Recovery of phosphorus from sewage sludge ash: Influence of incineration temperature on ash mineralogy and related phosphorus and heavy metal extraction

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Abstract

Phosphorus (P) can be effectively recovered from sewage sludge ash (SSA) by applying wet chemical extraction techniques. However, considerable amounts of heavy metals can be co-extracted depending on the type of extraction liquid used. In this study, the influence of the incineration temperature on the ash mineralogy and related P and heavy metal extraction using sulfuric acid, hydrochloric acid, oxalic acid and sodium hydroxide was studied. Results showed that the P extraction efficiency with sodium hydroxide decreased with increasing incineration temperature, related to a decrease in Al/Fe-phosphates in the SSA. Furthermore, P extraction efficiency for the acidic extraction liquids reached a maximum for SSA obtained around 850 °C (> 86% P extracted). Heavy metal co-extraction generally decreased with increasing incineration temperature, which could be linked to the immobilization of the heavy metals in the SSA matrix. For all extraction liquids considered, the lowest heavy metal co-extraction was found in SSA samples obtained at 1000 °C (< 21% total heavy metals extracted). However, the incorporation of P into silicate melt agglomerates at that incineration temperature reduced the P extraction. As a result, an incineration temperature in the range 800 – 850 °C offered a good trade-off between high P extraction and low heavy metal co-extraction.

Keywords: Ash mineralogy; Heavy metal extraction; Incineration temperature; Phosphorus extraction; Sewage sludge.

Graphical abstract

Abbreviations

See footnote¹.

1. Introduction

Phosphorus (P) is an essential micronutrient for all living organisms. In 2019, the worldwide P consumption was around 20.5 million tonnes of which most was used for manufacturing fertilizers, animal feed and detergents [1,2]. However, P reserves, in the form of phosphate rock, are depleting and recycling of P becomes increasingly important [2].

Wastewater contains high amounts of P and during wastewater treatment (WWT) more than 90% of this P is transferred to the sewage sludge (SS) by applying enhanced biological removal techniques or chemical precipitation with Al- or Fe-salts [3–5]. In 2016, about 11.2 million tonnes (dry matter (DM)) of SS was produced in the EU28, of which about 28% was incinerated [6]. Incineration not only reduces the mass of the SS by up to 90%, but also destroys pathogens and

¹ DM = dry matter; EPMA = electron probe microanalysis; ICP-OES = inductively coupled plasma optical emission spectroscopy; L/S = liquid/solid; R_{wp} = weighted profile R-factor; SMT = standards, measurement and testing; SS = sewage sludge; SSA = sewage sludge ash; WWT = wastewater treatment; XRD = X-ray diffraction.

toxic organic compounds, whilst recovering part of its energy content [3,7,8]. Furthermore, upon incineration, P largely concentrates in the sewage sludge ash (SSA), which generally has a P content of 4 – 12%. Therefore, SSA is a good alternative for non-renewable phosphate rock, which has a P content of 2 – 18% [9–12]. However, both the low P bioavailability and the high heavy metal concentrations in the SSA exceeding legal limit values for agricultural use, impede the direct application of SSA as a P fertilizer [3,7,13]. In this case, an alternative way to close the P cycle is to recover the valuable P from the SSA.

Many experts prefer P recovery from SSA by wet chemical extraction over thermochemical treatment and other recovery methods because of the high efficiency, low costs and because it is similar to the process currently used for extraction of P from phosphate rock [3,5]. In previous work of the authors, it was found that the type of extraction liquid, extraction liquid concentration, liquid/solid (L/S) ratio, contact time, pH, ash composition and ash mineralogy all affect P and heavy metal extraction efficiency from SSA [13,14]. Moreover, other literature shows that the temperature at which the SS is incinerated can alter the P mineralogy of the SSA and in this way can also affect the P extractability [3,8,15,16]. Higher incineration temperatures stimulate the transformation in the ash of poorly soluble P minerals, in which P is bound to Al or Fe (Al/Fe-phosphates), to more soluble P minerals, in which P is bound to Ca or Mg (Ca/Mg-phosphates), which improves the P extraction efficiency and P bioavailability [3,7,8,16–20]. Gorazda et al. [16] found that the efficiency of P extraction from SSA with nitric acid increased with increasing SS incineration temperature up to 950 °C. Moreover, the research of Atienza-Martinez et al. [8] showed that higher SS incineration temperatures improved the efficiency of P extraction from SSA with sulfuric acid, whereas this was not the case with oxalic acid, for which the P extraction efficiency was close to 100% regardless of the SS incineration temperature. The latter was confirmed by the work of Liang et al. [3] (for SS incineration temperatures up to 850 °C). Somewhat contradictorily, Liang et al. [3] found that the efficiency of P extraction from SSA with sulfuric acid decreased with increasing SS incineration temperature even though the amount of acid-soluble Ca-phosphates in the ash increased. They related this phenomenon to the denser surface structure of SSA particles formed at higher incineration temperatures, inhibiting acid penetration towards the core of the particles, in this way decreasing the efficiency of P extraction [3].

The changes in P mineralogy with increasing SS incineration temperature have been discussed extensively in literature [3,8,16–23]. However, these changes in P mineralogy have only rarely been linked to the P extraction efficiency [3,8,16] and, as discussed in the previous paragraph, the results of the little existing studies were not consistent. Moreover, it is important to find out whether the SS incineration temperature also affects the co-extraction of the heavy metals and to which extent [3]. Lower heavy metal co-extraction could reduce the costs of further processing the P extract to a final product complying with legal limit values for heavy metals in fertilizers.

The primary aim of this study was to assess the influence of the SS incineration temperature on the P mineralogy in the ash and the related wet P extraction efficiency from the SSA in a comprehensive and systematic way. To this extent, the SS incineration temperature was varied between 550 and 1100 °C and the efficiency of P extraction from the obtained SSA with sulfuric acid, hydrochloric acid, oxalic acid and sodium hydroxide was investigated. Furthermore, the influence of the SS incineration temperature on the heavy metal co-extraction was investigated.

