Chemical State of Chromium, Sulfur, and Iron in Sewage Sludge Ash based Phosphorus Fertilizers

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ABSTRACT: As an essential element of all life forms, phosphorus (P) is vital to the fertilizer industry. With decreasing quantity and quality of phosphate rock resources, recycling P-fertilizers from wastewater is of increasing interest. The P-fertilizer products of a recently developed thermochemical process for P recovery from sewage sludge ash (SSA) were investigated by chromium, sulfur, and iron K-edge X-ray near-edge structure (XANES) spectroscopy. This paper focuses the formation and prevention of toxic chromium(VI) and toxic sulfides during the thermochemical processes. Reducing conditions prevent the oxidation of chromium(III) in the SSA to toxic chromium(VI). Sulfides formed under the reducing conditions are nontoxic iron sulfides. Hematite (Fe_2O_3) present in the SSA is reduced to magnetite (Fe_3O_4). A gentle post-treatment at 400 °C under oxidizing conditions converts the iron sulfides into plant-available iron sulfates. This oxidative post-treatment does not form undesired chromium(VI) compounds.

KEYWORDS: *X-ray absorption near-edge structure (XANES) spectroscopy, Phosphorus recovery, Sewage sludge ash, Chromium, sulfur, Iron*
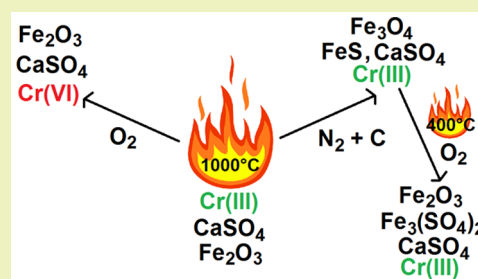
■ INTRODUCTION

Phosphorus (P) has fundamental importance for all living organism. For that reason, P in form of phosphates is applied as fertilizer in the agricultural industry. Currently, organic and phosphate rock based fertilizers are used. Because of a possible shortage of phosphate rock resources[1] in the next decades and increasing phosphate rock prices, sewage sludge has become an interesting secondary phosphate resource.

Sewage sludge is often contaminated with toxic heavy metals and the contained phosphorus exhibits low plant-availability. Previously, we worked on a thermochemical process using chlorine-donors[2,3] to separate toxic heavy metals from sewage sludge ash (SSA) and increase the plant-availability of the phosphorus in the SSA. However, the fertilizing performance of the products was limited especially on alkaline soils and thus a new approach was investigated to overcome this drawback. The new approach is based on thermochemical treatment of SSA at approximately 950 °C with sodium carbonate/sulfate under reducing conditions.[4,5] Some volatile heavy metals (As, Cd, Pb, Hg, Tl) can be separated via the gas phase and highly plant-available $CaNaPO_4$ (also called rhenatite) is formed.[4,6,7] This process was jointly patented together with the company Outotec Oyj (Finland).[5]

In a previous paper,[8] we showed that toxic chromium(VI) compounds were formed during thermochemical treatment of SSA with sodium carbonate under oxidizing conditions. It was

assumed that reducing conditions may prevent the development of toxic Cr(VI) during the thermochemical treatment. Therefore, we analyzed the oxidation state of chromium of these new SSA based P-fertilizers by Cr K-edge X-ray absorption near-edge structure (XANES) spectroscopy. Because of the appearance of a pre-peak for Cr(VI)-compounds in the XANES spectrum, these compounds are easily detectable by this method.[8−10]

Sodium carbonate and sodium sulfate were used as Na-additives for the process. Sodium sulfate has the advantages in that it is cheaper than sodium carbonate and the sulfur has a certain value as a nutrient in the fertilizer. However, thermal treatment of sodium sulfate under reducing conditions could potentially form toxic sodium sulfide.[11,12] SSA contains almost all elements of the periodic table. Thus, the developed toxic sodium sulfide can also react with other compounds to either toxic (e.g., calcium sulfide) or nonhazardous (e.g., iron sulfide) sulfides. To follow transformation processes between sulfides and sulfates under reducing and oxidizing conditions, S K-edge XANES spectroscopy was applied as an eligible method.[13,14] There is approximately 10 eV between the edge of sulfides and

sulfates in the XANES spectrum. Thus, sulfides and sulfates are easily detectable in parallel.

