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

4 Rosanna Kleemann^{a,b,*}, Jonathan Chenoweth^a, Roland Clift^a, Stephen
5 Morse^a, Pete Pearce^b, Devendra Saroj^c

6 ^a Centre for Environment and Sustainability, University of Surrey,
7 Guildford, GU2 7XH, UK

8 ^b Innovation Centre, Thames Water Utilities Ltd., Island Road,
9 Reading, RG2 0RP, UK

10 ^c Department of Civil & Environmental Engineering, University of
11 Surrey, Guildford, GU2 7XH, UK

12 *Corresponding author

13 Email: rosannakleemann@gmail.com

14 Address: Innovation Centre, Thames Water, Island Road, Reading,
15 RG2 0RP, UK

16

17 Abstract

18 This research compares and contrasts the physical and
19 chemical characteristics of incinerator sewage sludge ash

20 (ISSA) and pyrolysis sewage sludge char (PSSC) for the
21 purposes of recovering phosphorus as a P-rich fertiliser.
22 Interest in P recovery from PSSC is likely to increase as
23 pyrolysis is becoming viewed as a more economical method of
24 sewage sludge thermal treatment compared to incineration.
25 The P contents of ISSA and PSSC are 7.2-7.5% and 5.6%,
26 respectively. Relative to the sludge, P concentrations are
27 increased about 8-fold in ISSA, compared to roughly 3-fold in
28 PSSC. Both PSSC and ISSA contain whitlockite, an unusual form
29 of calcium phosphate, with PSSC containing more whitlockite
30 than ISSA. Acid leaching experiments indicate that a
31 liquid/solid ratio of 10 with 30 minutes contact time is optimal
32 to release $\text{PO}_4\text{-P}$ into leachate for both ISSA and PSSC. The
33 proportion of P extracted from PSSC is higher due to its higher
34 whitlockite content. Heavy metals are less soluble from PSSC
35 because they are more strongly incorporated in the particles.
36 The results suggest there is potential for the development of a
37 process to recover P from PSSC.

38 **Keywords:** incineration; incinerator sewage sludge ash (ISSA);
39 phosphorus recovery; pyrolysed sewage sludge char (PSSC);
40 pyrolysis; sewage sludge

41

42 **1. Introduction**

43 Each year approximately 11.6 million tonnes of dry municipal
44 sewage sludge is produced in Europe (Milieu Ltd., WRc and
45 RPA, 2010). Greece landfills more than 90% of its sludge, while
46 France, Spain and the UK use more than 65% sludge of their
47 sludge in agriculture, and the Netherlands and Switzerland
48 incinerate all their sludge (Milieu Ltd., WRc and RPA, 2010).
49 Energy recovery from sewage sludge using thermal processes
50 such as incineration, pyrolysis, and gasification are gaining
51 more consideration. On average, 27% of sewage sludge is
52 incinerated in Europe (Milieu Ltd., WRc and RPA, 2010).
53 However, incineration has been in decline in the UK because
54 of its high operating costs, while pyrolysis is seen as potentially
55 more viable due to its higher energy recovery (Mills et al.,
56 2014).

57 The fundamental difference between incineration and
58 pyrolysis is the presence or absence of oxygen. Incineration
59 refers to combustion in excess oxygen at high temperature,
60 usually with recovery of heat, for example to raise steam to
61 produce power through a steam turbine, leaving an inert solid

62 ash residue (Samolada & Zabaniotou, 2014; Tyagi & Lo, 2013).
63 By contrast, pyrolysis is thermal decomposition under oxygen-
64 starved conditions; for sewage sludge, pyrolysis produces a
65 'carbonized' solid char, ash, pyrolysis oils, water vapour and
66 combustible gases (Samolada & Zabaniotou, 2014; Tyagi & Lo,
67 2013). The low operating temperature (500°C) of conventional
68 pyrolysis compared to incineration leads to lower heavy metal
69 concentrations in pyrolysis gas (Samolada & Zabaniotou,
70 2014).

