Comparison of Phosphorus Recovery from Incinerated
Sewage Sludge Ash (ISSA) and Pyrolysed Sewage Sludge Char (PSSC)

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Abstract

This research compares and contrasts the physical and chemical characteristics of incinerator sewage sludge ash
(ISSA) and pyrolysis sewage sludge char (PSSC) for the purposes of recovering phosphorus as a P-rich fertiliser. Interest in P recovery from PSSC is likely to increase as pyrolysis is becoming viewed as a more economical method of sewage sludge thermal treatment compared to incineration. The P contents of ISSA and PSSC are 7.2-7.5% and 5.6%, respectively. Relative to the sludge, P concentrations are increased about 8-fold in ISSA, compared to roughly 3-fold in PSSC. Both PSSC and ISSA contain whitlockite, an unusual form of calcium phosphate, with PSSC containing more whitlockite than ISSA. Acid leaching experiments indicate that a liquid/solid ratio of 10 with 30 minutes contact time is optimal to release PO$_4$-P into leachate for both ISSA and PSSC. The proportion of P extracted from PSSC is higher due to its higher whitlockite content. Heavy metals are less soluble from PSSC because they are more strongly incorporated in the particles. The results suggest there is potential for the development of a process to recover P from PSSC.

**Keywords:** incineration; incinerator sewage sludge ash (ISSA); phosphorus recovery; pyrolysed sewage sludge char (PSSC); pyrolysis; sewage sludge
1. Introduction

Each year approximately 11.6 million tonnes of dry municipal sewage sludge is produced in Europe (Milieu Ltd., WRc and RPA, 2010). Greece landfills more than 90% of its sludge, while France, Spain and the UK use more than 65% sludge of their sludge in agriculture, and the Netherlands and Switzerland incinerate all their sludge (Milieu Ltd., WRc and RPA, 2010). Energy recovery from sewage sludge using thermal processes such as incineration, pyrolysis, and gasification are gaining more consideration. On average, 27% of sewage sludge is incinerated in Europe (Milieu Ltd., WRc and RPA, 2010). However, incineration has been in decline in the UK because of its high operating costs, while pyrolysis is seen as potentially more viable due to its higher energy recovery (Mills et al., 2014).

The fundamental difference between incineration and pyrolysis is the presence or absence of oxygen. Incineration refers to combustion in excess oxygen at high temperature, usually with recovery of heat, for example to raise steam to produce power through a steam turbine, leaving an inert solid
ash residue (Samolada & Zabaniotou, 2014; Tyagi & Lo, 2013). By contrast, pyrolysis is thermal decomposition under oxygen-starved conditions; for sewage sludge, pyrolysis produces a ‘carbonized’ solid char, ash, pyrolysis oils, water vapour and combustible gases (Samolada & Zabaniotou, 2014; Tyagi & Lo, 2013). The low operating temperature (500°C) of conventional pyrolysis compared to incineration leads to lower heavy metal concentrations in pyrolysis gas (Samolada & Zabaniotou, 2014).

There has been much interest in the recovery of phosphorus (P) from ISSA either as phosphoric acid or as a fertiliser (Adam et al., 2009; Donatello et al., 2010; Franz, 2008; Ottosen et al., 2013; Ateinza-Martinez et al., 2014; Azuara et al., 2013; Biswas et al., 2009; Cohen, 2009). P recovery from waste might be a partial solution to the uncertain future of rock phosphate supplies (Kleemann et al., 2015). ISSA has been the subject of considerable research, with its chemical and physical properties being frequently reported. However, there is much less information available on pyrolysed sewage sludge char (PSSC): much research has been devoted to determining the effects of temperature on pyrolysis products, with gas and oil
yields as the main focus, but there remain many gaps in
knowledge on the chemical and physical properties of PSSC. In
particular, there appear to be no studies on P recovery from
PSSC using techniques, primarily acid leaching, generally
applied to ISSA. A review by Fonts et al. (2012) confirms that P
recovery from ISSA has been explored but that recovery from
PSSC had been overlooked thus far.

P recovery from ISSA has been reported in literature, but little
research has compared P recovery from the two residues. The
research reported here was undertaken to compare and
contrast the physical and chemical profiles of ISSA and PSSC
before and after acid leaching. The release of P and heavy
metals from ISSA and PSSC using acid leaching are compared
and discussed.

2. Materials and methods

2.1 Ash and char source

ISSA was sourced from two different Thames Water Waste
Water Treatment Plants (WWTPs), Crossness and Beckton,
which treat wastewater from a population equivalent of 5.5
million. Beckton and Crossness sewage sludge incinerators operate at temperatures in the range 850-950°C: incinerators must operate above 850°C to ensure minimal dioxin formation, but below 950°C to ensure slag formation (melting of ash) does not occur. The ISSA samples discussed here were taken at two different dates: Table 1 refers to samples taken 12 months after the samples to which the other results refer.

For PSSC, dried sludge was imported from Malaga WWTP (Spain) and processed by Environmental Power International (EPi) Ltd. to produce char (PSSC) in a full scale flash-pyrolysis unit designed to maximise syngas production by minimising the amount of organic carbon left in the char. The process operates at 850°C and just above atmospheric pressure, with a residence time of 2 minutes. The same sludge and PSSC samples were used throughout the tests reported here.

