

Heavy metal removal from sewage sludge ash analyzed by thermogravimetry

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Abstract A high temperature (1000 °C) thermochemical process for heavy metal removal from sewage sludge ash via the chloride pathway was investigated by thermogravimetry/differential thermal analysis (TG/DTA). TG and DTA measurements gave information about secession and evaporation of water, HCl, and heavy metal chlorides at different temperatures. Additionally, gaseous water and hydrochloric acid which occurred in the process were detected by an FT-IR detector that was coupled to the TG/DTA-system. Heavy metal chlorides which were also formed in the process cannot be detected by this technique. For that reason the outlet gas of the TG/DTA-system was discharged into washing flasks filled with water for absorption. The washing flasks were replaced in temperature steps of 50 °C and the heavy metal concentrations of the solutions were determined by ICP-OES. The temperature-dependent formation/evaporation of different heavy metal chlorides was analyzed and compared for two different thermochemical processes using magnesium chloride hydrate or calcium chloride hydrate as Cl-donors. In both cases evaporation of Cd, Cu, Pb, and Zn was observed from 600 °C, whereas As, Cr, and Ni remained in the solid state. The results were discussed against the background of thermodynamic calculations.

Keywords Thermogravimetry/FT-IR · Sewage sludge ash · Heavy metal chloride · Thermodynamic simulation

Introduction

Phosphorus is an essential element of all life forms. It is necessary for the metabolism process (ADP/ATP) and part of the DNA. For this reason phosphorus is a macronutrient and must be applied in agricultural crop production in form of phosphorus fertilizers. In general, mineral phosphates from external sources (phosphate rock) are used for fertilizer production. However, phosphate rock is a non-renewable and limited resource and is often contaminated with cadmium and uranium. Thus, new sustainable options for the production of phosphate fertilisers must be searched. An alternative source of phosphate is sewage sludge. To protect local receiving waters from eutrophication the phosphorus in waste water is transferred into the sewage sludge by enhanced biological phosphorus removal and/or by precipitation with Ca^{2+} -, Fe^{2+} -, Fe^{3+} -, or Al^{3+} -salts in the waste water treatment plant. However, direct agricultural application of sewage sludge became a controversial issue as sewage sludge is often highly contaminated with organic pollutants and heavy metals. Consequently, the amount of sewage sludge thermally treated (mono- or co-incineration and subsequent disposal of the ashes) significantly increased in the last decade in the European Union.

In the European FP6-project SUSAN [1] (Sustainable and Safe Re-use of Municipal Sewage Sludge for Nutrient Recovery) a two-step thermal treatment of sewage sludge was developed aiming at the production of marketable mineral phosphorus fertilisers [2]. In a first step, sewage sludge is incinerated (mono-incineration) at 800–900 °C

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under destruction of all organic matter including the organic pollutants. The resulting sewage sludge ash (SSA) is rich in phosphorus and other nutrients (calcium, magnesium, potassium, etc.) but still contains most of the heavy metals that were present in the sludge. In a second step, the SSA is mixed with alkaline earth metal chlorides (MgCl_2 and CaCl_2) and thermally treated in a rotary kiln at a temperature of approx. 1000 °C. Heavy metal chlorides are formed and evaporated in this process and at the same time plant-available mineral phosphate phases are generated. The thermochemical process is already successfully operated in pilot-scale (7 Mg/days) by the Austrian company ASH DEC Umwelt AG and is planned to be implemented in industrial scale aiming at the production of marketable P-fertilizers from SSAs.

One major goal of the thermochemical process is the evaporation of heavy metal chlorides at high temperatures of approx. 1000 °C. Figure 1 shows the gaseous fractions of six heavy metal chlorides and oxides (Cd, Zn, Pb, Cu, Ni, and Cr as pure substances in nitrogen atmosphere) as a function of the temperature calculated with the thermodynamic modeling program HSC-Chemistry [3]. Except copper almost all heavy metal chlorides are completely in the vapor phase at 1000 °C, showing that the considered thermochemical process is principally possible. The respective heavy metal oxides have vapor pressures which are lower by several orders of magnitude and are not visible in Fig. 1, except for CdO and PbO.