71 There has been much interest in the recovery of phosphorus
72 (P) from ISSA either as phosphoric acid or as a fertiliser (Adam
73 et al., 2009; Donatello et al., 2010; Franz, 2008; Ottosen et al.,
74 2013; Ateinsa-Martinez et al., 2014; Azuara et al., 2013; Biswas
75 et al., 2009; Cohen, 2009). P recovery from waste might be a
76 partial solution to the uncertain future of rock phosphate
77 supplies (Kleemann et al., 2015). ISSA has been the subject of
78 considerable research, with its chemical and physical
79 properties being frequently reported. However, there is much
80 less information available on pyrolysed sewage sludge char
81 (PSSC): much research has been devoted to determining the
82 effects of temperature on pyrolysis products, with gas and oil

83 yields as the main focus, but there remain many gaps in
84 knowledge on the chemical and physical properties of PSSC. In
85 particular, there appear to be no studies on P recovery from
86 PSSC using techniques, primarily acid leaching, generally
87 applied to ISSA. A review by Fonts et al. (2012) confirms that P
88 recovery from ISSA has been explored but that recovery from
89 PSSC had been overlooked thus far.

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

97

98 **2. Materials and methods**

99 **2.1 Ash and char source**

100 ISSA was sourced from two different Thames Water Waste
101 Water Treatment Plants (WWTPs), Crossness and Beckton,
102 which treat wastewater from a population equivalent of 5.5

103 million. Beckton and Crossness sewage sludge incinerators
104 operate at temperatures in the range 850-950°C: incinerators
105 must operate above 850°C to ensure minimal dioxin
106 formation, but below 950°C to ensure slag formation (melting
107 of ash) does not occur. The ISSA samples discussed here were
108 taken at two different dates: Table 1 refers to samples taken
109 12 months after the samples to which the other results refer.

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

118 **2.2 Solid and liquid analyses methods**

119 Solids samples of ISSA and PSSC were characterised using X-ray
120 powder diffraction (XRD) at an accredited laboratory in Brunel
121 University (UK) to determine the elemental and mineralogical
122 composition before carrying out acid leaching tests. Scanning
123 electron microscope (SEM) was used to compare the physical

124 forms and ICP-MS analysis was used determine the elemental
125 concentrations of all samples pre- and post-acid leaching.

126 To quantify solubilised Ca-P, Al-P and Fe-P in the ISSA and PSSC
127 solid samples, a form of the Sekiya method first described in
128 1983 was utilised (Zhang et al., 2001). Details of the adapted
129 procedure can be found in Supplementary Data, along with
130 the procedure for acid leaching experiments using sulphuric
131 acid at a range of liquid/solid ratios and contact times.

132 In this research, the mineral whitlockite is of particular
133 importance with regards to the acid leaching of P into
134 leachate. Whitlockite $[(Ca_9X(PO_4)_7]$, where X is most commonly
135 Fe but may also be Cu, H, Al, Ni, or Sr] is an unusual form of
136 calcium phosphate, commonly found in human urinary stones
137 and salivary stones (Bazin et al., 2007). High quantities of
138 whitlockite are beneficial in the recovery of P, because it is
139 readily dissolved from the whitlockite particle using acids
140 (Donatello, et al., 2010). The quantities of whitlockite found in
141 ISSA and PSSC are discussed in section 3.2.

142 In this paper, “primary macronutrients” refers to P, N, and K,
143 and “secondary macronutrients” denotes S, Mg, and Ca.

144 “Micronutrients” encompasses Al, Cu, Zn, Fe, Ni, Mo, Mn, and
145 B, while heavy metals refers to Pb, Se, Cr, Hg, Cd, and As.

146

147 **3. Results**

148 **3.1 Elemental composition**

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

164 than the Beckton and Crossness sludges, but concentrations
165 after pyrolysis/incineration are similar.