2.2 Solid and liquid analyses methods

Solids samples of ISSA and PSSC were characterised using X-ray powder diffraction (XRD) at an accredited laboratory in Brunel University (UK) to determine the elemental and mineralogical composition before carrying out acid leaching tests. Scanning electron microscope (SEM) was used to compare the physical
forms and ICP-MS analysis was used to determine the elemental concentrations of all samples pre- and post-acid leaching.

To quantify solubilised Ca-P, Al-P and Fe-P in the ISSA and PSSC solid samples, a form of the Sekiya method first described in 1983 was utilised (Zhang et al., 2001). Details of the adapted procedure can be found in Supplementary Data, along with the procedure for acid leaching experiments using sulphuric acid at a range of liquid/solid ratios and contact times.

In this research, the mineral whitlockite is of particular importance with regards to the acid leaching of P into leachate. Whitlockite \([\text{Ca}_9X(\text{PO}_4)_7]\), where X is most commonly Fe but may also be Cu, H, Al, Ni, or Sr] is an unusual form of calcium phosphate, commonly found in human urinary stones and salivary stones (Bazin et al., 2007). High quantities of whitlockite are beneficial in the recovery of P, because it is readily dissolved from the whitlockite particle using acids (Donatello, et al., 2010). The quantities of whitlockite found in ISSA and PSSC are discussed in section 3.2.

In this paper, “primary macronutrients” refers to P, N, and K, and “secondary macronutrients” denotes S, Mg, and Ca.
Micronutrients” encompasses Al, Cu, Zn, Fe, Ni, Mo, Mn, and B, while heavy metals refers to Pb, Se, Cr, Hg, Cd, and As.

3. Results

3.1 Elemental composition

Table 1 shows the elemental concentrations of sludge before and ISSA/PSSC after incineration or pyrolysis. The imported sludge destined for pyrolysis and resulting PSSC contain greater concentrations of macro- and micro- nutrients than Beckton and Crossness sludges and their ashes, ISSA(b) and ISSA(c). Incineration and pyrolysis concentrates most elements, but Table 1 shows that N concentration decreases across all samples, significantly so in ISSA. Cd concentration is roughly halved by pyrolysis, but increased by 5.0 and 5.4 times in ISSA(b) and ISSA(c), respectively. Concentrations of As remain roughly constant in PSSC, but increase by 4.8 and 6.9 times in ISSA(b) and ISSA(c). Relative to the sludge, P concentrations are enriched by 7.9, 6.7, and 2.5 times in ISSA(b), ISSA(c) and PSSC, respectively. The sludge used for pyrolysis contains significantly higher concentrations of Fe
than the Beckton and Crossness sludges, but concentrations after pyrolysis/incineration are similar.

Table 2 compares the elemental composition of ISSA and PSSC solid samples; as noted above, Tables 1 and 2 refer to identical PSSC samples but the two tables refer to ISSA samples taken on different dates although the samples and their compositions are broadly comparable. Table 2 shows that the samples contain high concentrations of P, but differ in their K and especially N contents. Only PSSC contains significant concentrations of the primary macronutrient N. In terms of secondary macronutrients (Table 2), ISSA(b) contains less S and ISSA(c) contains more Ca than other samples. Viewing micronutrients in Table 2, PSSC contains significantly lower Al and Ni concentrations and higher Fe than ISSA. The two ISSA samples contain very similar concentrations of Cu, more than 1200 mg/kg, whereas the concentration in PSSC is less than 400 mg/kg. Referring to Table 1, Cu in the sludge is enriched by 6.5-6.9 times in the ISSA samples compared to 2.2 times in the PSSC. Table 2 shows that PSSC contains much lower concentrations of heavy metals than ISSA. Evidently a large
proportion of the heavy metals are volatilised in flash pyrolysis; the significance of this is discussed below.

3.2 XRD and SEM analysis before acid leaching

Mineralogical analysis reveals various similarities between the solids samples, quantified in Table 3. XRD analysis shows that ISSA(b), ISSA(c) and PSSC all contain quartz, anhydrite, and whitlockite compounds. Table 3 shows that ISSA(b) and PSSC both contain a phosphate identified with a strontium phase while only PSSC contains calcite.

SEM analysis was conducted to determine the difference in form between ISSA and PSSC solid samples. Figure 1 shows the striking difference between the structure of ISSA (Figure 1a) and PSSC (Figure 1b) at similar magnifications: PSSC consists of “honeycomb” porous particles whereas ISSA consists of smaller distinct particles with less obvious porosity. The BET surface area of PSSC measured during this research is 8.8 m$^2$/g compared to 18.0 m$^2$/g and 23.8 m$^2$/g of ISSA(b) and ISSA(c), respectively, reported for these materials by Donatello et al. (2010).

3.3 Fractionation
The applied fractionation method measures the concentrations of Ca-P, Al-P and Fe-P bound compounds using a series of leaching steps. Figure 2 shows that there is little Fe-P binding in any of the samples. The most prevalent type of P bond is Ca-P, with more Ca-P bonding in PSSC than in either ISSA sample.