The temperatures of formation and evaporation of different heavy metal chlorides were in the focus of the investigation presented in this article. The heavy metal chlorides are formed by the reaction of heavy metal compounds present in the SSA with the chlorine-donor. The

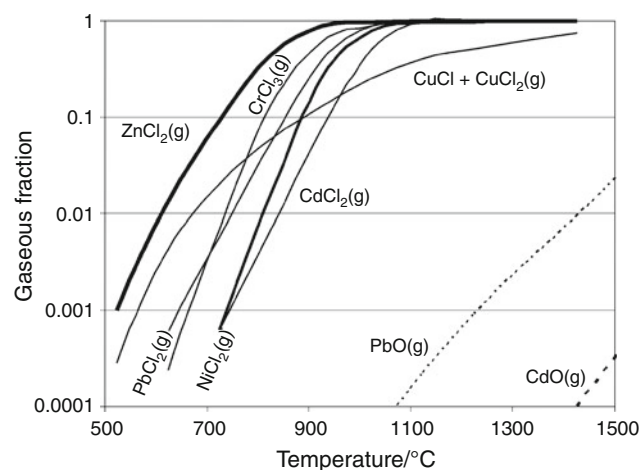
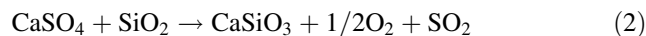


Fig. 1 Gaseous fractions of six heavy metal chlorides. Vapor pressure of the respective oxides is lower by several orders of magnitude. Therefore, CdO and PbO are the only oxides visible in the chart

temperatures of sublimation/boiling points for different relevant heavy metal chlorides are CdCl_2 : 967 °C, CuCl_2 : 525 °C, CuCl : 1367 °C, PbCl_2 : 954 °C, and ZnCl_2 : 732 °C [4]. CaSO_4 , which is also present in SSA, thermally decomposes below 1000 °C to CaO and SO_3 [5] (see Eq. 1). The presence of SiO_2 advantages the decomposition of CaSO_4 by formation of CaSiO_3 (see Eq. 2).



The chlorine-donor MgCl_2 -hexahydrate reacts at 97–117 °C to MgCl_2 -tetrahydrate, at 135–180 °C to MgCl_2 -dihydrate and in the range 185–230 °C to the respective monohydrate [4]. Furthermore, the thermal decomposition of MgCl_2 -hydrate is accompanied by the formation of $\text{Mg}(\text{OH})\text{Cl}$ and HCl at temperatures above 117 °C. The chlorine-donor CaCl_2 -dihydrate reacts at 45–175 °C to CaCl_2 -monohydrate and in the range 176–260 °C to the anhydride [4, 6].

Experimental

Materials and instrumentation

A representative Fe-rich SSA from an industrial fluidized bed incinerator (in the Netherlands) was used for the experiments. The mass fractions of main elements and heavy metals are listed in Table 1. For the thermal experiments, the SSA was mixed with the chlorine-donors $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (cryst., Ph. Eur., Merck, Darmstadt, Germany) or $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ($\geq 99\%$, Ph. Eur., Carl Roth GmbH, Karlsruhe, Germany). For all trials a Cl-content of 150 g Cl/kg ash was adjusted similar to the technical application of the thermochemical process. In addition, some water was added before mixing the ash with the Cl-donor.

Thermogravimetry/differential thermal analysis (TG/DTA) experiments were carried out on Netzsch STA 449 F3 Jupiter (Selb, Germany). Samples of 19–26 mg were heated with a rate of 5 °C/min from 30 to 1000 °C, afterwards the temperature was kept constant at 1000 °C for 30 min. For the TG experiments coupled with the analysis of heavy metal chlorides in the gaseous phase, larger samples of 600–700 mg were placed on a single TG-sample holder (plate) in order to increase the total mass of heavy metals. The off-gas was continuously discharged into washing flasks (10 mL) that were replaced in steps of 10 min (50 °C) starting from 100 °C. Heating rate, temperature range, and isothermal phase were similar to the experiments described above (5 °C/min, 30–1000 °C, 30 min at 1000 °C). The flow rate of the carrier gas (air) was 50 mL/min. The heavy metal concentrations of the