166 Table 2 compares the elemental composition of ISSA and PSSC
167 solid samples; as noted above, Tables 1 and 2 refer to identical
168 PSSC samples but the two tables refer to ISSA samples taken
169 on different dates although the samples and their
170 compositions are broadly comparable. Table 2 shows that the
171 samples contain high concentrations of P, but differ in their K
172 and especially N contents. Only PSSC contains significant
173 concentrations of the primary macronutrient N. In terms of
174 secondary macronutrients (Table 2), ISSA(b) contains less S
175 and ISSA(c) contains more Ca than other samples. Viewing
176 micronutrients in Table 2, PSSC contains significantly lower Al
177 and Ni concentrations and higher Fe than ISSA. The two ISSA
178 samples contain very similar concentrations of Cu, more than
179 1200 mg/kg, whereas the concentration in PSSC is less than
180 400 mg/kg. Referring to Table 1, Cu in the sludge is enriched
181 by 6.5-6.9 times in the ISSA samples compared to 2.2 times in
182 the PSSC. Table 2 shows that PSSC contains much lower
183 concentrations of heavy metals than ISSA. Evidently a large

184 proportion of the heavy metals are volatilised in flash
185 pyrolysis; the significance of this is discussed below.

186 **3.2 XRD and SEM analysis before acid leaching**

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

193 SEM analysis was conducted to determine the difference in
194 form between ISSA and PSSC solid samples. Figure 1 shows the
195 striking difference between the structure of ISSA (Figure 1a)
196 and PSSC (Figure 1b) at similar magnifications: PSSC consists of
197 “honeycomb” porous particles whereas ISSA consists of
198 smaller distinct particles with less obvious porosity. The BET
199 surface area of PSSC measured during this research is $8.8 \text{ m}^2/\text{g}$
200 compared to $18.0 \text{ m}^2/\text{g}$ and $23.8 \text{ m}^2/\text{g}$ of ISSA(b) and ISSA(c),
201 respectively, reported for these materials by Donatello et al.
202 (2010).

203 **3.3 Fractionation**

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

210 **3.4 Acid leaching**

211 **3.4.1 Contact time**

212 Figure 3a shows the concentrations of $\text{PO}_4\text{-P}$ released from
213 ISSA into leachate measured over a two hour period. These
214 experiments were conducted only on ISSA samples before
215 PSSC samples became available. The concentration of $\text{PO}_4\text{-P}$ in
216 the leachate increased by 49% between 15 and 30 minutes
217 contact times, after which $\text{PO}_4\text{-P}$ release remained unchanged
218 until the end of the experiment at 2 hours contact time. Figure
219 3b displays the concentrations of $\text{PO}_4\text{-P}$ and Total P measured
220 in the leachate after 30 minutes and 24 hours leaching time:
221 the extended contact time did not result in more P leaching.
222 Thus 30 minutes contact time would be sufficient in a process
223 to recover phosphorus from ISSA.

224 **3.4.2 Liquid/solid ratio**

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

231 **3.4.3 Phosphorus**

232 Figure 4 displays the %P extraction from ISSA and PSSC solid
233 samples across six different acid molar concentrations.
234 Maximum extraction from ISSA occurred around 0.6M: $90\pm1\%$
235 from ISSA(b) at 0.6M LS 20 and $93\pm2\%$ from ISSA(c) at 0.5M LS
236 20. Higher acid concentrations do not achieve significantly
237 greater P extraction.

238 The proportion of P extracted from PSSC was lower at the
239 optimal acid concentration for ISSA. Therefore, higher molar
240 concentrations, 0.8M and 1M, were tested in leaching
241 experiments for PSSC. The highest average extraction of P
242 achieved from PSSC was $89\pm9\%$ at 0.8M and LS 10. In an
243 individual PSSC sample an extraction of 97% was calculated at

244 0.8M LS 10, the highest %P extraction of any sample at 30
245 minutes contact time. Interestingly, for PSSC, highest acid
246 molar concentrations of 1M did not achieve best P release;
247 maximum P concentration in leachate and %P extraction were
248 measured at 0.8M.