3.4 Acid leaching

3.4.1 Contact time

Figure 3a shows the concentrations of PO$_4$-P released from ISSA into leachate measured over a two hour period. These experiments were conducted only on ISSA samples before PSSC samples became available. The concentration of PO$_4$-P in the leachate increased by 49% between 15 and 30 minutes contact times, after which PO$_4$-P release remained unchanged until the end of the experiment at 2 hours contact time. Figure 3b displays the concentrations of PO$_4$-P and Total P measured in the leachate after 30 minutes and 24 hours leaching time: the extended contact time did not result in more P leaching. Thus 30 minutes contact time would be sufficient in a process to recover phosphorus from ISSA.
3.4.2 Liquid/solid ratio

Detailed outcomes of experimental work on the effect of liquid/solid ratios (LS) on the dissolution of P, Mg, and Zn from all three materials are provided in Figure S-1. Increasing the solid/liquid ratio (LS) in the range 5 to 20 increases the percentage of nutrients extracted from each solid but reduces the resulting leachate concentration.

3.4.3 Phosphorus

Figure 4 displays the %P extraction from ISSA and PSSC solid samples across six different acid molar concentrations. Maximum extraction from ISSA occurred around 0.6M: 90±1% from ISSA(b) at 0.6M LS 20 and 93±2% from ISSA(c) at 0.5M LS 20. Higher acid concentrations do not achieve significantly greater P extraction.

The proportion of P extracted from PSSC was lower at the optimal acid concentration for ISSA. Therefore, higher molar concentrations, 0.8M and 1M, were tested in leaching experiments for PSSC. The highest average extraction of P achieved from PSSC was 89±9% at 0.8M and LS 10. In an individual PSSC sample an extraction of 97% was calculated at
0.8M LS 10, the highest %P extraction of any sample at 30 minutes contact time. Interestingly, for PSSC, highest acid molar concentrations of 1M did not achieve best P release; maximum P concentration in leachate and %P extraction were measured at 0.8M.

Comparing Figure 4 and Figure 5 shows that %P extraction and liquid P concentrations do not follow the same trend. Maximum P concentrations in the leachate were achieved by ISSA(b) and ISSA(c) at 0.6M LS 5 and by PSSC at 0.8M LS 5. This is in agreement with Figure S-1a which shows that the highest P concentrations in liquid were measured at LS 5.

3.4.4 Macronutrients

Figure S-2 shows that low %Ca extractions were measured across the series of experiments, ranging from 3 to 13% for ISSA(b), 3 to 11% for ISSA(c) and 2 to 27% for PSSC. Figure S-3 confirms that significant concentrations of Ca remain unleached in ISSA and PSSC solid samples. K and Mg percentage extractions are much higher than Ca: 9 to 61% and 22 to 78% extraction respectively from ISSA(b), 11 to 54% and 35 to 75% respectively from ISSA (c) and 12 to 76% and 26 to
85% from PSSC. However, while the fractions of Ca extracted are lower than for K and Mg, higher concentrations of Ca are measured in leachate than K (Supplementary Data Figure S-4).

3.4.5 Micronutrients

As molar acid concentrations increase, extraction of micronutrients from ISSA and PSSC and their concentration in the resultant leachates generally increase (see Figures S-5 and S-6 in Supplementary Data). Leachates from PSSC contain higher concentrations of micronutrients than those from ISSA (Figure S-5).

Comparing Figures S-7 and 6a reveals a different response of Fe and Cu to acid leaching of PSSC and ISSA: PSSC releases more Fe whereas ISSA releases more Cu. Table 2 shows that PSSC contains lower concentrations of Cu in the unleached solid compared to ISSA: concentrations of Cu in PSSC range from 0.1 to 17mg/l, while in ISSA(b) Cu ranges from 43 to 175mg/l and in ISSA(c) from 32 to 155mg/l. Whereas P extraction is dependent upon LS ratio (see above), Cu extraction is not. However, it was found in this work that Cu extraction depends very strongly on LS ratio for both PSSC and ISSA (Figure 6b), with the highest % extractions occurring at
high LS ratios. Figures S-8 to S-16 of Supplementary Data provides further details on extractions and concentrations of macro- and micro- nutrients in ISSA and PSSC samples.

### 3.4.6 Heavy metals

Figure S-17 of Supplementary data shows there are very low concentrations of heavy metals in PSSC leachate compared to both ISSA leachate samples. This is especially clear when viewing As and Cd in the separate graphs of Figure S-18 and S-19. Table 2 shows that PSSC contains low levels of As and Cd in unleached solid samples, explaining the low concentrations in leachate. PSSC maximum extraction for As is 72% compared to 97% and 98% measured by ISSA(b) and ISSA(c).

### 3.5 Summary

There are major differences between the ways nutrients and heavy metals in sludge behave in pyrolysis and incineration. Relative to the sludge, P concentrations are enriched by 7.9, 6.7, and 2.5 times in ISSA(b), ISSA(c) and PSSC, respectively. Following thermal treatment only PSSC contains significant residual concentrations of N, compared to ISSA samples. PSSC contains much lower concentrations of heavy metals than
ISSA; evidently a large proportion of the heavy metals are volatilised in flash pyrolysis. XRD analysis shows that all solid samples contain quartz, anhydrite, and whitlockite minerals. PSSC consists of “honeycomb” porous particles whereas ISSA consists of smaller distinct particles with less obvious porosity. During acid leaching most \( \text{PO}_4 \)-P was released into leachate in the first 15-30 minutes contact time. Increasing the LS ratio in the range 5 to 20 increases the percentage extraction of P from solid but reduces the leachate P concentration. High P extractions, around 90%, were achieved from both ISSA solid samples at acid molar concentrations of 0.3M and LS 20. PSSC showed the highest extraction of P, greater than 90%, at 0.8M and LS 10. Maximum P concentrations in leachate were achieved for ISSA(b) and ISSA(c) each at 0.6M LS 5 and for PSSC at 0.8M LS 5. Significant concentrations of Ca remain unleached in all solid samples. Low concentrations of heavy metals in PSSC acid leachate were measured compared to both ISSA samples.