Furthermore, the iron in the SSA in the chemical form of iron(III) oxide (Fe_2O_3, hematite)[15] may reduce to iron(II) compounds. Therefore, we applied also Fe K-edge XANES spectroscopy for the analysis of the chemical state of iron in the SSA based fertilizers. Previously, this technique was already applied for iron in other environmental applications.[16−18]

■ EXPERIMENTAL SECTION

Preparation of SSA based P-Fertilizers. The SSA used for the experiments stemmed from a sewage sludge mono-incineration plant in Germany that incinerates sludge from wastewater treatment plants primarily using Fe-salts for phosphate precipitation. Table 1 shows the

Table 1. Mass Fractions and Standard Deviations (SD; n = 3) of Main Elements and Trace Elements Determined for the Used SSA by ICP-OES and ICP-MS after Total Digestion with $HClO_4/HNO_3/HF$ in a Microwave (240 °C)

	SSA (mg/kg)	SD (mg/kg)
Al	29717	787
Ca	123735	803
Fe	190596	2232
K	13055	540
Mn	5255	45
Mg	13203	119
Na	14746	1682
P	111976	1621
S	8905	180
Si	110373	3625
Ti	3996	2
As	25.1	0.6
Cd	2.8	0.1
Cr	79.6	8.0
Cu	2698	21
Hg	1.2	0.0
Mo	25.7	0.5
Ni	49.0	1.0
Pb	142	9
Sn	86.9	1.8
Sr	718	5
Th	2.2	0.1
U	4.1	0.1
Zn	2985	36

mass fractions of main and trace elements. Thermochemical treatments of SSA (3 kg) with sodium carbonate (0.9 kg, Na_2CO_3; Fisher Chemicals Loughborough, UK) and sodium sulfate (1.2 kg, Na_2SO_4; AppliChem, Darmstadt, Germany), respectively, were carried out in a rotary furnace (Thermal Technology, RT1700, Bayreuth, Germany) with a corundum tube for approximately 30 min at 900 °C under reducing conditions (0.3 kg lignite (mixed with the SSA) + nitrogen gas; hereafter, the products of this treatment are referred to as SSA-Na1 (Na_2CO_3) and SSA-Na2 (Na_2SO_4), respectively). Samples of SSA-Na2 were also post-treated in corundum crucibles under oxidizing conditions (air) at 400 °C in a muffle furnace (Nabertherm LH 15/14, Lillenthal, Germany; product hereafter referred as SSA-Na3).

The elemental composition of the SSA was measured by ICP-OES (Thermo iCAP 7000 Series, Dreieich, Germany) and ICP-MS (Thermo iCAP Q, Dreieich, Germany) after total digestion (HNO$_3$/ HClO$_4$/HF) in a microwave (mikroPrepA, MLS GmbH, Leutkirch, Germany; heating with 1000 W; 20 min isotherm segment at 240 °C). For all samples digestion and ICP-OES and ICP-MS, respectively, measurements were carried out three times.