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

255 **3.4.4 Macronutrients**

256 Figure S-2 shows that low %Ca extractions were measured
257 across the series of experiments, ranging from 3 to 13% for
258 ISSA(b), 3 to 11% for ISSA(c) and 2 to 27% for PSSC. Figure S-3
259 confirms that significant concentrations of Ca remain
260 unleached in ISSA and PSSC solid samples. K and Mg
261 percentage extractions are much higher than Ca: 9 to 61% and
262 22 to 78% extraction respectively from ISSA(b), 11 to 54% and
263 35 to 75% respectively from ISSA (c) and 12 to 76% and 26 to

264 85% from PSSC. However, while the fractions of Ca extracted
265 are lower than for K and Mg, higher concentrations of Ca are
266 measured in leachate than K (Supplementary Data Figure S-4).

267 **3.4.5 Micronutrients**

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

274 Comparing Figures S-7 and 6a reveals a different response of
275 Fe and Cu to acid leaching of PSSC and ISSA: PSSC releases
276 more Fe whereas ISSA releases more Cu. Table 2 shows that
277 PSSC contains lower concentrations of Cu in the unleached
278 solid compared to ISSA: concentrations of Cu in PSSC range
279 from 0.1 to 17mg/l, while in ISSA(b) Cu ranges from 43 to
280 175mg/l and in ISSA(c) from 32 to 155mg/l. Whereas P
281 extraction is dependent upon LS ratio (see above), Cu
282 extraction is not. However, it was found in this work that Cu
283 extraction depends very strongly on LS ratio for both PSSC and
284 ISSA (Figure 6b), with the highest % extractions occurring at

285 high LS ratios. Figures S-8 to S-16 of Supplementary Data
286 provides further details on extractions and concentrations of
287 macro- and micro- nutrients in ISSA and PSSC samples.

288 **3.4.6 Heavy metals**

289 Figure S-17 of Supplementary data shows there are very low
290 concentrations of heavy metals in PSSC leachate compared to
291 both ISSA leachate samples. This is especially clear when
292 viewing As and Cd in the separate graphs of Figure S-18 and S-
293 19. Table 2 shows that PSSC contains low levels of As and Cd in
294 unleached solid samples, explaining the low concentrations in
295 leachate. PSSC maximum extraction for As is 72% compared to
296 97% and 98% measured by ISSA(b) and ISSA(c).

297 **3.5 Summary**

298 There are major differences between the ways nutrients and
299 heavy metals in sludge behave in pyrolysis and incineration.
300 Relative to the sludge, P concentrations are enriched by 7.9,
301 6.7, and 2.5 times in ISSA(b), ISSA(c) and PSSC, respectively.
302 Following thermal treatment only PSSC contains significant
303 residual concentrations of N, compared to ISSA samples. PSSC
304 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 $\text{PO}_4\text{-P}$ 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.

323

324 **4. Discussion**

325 **4.1 Elemental composition**

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

333 During incineration N-containing volatiles evolve early in the
334 process, N is oxidised and NO_x emissions produced (Rink et al.,
335 1993). In comparison, the oxygen-starved conditions of
336 pyrolysis ensure that N and S are not oxidised but are retained
337 in the solid residue (Pokorna et al., 2009). Table 2 shows the
338 resulting differences in the concentrations of primary
339 macronutrients in ISSA and PSSC. The percentage P contents of
340 ISSA(b), ISSA(c), and PSSC are 7.5, 7.2 and 5.6, respectively,
341 broadly consistent with the values of 5.6% and 4.3% P
342 reported by Bridle & Pritchard (2004) and Gao et al. (2014),
343 respectively, and with P contents in the range 5.7% to 7.6%
344 reported by Donatello et al. (2010). The variation of P contents
345 and other nutrients are attributed to different WWTP influent

346 characteristics, WWTP processes, and incineration/pyrolysis
347 characteristics.