4. Discussion
4.1 Elemental composition

Table 1 shows that a major difference between the residues from incineration and pyrolysis lies in the enrichment of nutrients and heavy metals. Table 2 confirms that PSSC contains significantly more N and less Cd, Hg, and Pb than ISSA. Presence of N with low heavy metal concentration is important when producing a nutrient-rich fertiliser from ISSA or PSSC.

During incineration N-containing volatiles evolve early in the process, N is oxidised and NO\textsubscript{x} emissions produced (Rink et al., 1993). In comparison, the oxygen-starved conditions of pyrolysis ensure that N and S are not oxidised but are retained in the solid residue (Pokorna et al., 2009). Table 2 shows the resulting differences in the concentrations of primary macronutrients in ISSA and PSSC. The percentage P contents of ISSA(b), ISSA(c), and PSSC are 7.5, 7.2 and 5.6, respectively, broadly consistent with the values of 5.6% and 4.3% P reported by Bridle & Pritchard (2004) and Gao et al. (2014), respectively, and with P contents in the range 5.7% to 7.6% reported by Donatello et al. (2010). The variation of P contents and other nutrients are attributed to different WWTP influent...
characteristics, WWTP processes, and incineration/pyrolysis characteristics.

The fate of the heavy metals depends on the operating conditions during thermal processing. At the higher temperatures used for incineration, the heavy metals are largely volatilised (Jin et al., 2014; Yuan et al. 2015). This is also evident in this work, although the small yields of ISSA mean that the concentrations of heavy metals in ISSA appear as substantial. The wide variety of enrichment values reported for different processes is attributable to the different thermal stabilities of heavy metal species in sewage sludge during thermal treatment (Yuan et al., 2015) and to differences in process design. Volatile metals such as Cd and Hg can escape the precipitators because they are in a gaseous form. However, as temperatures fall they condense onto fine particle surfaces. The resultant particles are captured in the filtration system and may then be added back into the bulk of the ash from the precipitators.

A wider range of temperatures is used in pyrolysis. In conventional pyrolysis processes operating up to 500°C volatilisation is limited (Samolada & Zabaniotou, 2014). If the
pyrolysis gases remain at high enough temperature, the metals can remain as vapour to condense in the oil quench to form part of the oil cake which leaves the process as a separate stream and so will not appear in the resulting PSSC solids. At higher temperatures, many metals are essentially volatilised completely and are therefore not present in the remaining PSSC (Bridle & Pritchard, 2004; Hossain et al., 2011; Kistler et al., 1987). At temperatures above 750°C, Cd reduces to its metallic form and evaporates during pyrolysis (Kistler et al., 1987). Hg behaves similarly to Cd, evaporating during pyrolysis at temperatures as low as 350°C (Kistler et al., 1987). Both of these effects agree with the PSSC compositions found here (Table 1). According to Hwang et al. (2007), Pb and Zn also volatilise during pyrolysis up to 500°C; for this work, Table 1 shows higher Pb and Zn concentrations in the PSSC relative to the sludge but this represents a loss when the lower PSSC mass is accounted for. For As, Jin et al. (2014) note a loss of between 19% and 33% in their PSSC samples; in this research, As concentrations were essentially the same in the sludge and the PSSC (Table 1), representing a loss corresponding to the loss of total material between the sludge and the residue. The movement and behaviour of heavy metals in incineration and...
Pyrolysis is important to understand as this informs the heavy metal content of leachate following acid leaching, which will ultimately be used to produce a low heavy metal, nutrient-rich fertiliser.

The different pH values of ISSA and PSSC samples are attributed to the presence of Ca which is the main element responsible for alkalinity (Hwang et al., 2007; Kuligowski & Poulsen, 2010). The removal of acidic oxygen-containing surface groups during pyrolysis may also be responsible for the high pH of PSSC (Stammbach et al., 1989).

### 4.2 XRD analysis before acid leaching

According to this research, the inorganic fraction of PSSC is mineralogically similar to ISSA but contains calcite and greater amounts of whitlockite compounds. Calcite is stable up to ~825°C above which it decomposes to calcium oxide (Sikes et al., 2000). ISSA(c) and PSSC samples contain anhydrite, associated with the fact that they each contain more Ca than ISSA(b), see Table 2. The only other mineralogical analysis of PSSC appears to be that reported by Abrego et al. (2009). Following pyrolysis at 800°C, Abrego et al. report the presence of quartz, feldspars (albite and anorthite), calcium oxide,
oldhamite, troilite, pyrrhotite, and barringerite in undigested PSSC samples (Abrego et al., 2009). Only the presence of quartz is common between this study and that of Abrego et al. (2009). The mineral content, especially whitlockite, of ISSA and PSSC is important to measure because this influences the dissolution of elements into leachate.