Reference Compounds. The following reference compounds were used for the experiments: calcium chromate ($CaCrO_4$), chromium sulfate ($Cr_2(SO_4)_3·H_2O$), chromium sulfide (Cr_2S_3), iron disulfide (FeS_2), iron(II,III) oxide (Fe_3O_4) (all ABCR, Karlsruhe, Germany), iron(II) oxide (Fe_2O_3) and magnesium sulfate ($MgSO_4·$ $7H_2O$) (both Sigma-Aldrich, Steinheim, Germany), chromium phosphate ($CrPO_4·4H_2O$), calcium sulfide (CaS), iron(III) phosphate ($FePO_4·H_2O$) (all Alfa Aesar, Karlsruhe, Germany), sodium sulfate (Na_2SO_4), sodium sulfite (Na_2SO_3), iron sulfate ($FeSO_4·7H_2O$) (all AppliChem, Darmstadt, Germany), chromium(III) oxide (Cr_2O_3) and iron sulfide (FeS) (both Merck, Darmstadt, Germany), barium sulfate ($BaSO_4$) and calcium sulfate ($CaSO_4$) (both Acros Organics, Geel, Belgium), sodium carbonate (Na_2CO_3; Fisher Chemicals, Loughborough, UK) and sodium sulfide ($Na_2S·9H_2O$; Tessenderlo, Brussels, Belgium). Chromium hydroxide ($Cr(OH)_3$) was precipitated from an aqueous solution of chromium chloride ($CrCl_3$; p.a., Sigma-Aldrich, Australia) with ammonia. Calcium chromite ($CaCr_2O_4$), magnesium chromite ($MgCr_2O_4$), and chromite ($FeCr_2O_4$) were prepared from Cr_2O_3 (p.a., Merck, Darmstadt, Germany) with calcium carbonate ($CaCO_3$; p.a., Sigma-Aldrich, Steinheim, Germany), magnesium carbonate ($MgCO_3$; p.a., Merck, Darmstadt, Germany), and Fe_3O_4 (ABCR, Karlsruhe, Germany) at 1250, 1000, and 1500 °C, respectively, in platinum crucibles by thermal treatment (6−16 h) in a muffle furnace (Nabertherm LH 15/14, Lillenthal, Germany). Iron(II) phosphate ($Fe_3(PO_4)_2·6H_2O$) was precipitated from an aqueous solution of ammonium phosphate dibasic ($(NH_4)_2HPO_4$; Sigma-Aldrich, Steinheim, Germany) with an aqueous solution of iron(II) sulfate ($FeSO_4·7H_2O$; AppliChem, Darmstadt, Germany).

XANES Measurements. XANES measurements were carried out at the BAM*line* and KMC-1[19] beamline, both at the electron storage ring BESSY II of the Helmholtz-Zentrum Berlin. The ring was operated in top-up mode at a current of I = 300 mA. The two beamlines use Si(111) double-crystal monochromators. The scans were acquired at room temperature in fluorescence mode. The XANES scan range was 2450−2520 eV in steps of 0.5 eV at the S-edge, 5950−6100 eV for Cr, and 7100−7200 eV for Fe with a step width of 0.5 eV in the pre-edge and edge region, respectively. The energy resolution of the KMC-1 beamline increases from 250 meV at the S K-edge to appr. 1 eV at the Fe K-edge. Data were recorded in fluorescence mode by a silicon drift detector XFlash 30 (BAM*line*; Bruker, Berlin, Germany) and silicon drift detector XFlash 4010 (KMC-1; Bruker, Berlin, Germany) for the SSA based P-fertilizers and for the set of reference materials mentioned above.

Data were analyzed using the freeware Demeter Athena.[20] Therefore, spectra were normalized to an edge jump of $\Delta\mu d$ = 1 after background subtraction, and reference spectra were corrected for self-absorption. Chemical species were evaluated using linear combination fitting assisted by target transformation as available in Demeter Athena.

Thermodynamic Calculations. The thermodynamic calculations were done with the software HSC Chemistry 6.1 (Outotec, Oberursel, Germany).