2. Materials and methods

2.1. SSA samples

Dewatered SS was sampled from the SS storage bunker at the WWT plant of Aquafin in Leuven (Belgium). One tenth of all SS produced in Flanders (Belgium) is collected in this bunker before it is further treated in a digester. About 1.2 kg of dewatered SS (25% DM) was sampled once a day over a ten-day period (February 2020). All SS samples were dried at 105 °C for 24 h (VENTI-Line 56 Prime), ground (Retsch RS 200, 30 s, 1100 rpm) and mixed thoroughly with the samples collected on the other days after which the pooled sample was stored in a closed container at room temperature.

Of the pooled SS sample, subsamples of 45 g each were weighed in a porcelain dish with flat bottom (diameter of 10 cm) and incinerated in a muffle furnace (Nabertherm L3/11, heating rate of 15 °C/min) at 550, 650, 750, 800, 825, 850, 875, 900, 1000 and 1100 °C for 2 h. Next, each SSA sample was left to cool down to room temperature in the ambient air after which it was ground in a mortar and mixed thoroughly. The amount of SS used for the incineration experiments (45 g) was chosen to obtain sufficient amount of SSA for all characterization and extraction experiments, yet assured the SS to be evenly spread in a thin layer over the bottom surface of the porcelain dish. The duration of 2 h was based on the literature [3,18,24,25] and on preliminary experiments that showed no additional mass loss at longer incineration times.

2.2. SSA characterization

The elemental composition of the SSA obtained at the different incineration temperatures was determined by microwave-assisted digestion of 250 mg samples using a combination of aqua regia and hydrofluoric acid, as described in detail in previous work [13]. The digestion solutions were analyzed for Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, P, Pb, S, Si, Ti and Zn by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Varian 720-ES ICP-OES).

The SSA mineralogy in the crystalline phase was determined by quantitative X-ray diffraction (XRD) (D8 Bruker) with a corundum (Al₂O₃) internal standard and Cu K_α radiation. The data obtained was refined based on the Rietveld method and the weighted profile R-factor (R_{wp}) ranged between 6.50 and 7.59. The obtained XRD spectra can be consulted in Supplementary Material (Figure S1). The ‘standards, measurement and testing (SMT)’ protocol [26,27] was used to distinguish between inorganic P and organic P in the SSA. The same protocol was used to distinguish between Al/Fe-

phosphates (non-apatite inorganic P) and Ca-phosphates (apatite inorganic P) in the SSA. Furthermore, electron probe microanalysis (EPMA) (JXA-8530F) was used to determine the elemental distribution of Al, Ca, Fe, P and Si in selected areas of subsamples of the SSA obtained at 550, 850 and 1100 °C. The SSA samples obtained at these three temperatures were selected for EPMA as they showed the largest differences in P mineralogy (XRD analysis and SMT protocol) and P extraction efficiency. For EPMA, the powder SSA subsamples were embedded in a resin, grinded, polished and coated with a carbon layer.

2.3. Extraction experiments

The extraction liquids selected were sulfuric acid, hydrochloric acid, oxalic acid and sodium hydroxide. Sulfuric acid and oxalic acid were selected since previous work of the authors showed that they were optimal for P extraction from SSA [13]. However, sulfuric acid and oxalic acid have the disadvantage that large amounts of solid extraction residue are formed, i.e., gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcium oxalate (CaC_2O_4), respectively. These extraction residues require further treatment or a suitable application as secondary resource has to be found [13,28]. Hydrochloric acid was selected because it is available on an industrial scale, and upon extraction, no additional solid residue is formed, only the ash extraction residue remains. Sodium hydroxide was selected because previous work showed that it co-extracts less heavy metals during P extraction compared to the beforementioned acids [13,14,29,30]. The experiments were carried out at the optimal extraction conditions determined in previous work of the authors [13]: sulfuric acid, hydrochloric acid and oxalic acid were applied at a concentration of 0.5 N, an L/S ratio of 10 ml/g ash and a contact time of 2 h; sodium hydroxide was applied at a concentration of 0.5 N, an L/S ratio of 50 ml/g ash and a contact time of 2 h.

The extraction experiments were carried out at room temperature and all glassware was first rinsed with a 3% nitric acid solution. A well-sealed 50 ml PP falcon tube (HDPE flat cap) with 2.5 g of SSA and 25 ml 0.5 N sulfuric acid, hydrochloric acid or oxalic acid was placed horizontally on a reciprocating shaker (Heidolph Promax 2020) for 2 h at maximum speed (400 rpm). The same was done for the experiments with sodium hydroxide but 0.5 g of SSA was used in combination with 25 ml 0.5 N sodium hydroxide. The pH of the extraction liquid was for each run measured at the start and at the end of the extraction procedure (SenTix 21 electrode). Next, the solutions were filtered (0.45 μm) and analyzed for Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, P, Pb, S, Si, Ti and Zn by ICP-OES (Varian 720-ES ICP-OES). The extraction efficiency was calculated as the amount of element extracted according to Eq. (1):

$$\text{Extraction efficiency (\%)} = \frac{\text{Element extracted (\% of DM)}}{\text{Element in ash (\% of DM)}} \times 100\% \quad (1)$$

2.4. FactSage thermochemical calculations

Thermochemical equilibrium calculations were performed with the Equilib module of FactSage (version 8.0), which is based on the Gibbs free energy minimization principle, using FToxid and FactPS databases. These thermochemical calculations were used to predict the heavy metal mineralogy in the SSA. The elemental composition of the SSA samples obtained in the lab experiments (Table 1) was used as input for the thermochemical calculations, in combination with an excess of oxygen.