XRD analysis of ISSA agrees well with the literature in which whitlockite compounds are frequently reported (Cheeseman et al., 2003; Cyr et al., 2007; Donatello et al., 2010; Mahieux et al., 2010; Nowak et al., 2013; Petzet et al., 2012). Ca is a common element found in wastewaters and is responsible for hard water, which explains the high whitlockite content of all samples. As shown in Figure 2, calcium phosphorus bonding is present in both ISSA and PSSC. This may be in the form of whitlockite or hydroxylapatite \([\text{Ca}_5(\text{PO}_4)_3\text{OH}]\) depending upon the sludge composition and incineration or pyrolysis temperature and residence time (Cyr et al., 2007). Adam et al. (2009) reported that above 750°C whitlockite is not present in ISSA because it reacts with CaCl\(_2\), forming chlorspodiosite and chlorapatite. However, whitlockite compounds were observed here in ISSA produced at 850-950°C. Quartz appears to be a
common mineral in ISSA with many researchers reporting its presence (Cheeseman & Virdi, 2005; Cyr et al., 2007; Donatello et al., 2010; Franz, 2008; Mahieux et al., 2010; Nowak et al., 2013) due to the universal presence of silica in sewage sludge (Cohen, 2009). Quartz has also been detected in ISSA formed at even higher temperature, up to 1050°C (Adam et al., 2009), confirming the stability of quartz.

Nowak et al. (2013) reported concentrations of 34.4% whitlockite, 28.9% quartz, 6.8% anhydrite and 2.9% calcite in ISSA samples, along with lower concentrations of hematite, potassium-calcium sulphate and magnetite. Cyr et al. (2007) measured 26% calcium phosphates (whitlockite) and 14% quartz along with gypsum, feldspar, micas and glass in their ISSA samples. The results of the analysis here agrees well with Nowak et al. (2013) and Cyr et al. (2007), showing whitlockite as the most abundant mineral (60-65%), followed by quartz (20-31%) and anhydrite (4-15%).

The structure of PSSC (Figure 2) is typical of that formed in rapid pyrolysis: rapid evolution of gas and carbonisation of the organic fraction of the solid leads to the hardened honeycomb structure. It is likely that PSSC from different pyrolysis
processes will have a different structure and therefore could leach at different rates.

4.3 Fractionation

Results of fractionation displayed in Figure 2 show that Ca-P bonding is most prevalent in all samples. This agrees with the XRD analysis which concludes that whitlockite compounds are the most abundant mineral in each sample (Table 3). The high abundance of Ca-P is due to the conversion of organic P in the pyrolysis process (Zhang et al., 2001). XRD analysis revealed that ISSA(b) contains approximately 5% less whitlockite compound than ISSA(c) (Table 3) which may explain the difference in Ca-P concentrations as seen in Figure 2. Table 2 shows that PSSC contains less Al and more Fe than ISSA samples, which explains the Al-P and Fe-P binding displayed in Figure 2. Higher Ca-P bonding points towards greater dissolution of P using acid compared to Fe- or Al-P bonding.

4.4 Acid leaching

4.4.1 Contact time

Figure 3a shows that 30 minutes contact time is optimum to release the majority of PO₄-P from ISSA solid samples into
leachate; this was applied to PSSC experiments also. Mixing for longer than 30 minutes would require more energy without significantly increasing \( \text{PO}_4 \)-P release, stretching the economics of a full scale process. However, the contact time needed depends on the characteristics of the solid and may therefore differ between materials produced by different processes. A two-hour contact time was used by Ateinza-Martinez et al. (2014) on their combusted char sample and by Biswas et al. (2009), each using a low concentration of 0.05-0.53M \( \text{H}_2\text{SO}_4 \) acid. In contrast Franz (2008) found a contact time of 10 minutes was optimum, while Donatello et al. (2010) achieved 85% P extraction after 30 minutes, comparable to the results found in this work. The shorter contact time of approximately 30 minutes is sufficient because whitlockite readily dissolves in acid (Donatello, et al., 2010). The essentially unchanging dissolution after 30 minutes may be due to the formation of gypsum crystals on the whitlockite particle surfaces (see Section 4.4.3) or to quartz phases restricting acid contact with whitlockite particles (Donatello et al., 2010). Kalmykova & Karlfeldt Fedje (2013) found that, as in the present work (Figure 3b), two hours contact time achieved greater extraction compared to 24 hours.
4.4.2 Liquid/solid ratio

Increasing the LS ratio in the range 5 to 20 increases the percentage extraction of P from solid but reduces the leachate concentration (see Section 3.4.3 and Figure S-1a of Supplemental Data). Lower LS ratios are preferred to reduce the costs of handling and processing the leachate: a balance must be struck between %extraction, nutrient concentrations in the leachate and LS ratio. Ateinza-Martinez et al. (2014), report that LS 20 compared to LS 150 provides lowest % P extraction efficiencies in ISSA, due to the decrease in liquid-solid contact. Franz (2008) concluded that LS ratio of 2 was favourable for their ISSA samples.

4.4.3 Phosphorus

Table 4 summarises the optimum P recovery parameters and % P extractions reported by other authors. High LS ratios along with relatively low acid molar concentrations have generally been favoured by other authors. However, this work has shown that, due to the lower surface area of PSSC, higher acid concentrations may be needed to penetrate and dissolve nutrients contained within the PSSC particle. A rise in %P
extraction with increasing acid concentration is frequently reported in literature (Cohen et al., 2009; Donatello et al., 2010; Ottosen et al., 2013; Ateinza-Martinez et al., 2014). Figure 4 confirms this effect for low acid strengths but shows that P extraction from ISSA plateaus at approximately 90% at 0.3M H$_2$SO$_4$ acid; a similar plateau of %P extraction was reported by Cohen et al. (2009) and Kuligowski & Poulsen (2010) for ISSA. This effect results from the formation of gypsum around ash aggregates which prevents acid reaching the particle core, reducing dissolution (Cohen, 2009). A similar plateau effect is seen in PSSC samples, but at a higher concentration of 0.8M acid concentration. The highest %P extractions were achieved for PSSC, due to its higher whitlockite content compared to ISSA samples (Table 3).

