



## Chemical state of chromium in sewage sludge ash based phosphorus-fertilisers



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### HIGHLIGHTS

- Chromium(VI) did not develop during thermochemical treatment of SSA with Cl-donors.
- Chromium(VI) develops by thermal treatment of SSA with Ca- and Na-carbonate.
- A Cr-solubility in water >10% detect Cr(VI) in SSA based P-fertilisers.

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### ABSTRACT

Sewage sludge ash (SSA) based P-fertilisers were produced by thermochemical treatment of SSA with Cl-donors at approximately 1000 °C. During this thermochemical process heavy metals are separated as heavy metal chlorides via the gas phase. Chromium cannot be separated under normal conditions. The risk of the development of toxic Cr(VI) during the thermochemical process was investigated. X-ray Absorption Spectroscopy measurements showed that SSA and thermochemically treated SSA with CaCl<sub>2</sub>, MgCl<sub>2</sub> and NaCl contain Cr(III) compounds only. In contrast, treating SSA with elevated quantities of Na<sub>2</sub>CO<sub>3</sub>, to enhance the plant-availability of the phosphate phases of the fertiliser, developed approximately 10–15% Cr(VI). Furthermore, Raman microspectroscopy showed that using Mg-carbonate reduces the risk of a Cr(VI) development during thermochemical treatment. Additionally, leaching tests showed that only a Cr-water solubility >10% is an indicator for Cr(VI) in SSA based P-fertilisers.

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### 1. Introduction

Phosphorus is an essential element of all life forms. It is necessary for the metabolism process (ADP/ATP) and part of the DNA. Accordingly, phosphorus is inserted in form of phosphate fertilisers in the agricultural food production. Usually, the limited natural resource phosphate rock is used for fertiliser production. Due to the increase of the phosphate rock price and decreasing amount (Cordell et al., 2009) and quality of mineral phosphate resources, new alternatives for the production of phosphate fertilisers for agriculture must be found. An important source of secondary

phosphates is sewage sludge. The use of such materials poses challenges due to the presence of heavy metals in the sludges.

In the European FP6-project SUSAN (SUSAN, 2013) a thermochemical process with Cl-donors at 1000 °C was developed that separates heavy metals from sewage sludge ash (SSA) originating from mono-incineration of sewage sludge (Adam et al., 2009). The process transfers the ash into a fertiliser containing mineral phosphate phases that are plant-available. However, both, chromium and nickel cannot be separated from the SSA via the thermochemical treatment under normal operating conditions (Adam et al., 2009; Vogel and Adam, 2011). In fact, high concentrations of chlorine gas would be required to separate these elements, and although such processes are well established in the production of TiO<sub>2</sub>, this might not be economically viable for the treatment of sewage sludge ashes.

Chromium in SSA is thus a critical issue to address. Chromium in the hexavalent state is very toxic. In contrast, trivalent Cr is less

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mobile in the environment and therefore less bioavailable and markedly less toxic (Shanker et al., 2005). The Cr concentration permitted in SSA based fertilisers thus requires tight regulation. For example, the German Fertiliser Ordinance mandates that the total Cr of fertilisers must be labelled above a content of 300 ppm (German Fertiliser Ordinance, 2008). Furthermore, the Cr(VI) mass fraction is limited to 2 ppm irrespective of the overall amount of Cr present in the fertiliser. The SSA based fertilisers used for this study contain approximately 170 ppm of total Cr, whereby no chromium species information was available on these fertilisers.

Takaoka et al. (2008) found by X-ray Absorption Spectroscopy measurements that Japanese SSA contains chromium as Cr(III) species, specifically  $\text{FeCr}_2\text{O}_4$ ,  $\text{Cr}(\text{OH})_3$  and  $\text{CaCr}_2\text{O}_4$ . Kirk et al. (2002) showed that Cr(VI) compounds can develop during thermal treatment of Cr(III) oxide with Ca-compounds at 1000 °C. XRD measurements of the used SSA (Peplinski et al., 2009) determined, in addition to calcium phosphates, the following Ca-compounds:  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{CaSO}_4$  and  $\text{CaCO}_3$ . Thus, oxidation of Cr(III) in the SSA during the thermal treatment process is possible.

In this study, we investigated the presence of Cr(VI) and the makeup of chemical species of Cr in SSA based fertilisers after thermochemical treatment in oxidising conditions ( $\text{HCl}/\text{Cl}_2/\text{O}_2$ ) at approximately 1000 °C. This work forms an important part of developing fertiliser production processes using Cl-donors as outlined above. Raman microspectroscopy was used to provide reference information on possible reactions between Cr and Ca- and Mg-compounds of the SSA during thermochemical treatment. Correspondingly, the products of thermal treatment of  $\text{Cr}_2\text{O}_3$  with  $\text{CaCO}_3$  and  $\text{MgCO}_3$  were analysed.

In the case of the SSA based fertilisers, the low mass fraction of Cr prevented detection by Raman microspectroscopy. Hence, X-ray Absorption Near Edge Structure (XANES) spectroscopy measurements were carried out to determine the chemical state and species of the chromium. The suitability of XANES to analyse chemical species of Cr at relatively low concentrations is well established (Arcon et al., 1998; Manning et al., 2007; Takaoka et al., 2008; Kappen et al., 2008). In addition, the Cr-solubility of Cr-reference compounds and SSA based fertilisers in dist. water, 5% HCl and 5%  $\text{HNO}_3$  was determined to observe Cr(VI) in the SSA based fertilisers. We used 5% HCl and 5%  $\text{HNO}_3$  solutions, because in the literature (HHS, 2012) it was mentioned that Cr(VI) compounds, in opposite to Cr(III) compounds, are soluble in weak acids.