Table 1 Mass fractions of main elements and heavy metals determined in raw SSA by ICP-OES after total digestion with HNO₃/HCl/HF in the microwave

Raw SSA/mg/kg	
Al	55920
As	34
Ca	134200
Cd	4
Cr	146
Cu	1113
Fe	100100
Hg	<0.07
K	10580
Mg	15020
Mn	1043
Na	5586
Ni	83
P	90040
Pb	237
S	12970
Sn	48
Zn	2543

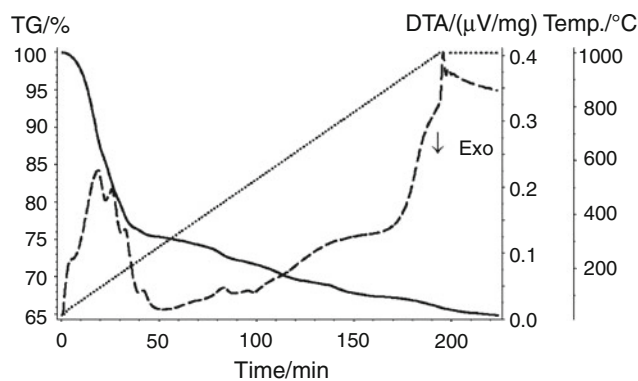
solutions from the washing flasks were measured by ICP-OES (Thermo IRIS Intrepid II XSP in combination with Thermo Timberland IIS Autosampler, Thermo Fisher Scientific GmbH, Dreieich, Germany).

Thermogravimetry/FT-IR experiments were carried out on a Netzsch STA 409 PC Luxx system (Selb, Germany) coupled by a heated transfer line (volume 50 mL; heated at 180 °C) to a Bruker Vertex 70 FT-IR spectrometer (Ettlingen, Germany) with a liquid-cooled mercury cadmium telluride detector. Samples of 37–63 mg were heated with a heating rate of 10 °C/min from 30 to 1000 °C. Afterwards temperature of 1000 °C was kept constant for 30 min. The flow rate of the carrier gas (oxygen) was 50 mL/min. FT-IR gas-phase spectra were collected with a spectral resolution of 4 cm⁻¹ and 32 scans were coadded per spectrum.

Results and discussion

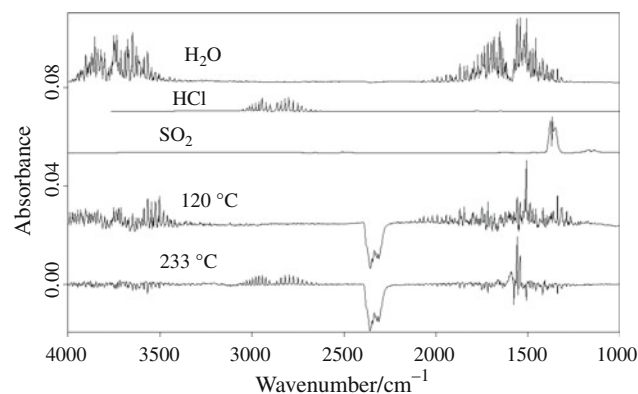
Trials with magnesium chloride hexahydrate and SSA

Figure 2 shows the TG/DTA diagram of the thermochemical treatment of SSA with MgCl₂·6H₂O as chlorine-donor. At around 100 °C the TG curve decreased intensely due to evaporation of water, which was also detected in the DTA curve as an endothermic signal. Between 200 °C and approx. 400 °C the mass loss was low but increased again

**Fig. 2** TG/DTA diagram for a mixture of SSA and MgCl₂·6H₂O; 30–1000 °C with 5 °C/min afterwards 30 min isotherm segment at 1000 °C (TG, solid line; DTA, dashed line; and temperature, dotted line)

at higher temperatures and a nearly constant mass loss was observed in the range 400–1000 °C.