4.4.4 Macro- and micro- nutrients

Across all the samples, Ca displayed low % extractions with high Ca concentrations remaining unleached in solids (Figures S-2 and S-3). The low % extraction of Ca may be due to the precipitation of CaSO$_4$.2H$_2$O (basanite) during the acid leaching (Donatello et al., 2010). High basanite contents in PSSC samples were measured in this work using XRD analysis of
solid samples after acid leaching (Kleemann, 2015). Biswas et al. (2009) suggest that Ca may nucleate to the centre of the PSSC or ISSA matrices, making it harder to extract into leachate.

There is a clear distinction between the samples’ responses to micronutrient leaching, with Fe dissolving easily from PSSC and Cu dissolving easily from ISSA. The low release of Fe into ISSA liquid may be due to the transformation of Fe into an acid-insoluble Fe compound such as hematite during incineration (Stark et al., 2006; Cohen, 2009). Due to the lack of oxygen in pyrolysis, Fe did not transform into an iron oxide in PSSC, but remained in its more easily soluble form, whitlockite. Ottosen et al. (2013), report that, whereas P extraction is dependent upon LS ratio (see above), Cu extraction is not. However, it was found in this work that Cu extraction depends very strongly on LS ratio for both PSSC and ISSA (Figure 6b), with the highest % extractions occurring at high LS ratios. The presence of fulvic acid-type compounds in municipal solid waste incineration (MSWI) bottom ash are responsible for increased leaching of Cu (Van Zomeren & Comans, 2004; Johnson et al., 1996). This may explain the increased Cu and
heavy metal leaching into leachate from ISSA compared to PSSC found here. This is again important to consider in the production of a fertiliser.

4.4.5 Heavy metals

Figure S-17 of Supplementary Data shows that PSSC releases less heavy metal into leachate than ISSA. Heavy metals are highly immobile in PSSC due to the well buffered alkaline properties of PSSC and because the metals are more strongly incorporated into PSSC particles compared to ISSA particles (Kistler et al., 1987; Caballero et al., 1997; Conesa et al., 1998; Furness et al., 2000; Kaminsky & Kummer, 1989). Both pyrolysis and incineration are thought to suppress the leachability of heavy metals, but Figure S-17 shows this does not hold true for ISSA: even at low acid concentrations of 0.19M H$_2$SO$_4$, higher quantities of heavy metals were released into leachate for ISSA compared to PSSC. Heavy metals such as Cd, Cr, and Pb are water-soluble components of MSWI fly ash, because the particles deposit on the ash particle surface (Buchholz & Landsberger, 1995). During pyrolysis As and Cd are volatilised, leading to reduced concentrations in PSSC and leachate compared to ISSA. The concentrations of heavy
metals in PSSC leachate may be reduced further by the lower BET surface area of PSSC, reducing contact with acid to release heavy metals into liquid.

5. Conclusions

This research compares and contrasts the physical and chemical characteristics of ISSA and PSSC for the purposes of P recovery with a view to producing a P rich fertiliser. PSSC is mineralogically similar to ISSA with each containing significant quantities of whitlockite. However, PSSC contains calcite and greater amounts of whitlockite compared to ISSA. ISSA samples contain significantly more quartz than PSSC.

The P contents of ISSA(b), ISSA(c), and PSSC are 8%, 7%, and 6%, enriched relative to the sludge by 8, 7, and 3 times in ISSA(b), ISSA(c) and PSSC, respectively.

A further difference between ISSA and PSSC lies in their N and heavy metals contents. During incineration N-containing volatiles evolve early in the process, N is oxidised lowering concentrations in the resulting ISSA. During pyrolysis many heavy metals are essentially volatilised completely and are
therefore not present in the remaining PSSC. Cd concentrations are halved during pyrolysis, but increased relative to the sludge by 5.0 and 5.4 times in ISSA(b) and ISSA(c), respectively.

Acid leaching of ISSA and PSSC showed a variety of similarities and dissimilarities between samples. For both materials, a contact time of 30 minutes is optimum to release PO$_4$-P into liquid, because P-rich whitlockite is readily dissolvable in acid.

In a full scale P recovery process, lower liquid-to-solid (LS) ratios are preferred to reduce the costs of handling and processing the leachate. The optimum LS ratio for the materials tested here appears to be about 10. However, it is uncertain whether materials from different processes will show the same characteristics; this is a particular question for PSSC because the material tested here came from a high temperature flash pyrolysis process and showed a very specific particle form. In both ISSA and PSSC, extraction of Ca was low with high Ca concentrations remaining in the solids after leaching. ISSA and PSSC samples show different behaviours for micronutrient leaching, with Fe dissolving more readily from PSSC samples and Cu dissolving more easily from ISSA.
Concentrations of heavy metals were low in PSSC leachate due to the well buffered alkaline properties strongly incorporating heavy metals into PSSC particles.

Interest in P recovery from PSSC is expected to increase as pyrolysis is becoming viewed as more economical method of sewage sludge thermal treatment compared to incineration.