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

364 A wider range of temperatures is used in pyrolysis. In
365 conventional pyrolysis processes operating up to 500°C
366 volatilisation is limited (Samolada & Zabaniotou, 2014). If the

367 pyrolysis gases remain at high enough temperature, the
368 metals can remain as vapour to condense in the oil quench to
369 form part of the oil cake which leaves the process as a
370 separate stream and so will not appear in the resulting PSSC
371 solids. At higher temperatures, many metals are essentially
372 volatilised completely and are therefore not present in the
373 remaining PSSC (Bridle & Pritchard, 2004; Hossain et al., 2011;
374 Kistler et al., 1987). At temperatures above 750°C, Cd reduces
375 to its metallic form and evaporates during pyrolysis (Kistler et
376 al., 1987). Hg behaves similarly to Cd, evaporating during
377 pyrolysis at temperatures as low as 350°C (Kistler et al., 1987).
378 Both of these effects agree with the PSSC compositions found
379 here (Table 1). According to Hwang et al. (2007), Pb and Zn
380 also volatilise during pyrolysis up to 500°C; for this work, Table
381 1 shows higher Pb and Zn concentrations in the PSSC relative
382 to the sludge but this represents a loss when the lower PSSC
383 mass is accounted for. For As, Jin et al. (2014) note a loss of
384 between 19% and 33% in their PSSC samples; in this research,
385 As concentrations were essentially the same in the sludge and
386 the PSSC (Table 1), representing a loss corresponding to the
387 loss of total material between the sludge and the residue. The
388 movement and behaviour of heavy metals in incineration and

389 pyrolysis is important to understand as this informs the heavy
390 metal content of leachate following acid leaching, which will
391 ultimately be used to produce a low heavy metal, nutrient-rich
392 fertiliser.

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

399 **4.2 XRD analysis before acid leaching**

400 According to this research, the inorganic fraction of PSSC is
401 mineralogically similar to ISSA but contains calcite and greater
402 amounts of whitlockite compounds. Calcite is stable up to
403 ~825°C above which it decomposes to calcium oxide (Sikes et
404 al., 2000). ISSA(c) and PSSC samples contain anhydrite,
405 associated with the fact that they each contain more Ca than
406 ISSA(b), see Table 2. The only other mineralogical analysis of
407 PSSC appears to be that reported by Abrego et al. (2009).
408 Following pyrolysis at 800°C, Abrego et al. report the presence
409 of quartz, feldspars (albite and anorthite), calcium oxide,

410 oldhamite, troilite, pyrrhotite, and barringerite in undigested
411 PSSC samples (Abrego et al., 2009). Only the presence of
412 quartz is common between this study and that of Abrego et al.
413 (2009). The mineral content, especially whitlockite, of ISSA and
414 PSSC is important to measure because this influences the
415 dissolution of elements into leachate.

416 XRD analysis of ISSA agrees well with the literature in which
417 whitlockite compounds are frequently reported (Cheeseman
418 et al., 2003; Cyr et al., 2007; Donatello et al., 2010; Mahieux et
419 al., 2010; Nowak et al., 2013; Petzet et al., 2012). Ca is a
420 common element found in wastewaters and is responsible for
421 hard water, which explains the high whitlockite content of all
422 samples. As shown in Figure 2, calcium phosphorus bonding is
423 present in both ISSA and PSSC. This may be in the form of
424 whitlockite or hydroxylapatite $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$ depending upon
425 the sludge composition and incineration or pyrolysis
426 temperature and residence time (Cyr et al., 2007). Adam et al.
427 (2009) reported that above 750°C whitlockite is not present in
428 ISSA because it reacts with CaCl_2 , forming chlorspodiosite and
429 chlorapatite. However, whitlockite compounds were observed
430 here in ISSA produced at 850-950°C. Quartz appears to be a

431 common mineral in ISSA with many researchers reporting its
432 presence (Cheeseman & Viridi, 2005; Cyr et al., 2007; Donatello
433 et al., 2010; Franz, 2008; Mahieux et al., 2010; Nowak et al.,
434 2013) due to the universal presence of silica in sewage sludge
435 (Cohen, 2009). Quartz has also been detected in ISSA formed
436 at even higher temperature, up to 1050°C (Adam et al., 2009),
437 confirming the stability of quartz.