2.5. Quality assurance/quality control procedures of analytical techniques

The microwave assisted digestion was based on the European standard EN 13656:2002 [31]. For the digestion, extraction and SMT protocol, a method/reagent blank was analyzed after going through all steps of the procedure parallel to the SSA samples. The balance, pipettes, pH meter, and other instruments and measuring devices used were calibrated, standardized and serviced frequently according to internal good laboratory practice standards. A corundum internal standard was used for the quantitative XRD analysis. The calibration curve for the ICP-OES measurements was prepared with 1000 ppm standards and the calibration standards were rerun once each ten or twenty samples measured. All glassware was stored in closed containers and rinsed with at 3% nitric acid solution before use. Ultrapure water was used for all experiments (18.2 M Ω .cm, Millipore Direct-Q 3 UV).

3. Results and discussion

3.1. SSA characterization

Table 1 gives the concentrations of the major elements (% of DM) and of the heavy metals of concern (mg/kg DM) in the SSA samples as function of the incineration temperature. This table shows that the P concentration in the SSA remained almost constant with increasing incineration temperature (6.65 – 6.89% of DM), which was to be expected since P is not volatilized during incineration [20,32]. Furthermore, Table 1 shows that the concentration of most elements in the SSA was slightly lower in the sample obtained at 550 °C compared to higher incineration temperatures. This might be explained by the presence of a small amount of carbonates diluting the other elements in the SSA obtained at 550 °C. Indeed, whereas temperatures below 600 °C merely cause the oxidation of organic compounds, temperatures above 600 °C also result in the decomposition of inorganic compounds such as carbonates [3,33]. XRD analysis (see Figure 1.a) confirmed that no carbonates were present in the crystalline phase of the SSA samples obtained at incineration temperatures above 650 °C.

Table 1 Elemental composition of the SSA samples obtained at different incineration temperatures (% of DM or mg/kg DM).

		Temperature (°C)									
		550	650	750	800	825	850	875	900	1000	1100
Al	(% of DM)	6.01	6.21	6.19	6.26	6.25	6.20	6.26	6.20	6.29	6.30
Ca	(% of DM)	5.45	5.59	5.50	5.64	5.76	5.63	5.61	5.61	5.56	5.62
Fe	(% of DM)	9.67	9.97	10.04	9.86	10.04	10.06	10.09	10.04	10.07	10.04
K	(% of DM)	1.94	2.01	1.98	2.01	2.02	2.02	2.02	1.98	2.00	2.01
Mg	(% of DM)	1.24	1.29	1.29	1.28	1.30	1.30	1.32	1.29	1.31	1.30
Na	(% of DM)	0.34	0.35	0.36	0.34	0.35	0.35	0.35	0.35	0.38	0.39
P	(% of DM)	6.65	6.78	6.82	6.85	6.82	6.83	6.81	6.89	6.88	6.83
S	(% of DM)	0.50	0.49	0.43	0.36	0.29	0.25	0.19	0.14	0.03	0.02
Si	(% of DM)	18.79	19.19	19.16	19.22	19.58	19.56	19.33	19.42	19.35	19.05
Ti	(% of DM)	0.37	0.37	0.37	0.37	0.37	0.38	0.38	0.38	0.38	0.38
Cd	(mg/kg DM)	8.3	8.7	8.5	7.9	7.7	7.4	7.5	7.7	7.2	7.5
Cr	(mg/kg DM)	139	141	138	144	145	148	147	145	146	156
Cu	(mg/kg DM)	582	592	598	603	603	605	609	608	605	587
Ni	(mg/kg DM)	60	61	58	57	59	66	62	59	61	63
Pb	(mg/kg DM)	156	160	159	159	157	157	151	147	107	120
Zn	(mg/kg DM)	2114	2177	2151	2129	2147	2169	2161	2175	2042	2124

Several authors found that the release of alkali and alkaline earth metals (specifically Ca, K, Mg and Na) from biomass fuels in general increases with increasing incineration temperature [34–37]. Yet, in this work, the Ca, K, Mg and Na concentration in the SSA remained relatively constant with increasing incineration temperature (5.45 – 5.76% of DM, 1.94 – 2.02% of DM, 1.24 – 1.32% of DM and 0.34 – 0.39% of DM for a temperature increase from 550 to 1100 °C, respectively). This is related to the high concentration of Si in the SS and hence also in the SSA (18.79 – 19.58% of DM), retaining Ca, K, Mg and Na in the silicate fraction [34–37]. XRD analysis (see Figure 1.d) indeed showed that these alkali and alkaline earth metals are bound in the silicate fraction as diopside ($\text{CaMgSi}_2\text{O}_6$), microcline (KAlSi_3O_8), muscovite ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH},\text{F})_2$), plagioclase ($(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$) and smectite-related minerals (e.g., $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_{2-x}\text{H}_2\text{O}$), all having high boiling points. Table 1 also shows that in general the concentration of most major elements increased very slightly with increasing incineration temperature, which is related to a slight increase in incineration loss with increasing incineration temperature. This increasing incineration loss may reflect the losses of sulfates, chlorides (not measured in this research), oxides and other compounds with low boiling points [32]. Indeed, unlike all other major elements, the concentration of S in SSA decreased with increasing incineration temperature (from 0.50 to 0.02% of DM for a temperature increase from 550 to 1100 °C, respectively). Knudsen et al. [34] found that the release of S at high temperatures is highly influenced by the Si content in incinerated waste samples. For Si-rich waste samples, such as the SS investigated in this research, the alkali and alkaline earth metals originally bound in sulfates are more likely to be incorporated into (alumino-)silicates with increasing incineration temperature, in this way releasing the S as sulfur dioxide (SO_2) gas [34,38,39].

Table 1 also shows that the concentration of the heavy metals of concern, except Pb, remained almost constant with increasing incineration temperature (respectively, 7.2 – 8.7 mg/kg DM for Cd, 138 – 156 mg/kg DM for Cr, 582 – 609 mg/kg DM for Cu, 57 – 66 mg/kg DM for Ni and 2042 – 2177 mg/kg DM for Zn). Previous research showed that retention of heavy metals in SSA is related to high contents of Si, Al and Ca. In this case, heavy metals are likely to be incorporated into silicates and aluminates impeding their volatilization [35,40–46]. Pb is the only heavy metal for which the concentration in the SSA decreased at temperatures above 900 °C (see Table 1), which might be related to Pb volatilization [35,41,46,47].

