<b>ESRF</b>	<b>Experiment title:</b> The chemical state of antimony and vanadium species in municipal solid waste incineration bottom ash	Experiment number: EV-511
Beamline:	Date of experiment:	Date of report:
ID26	from: 17.01.2023 to: 23.01.2023	
Shifts:	Local contact(s):	Received at ESRF:
18	Sami Juhani Vasala	
Names and affiliations of applicants (* indicates experimentalists):		
Christian Vogel*, Bundesanstalt für Materialforschung und -prüfung (BAM)		
Franz-Georg Simon*, Bundesanstalt für Materialforschung und -prüfung (BAM)		
Philipp Scholz*, Bundesanstalt für Materialforschung und -prüfung (BAM)		

## **Report:**

Due to the large quantity as residual mineral waste, municipal solid waste incineration - bottom ash (MSWI-BA) is an interesting secondary raw material that can be utilized for road construction or to produce building materials. However, leaching of chloride, sulfate and potentially toxic elements (PTE) from MSWSI-BA into the environment may cause problems in utilization of it in civil engineering. In a previous study, we performed a long-term leaching test of a wet-mechanically treated MSWI-BA in a lysimeter for almost six years to investigate the efficiency of the treatment process on the release of PTEs. While concentrations of chloride, sulfate and the majority of PTEs started to decrease rapidly with progressive liquid-to-solid ratio (L/S), the ecotoxic elements antimony (Sb) and vanadium (V) behaved differently. At the beginning of the lysimeter test, the Sb and V concentrations were low, but after approximately one year of operation at an L/S ratio of around 0.8 L/kg, a steady increase was observed. To unravel the chemical state of Sb and V in MSWI-BA we applied HERFD-XANES spectroscopy at ID21 beamline to various MSWI ashes from different locations and treatments.

Antimony is a critical element, because released toxic Sb(V) from secondary construction materials can sorb onto inorganic oxides and organic matter in soils which may affect environmental health by ecotoxic effects and bioaccessibility. The source for Sb in MSWI-BA is very likely plastic in municipal solid waste, in which it is used as a flame-retardant agent or catalyst. To determine the chemical state of Sb in plastics we analyzed a plastic with antimony flame retardant (see Fig. 1). The Sb  $L_1$ -edge HERFD-XANES spectrum of the plastic shows clearly the presence of Sb(III)-oxide in the plastic sample. In opposite, the XANES spectra of fly and bottom ashes, respectively, from various MSWI plants showed that the chemical state of antimony after treatment is Sb(V) (see Fig. 1). Thus, there is a conversion of Sb(III) to Sb(V) during thermal treatment.



Figure 1: Antimony L<sub>1</sub>-edge XANES spectra of standards and a fly ashes (FA) from municipal waste incineration and a plastic fame retardant (FR)

Vanadium is a metal that receives increasing attention due to its possible toxicity and its increased use in the society, i.e. in high-grade steel and in vanadium redox-flow batteries. However, at high concentrations vanadium is toxic to many organisms. Therefore, we analyzed the chemical state of V in various treated MSWI-BAs by V K-edge HERFD-XANES spectroscopy (see Fig. 2). Vanadium was mainly found in the analyzed bottom and fly ashes in the oxidation state V(V). Additionally performed linear combination fitting strongly suggest that V is mainly bond as CaV<sub>2</sub>O<sub>6</sub> (V(V) compound) in the MSWI-BAs. However, the >16mm fraction of a MSWI-BA also showed a larger amount of V(IV) compounds (see Fig. 2), which was also confirmed by linear combination fitting. The coarser fraction of the MSWI-BA contains more metal parts. The V(IV) compound vanadium carbide (VC) is commercially used in metal tool bits and cutting tools because of its great hardness and temperature resistance, therefore it is a conclusive explanation for our finding.



*Figure 2: Vanadium K-edge XANES spectra of standards and bottom ashes (BAs) from municipal waste incineration* 

Summarized, we were able to determine the chemical state of antimony and vanadium in various MSWI ashes. A paper with these results is currently in preparation.