438 Nowak et al. (2013) reported concentrations of 34.4%
439 whitlockite, 28.9% quartz, 6.8% anhydrite and 2.9% calcite in
440 ISSA samples, along with lower concentrations of hematite,
441 potassium-calcium sulphate and magnetite. Cyr et al. (2007)
442 measured 26% calcium phosphates (whitlockite) and 14%
443 quartz along with gypsum, feldspar, micas and glass in their
444 ISSA samples. The results of the analysis here agrees well with
445 Nowak et al. (2013) and Cyr et al. (2007), showing whitlockite
446 as the most abundant mineral (60-65%), followed by quartz
447 (20-31%) and anhydrite (4-15%).

448 The structure of PSSC (Figure 2) is typical of that formed in
449 rapid pyrolysis: rapid evolution of gas and carbonisation of the
450 organic fraction of the solid leads to the hardened honeycomb
451 structure. It is likely that PSSC from different pyrolysis

452 processes will have a different structure and therefore could
453 leach at different rates.

454 **4.3 Fractionation**

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

468 **4.4 Acid leaching**

469 **4.4.1 Contact time**

470 Figure 3a shows that 30 minutes contact time is optimum to
471 release the majority of $\text{PO}_4\text{-P}$ 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 $\text{PO}_4\text{-P}$ 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 Ateinsa-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 H_2SO_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.

494 **4.4.2 Liquid/solid ratio**

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

506 **4.4.3 Phosphorus**

507 Table 4 summarises the optimum P recovery parameters and
508 % P extractions reported by other authors. High LS ratios along
509 with relatively low acid molar concentrations have generally
510 been favoured by other authors. However, this work has
511 shown that, due to the lower surface area of PSSC, higher acid
512 concentrations may be needed to penetrate and dissolve
513 nutrients contained within the PSSC particle. A rise in %P

514 extraction with increasing acid concentration is frequently
515 reported in literature (Cohen et al., 2009; Donatello et al.,
516 2010; Ottosen et al., 2013; Ateinsa-Martinez et al., 2014).
517 Figure 4 confirms this effect for low acid strengths but shows
518 that P extraction from ISSA plateaus at approximately 90% at
519 0.3M H₂SO₄ acid; a similar plateau of %P extraction was
520 reported by Cohen et al. (2009) and Kuligowski & Poulsen
521 (2010) for ISSA. This effect results from the formation of
522 gypsum around ash aggregates which prevents acid reaching
523 the particle core, reducing dissolution (Cohen, 2009). A similar
524 plateau effect is seen in PSSC samples, but at a higher
525 concentration of 0.8M acid concentration. The highest %P
526 extractions were achieved for PSSC, due to its higher
527 whitlockite content compared to ISSA samples (Table 3).

528 **4.4.4 Macro- and micro- nutrients**

529 Across all the samples, Ca displayed low % extractions with
530 high Ca concentrations remaining unleached in solids (Figures
531 S-2 and S-3). The low % extraction of Ca may be due to the
532 precipitation of CaSO₄·2H₂O (basanite) during the acid leaching
533 (Donatello et al., 2010). High basanite contents in PSSC
534 samples were measured in this work using XRD analysis of

535 solid samples after acid leaching (Kleemann, 2015). Biswas et
536 al. (2009) suggest that Ca may nucleate to the centre of the
537 PSSC or ISSA matrices, making it harder to extract into
538 leachate.

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

556 heavy metal leaching into leachate from ISSA compared to
557 PSSC found here. This is again important to consider in the
558 production of a fertiliser.

559 **4.4.5 Heavy metals**

560 Figure S-17 of Supplementary Data shows that PSSC releases
561 less heavy metal into leachate than ISSA. Heavy metals are
562 highly immobile in PSSC due to the well buffered alkaline
563 properties of PSSC and because the metals are more strongly
564 incorporated into PSSC particles compared to ISSA particles
565 (Kistler et al., 1987; Caballero et al., 1997; Conesa et al., 1998;
566 Furness et al., 2000; Kaminsky & Kummer, 1989). Both
567 pyrolysis and incineration are thought to suppress the
568 leachability of heavy metals, but Figure S-17 shows this does
569 not hold true for ISSA: even at low acid concentrations of
570 0.19M H₂SO₄, higher quantities of heavy metals were released
571 into leachate for ISSA compared to PSSC. Heavy metals such as
572 Cd, Cr, and Pb are water-soluble components of MSWI fly ash,
573 because the particles deposit on the ash particle surface
574 (Buchholz & Landsberger, 1995). During pyrolysis As and Cd
575 are volatilised, leading to reduced concentrations in PSSC and
576 leachate compared to ISSA. The concentrations of heavy

577 metals in PSSC leachate may be reduced further by the lower
578 BET surface area of PSSC, reducing contact with acid to release
579 heavy metals into liquid.

