



	Experiment title: Determination of the chemical state of mercury in sewage sludge ash based phosphorus fertilisers	Experiment number: EV 142
Beamline: ID26	Date of experiment: from: 15.07.2015 to: 21.07.2015	Date of report: 17.08.2015
Shifts: 21	Local contact(s): Lucia Amidani	<i>Received at ESRF:</i>
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Report:

We analyzed the chemical state of mercury and selenium in sewage sludge ash (SSA) before and after thermochemical treatment under different conditions for phosphorus-fertilizer production by X-ray absorption near edge structure (XANES) spectroscopy.

Sewage sludge is a secondary resource for the production of P-fertilizers. For landfilling and phosphorus recycling sewage sludge is often mono-incinerated to destroy organic pollutants. However, the resulting sewage sludge ash (SSA) is often polluted with toxic heavy metals and contains phosphorus with a low plant-availability. The limit for mercury in the German fertilizer ordinance is 1 mg/kg. Previous analyses of German SSAs showed mercury mass fractions of 0.1 to 3.6 mg/kg. At BAM two different processes were developed to separate heavy metals and to increase the plant availability of P. Previously, we worked on a thermochemical method using chlorine-donors under oxidizing conditions at approx. 1000°C. Due to the low plant-availability of these recycling P-fertilizers on neutral and alkaline soils a second process was developed. Nowadays, a more promising process was applied where SSA is thermochemically treated with Na₂SO₄ at 850-1000°C under reducing conditions. Due to the formation of CaNaPO₄ these P-fertilizers have a much higher plant-availability.

We analyzed several SSAs (1-4) and SSA 1 thermochemically treated with chlorine donors under oxidizing conditions (SSA 1-O) and with Na₂SO₄ under reducing conditions (SSA 1-R), respectively. With both processes some mercury was separated from the SSA whereby the limit of the German fertilizer ordinance was met. However, mercury compounds are very volatile already at low temperature, only HgSe and HgS are thermal stable until

approx. 1000°C and 600°C, respectively. Thus, all of the mercury should be separated in normal state during thermochemical treatments at 900-1000°C.