3.2. SSA mineralogy

XRD analysis (see Figure 1) showed that the major minerals present in the crystalline phase of the SSA samples were quartz (SiO_2), whitlockite ($\text{Ca}_9(\text{Mg,Fe})(\text{PO}_4)_6(\text{PO}_3\text{OH})$), hematite (Fe_2O_3) and smectite-related minerals. Furthermore, Figure 1.f shows that the SSA samples contained a large amorphous fraction (26 – 48% of DM), of which the mineralogy could not be determined by XRD analysis. Between 550 and 650 °C, there was a decrease in the amount of amorphous fraction, after which it remained more or less constant between 650 and 900 °C. At temperatures above 900 °C, the amount of amorphous fraction started to increase again since higher incineration temperatures imply more glassy SSA due to agglomeration caused by silicate melting [37,48–51]. Unfortunately, the mineralogy of the heavy metals could not be detected by XRD analysis because of their low concentrations in the SSA samples [45,46].

With increasing incineration temperature, in general the amount of hematite, stanfieldite ($\text{Ca}_4(\text{Mg,Fe,Mn})_5(\text{PO}_4)_6$), whitlockite and microcline in the crystalline phase of the SSA samples increased, whereas the amount of Mg-Al-Fe-oxide ($\text{MgAl}_{0.6}\text{Fe}_{1.4}\text{O}_4$) and smectite-related minerals decreased.

According to the XRD analysis, the P in the crystalline phase of the SSA samples was only present in Ca-phosphates (stanfieldite and whitlockite). However, the results of the SMT protocol showed that a fraction of P in the SSA samples was bound as Al- and/or Fe-phosphates, which was confirmed in the EPMA analysis (see Supplementary Material, Figure S2 – S4). Since XRD analysis did not detect Al/Fe-phosphates in the crystalline phase, they were most likely present in the amorphous phase. The literature shows that Al/Fe-phosphates in the crystalline phase of SSA samples are mainly present in the form of berlinite (AlPO_4) and iron(III) phosphate (FePO_4) [3,7,8,19,52].

Figure 1 Mineral composition of the crystalline phase of the SSA samples obtained at different incineration temperatures (quantitative XRD analysis) (% of DM). (a) Carbonates; (b) Oxides; (c) Phosphates; (d) Silicates; (e) Sulfates; (f) Amorphous phase.²

* The mineral present is a "heat modified" smectite and it is unclear how closely its composition is related to that of "true" smectite.

² Calcite = CaCO_3 ; Hematite = Fe_2O_3 ; Mg-Al-Fe-oxide = $\text{MgAl}_{0.6}\text{Fe}_{1.4}\text{O}_4$; Stanfieldite = $\text{Ca}_4(\text{Mg,Fe,Mn})_5(\text{PO}_4)_6$; Whitlockite = $\text{Ca}_9(\text{Mg,Fe})(\text{PO}_4)_6(\text{PO}_3\text{OH})$; Cristobalite = SiO_2 ; Diopside = $\text{CaMgSi}_2\text{O}_6$; Microcline = KAlSi_3O_8 ; Muscovite = $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH,F})_2$; Plagioclase = $(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$; Quartz = SiO_2 ; Smectite-related = e.g. $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$; Tridymite = SiO_2 ; Anhydrite = CaSO_4 ; Gypsum = $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Based on the XRD results (Figure 1), the elemental composition (Table 1) and the results from the SMT protocol, the mass fraction of P bound in crystalline Ca-phosphates (whitlockite and stanfieldite), in amorphous Al/Fe-phosphates, and remaining P of unknown mineralogy in the amorphous phase was calculated as shown in Figure 2. This figure shows that the share of P bound in crystalline Ca-phosphates increased with increasing incineration temperature to reach a maximum of 51% at 875 °C, after which it decreased again with increasing incineration temperature. Furthermore, Figure 2 shows that the amount of P bound in Al/Fe-phosphates decreased with increasing incineration temperature. The observed conversion of Al/Fe-phosphates into Ca-phosphates with increasing incineration temperature is in line with previous research [3,17–19,23]. This conversion can be explained by reaction of Al/Fe-phosphates with Ca and Si compounds, forming Ca-phosphates and acid insoluble hematite, corundum or aluminosilicates [3,8,16,53]. In this work, EPMA showed that at least part of the P in the SSA sample obtained at 550 °C consisted of Fe-phosphates (see Supplementary Material, Figure S2). The increasing amount of crystalline hematite in Figure 1.b and the decreasing amount of P bound in amorphous Al/Fe-phosphates in Figure 2 confirm that Fe-phosphates were converted into Ca-phosphates and hematite with increasing temperature. Accordingly, the mass fraction of Fe bound in hematite increased from 19% of total Fe at 550 °C up to 91% of total Fe at 1000 °C, at which point hardly any Fe-phosphates could be present because almost all Fe was bound in crystalline hematite. On the other hand, the conversion of Al-phosphates into Ca-phosphates and corundum or aluminosilicates could not be observed from the XRD analysis in this work, since between 64 and 94% of total Al in the SSA samples was bound in the amorphous phase from which the mineralogy is unknown. Yet, extraction data for Al and Fe as function of the incineration temperature (see Supplementary Material, Figure S5 – S6) showed that the solubility of Al and Fe in sulfuric acid, hydrochloric acid and oxalic acid decreased with increasing incineration temperature. This confirms that with increasing incineration temperature the Al/Fe-phosphates in the SSA were converted to other P compounds and Al and Fe compounds poorly soluble in acids.

Figure 2 Mass fraction of P bound in crystalline Ca-phosphates (Ca-P) (whitlockite and stanfieldite), in amorphous Al/Fe-phosphates (Al/Fe-P), and remaining P of unknown mineralogy in the amorphous phase of the SSA samples obtained at different incineration temperatures (% of total P).