580

581 **5. Conclusions**

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

589 The P contents of ISSA(b), ISSA(c), and PSSC are 8%, 7%, and
590 6%, enriched relative to the sludge by 8, 7, and 3 times in
591 ISSA(b), ISSA(c) and PSSC, respectively.

592 A further difference between ISSA and PSSC lies in their N and
593 heavy metals contents. During incineration N-containing
594 volatiles evolve early in the process, N is oxidised lowering
595 concentrations in the resulting ISSA. During pyrolysis many
596 heavy metals are essentially volatilised completely and are

597 therefore not present in the remaining PSSC. Cd
598 concentrations are halved during pyrolysis, but increased
599 relative to the sludge by 5.0 and 5.4 times in ISSA(b) and
600 ISSA(c), respectively.

601 Acid leaching of ISSA and PSSC showed a variety of similarities
602 and dissimilarities between samples. For both materials, a
603 contact time of 30 minutes is optimum to release $\text{PO}_4\text{-P}$ into
604 liquid, because P-rich whitlockite is readily dissolvable in acid.
605 In a full scale P recovery process, lower liquid-to-solid (LS)
606 ratios are preferred to reduce the costs of handling and
607 processing the leachate. The optimum LS ratio for the
608 materials tested here appears to be about 10. However, it is
609 uncertain whether materials from different processes will
610 show the same characteristics; this is a particular question for
611 PSSC because the material tested here came from a high
612 temperature flash pyrolysis process and showed a very specific
613 particle form. In both ISSA and PSSC, extraction of Ca was low
614 with high Ca concentrations remaining in the solids after
615 leaching. ISSA and PSSC samples show different behaviours for
616 micronutrient leaching, with Fe dissolving more readily from
617 PSSC samples and Cu dissolving more easily from ISSA.

618 Concentrations of heavy metals were low in PSSC leachate due
619 to the well buffered alkaline properties strongly incorporating
620 heavy metals into PSSC particles.

621 Interest in P recovery from PSSC is expected to increase as
622 pyrolysis is becoming viewed as more economical method of
623 sewage sludge thermal treatment compared to incineration.
624 Results from this research can be used to inform the
625 development of a novel P recovery process through PSSC
626 route.

627

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634

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

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

Figure 1: a) SEM image of ISSA at 1,500 magnification; b) SEM image of PSSC at 1,700 magnification. Scale shown on SEM pictures.

Figure 2: Results from Sekiya fractionation

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Figure 6: a) Concentrations of Cu measured in ISSA and PSSC leachate samples at 30 minutes contact time, LS ratios 5, 10, and 20, and acid molar concentrations from 0.19M to 1M; **b)**

Concentrations of Cu remaining in ISSA and PSSC samples versus % Cu extractions from ISSA and PSSC with linear trend lines