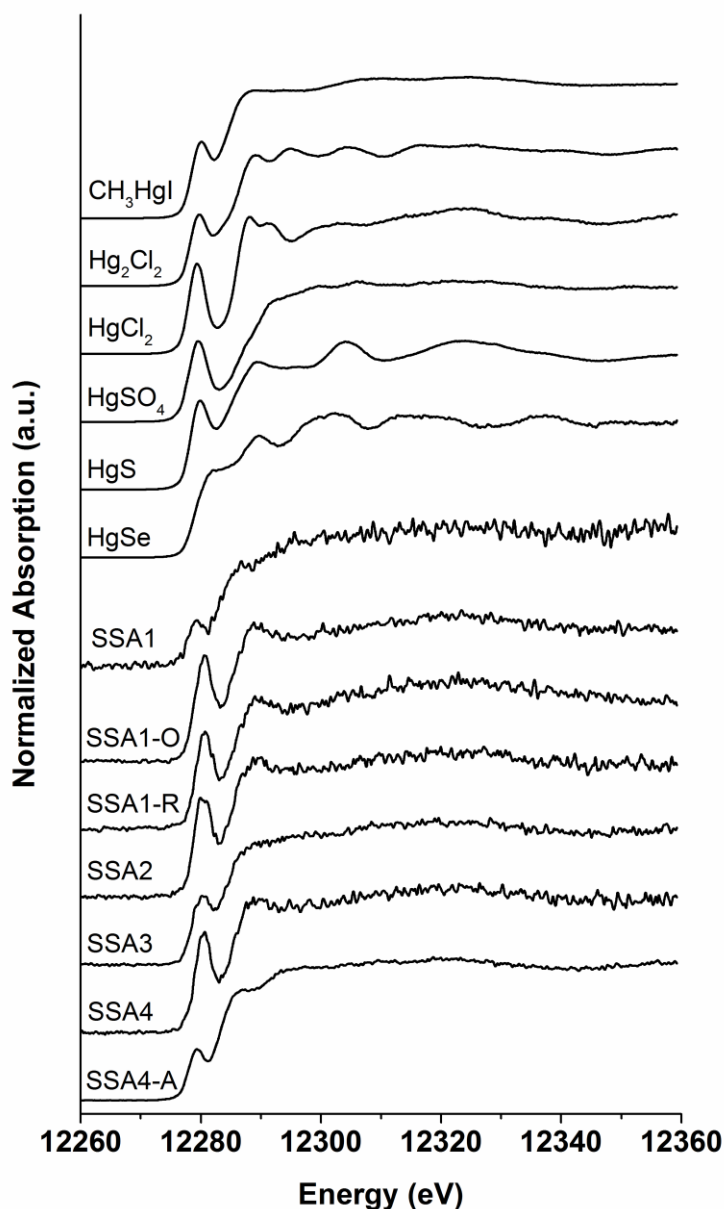


Figure 1: Hg L_3 -edge XANES spectra of mercury references, the SSAs and SSA based P-fertilizers

Figure 1 shows the Hg L_3 -edge XANES spectra of mercury references, the SSAs and SSA based P-fertilizers. The Hg XANES spectra of SSA 1 and 3 are different to those of SSA 2 and 4. Linear combination fitting (LCF) of SSA 1 determined approx. 42 % CH_3HgI , 34% HgSO_4 and 24% HgSe . Also other combination with HgS and HgCl_2 are possible, but always with CH_3HgI as the major component. For SSA 3 a composition of approx. 95-90 % CH_3HgI and 10-5 % HgSe was determined. Thus, these two SSAs contain mercury adsorbed to carbon, which indicate that the carbon adsorber from the off-gas cleaning after the electric precipitator was disposed together with the SSA.

In opposite, SSA 2 and 4 have a much stronger pre-peak, which indicates the presence of HgS and/or HgCl_2 . Linear combination fitting of these two SSAs determined approx. 50 % HgS , 25 % HgCl_2 and 25% HgSe . HgS and HgCl_2 should not be thermal stable at the incineration temperature of 815°C but presumably the contact time was very short whereby they did not decompose or due to HCl and SO_2 gas in the atmosphere these mercury

compounds were stabilized. Furthermore, they could be also build in into other stabile minerals like calcium phosphates.

Furthermore, in SSA 4 no mercury adsorbed to organic material was found. Additionally we analyzed the carbon absorber of the off-gas cleaning after the electric precepitator of this incineration plant (SSA 4-A), which contains much more mercury than the SSA (approx. 132 mg/kg). LCF determined for SSA 4-A approx. 80% CH_3HgI and 20% HgSO_4 . Thus, most of the mercury is adsorbed to carbon material of the adsorber. HgSO_4 could have been emerged from interactions of mercury on the adsorber with SO_2 in the off-gas.

During thermochemical treatment of SSA 1 the mercury mass fraction decreased from 2.1 mg/kg to 0.6 mg/kg with both oxidizing (SSA 1-O) and reducing (SSA 1-R) conditions. LCF determined for SSA 1-O approx. 77% HgS and 23% HgCl_2 , which are similar mercury compounds as detected in SSA 2 and 4. Furthermore, in SSA 1-R, the thermochemically treated SSA 1 under reducing conditions, approx. 82 % HgS and 18% HgSe was detected. However, as mentioned above HgS and HgCl_2 should not be thermally stabile at temperatures of approx. 950-1000°C. Probably the reason is a stabilization of mercury in the SSA matrix. Several processes are in development to stabilize mercury waste in form of ceramics or cements. Cho et al. (J. Hazard. Mater. 278 (2014) 474–482) showed a process where mercury is stabilized in form of HgS in a matrix of CaNaPO_4 or MgKPO_4 . Possibly, the stabilization of mercury in SSAs proceeds very similar. Thus, during the thermochemical treatments under oxidizing and reducing conditions mercury adsorbed to organic material was separated from the SSA and only some of the more stabile inorganic mercury compounds remain in the SSA.