The same sample was also analyzed by thermogravimetry coupled with an FT-IR detector. In Fig. 3 the FT-IR spectra of 120 and 233 °C together with reference spectra of gaseous water, hydrochloric acid, and sulfur dioxide are mapped. It is visible that the first sharp decrease in the TG curve in the range 100–200 °C was caused by evaporation of water. At 233 °C additionally gaseous hydrochloric acid was detected, which was formed by the thermal decomposition of magnesium chloride hexahydrate. Other decomposition products were not detected. Chlorine gas formed in the process by the thermal decomposition of MgCl₂ or CaCl₂ in absence of gaseous water was not detectable due to its IR-inactivity. In Fig. 4 the spectral absorbance of water (3532 cm⁻¹) and hydrochloric acid (2802 cm⁻¹) was plotted versus the temperature. A strong peak at the wavelength 3532 cm⁻¹ was observed in the range 100–200 °C, which was due to vaporization of water.

**Fig. 3** FT-IR spectra at 120 and 233 °C of the thermogravimetric set-up coupled with FT-IR spectrometer of SSA with MgCl₂·6H₂O and reference spectra of gaseous water, hydrochloric acid, and sulfur dioxide

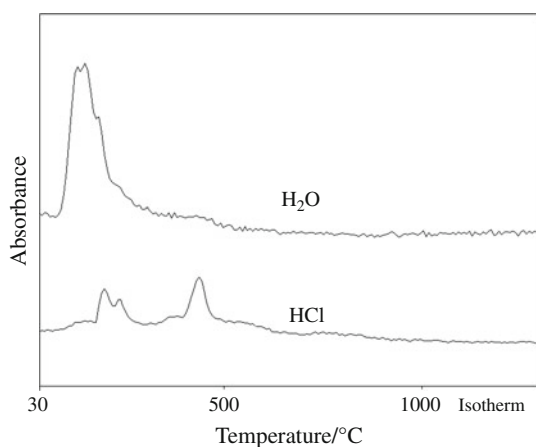


Fig. 4 Spectral absorbance (from the FT-IR spectra) versus temperature plot of gaseous water (3532 cm^{-1}) and hydrochloric acid (2802 cm^{-1}) for the thermogravimetric analysis of SSA with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

The spectral absorbance of gaseous hydrochloric acid showed two peaks at 180 and 450 °C.

Only water and hydrochloric acid were detectable with the FT-IR detector. In order to follow the pathway of heavy metal chlorides formed at high temperatures, the concentrations of the dissolved heavy metals absorbed in the washing flasks were determined by ICP-OES. In Fig. 5 the temperature-dependent concentrations of some heavy metals and sulfur plus the TG diagram are shown. The heavy metals Cd, Cu, Pb, and Zn were detected in the washing solutions starting from 600 °C. Other heavy metals such as Cr and Ni and also As were not detected. Adam et al. [7] observed also in technical trials with a rotary furnace that the transfer rates for these elements are very low compared to those of Cd, Cu, Pb, and Zn. Furthermore, the main (matrix)

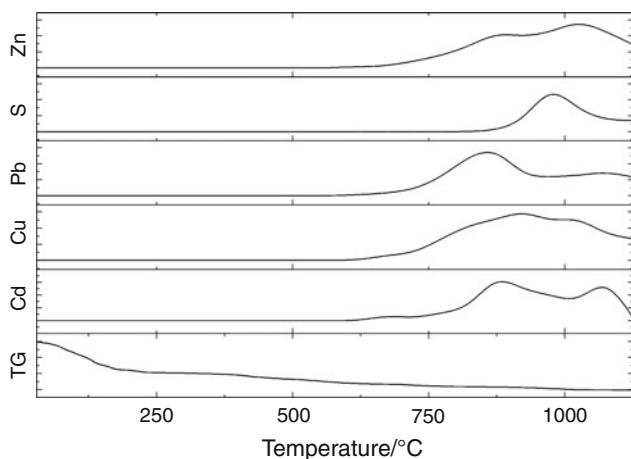


Fig. 5 Concentration of different elements of the outgoing gas flow from the thermogravimetric set-up initiated in water (measured by ICP-OES) and the TG-diagram versus the temperature for SSA with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