3.3. P extraction

Figure 3 gives the efficiency of P extraction from the SSA samples with sulfuric acid, hydrochloric acid, oxalic acid and sodium hydroxide as function of the incineration temperature. This figure shows that the P extraction efficiency for sodium hydroxide was lower than for the acidic extraction liquids. Sulfuric acid and hydrochloric acid, both inorganic acids, behaved similarly in terms of P extraction efficiency as function of the incineration temperature, whereas oxalic acid behaved differently at low (550 °C) and high (1000 and 1100 °C) incineration temperatures (see Figure 3).

Figure 3 shows that the P extraction efficiency with sodium hydroxide gradually decreased with increasing incineration temperature, which is related to the decreasing mass fraction of Al/Fe-phosphates in the SSA (see Figure 2). In general, Al- and/or Fe-phosphates dissolve well in alkaline extraction liquids such as sodium hydroxide, whereas Ca-phosphates do almost not dissolve in alkaline environment [14,30,54,55]. However, the P extraction efficiency with sodium hydroxide was generally lower than the mass fraction of Al/Fe-phosphates in the SSA samples obtained from the SMT protocol. The Al/Fe-phosphates mass fraction in the SSA samples decreased from 54 to 18% of total P (see Figure 2) over the considered temperature range, whereas the P extraction efficiency for sodium hydroxide decreased from 46 to 5% of total P (see Figure 3). Hence, a sodium hydroxide concentration higher than 0.5 N, an L/S ratio higher than 50 ml/g ash and/or a contact time longer than 2 h is required to extract all Al/Fe-phosphates from the SSA samples. This will, however, undesirably increase the extraction costs while still only a maximum of 54% of total P will be extracted, making the economic viability of P extraction with sodium hydroxide rather doubtful. In this regard, it seems interesting to investigate whether the addition of certain chemicals during the incineration process might shift the P mineralogy towards more Al/Fe-phosphates in the SSA, in this way increasing the P extraction efficiency for sodium hydroxide extraction. An interesting aspect of P extraction with sodium hydroxide is that the heavy metal co-extraction is relatively low [13,29,30], resulting in less elaborate extract purification, which in its turn might offset the costs of the chemical addition necessary to increase the share of Al/Fe-phosphates.

Figure 3 Efficiency of P extraction from the SSA samples obtained at different incineration temperatures (%). Extraction with sulfuric acid, hydrochloric acid and oxalic acid was performed with an L/S ratio of 10 ml/g ash, whereas extraction with sodium hydroxide was performed with an L/S ratio of 50 ml/g ash.

For sulfuric acid and hydrochloric acid, Figure 3 shows a parabolic correlation between the P extraction efficiency and the incineration temperature, with a maximum P extraction efficiency obtained around 850 °C (> 86% P extracted). The increasing P extraction efficiency between 550 and 850 °C could be related to the decreasing mass fraction of P bound as Al/Fe-phosphates in this temperature range (Figure 2). According to the EPMA results, at least part of the P in the SSA sample obtained at 550 °C was bound as Fe-phosphates (see Supplementary Material, Figure S2). However, it is unknown whether this P was bound as iron(III) phosphate (FePO_4), iron(II) phosphate ($\text{Fe}_3(\text{PO}_4)_2$) or other Fe-phosphates. Yet, this information is crucial to explain the P extraction trend because these Fe-phosphates show different behavior upon acid extraction. Iron(III) phosphate, for instance, is poorly soluble in acidic environment, whereas this is the opposite for iron(II) phosphate ($\text{pH} < 2$) (data from Visual MINTEQ and Levlin and Hultman [56]). Accordingly, if some of the Fe-phosphates in the SSA sample obtained at 550 °C consisted of iron(III) phosphate (which was previously detected in SSA samples by Liang et al. [3] and Atienza-Martinez et al. [8]), this would explain the somewhat lower P extraction with sulfuric acid and hydrochloric acid from this SSA sample. Increasing the incineration temperature would shift the P bound in this iron(III) phosphate towards Ca-phosphates, as previously discussed in section 3.2 [3,8,16], resulting in higher P extraction efficiencies since Ca-phosphates are generally well soluble in acids [3,30].

Furthermore, in Figure 3, it can be seen that the P extraction efficiency with oxalic acid remained relatively constant for SSA samples obtained between 550 and 850 °C, whereas it slightly increased with sulfuric acid and hydrochloric acid. This can be related to the decrease in organic bound P from 10 to 5% of total P in the SSA in this temperature range (shown by the results of the SMT protocol). Organic bound P can exist, for instance, in the form of orthophosphate mono- or diesters, which also occur in SS [3,22,57]. Szögi et al. [58] showed that both inorganic acids and (strong) organic acids can easily dissolve inorganic bound P, whereas (strong) organic acids can more easily dissolve organic bound P compared to inorganic acids.

For the acidic extraction liquids, the P extraction efficiency decreased with increasing incineration temperature above 850 °C (see Figure 3). This decreasing P extraction efficiency is related to the formation of agglomerates caused by silicate melting [3,8,48,59]. At incineration temperatures up to 850 °C, the SSA samples were rather brittle and could be ground easily into fine powders. In contrast, the SSA sample obtained at 1000 °C showed some agglomerates and at 1100 °C the whole SSA sample was agglomerated into hard chunks that were difficult to ground (see pictures in Supplementary Material, Figure S7). These agglomerates complicate the P extraction since the extraction liquid cannot properly penetrate the agglomerates and therefore cannot react with all P in the SSA [3,48]. In this study, however, the SSA samples were ground before extraction, which slightly promoted the acid penetration due to an increase in the solid/liquid contact surface [3,48]. For sulfuric acid and hydrochloric acid, the P extraction efficiency dropped from 87 to 46% and from 90 to 52%, respectively, in the temperature range of 850 to 1100 °C. In contrast, the decrease in the P extraction efficiency was larger for oxalic acid in the same temperature range, i.e., from 87 to 18%. This is probably related to the fact that oxalic acid ($\text{pK}_{a1} = 1.25$, $\text{pK}_{a2} = 4.27$) is a weaker acid than sulfuric acid ($\text{pK}_{a1} = -3$, $\text{pK}_{a2} = 1.99$) and hydrochloric acid ($\text{pK}_a = -7$).