Results from this research can be used to inform the development of a novel P recovery process through PSSC route.

Acknowledgements

The authors gratefully acknowledge the UK Engineering and Physical Sciences Research Council (EPSRC) Grant number EP/G037612/1, the University of Surrey Engineering Doctorate Programme and the sponsor company Thames Water Ltd. for their support in this research.

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Comparison of Phosphorus Recovery from Incinerated Sewage Sludge Ash (ISSA) and Pyrolysed Sewage Sludge Char (PSSC)

Rosanna Kleemann\textsuperscript{a,b,*}, Jonathan Chenoweth\textsuperscript{b}, Roland Clift\textsuperscript{a}, Stephen Morse\textsuperscript{b}, Pete Pearce\textsuperscript{b}, Devendra Saroj\textsuperscript{c}

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Table 1: Elemental analysis of sludge before and after pyrolysis/incineration

<table>
<thead>
<tr>
<th>Element</th>
<th>Units</th>
<th>Pyrolysis sludge</th>
<th>PSSC</th>
<th>Beckton sludge</th>
<th>ISSA(b)</th>
<th>Crossness sludge</th>
<th>ISSA(c)</th>
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<td>P</td>
<td>mg/kg</td>
<td>22,610±180</td>
<td>56,220±70</td>
<td>7,271±6</td>
<td>57,140±509</td>
<td>7,282±112</td>
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<td>N</td>
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<td>52,820±24</td>
<td>19,519±1,102</td>
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<td>872±9</td>
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<td>45,208±57</td>
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<td>Zn</td>
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<td>271±9</td>
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<td>204±3</td>
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<tr>
<td>As</td>
<td>mg/kg</td>
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<td>0.7±0.2</td>
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<td>Cr</td>
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<td>31±1</td>
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<td>27±0.1</td>
<td>119±1</td>
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<tr>
<td>Al</td>
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### Table 2: Elemental analysis of solids used in experiments

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<th>ISSA(b)</th>
<th>ISSA(c)</th>
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<td>P</td>
<td>mg/kg</td>
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<td>S</td>
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<td>Mg</td>
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<tr>
<td>Ca</td>
<td>mg/kg</td>
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<tr>
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<td>Cu</td>
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<tr>
<td>Fe</td>
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<td>36,716±6</td>
<td>29,924±315</td>
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<tr>
<td>Ni</td>
<td>mg/kg</td>
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<td>95±2</td>
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<td>Mo</td>
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<tr>
<td>Mn</td>
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<tr>
<td>B</td>
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<td>96±0.4</td>
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<td>Pb</td>
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<td>Se</td>
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<td>Cr</td>
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<td>Hg</td>
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<tr>
<td>Cd</td>
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<tr>
<td>As</td>
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### Table 3: Quantitative mineralogical analysis

<table>
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<tr>
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<th>ISSA(b)</th>
<th>ISSA(c)</th>
<th>PSSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whitlockite-like compounds (\text{Ca}_9\text{X}(\text{PO}_4)_7)</td>
<td>60%</td>
<td>65%</td>
<td>70%</td>
</tr>
<tr>
<td>Quartz (\text{SiO}_2)</td>
<td>31%</td>
<td>20%</td>
<td>9%</td>
</tr>
<tr>
<td>Calcite (\text{CaCO}_3)</td>
<td>6%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{SrH(PO}_4)</td>
<td>5%</td>
<td>4%</td>
<td></td>
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<tr>
<td>Anhydrite (\text{CaSO}_4)</td>
<td>4%</td>
<td>15%</td>
<td>12%</td>
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Table 4: Optimum acid leaching parameters & P recovery reported in literature

<table>
<thead>
<tr>
<th>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; acid concentration</th>
<th>Contact time</th>
<th>LS Ratio</th>
<th>Sample</th>
<th>P recovery</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>0.05-0.53 M</td>
<td>2-24 hours</td>
<td>150</td>
<td>Combusted PSSC</td>
<td>90%</td>
<td>Ateinza-Martinez et al., (2014)</td>
</tr>
<tr>
<td>20 M</td>
<td>2 hours</td>
<td>500</td>
<td>Pyrolysed pig manure ash</td>
<td>100%</td>
<td>Azuara et al., (2013)</td>
</tr>
<tr>
<td>0.05 M</td>
<td>4 hours</td>
<td>150</td>
<td>ISSA</td>
<td>100%</td>
<td>Biswas et al., (2009)</td>
</tr>
<tr>
<td>1 M</td>
<td>30 minutes</td>
<td>20</td>
<td>ISSA</td>
<td>&gt;85%</td>
<td>Cohen, (2009)</td>
</tr>
<tr>
<td>0.5 M</td>
<td>30 minutes</td>
<td>20</td>
<td>ISSA</td>
<td>80%</td>
<td>Donatello et al., (2010)</td>
</tr>
<tr>
<td>0.19 M</td>
<td>2 hours</td>
<td>20</td>
<td>Fe-rich sludge</td>
<td>~100%</td>
<td>Ottosen et al., (2013)</td>
</tr>
</tbody>
</table>
Comparison of Phosphorus Recovery from Incinerated Sewage Sludge Ash (ISSA) and Pyrolysed Sewage Sludge Char (PSSC)

Rosanna Kleemann\textsuperscript{a,b,}, Jonathan Chenoweth\textsuperscript{a}, Roland Clift\textsuperscript{a}, Stephen Morse\textsuperscript{a}, Pete Pearce\textsuperscript{b}, Devendra Saroj\textsuperscript{c}