■ RESULTS AND DISCUSSION

Cr K-Edge XANES. Figure 1 shows the Cr K-edge XANES spectra of the investigated SSA, SSA based P-fertilizers (SSA-Na1 to SSA-Na3), and Cr reference compounds. Similar to a previous analysis,[8] the used SSA contains mainly chromites (XCr_2O_4; X = Ca, Mg, Fe). Also, Cr-substituted hematite is possible (XANES spectra very similar).[21] Linear combination fitting (LCF) of SSA also indicates a mixture of Cr_2O_3 and $Cr_2(SO_4)_3$ as possible Cr compounds in the SSA (see Figure 2). The SSA thermochemically treated with Na_2CO_3 under reducing conditions (SSA-Na1) contains also mainly chromites or Cr-substituted hematite. Thus, reducing conditions avoid the development of toxic Cr(VI) in the thermochemical process. Furthermore, the thermochemical treatment with Na_2SO_4 under reducing conditions (SSA-Na2) shows very similar Cr
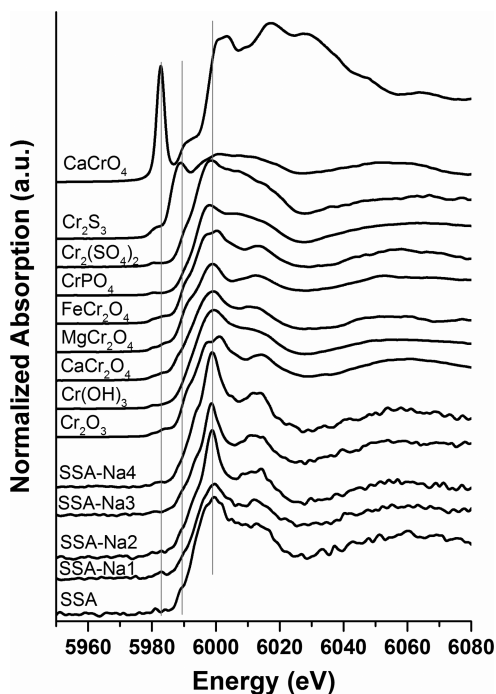
Figure 1. Cr K-edge XANES spectra of SSA, SSA based P-fertilizers, and Cr reference compounds.
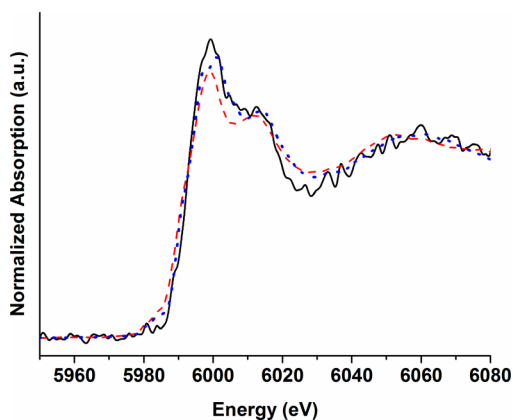

Figure 2. Linear combination fitting of SSA (—), 50% $CaCr_2O_4$ + 50% $MgCr_2O_4$ (---), and 97% Cr_2O_3 + 3% $Cr_2(SO_4)_3$ (⋯).

Figure 3. S K-Edge XANES spectra of SSA and SSA based P-fertilizers.

Figure 4. S K-Edge XANES spectra of sulfur reference compounds.

Figure 5. Comparison of the S K-edge XANES spectra of SSA-Na1 (—) with $CaSO_4$ (---), Na_2SO_4 (⋯), and FeS (—·—·).

reaction products. Possible Cr_2S_3, which could be developed by reducing of the sulfate, was not detected. Also, during a gentle post-treatment of SSA-Na2 at 400 °C under oxidizing conditions, no toxic Cr(VI) was formed (see SSA-Na3). This temperature is probably too low for the oxidation of Cr(III). Thus, by changing of the conditions of the thermochemical process (atmosphere, post-treatment) undesired oxidation of Cr(III) in the SSA to toxic Cr(VI) can be prevented.