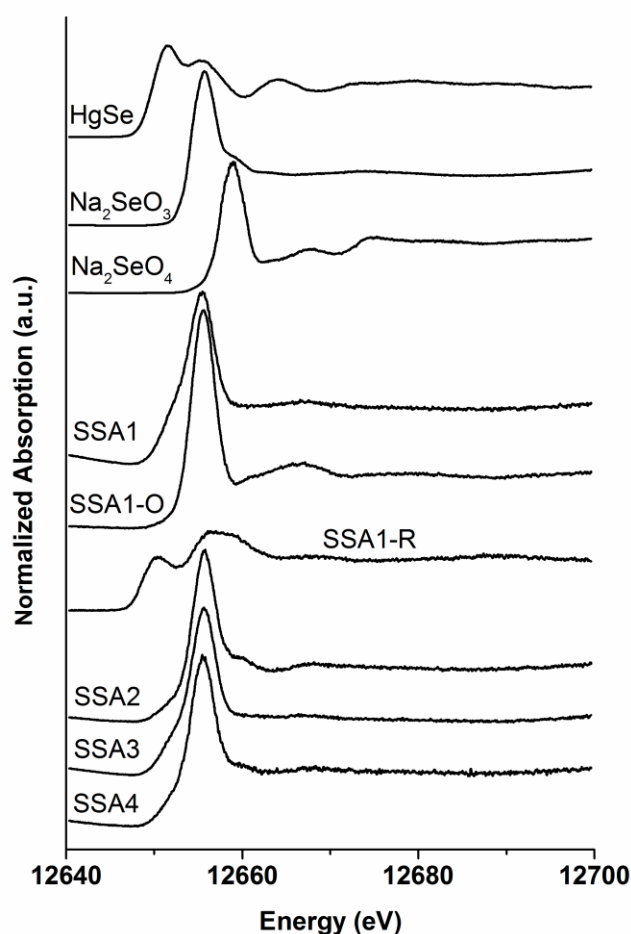


Figure 2: Se K-edge XANES spectra of selenium references, the SSAs and SSA based P-fertilizers

Figure 2 shows the Se K-edge XANES spectra of selenium references, the SSAs and SSA based P-fertilizers. The different oxidation states of selenium in the references (HgSe (Se^{2+}), Na_2SeO_3 (Se^{4+}), Na_2SeO_4 (Se^{6+})) shows a strong shift of the edge. Thus, the oxidation state of selenium in the SSAs is easily detectable on the position of the edge. LCF determined approx. 15% Se^{2+} and 85% Se^{4+} for SSA 1 and 3. In opposite, SSA 2 and 4 mainly contain Se^{4+} and contain only small amounts on Se^{2+} (SSA2: approx. 2%; SSA4: approx. 7%). Thus, a part of the mercury could be bond as HgSe .

After thermochemical treatment of SSA 1 with chlorine donors (SSA 1-O) all Se^{2+} was oxidized to Se^{4+} . In opposite, after thermochemical treatment of SSA 1 under reducing conditions (SSA 1-R) 70% of the selenium was determined as Se^{2+} and only 30% remain as Se^{4+} . Thus, the chemical state of selenium in the SSAs is very sensitive to the thermochemical treatment processes.

Summarized, we were able to determine the chemical state of mercury in very diluted SSAs and SSA based P-fertilizers by Hg L_3 -edge XANES spectroscopy at ID26. In some SSAs the mercury loaded carbon adsorber of the off-gas cleaning after the electric precipitator was added to the SSA for waste disposal. These SSAs contain mostly mercury bond to carbon/organic material. The other SSAs mainly contain the inorganic mercury compounds HgS , HgCl_2 and HgSe . During thermochemical treatment mercury bond to carbon material was separated and only some of the inorganic mercury compounds remain in the SSA. Furthermore, Se K-edge XANES spectroscopy supports the theory that HgSe is a part of the inorganic mercury compounds.