elements such as Al, Ca, Mg, P, and Si remained in the solid state and were not detected in the washing solutions. Thus, from 600 °C the respective heavy metal chlorides were simultaneously formed and evaporated in the thermochemical process. Sulfur was detected in the washing solutions from around 850 °C. Peplinski et al. [8] showed by XRD measurements that anhydrite (CaSO_4) completely disappeared in the thermochemical process in the temperature range 900–1000 °C. In the literature [5] it was found that anhydrite degrades below 1000 °C to CaO and SO_3 . At high temperatures SO_3 is not stable; it decays to SO_2 and $\frac{1}{2}\text{O}_2$. However, both SO_3 and SO_2 are IR-active molecules but were not detected with the FT-IR detector. The most likely reason is the low concentration of SO_2 gas formed in the trials with FT-IR (37 mg sample).

Results of trials with calcium chloride dihydrate and SSA

Similar measurements were carried out using $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ as chlorine-donor. In Fig. 6 the TG and DTA curves of the thermochemical process are mapped. Analogous to the process with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ an endothermic reaction with a strong mass loss was detected at around 100 °C due to the vaporization of water. Heating to higher temperatures showed a constant mass loss without major steps.

The analysis of this SSA/chlorine-donor combination by TG coupled with FT-IR showed only water as gaseous IR-active product. In Fig. 7 the spectral absorbance of water (3532 cm^{-1}) was plotted versus the temperature. Water was detected between 100 and 200 °C correlating with the high mass loss observed in the TG curve in this temperature range. Instead of HCl which is formed by thermal decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ IR-inactive chlorine gas was formed by the thermal decay of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and was thus not detected.

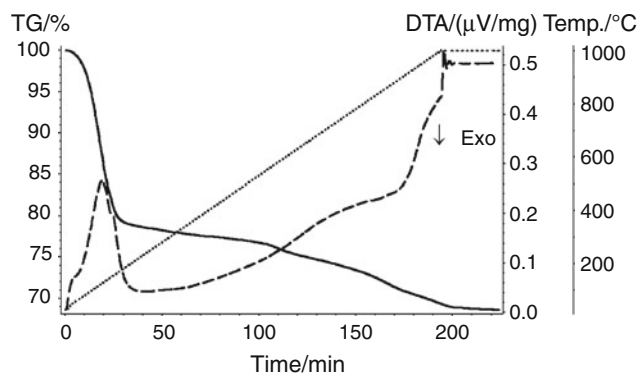


Fig. 6 TG/DTA diagram for a mixture of SSA and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; 30–1000 °C with 5 °C/min afterwards 30 min isotherm segment at 1000 °C (TG, solid line; DTA, dashed line, and temperature, dotted line)

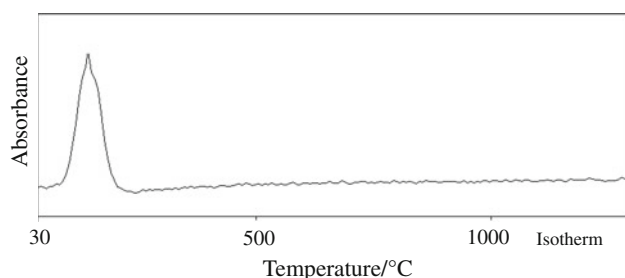


Fig. 7 Spectral absorbance (from the FT-IR spectra) versus temperature plot of gaseous water (3532 cm^{-1}) for the thermogravimetric analysis of SSA with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