S K-Edge XANES. Figure 3 shows the S K-edge XANES spectra of the investigated SSA and SSA based P-fertilizers. The sulfate present in the used SSA was mainly $CaSO_4$. This was also detected by XRD measurements.[15] In SSA-Na1, small amounts of FeS and Na_2SO_4 were detected besides $CaSO_4$ (see for comparison the XANES spectra of reference compounds in Figure 4). Because of the strong white line of the samples, a LCF with the references was very difficult. Figure 5 shows a comparison of the S K-edge XANES spectrum of SSA-Na1 with those of $CaSO_4$, Na_2SO_4 and FeS. In the pre-edge region
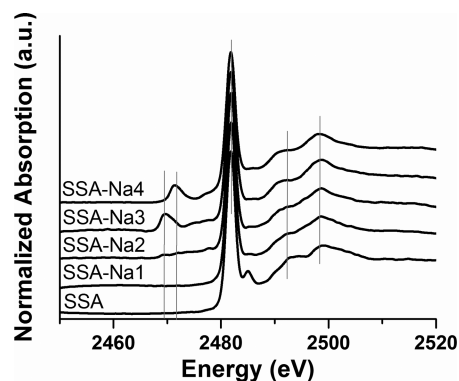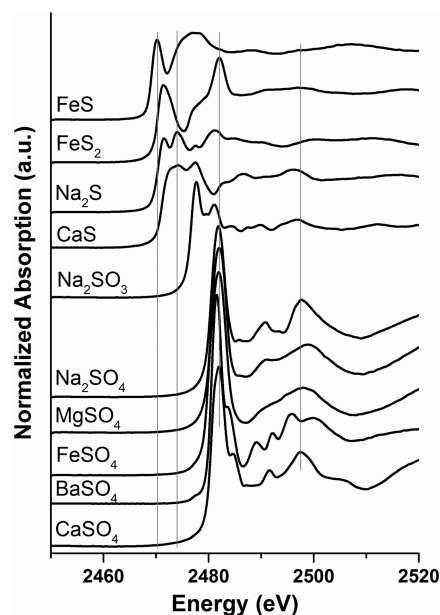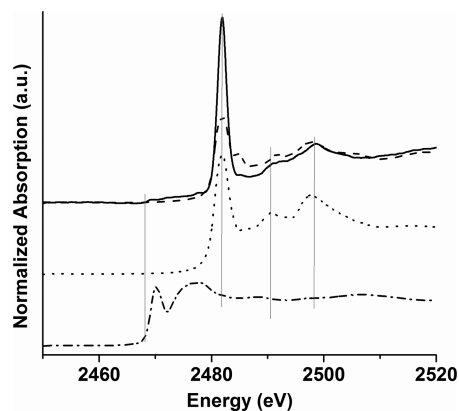
(between 2468 and 2478 eV) of the XANES spectrum of SSA-Na1, a sulfide compound was detected. Because of the edge at very low energy (see also Figure 4), it was identified as FeS. Furthermore, the oscillations in the post-edge region (2490−2500 eV) are a little bit broader than those of pure $CaSO_4$, which suggests that some Na_2SO_4 was formed during the thermochemical treatment. Because of the higher amount of

sulfur, SSA-Na2 showed an even stronger signal of FeS, which was developed by the thermochemical treatment under reducing conditions. Thus, the products from reductive degradation of Na_2SO_4 directly react with iron compounds present in the SSA to nontoxic FeS. Surprisingly, after the gentle post-treatment of SSA-Na2 at 400 °C under oxidizing conditions, FeS_2 was detected in SSA-Na3. This could be due to the experimental setup with crucibles that might cause a limited contact between gas phase (oxygen) and solid SSA-Na2.

Thermodynamic Calculations. Figure 6 shows the results of a thermodynamic calculation for the reaction of FeS with an
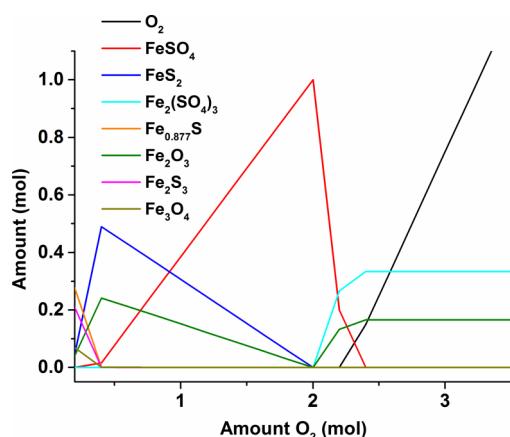

Figure 6. Results of a thermodynamic equilibrium calculation for the reaction of FeS (1 mol) with oxygen (0.2−3.5 mol) at 400 °C.

increasing amount of oxygen at 400 °C. With low amounts of oxygen (<1 mol O_2), FeS_2 is the major reaction product together with some Fe_2O_3. This result is in agreement with our findings of the S K-edge XANES measurements. After increasing the oxygen amount to 1−2 mol O_2, $FeSO_4$ is the major reaction product. Higher amounts of oxygen (>2 mol O_2) lead to the formation of $Fe_2(SO_4)_3$ and Fe_2O_3. A further increase of the oxygen amount does not change the reaction compounds. It can be assumed that an improved solid−gas contact in the thermal post-treatment (e.g., in a fluidized bed reactor or rotary kiln) would be suitable to transform completely iron sulfide into plant-available sulfates.