3.4. Heavy metal extraction

As previously cited, it is assumed that many of the heavy metals are likely to be incorporated in silicates or aluminates [35,40–42,45,46]. Also in this work, neither XRD nor EPMA analysis could confirm the presence of these heavy metal silicates or aluminates because of their low concentrations in the SSA. Therefore, to explain the trends in heavy metal extraction efficiency as function of the SS incineration temperature, FactSage thermochemical calculations were used to predict the mineralogy of the heavy metals in the SSA. The results of two thermochemical calculations (with and without the selection of solution phases) are given in Supplementary material (Figure S8 – S9). However, FactSage thermochemical calculations have certain limitations: (1) thermodynamic data is lacking for complex phosphates and silicates; (2) only thermodynamics and no kinetics are taken into account; (3) infinite reaction times are assumed; (4) perfect mixing is assumed

[60–63]. Therefore, the statements below are to be considered as hypotheses based on the FactSage thermochemical calculations and literature data.

Figure 4 Amount of Cd, Cr, Cu, Ni, Pb and Zn extracted from the SSA samples obtained at different incineration temperatures (mg/kg DM). Extraction with sulfuric acid, hydrochloric acid and oxalic acid was performed with an L/S ratio of 10 ml/g ash, whereas extraction with sodium hydroxide was performed with an L/S ratio of 50 ml/g ash. The total amount of Cd, Cr, Cu, Ni, Pb and Zn in the SSA samples is given by the yellow line (data from Table 1). The sodium hydroxide extraction data for Cd, Cr, Ni and Pb was below the detection limit value of the ICP-OES measurements and is therefore not given in this figure (for sodium hydroxide extraction < 2.5 mg/kg DM for Cd, Cr and Ni, and < 7.5 mg/kg DM for Pb). (a) Cd extraction (mg/kg DM); (b) Cr extraction (mg/kg DM); (c) Cu extraction (mg/kg DM); (d) Ni extraction (mg/kg DM); (e) Pb extraction (mg/kg DM); (f) Zn extraction (mg/kg DM); (g) Total heavy metal extraction (Cd + Cr + Cu + Ni + Pb + Zn) (mg/kg DM).

Figure 4 gives the amount of Cd, Cr, Cu, Ni, Pb and Zn extracted from the SSA samples with sulfuric acid, hydrochloric acid, oxalic acid and sodium hydroxide as function of the incineration temperature. No data is given on the sodium hydroxide extraction for Cd, Cr, Ni and Pb since the concentrations in the extracts were below the ICP-OES detection limits (which was for the sodium hydroxide extraction liquid < 2.5 mg/kg ash for Cd, Cr and Ni, and < 7.5 mg/kg ash for Pb). In general, it can be concluded that sulfuric acid and hydrochloric acid resulted in the highest heavy metal extraction, whereas oxalic acid resulted in a slightly lower extraction for most of the heavy metals. Extraction with sodium hydroxide resulted in the lowest heavy metal extraction, which can be explained by the fact that most heavy metal compounds show

low solubility in alkaline environment [29,30,64]. The heavy metal extraction for the acidic extraction liquids is discussed more in detail in the following paragraphs.

Only small amounts of Cd were extracted from all SSA samples, ranging between 0.1 and 1.8 mg/kg DM (see Figure 4.a). According to the thermochemical calculations, Cd in the SSA is mainly bound by silicates or titanates. These minerals are in general poorly soluble, which is sustained by the fact that maximum 3% of all Si and maximum 2% of all Ti was extracted from the SSA samples in this work (data not shown). Studies by Pazos et al. [65] and Xiao et al. [66] also showed, by means of sequential extraction experiments, that > 80% of Cd in SSA is bound in a residual fraction consisting mainly of poorly soluble (alumino-)silicates. According to the thermochemical calculations, Cd would start to evaporate at temperatures above 800 °C and would be completely evaporated at temperatures above 1000 °C. However, the lab scale experiments in this work showed Cd stabilization in the SSA over the whole temperature range (see Figure 4.a). This again confirms the hypothesized formation of stable Cd-silicates or Cd-titanates, retaining the Cd in the SSA [40,45,46,60]. For sulfuric acid and hydrochloric acid, the Cd extraction remained fairly constant with increasing incineration temperature between 550 and 900 °C. Differently, for oxalic acid, the Cd extraction decreased with increasing incineration temperature in this temperature range. For all three extraction liquids, the decrease above 900 °C might be related to the formation of SSA agglomerates (see last paragraph in section 3.3). Furthermore, Figure 4.a shows that the Cd extraction was lower for oxalic acid compared to sulfuric acid and hydrochloric acid, which might be related to the formation of poorly soluble cadmium oxalate (CdC_2O_4) ($K_{\text{sp}} = 1.42 \times 10^{-8}$).

Figure 4.b shows that the amount of Cr extracted was relatively low (< 16 mg/kg DM) and that it decreased with increasing incineration temperature. According to the thermochemical calculations, soluble calcium chromate (CaCrO_4) occurs in SSA obtained at 550 °C, whereas at higher temperatures, the Cr mainly occurs as less soluble chromium oxide (Cr_2O_3) or bound in a molten slag phase. The thermochemical calculations show a sudden mineralogy change from chromate to oxide at 580 °C, while Figure 4.b rather shows a steady decrease in the Cr extraction between 550 and 850 °C. It is therefore difficult to link the lab experiments to the sudden mineralogy change predicted by the thermochemical calculations. Verbinnen et al. [67] reported a similar decrease when leaching Cr with water from contaminated sludge incinerated at temperatures ranging between 400 and 900 °C. They suggested that the highly soluble chromates present at low temperatures will start to form a silicate melt as the incineration temperature increases, in this way preventing the Cr from leaching [67].