## 2. Materials and instrumentation

### 2.1. Fertiliser preparation

The SSA used for this study originated from an incineration plant in the Netherlands; the corresponding sludges came from waste water treatment plants (WWTPs) primarily using Fe-salts for phosphate precipitation. The incineration temperature was 850 °C. The elemental composition of the SSA (see Table 1) was determined using ICP-OES (Thermo IRIS Intrepid II XSP in combination with Thermo Timberland IIS Autosampler) after total digestion ( $\text{HClO}_4/\text{HNO}_3/\text{HF}$ ) in a microwave (mikroPrepA, MLS GmbH, Leutkirch, Germany; heating with 1000 W; 20 min isotherm segment at 240 °C).

Thermochemical treatments of SSA with calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ; extra pure, Merck, Darmstadt, Germany), magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; cryst., Merck, Darmstadt, Germany), sodium chloride (p.a., Merck, Darmstadt, Germany) (all 150 g Cl per kg SSA) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ , Merck, Darmstadt, Germany) (270 g  $\text{Na}_2\text{CO}_3$  per kg SSA), respectively, were carried out in a

**Table 1**

Mass fractions and standard deviations (SD;  $n=3$ ) of main elements and trace elements determined for the used SSA by ICP-OES after total digestion with  $\text{HClO}_4/\text{HNO}_3/\text{HF}$  in a microwave oven (240 °C).

|    | SSA                                    |                            |
|----|--|----------------------------|
|    | Mass fractions ( $\text{mg kg}^{-1}$ ) | SD ( $\text{mg kg}^{-1}$ ) |
| Al | 48816                                  | 1301                       |
| Ca | 89479                                  | 1013                       |
| Fe | 87510                                  | 763                        |
| K  | 11972                                  | 508                        |
| Mg | 14090                                  | 174                        |
| Mn | 848                                    | 21                         |
| Na | 8009                                   | 1115                       |
| P  | 95741                                  | 1330                       |
| S  | 11875                                  | 256                        |
| Si | 132344                                 | 15054                      |
| Ti | 2567                                   | 46                         |
| As | 21.0                                   | 0.6                        |
| Cd | 4.6                                    | 0.1                        |
| Cr | 176                                    | 5                          |
| Cu | 1121                                   | 26                         |
| Mo | 30.6                                   | 0.4                        |
| Ni | 64.7                                   | 1.6                        |
| Pb | 370                                    | 4                          |
| Sn | 65.8                                   | 1.0                        |
| Zn | 3017                                   | 51                         |

rotary furnace (Thermo Technology, RT1700, Bayreuth, Germany). For these treatments a corundum furnace was used for a retention time of approximately 30 min at 950 °C (hereafter the products of this treatment are referred to as SSA-Ca1, SSA-Mg1, SSA-Na1 and SSA-Na2, respectively). The thermochemical treatment with  $\text{Na}_2\text{CO}_3$  was done to increase the plant-availability of the phosphate phases in the fertiliser due to the formation of Na-Ca-phosphates.

### 2.2. Thermal treatment of $\text{Cr}_2\text{O}_3$

$\text{Cr}_2\text{O}_3$  (p.a., Merck, Darmstadt, Germany) was thermally treated in corundum crucibles for 2 h at 1000 °C in a muffle furnace in two separate batches (1 g each) with 3.57 g  $\text{CaCO}_3$  (p.a., Sigma-Aldrich, Steinheim, Germany) and 4.18 g  $\text{MgCO}_3$  (p.a., Merck, Darmstadt, Germany), respectively, after mixing in a gyrowheel-mixer (hereafter the products of this treatment are referred to as Cr-Ca and Cr-Mg, respectively).

### 2.3. Reference samples

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (p.a., Sigma-Aldrich, Australia) was used for the solubility-tests and XANES experiments.  $\text{Cr}(\text{OH})_3$  was precipitated from an aqueous solution of  $\text{CrCl}_3$  with ammonia.  $\text{CaCr}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$  were prepared from  $\text{Cr}_2\text{O}_3$  (p.a., Merck, Darmstadt, Germany) with  $\text{CaCO}_3$  (p.a., Sigma-Aldrich, Steinheim, Germany) and  $\text{MgCO}_3$  (p.a., Merck, Darmstadt, Germany) at 1250 °C and 1000 °C, respectively, in platinum crucibles by thermal treatment (6 h) in a muffle furnace. The chemical state of these compounds was determined by Raman microspectroscopy (see instrument settings below).

### 2.4. Cr-solubility

The Cr-solubility was analysed by ICP-OES (Thermo IRIS Intrepid II XSP in combination with Thermo Timberland IIS Autosampler, Thermo Fisher Scientific GmbH, Dreieich, Germany) after extraction with dist. water, 5% HCl and 5%  $\text{HNO}_3$ . The pH-value of the solutions was analysed with the WTW pH/Cond 340i pH-meter in combination with the WTW pH-electrode Sentix 41 (both WTW, Weilheim, Germany). Samples of 0.5 g were extracted with 50 mL

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