Fe K-Edge XANES. The S K-edge XANES spectra show that iron sulfide was formed in the thermochemical process from Fe_2O_3 present in the SSA and the additive Na_2SO_4 under reducing conditions. Therefore, we analyzed also the chemical state of iron during the thermochemical processes. Figure 7 shows the Fe K-edge XANES spectra of SSA, the SSA based P-fertilizers, and Fe reference compounds. The XANES spectrum of SSA is very similar to that of $Fe_3(PO_4)_2$. Linear combination fitting indicates $Fe_3(PO_4)_2$ as a major Fe compound and some Fe_2O_3 (see Figure 8a). Previous XRD measurements[15] determined Fe_2O_3 (hematite) as a major iron compound in the SSA. Normally, during sewage sludge incineration, the precipitated iron phosphates from the wastewater treatment plant react with calcium compounds to Fe_2O_3 and calcium phosphates. However, both duplicates of XANES measurements from this SSA sample showed $Fe_3(PO_4)_2$ as the major Fe-bearing mineral phase. The LCF of SSA-Na1 determines a mixture of Fe_3O_4 and Fe_2O_3 as major iron phases (see Figure 8b). Because of the reducing conditions in the thermochemical process, a reduction of Fe(III) to Fe(II) is comprehensible.
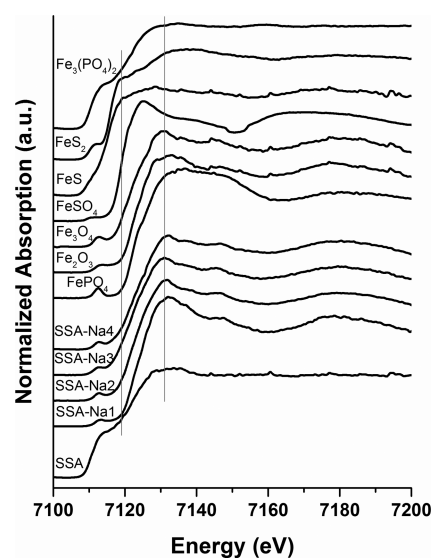

Figure 7. Fe K-Edge XANES spectra of SSA, SSA based P-fertilizers, and Fe reference compounds.
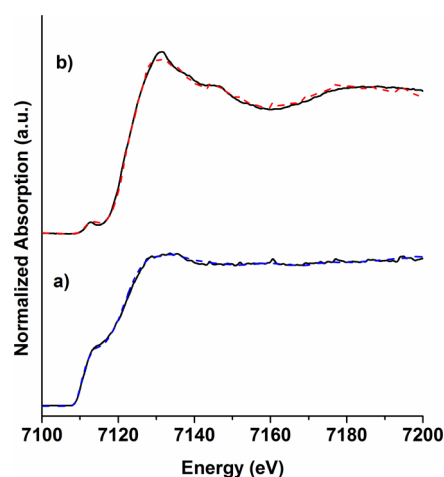

Figure 8. Linear combination fitting of (a) SSA (—) and 93% $Fe_3(PO_4)_2$ + 7% Fe_2O_3 (---) and (b) SSA-Na1 (—) and 65% Fe_2O_3 + 35% Fe_3O_4 (---).

Furthermore, the color of the SSA changed from red to black during the thermochemical treatment, which is also an indicator for the reduction of the iron oxides in the SSA. Because of the high mass fraction of iron in the SSA (approximately 19%), a high mass fraction of oxygen is liberated during the reduction whereby the mass fraction of phosphorus increases, which is beneficial for the sales of the fertilizer. In SSA-Na2 additional to Fe_3O_4 and Fe_2O_3, some iron sulfide (FeS/FeS_2) was determined by LCF. This is related to the use of Na_2SO_4 as an additive and the resulting higher S mass fraction (approximately 4.2% instead of 0.9%) in the product. During the oxidizing post-treatment (SSA-Na3) parts of the Fe_3O_4 are reoxidized to Fe_2O_3.

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Notes
The authors declare no competing financial interest.

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