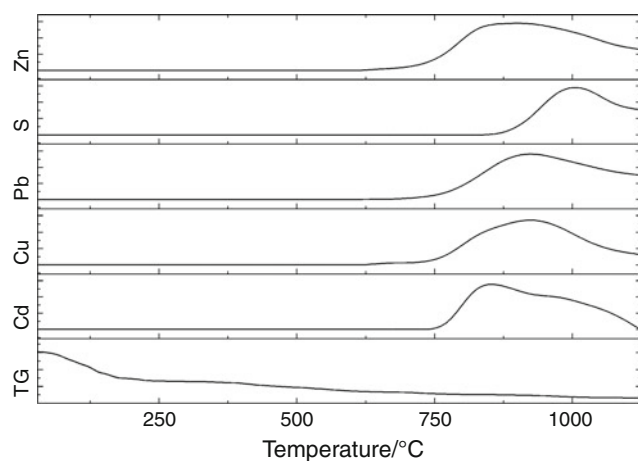


Fig. 8 Concentration of different elements of the outgoing gas flow from the thermogravimetric set-up initiated in water (measured by ICP-OES) and the TG diagram versus the temperature for SSA and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

Figure 8 shows the temperature-dependent concentration of some heavy metals and sulfur plus the TG-diagram for the thermochemical treatment of SSA with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Evaporation of Cd, Cu, Pb, and Zn was again detected from around $600\text{ }^\circ\text{C}$. Furthermore, As, Cr, and Ni as well as the matrix elements were not detected in the washing solutions similar to the observations of the trials with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as Cl-donor. Consequently, the chlorinating mechanisms taking place by the treatment with the two different Cl-donors were probably similar. The form of gaseous Cl-species (HCl or Cl_2) had obviously no effect on the transfer of heavy metals into the gaseous phase. Again, sulfur was detected from $850\text{ }^\circ\text{C}$ due to degradation of anhydrite at higher temperature.

Thermodynamic considerations

Thermodynamic calculations were carried out with the software HSC-Chemistry[®] [3]. The formation of element species in the temperature range $100\text{--}1000\text{ }^\circ\text{C}$ of a mixture containing the chlorine-donor MgCl_2 or CaCl_2 and the

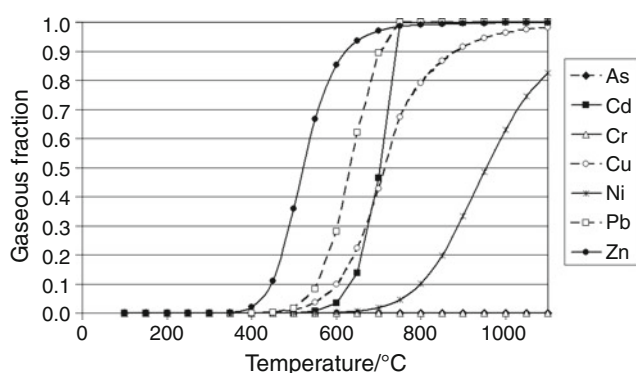


Fig. 9 Results of thermodynamic calculation for a mixture of magnesium chloride and heavy metal oxides in an air-atmosphere between 100 and $1100\text{ }^\circ\text{C}$ (Input data: N_2 (80 kmol), O_2 (20 kmol), MgCl_2 (10 kmol), As_2O_3 (0.25 kmol), CdO (0.5 kmol), Cr_2O_3 (0.25 kmol), CuO (0.5 kmol), NiO (0.5 kmol), PbO (0.5 kmol), and ZnO (0.5 kmol))

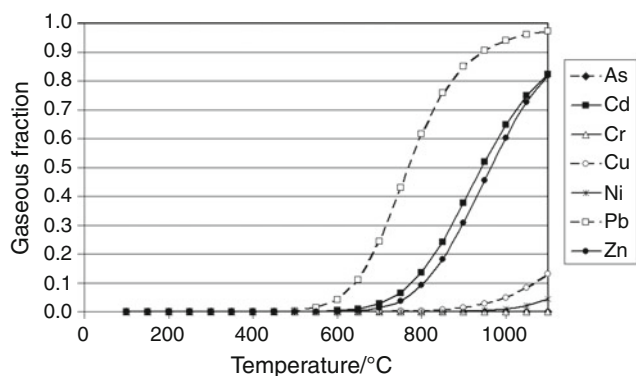


Fig. 10 Results of thermodynamic calculation for a mixture of calcium chloride and heavy metal oxides in an air-atmosphere between 100 and $1100\text{ }^\circ\text{C}$ (Input data: N_2 (80 kmol), O_2 (20 kmol), CaCl_2 (10 kmol), As_2O_3 (0.25 kmol), CdO (0.5 kmol), Cr_2O_3 (0.25 kmol), CuO (0.5 kmol), NiO (0.5 kmol), PbO (0.5 kmol), and ZnO (0.5 kmol))