The Cu extraction with sulfuric acid and hydrochloric acid fluctuated slightly with increasing incineration temperature (see Figure 4.c), ranging between 120 and 180 mg/kg DM. The Cu extraction with oxalic acid also fluctuated slightly in the SS incineration temperature range of 550 to 1000 °C (110 – 150 mg/kg DM) and then clearly decreased from 110 mg/kg DM (1000 °C) to 59 mg/kg DM (1100 °C). The Cu extraction with sodium hydroxide was much lower than with the acids, ranging between 2.9 and 6.2 mg/kg DM. The thermochemical calculations show that up to temperatures of 800 °C, all Cu is bound to ferrite (CuFe_2O_4), which is confirmed by research from Cai et al. [45] and Fraissler et al. [60]. Furthermore, the thermochemical calculations show that at temperatures above 800 °C, the fraction of Cu bound to ferrite decreases whereas the fraction of Cu bound in a molten slag phase increases up to 100% at temperatures above 875 °C. In contrast to the thermochemical calculations, heavy metal sequential extraction experiments for different SSA samples by Latosińska and Czapik [68], J. Li et al. [64,69], Li et al. [70], Pazos et al. [65] and Xiao et al. [66] showed only between 0.5 and 15% of total Cu bound to Fe- or Mn-oxides. In their research, they divided the heavy metal minerals into four fractions: (1) acid soluble/exchangeable fraction (metals bound to carbonates); (2) reducible fraction (metals bound to Fe and Mn-oxides); (3) oxidizable fraction (metals bound with organic matter or occurring in the form of sulfides); (4) residual fraction (metals bound with (alumino-)silicates). The oxidizable and residual fraction are considered to be rather stable and immobile. They found that between 55 and 90% of all Cu in SSA occurred in the residual fraction and was hence bound with for instance (alumino-)silicates. Moreover, between 8 and 40% of all Cu occurred in organic or sulfide bounds (oxidizable fraction). From their research, it could be concluded that most of the Cu (> 80%) in SSA was bound in the immobile fractions [64–66,68–70]. Research by J. Li et al. [69] demonstrated that small amounts of these immobile fractions still dissolved upon extraction with sulfuric acid and oxalic acid (no hydrochloric acid used in their experiments). Furthermore, they showed that the Cu in the reducible fraction almost completely dissolved upon extraction with sulfuric acid and oxalic acid. However, it should be noted that the sulfuric acid and oxalic acid concentrations used by J. Li et al. [69] were twice as high as in this work, which affects the extraction efficiency of the heavy metals [3,13]. In this work, between 20 and 30% of all Cu was extracted with sulfuric acid and hydrochloric acid, while this was between 10 and 26% with oxalic acid. Hence, following the results from J. Li et al. [69], it is assumed that only a small fraction of Cu-ferrite was present in the SSA samples which was completely dissolving upon extraction, whereas the rest of the Cu occurred in poorly soluble compounds such as (alumino-)silicates or sulfides.

Figure 4.d shows that the amount of Ni extracted was < 7 mg/kg DM over the full temperature range. Furthermore, from Figure 4.d it is clear that the incineration temperature had little effect on the Ni extraction, except for the slight decrease between 550 and 650 °C. However, the thermochemical calculations reveal no difference in Ni mineralogy for SSA samples at 550 and 650 °C that can explain this slight decrease. The thermochemical calculations show that all Ni is bound by silicates, titanates or aluminate and ferrite spinels and with increasing incineration temperature above 850 °C, an increasing share of Ni is incorporated into a molten slag phase. The binding of Ni in ferrite spinel in SSA was previously discussed in a study of Fraissler et al. [60], whereas the binding of Ni in silicates was previously discussed in a study of Cai et al. [45]. Silicates, titanates and ferrite and aluminate spinels were shown to immobilize Ni, in this way preventing the Ni from extracting [45,71]. This is confirmed by sequential extraction experiments showing that a substantial fraction of Ni in SSA is bound in an immobile fraction [64,66,68,69].

For Pb, there was a substantial difference between extraction with hydrochloric acid and extraction with sulfuric acid or oxalic acid (see Figure 4.e). The low Pb extraction with sulfuric acid and oxalic acid (< 3 mg/kg DM) can be explained

by the formation of poorly soluble lead(II) sulfate (PbSO_4) ($K_{\text{sp}} = 2.53 \times 10^{-8}$) and lead(II) oxalate (PbC_2O_4) ($K_{\text{sp}} = 4.8 \times 10^{-10}$), respectively [72,73]. With hydrochloric acid, the Pb extraction increased from 18 to 45 mg/kg DM between 550 and 850 °C, after which it remained fairly constant between 850 and 900 °C, and then decreased again sharply to 15 mg/kg DM between 900 and 1100 °C (see Figure 4.e). The decrease in Pb extraction between 900 and 1100 °C has two clear explanations. First, the total amount of Pb in the SSA samples decreased in this temperature range due to partial Pb volatilization (yellow line in Figure 4.e) [41,60]. Second, agglomerate formation incorporated Pb in the silicate melt [35,41,42], which showed low solubility (maximum 3% of all Si extracted in this research). The thermochemical calculations indeed confirm that a molten slag phase is formed at temperatures from around 800 °C. However, the increase in Pb extraction between 550 and 850 °C with hydrochloric acid is not so obvious to explain. According to the thermochemical calculations, there are three temperature zones in which the Pb mineralogy remains relatively constant. Between 550 and 750 °C all Pb occurs bound as lead(II) hexaaluminate ($\text{PbAl}_{12}\text{O}_{19}$). Furthermore, between 750 and 825 °C almost all Pb occurs bound as lead(II) sulfate, whereas between 825 and 1100 °C, Pb mainly occurs bound in a molten slag phase with a small amount of Pb evaporating as gaseous lead(II) oxide (PbO). The extraction data in Figure 4.e show a gradual increase in Pb extraction, whereas the thermochemical calculations only indicate sudden mineralogy changes around 750 and 825 °C, making it difficult to link this quantitatively to the increasing Pb extraction. Besides, in general, lead(II) hexaaluminate, lead(II) sulfate and Pb bound in a molten slag phase all exhibit poor solubility [74]. Therefore, the mineralogy changes predicted by the thermochemical calculations did not give a clear explanation for the increasing Pb extraction with increasing temperature.