S-1 Fractionation Method

The procedure outlined here follows Zhang et al. (2001): 2.5g of solid was extracted with 150ml of 2\% (v/v) acetic acid and agitated for 2 hours. The solid/liquid suspension was centrifuged at 2500rpm for 10 minutes; the supernatant was decanted and retained in a beaker. The remaining solid was twice washed with 75ml 1M NH\textsubscript{4}Cl solution. Both washing liquids and supernatant were added to the acetic acid extract providing the Ca-P fraction. The remaining solid was extracted with 150ml 1M NH\textsubscript{4}F and shaken for 1 hour at 250rpm. The suspension was centrifuged at 2500rpm for 10 minutes and the supernatant collected giving the Al-P fraction. The residual solid was twice washed with 75ml of saturated NaCl solution and the liquid discarded. The solid was mixed with 150ml 0.1M NaOH and shaken for 17 hours at 250rpm. The solution was centrifuged as previously described and the supernatant kept providing the Fe-P fraction. Total P, Ca, Al, and Fe concentrations of the supernatant samples were measured by ICP-MS.

S-2 Acid Leaching Method

To investigate the effects of acid leaching, sulphuric acid was used with a range of liquid/solid (LS) ratios, H\textsubscript{2}SO\textsubscript{4} concentrations and contact times. Sulphuric acid is most commonly used in industry to dissolve P from phosphate rock (Ateinza-Martinez et al., 2014). In this research LS ratios of 5, 10, and 20 were used. Acid concentration of 0.19M was selected since this is the minimum required to achieve efficient P extraction (Donatello et al., 2010). Two contact times, 30 minutes and 24 hours, were used in experiments, and the solution was vacuum filtered through Whatman GF/C filter paper (1.2 μm) and oven dried at 105°C for 1 hour. Filtrate and dry solid sample were analysed for elemental composition by ICP-MS. The fraction extracted was calculated as the weight of material in the solution divided by the total of the material in the solution and the solid.
R² = 0.7912

R² = 0.8221

R² = 0.9319

0 20 40 60 80 100

0 2000 4000 6000 8000 10000 12000

% P Extraction

P liquid concentration (mg/l)

LS 5

LS 10

LS 20

R² = 0.7492

R² = 0.6056

R² = 0.9129

0 10 20 30 40 50 60 70 80 90 100

0 500 1000 1500 2000 2500 3000 3500

% Mg Extraction

Mg liquid concentration (mg/l)

LS 5

LS 10

LS 20

R² = 0.9129

R² = 0.6056

R² = 0.7492
Figure S-1: a) P concentration in liquid versus % P extraction at LS ratios 5, 10, and 20 with linear trend lines; b) Mg concentration in liquid versus % Mg extraction at LS ratios 5, 10, and 20 with linear trend lines; c) Zn concentration in liquid versus % Zn extraction at LS ratios 5, 10, and 20 with linear trend lines
**Figure S-2**: % Extraction of macronutrients calculated from ISSA and PSSC samples at 30 minutes contact time, LS ratios 5, 10, and 20, and acid molar concentrations from 0.19M to 1M
Figure S-3: Concentrations of macronutrients measured in ISSA and PSSC solids at 30 minutes contact time, LS ratios 5, 10, and 20, and acid molar concentrations from 0.19M to 1M
Figure S-4: Concentrations of macronutrients remaining in liquid remaining after acid leaching at 30 minutes and 24 hour contact time at LS ratios 5 and 10 at acid molar concentrations 0.19M and 0.3M.
**Figure S-5:** Concentrations of micronutrients measured in ISSA and PSSC liquid samples at 30 minutes contact time, LS ratios 5, 10, and 20, and acid molar concentrations from 0.19M to 1M
Figure S-6: % extraction of micronutrients from solid after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 1M
Figure S-7: Concentrations of Fe measured in ISSA and PSSC liquid samples at 30 minutes contact time, LS ratios 5, 10, and 20, and acid molar concentrations from 0.19M to 1M
Figure S-8: Nutrient % extractions from PSSC after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 1M
Figure S-9: Macronutrient concentrations in PSSC liquid after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 1M
Figure S-10: Macronutrient concentrations in PSSC solid after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 1M
Figure S-11: Macronutrient % extractions from ISSA(b) after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 0.6M
Figure S-121: Macronutrient concentrations in ISSA(b) liquid after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 0.6M
**Figure S-23**: Macronutrient concentrations in ISSA(b) solid after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 0.6M
Figure S-34: Macronutrient % extractions from ISSA(c) after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 0.6M
Figure S-15: Macronutrient concentrations in ISSA(c) liquid after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 0.6M
Figure S-16: Macronutrient concentrations in ISSA(c) solid after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 0.6M
Figure S-17: Concentrations of heavy metals in liquid after acid leaching at 30 minutes contact time at LS ratios 5, 10, and 20 at acid molar concentrations from 0.19M to 1M
Figure S-18: Concentrations of As measured in ISSA and PSSC liquid samples at 30 minutes contact time, LS ratios 5, 10, and 20, and acid molar concentrations from 0.19M to 1M
Figure S-19: Concentration of Cd measured in ISSA and PSSC liquid samples at 30 minutes contact time, LS ratios 5, 10, and 20, and acid molar concentrations from 0.19M to 1M