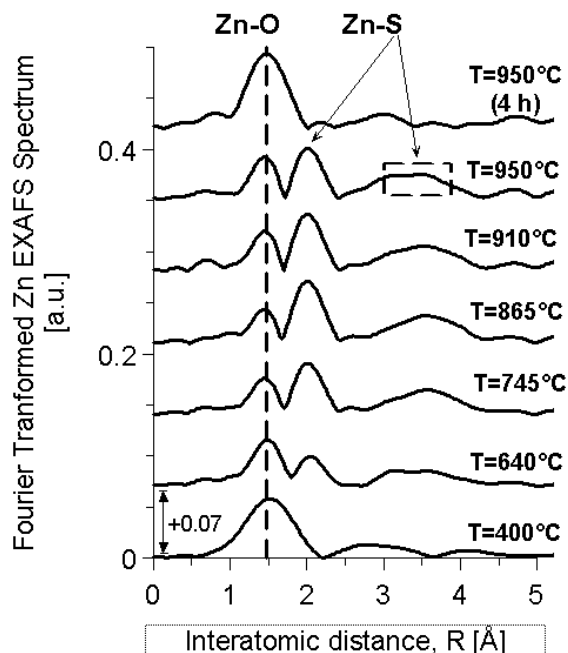


Fig. 4: Radial structure functions (RSF) derived from Zn EXAFS spectra with fly ash samples {1}-{7}.

The decomposition of Zn-S (which is likely also invoked by a $\text{ZnCl}_2 \uparrow$ forming reaction, but at a somewhat higher temperature than with ZnO) is evidenced by the gradual drop in the ZnS intensity going from samples {4} to {6} (viz., $T = 865 \rightarrow 950^\circ\text{C}$). ZnS is removed totally after 4h thermal treatment at 950°C (sample {7}). Speciation of the various zinc compounds residing in the respective fly ash samples is feasible by modelling the background corrected and normalized EXAFS spectra with a linear combination of spectra from different reference spectra. Figure 5 presents these

results multiplied with the Zn fraction in the respective fly ash samples, which we estimated from the respective area involved in the Zn evaporation rate course shown in Figure 1. In sample {7}, the Zn content (which was 100% with sample {1}) dropped by ca. 70% after 4h at 950°C and consists mainly of zinc aluminate (ZnAl_2O_4) and zinc silicate (Zn_2SiO_4). At the intermediate temperature range between 400 and 745°C , ZnS is formed on the cost of both, ZnO and Zn_2SiO_4 . With ZnO, we note that it is a sulphur scavenger known from hot gas cleaning techniques.

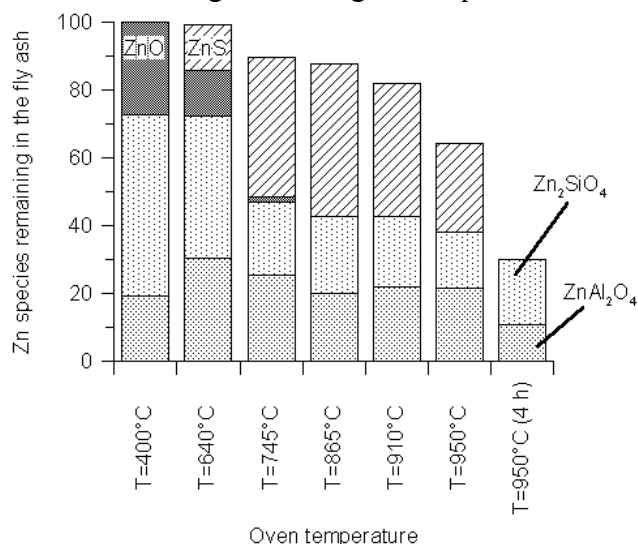


Fig. 5: Speciation of Zn compounds residing in the fly ash samples {1}-{7}, as discussed in the text.

CONCLUSION & OUTLOOK: The Zn K-edge EXAFS analysis provided valuable information on the speciation and fate of zinc species residing in fly ash during thermal treatment. The study underlined the role of indigenous sulphur and its competition with indigenous chloride, shifting the formation of volatile ZnCl_2 to substantially higher, hence, less desirable temperatures. Among other questions, the chemical form of sulphur in the original fly ash is not known yet. It could not be resolved with powder XRD, due to its low content, and may necessitate soft X-ray EXAFS analysis.

4 ACKNOWLEDGEMENT to I. Bonhoure, O. Haas, B. Schnyder (all at PSI), and the skilled assistance of the SNBL personnel, particularly, W. van Beek and Hermann Emerich.

5 REFERENCES

- [1] H. Lutz, Chr. Ludwig, R.P.W.J. Struis, *ICP Information Newsletter*, **27(3)**, 1-7 (2001).
- [2] *Thermochemical properties of inorganic substances*, O. Knacke, O. Kubaschewski, K. Hesselmann (Eds.), 2nd Edition, Springer, Berlin (1991).
- [3] T. Ressler, *J. Synchr. Rad.* **5**, 118 (1998).