Of the considered heavy metals, Zn was not only present in the SSA at the highest concentrations but was also extracted to the highest extent (see Figure 4.f). With increasing incineration temperature, Zn extraction showed a decreasing tendency for both acidic extraction and alkaline extraction (see Figure 4.f). This is in line with results found by Liang et al. [3] for acidic extraction. Furthermore, Li et al. [70] found that in SSA obtained at 500 °C, about 60% of all Zn showed high mobility and leachability, whereas in SSA obtained at 800 °C, this decreased to about 35%. The increase in Zn extraction between 1000 and 1100 °C observed in Figure 4.f was rather unexpected since it was presumed that the formation of agglomerates at 1100 °C would decrease the Zn extraction. At temperatures below 1000 °C, the thermochemical calculations show the incorporation of Zn in a silicate or an aluminate and ferrite spinel phase. Furthermore, the thermochemical calculations show that above 800 °C a Zn containing slag phase starts to form, while Zn mainly occurs in a molten slag phase at temperatures above 1000 °C. The presence of Zn bound in aluminate spinel, ferrite spinel and silicates in SSA was previously discussed in studies by Cai et al. [45], Fraissler et al. [60], Guo et al. [46], Liu et al. [75] and Nowak et al. [42]. However, aluminate spinels, ferrite spinels and silicates generally show poor solubility, so the results of the thermochemical calculations do not sustain the Zn extraction trend observed for SSA samples obtained at 550 and 650 °C. Since high Zn extraction was obtained at 550 and 650 °C, it is hypothesized that some of the Zn at these temperatures was bound in well soluble compounds such as for instance zinc sulfate (ZnSO_4) or zinc chloride (ZnCl_2). At higher temperatures, the Zn was most likely bound as aluminate spinel, ferrite spinel or silicates as predicted by the thermochemical calculations. This is confirmed by sequential extraction experiments performed by Chen et al. [51], showing an increase in Zn bound in a stable residual fraction with increasing incineration temperature. Furthermore, Figure 4 shows that Zn was the only heavy metal showing relatively high extraction for sodium hydroxide, which is related to its amphoteric character allowing it to dissolve in both acid and alkaline environment [76].

3.5. Selection of optimal incineration temperature

A general conclusion is that higher incineration temperatures immobilized the heavy metals in the SSA, in this way decreasing the heavy metal extraction (see Figure 4). Figure 4.g shows that the total heavy metal extraction was lowest at a SS incineration temperature of 1000 °C. However, at 1000 °C, the P extraction efficiency was below 73% due to agglomerate formation (see Figure 3). Hence, if SS would be incinerated at 1000 °C, the heavy metal co-extraction would be minimal, in this way reducing the downstream processing costs for heavy metal removal. However, in this case, more than 27% of P is not extracted from the SSA. Therefore, the selection of the optimal incineration temperature will depend on economic considerations such as the trade-off between P extraction efficiency (affecting the revenue) and heavy metal co-extraction (affecting the downstream processing costs). Hence, combining the data in Figure 3 and Figure 4.g and taking into account the above mentioned economic considerations, it can be concluded that an incineration temperature in the range of 800 to 850 °C seems most optimal for obtaining sufficiently high P extraction combined with low co-extraction of heavy metals. In this temperature range, all acidic extraction liquids showed similar P extraction efficiencies (respectively, 87 – 90%, see Figure 3). In contrast, oxalic acid showed lower co-extraction of heavy metals compared to sulfuric acid and hydrochloric acid (respectively, about 17% of heavy metals extracted compared to about 23%, see Figure 4.g). However, from an economic point of view, it might be most interesting to use sulfuric acid because it is cheaper than oxalic acid and hydrochloric acid [13,14,77].

4. Conclusions

Whereas the total content of P and heavy metals in the SSA remained fairly constant with increasing SS incineration temperature, the extraction of these elements with sulfuric acid, hydrochloric acid, oxalic acid and sodium hydroxide showed considerable variation, which can be related to changes in P and heavy metal mineralogy:

- Increasing incineration temperature decreased the mass fraction of P bound in Al/Fe-phosphates in SSA, in this way decreasing the efficiency of P extraction with sodium hydroxide.
- The efficiency of P extraction with sulfuric acid, hydrochloric acid and oxalic acid increased in the temperature range 550 – 850 °C. There are two possible explanations for this: (1) with increasing incineration temperature, iron(III) phosphate, which is poorly soluble in acidic environment, was converted into more soluble Ca-phosphates; (2) with increasing incineration temperature, the fraction of organic bound P decreased, which increased the P extraction with the inorganic acids sulfuric acid and hydrochloric acid, but hardly affected the P extraction with oxalic acid.
- The efficiency of P extraction with acids decreased in the temperature range 850 – 1100 °C, which is related to the incorporation of P into a poorly soluble silicate melt (agglomerate formation).
- Increasing incineration temperature enhanced heavy metal immobilization in the SSA, in this way decreasing the heavy metal co-extraction. SSA obtained at 1000 °C resulted in lowest total heavy metal co-extraction.

Overall, it can be concluded that incinerating SS between 800 and 850 °C offers the best compromise between high P extraction and low heavy metal co-extraction from the obtained SSA. In this temperature range, all acidic extraction liquids showed similar P extraction efficiencies, whereas the heavy metal co-extraction was lowest for oxalic acid.

5. Suggestions for further research

The scope of this research was to evaluate the influence of the incineration temperature on the P and heavy metal extraction from SSA. Further research could also evaluate the influence of chemical addition during the incineration process to examine whether and to which extent this affects the P and heavy metal extraction from SSA. For instance, chemical addition might increase the Al/Fe-phosphates content of SSA in this way improving the economic viability of sodium hydroxide extraction. Besides, it is interesting to evaluate whether chemical addition affects the immobilization of the heavy metals so that less heavy metals would be co-extracted in acidic environment.

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Supplementary Material

See appendix.

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