heavy metal oxides (and arsenic oxide) in an air-atmosphere was calculated. The amounts of gaseous element species were summed up for each element. The formation of PbCl_4 was excluded in the calculation as it is already the thermodynamically preferred species at low temperature ($100\text{ }^\circ\text{C}$). In this case already at the lowest temperature of $100\text{ }^\circ\text{C}$ Pb would be quantitatively transferred into the gaseous phase in form of PbCl_4 which was not observed in the trials. Figure 9 shows the results of the thermodynamic equilibrium calculation with MgCl_2 as chlorine-donor. The calculation shows that the formation of gaseous heavy metal chlorides of Cd, Cu, Pb, and Zn starts between 400 and $750\text{ }^\circ\text{C}$ which is in agreement with the experimental results. The major volatile species are CdCl_2 , CuCl_2 , PbCl_2 , and ZnCl_2 . The elements As and Cr did not form gaseous species in this temperature range which is also in agreement with experimental results. However, gaseous

NiCl_2 was formed from 750 °C which was not observed in the experiments. The results of the thermodynamic calculation with CaCl_2 as chlorine-donor are shown in Fig. 10. The calculated data show that gaseous CdCl_2 , PbCl_2 , and ZnCl_2 are formed at slightly higher temperatures starting in the range 550–750 °C. In contrast to experimental results and the results of the simulation with the Cl-donor MgCl_2 the formation of gaseous copper compounds starts not before 900 °C. The reason is the thermodynamically preferred formation of CuCl (sublimation point: 1367 °C) instead of CuCl_2 which was not observed in the calculation with MgCl_2 . The elements As, Cr, and Ni do not form gaseous compounds in the calculation with CaCl_2 which is in agreement with experimental observations.

Conclusions

During the thermochemical process of heavy metal elimination from SSA with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ the gaseous products water and hydrochloric acid were detected by TG coupled with FT-IR in the temperature range 100–450 °C. These products are formed by the well-known thermal decay of magnesium chloride hexahydrate. Formation and evaporation of the heavy metal chlorides of Cd, Cu, Pb, and Zn occurred in the same temperature range starting nearly at the same temperature of around 600 °C. In contrast the elements As, Cr, and Ni were not detected in the gas phase which is in accordance with previous investigations and thermodynamic considerations. The result of simultaneous heavy metal evaporation is in agreement with the TG curve which also shows a relatively constant mass loss without major steps. Sulfur was detected in the washing solutions due to the degradation of anhydrite above a temperature of 850 °C.

During the heavy metal elimination from SSA with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ only water was detected by FT-IR at low temperature. In contrast to the trial with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ chlorine gas is formed by thermal degradation of CaCl_2 (in absence of gaseous water) which is IR-inactive [6]. However, heavy metal elimination was comparable for both types of Cl-donors used for the thermochemical treatment. Thus, the heavy metal chlorides can either be formed by solid-state reactions between the chlorine-donor and the

heavy metals present in the SSA or by the reaction of heavy metals with gaseous HCl or Cl_2 generated in the process.

Thermodynamic calculations for the Cl-donor MgCl_2 showed results that were close to the experimental results for the elements As, Cr, Cd, Cu, Pb, and Zn. In contrast, Ni was calculated to be present in the gaseous phase from 750 °C which was not observed in the experiments. Also the calculation of the system with CaCl_2 as Cl-donor showed data close to experimental results for As, Cd, Cr, Ni, Pb, and Zn. In contrast to experimental results in this case Cu was not transferred into the gaseous phase already at 600 °C which was due to the formation of CuCl instead of CuCl_2 in the calculation. Thus, thermodynamic calculations of such complex systems can be used as an overview of possible reactions only.

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