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

Element	Units	Pyrolysis sludge	PSSC	Beckton sludge	ISSA(b)	Crossness sludge	ISSA(c)
pH			12±0.1		7±0.1		10±0.1
P	mg/kg	22,610±180	56,220±70	7,271±6	57,140±509	7,282±112	48,770±396
N	mg/kg	52,820±24	19,519±1,102	41,461±50	411±10	41,295±44.5	390±38
K	mg/kg	1,750±10	5,150±60	1,380±10	9,895±64	845±7	6,610±14
Ca	mg/kg	42,369±79	116,120±2,330	15,633±19	99,316±90	14,796±213	103,205±870
Mg	mg/kg	8,452±76	19,835±256	2,269±13	14,090±54	1,609±26	13,309±68
Mn	mg/kg	238±2.3	614±12	85±0.3	479±2	111±3	872±9
Fe	mg/kg	21,450±33	49,119±572	8,902±26	45,208±57	5,764±156	42,869±61
Zn	mg/kg	903±5	2343±6	578±6		434±14	
Ni	mg/kg	23±0.3	45±2	18±0.4	113±1	17±1	122±5
Cu	mg/kg	170±1	372±7	271±9	1,771±101	204±3	1,416±21
As	mg/kg	5±0.1	5±0.3	8±0.1	37±2	3±0.1	23±0.2
Cd	mg/kg	0.7±0.0	0.4±0.1	0.8±0.01	4±0.1	0.7±0.2	4±0.1
Cr	mg/kg	31±1	53±0.3	27±0.1	119±1	20±1	111±3
Pb	mg/kg	46±1	99±1	153±2	641±23	73±4	704±3
Hg	mg/kg	0.7±0.01	0.2±0.0				
Al	mg/kg	6,872±162	21,215±355	5,197±127	37,020±76	3,376±26	30,131±102

Table 2: Elemental analysis of solids used in experiments

Elements	Units	PSSC	ISSA(b)	ISSA(c)
P	mg/kg	56,220±70	75,205±645	71,610±70
N	mg/kg	19,519±1,102	515±17	481±11
K	mg/kg	5,150±60	23,560±70	8,605±235
S	mg/kg	14,294±275	4,963±25	12,664±92
Mg	mg/kg	19,835±256	15,931±95	16,106±179
Ca	mg/kg	116,120±2,330	109,050±340	143,410±670
Al	mg/kg	21,215±355	34,350±604	28,796±206
Cu	mg/kg	372±7	1,256±15	1,225±8
Zn	mg/kg	2,343±6.0	2,562±9	3,114±9
Fe	mg/kg	49,119±572	36,716±6	29,924±315
Ni	mg/kg	45±2	85±4	95±2
Mo	mg/kg	19±0.4	43±0.3	35±0.2
Mn	mg/kg	614±12	541±4	453±2
B	mg/kg	61±0.3	96±0.4	57±0.1
Pb	mg/kg	99±1	419±2	660±3
Se	mg/kg	3±0.03	11±0.1	13±0.04
Cr	mg/kg	53±0.3	84±2	79±1.2
Hg	mg/kg	0.2±0.1	3±0.2	9±0.2
Cd	mg/kg	0.4±0.1	3±0.1	5±0.1
As	mg/kg	5±0.3	18±0.1	22±0.1

Table 3: Quantitative mineralogical analysis

	ISSA(b)	ISSA(c)	PSSC
Whitlockite-like compounds ($\text{Ca}_9\text{X}(\text{PO}_4)_7$)	60%	65%	70%
Quartz (SiO_2)	31%	20%	9%
Calcite (CaCO_3)			6%
SrH(PO_4)	5%		4%
Anhydrite (CaSO_4)	4%	15%	12%

Table 4: Optimum acid leaching parameters & P recovery reported in literature

H₂SO₄ acid concentration	Contact time	LS Ratio	Sample	P recovery	Reference
0.05-0.53 M	2-24 hours	150	Combusted PSSC	90%	Ateinsa-Martinez et al., (2014)
20 M	2 hours	500	Pyrolysed pig manure ash	100%	Azuara et al., (2013)
0.05 M	4 hours	150	ISSA	100%	Biswas et al., (2009)
1 M			ISSA	>85%	Cohen, (2009)
0.5 M	30 minutes	20	ISSA	80%	Donatello et al., (2010)
0.19 M	2 hours	20	Fe-rich sludge	~100%	Ottosen et al., (2013)

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

Rosanna Kleemann^{a,b,*}, Jonathan Chenoweth^a, Roland Clift^a, Stephen Morse^a, Pete Pearce^b, Devendra Saroj^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 NH₄Cl 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 NH₄F 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, H₂SO₄ concentrations and contact times. Sulphuric acid is most commonly used in industry to dissolve P from phosphate rock (Ateinsa-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.

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