

1 **Element Speciation in UK Biomass Power Plant Residues Based on Composition, Mineralogy,**
2 **Microstructure and Leaching**

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12

13 **Abstract**

14 Biomass ash management is an escalating issue in many countries because of increasing numbers
15 of biomass power plants. Comprehensive characterization of biomass ashes with emphasis on element
16 speciation, and solubility of nutrients (e.g., K and P) and pollutants is essential for potential utilization
17 of these residues for soil nutrition. All the UK biomass ashes investigated, whether from combustion
18 of poultry litter, meat and bone meal, and straw, were alkaline and contained high concentrations of
19 P, K, and Ca. The biomass air pollution control (APC) residues were enriched in K, Cl, S and Zn, and
20 contained less lithophile elements, such as Al, Ca, P, Mg, Si, Ti, and Ba, compared to the bottom ashes.
21 P appeared in: 1) bottom ashes as apatite and other phosphates (potassium hydrogen phosphate and
22 potassium iron phosphate in the bottom ashes from combustion of poultry litter); 2) APC residues from
23 combustion of poultry litter as potassium sodium calcium phosphate. K is present mainly in sylvite,
24 arcanite, and some phosphates. Na, K, Cl, and S were easily leached by water from the biomass APC
25 residues. However, water leaching of P, Ca, and Mg was very low, with leaching of P possibly controlled

26 by hydroxyapatite. Aqueous Zn, Cu and Pb appear to prevail in the form of neutral and anionic
27 hydroxide complexes, which are toxic and easily accessible chemical forms for live organisms.
28 Application of the poultry litter bottom ashes as a PK fertiliser in agriculture is appropriate. However,
29 direct application of APC residues to agricultural fields is not appropriate but recovery of K and P from
30 that material should be considered.

31 **Keywords:** Biomass; bottom ash; fly ash; APC residue; element speciation; leaching; phosphorous;
32 potassium; fertiliser

33 **1. Introduction**

34 The combustion of biomass for heat and power generation is rising continuously because of limited
35 availability of fossil fuels and evidence of global warming caused by CO₂ emissions from fossil fuel
36 combustion [1]. In the UK, 29% of the current 25 GWe coal-fired generating capacity will be lost after
37 2016 due to the stringent emission limits in the Large Combustion Plant Directive [2]. There are already
38 20 biomass power plants in the UK (~1.1 GWe), and the urgent need to replace fossil fuels with
39 renewable energy sources has led to proposals for a further 37 UK biomass power plants, which will
40 generate ~6 GWe and result in >2 Mtpa of biomass ash [3,4]. According to Vassillev et al. [5], about 480
41 Mtpa of biomass ash, compared to 780 Mtpa of coal ash, may be generated worldwide. Therefore, it
42 is clear that biomass ash management is an escalating issue. In accordance with the waste hierarchy,
43 it would be desirable to reuse or recycle these wastes. Comprehensive characterisation of biomass
44 ashes is needed to consider their further possible application. Data published on the properties of
45 biomass ashes are not as detailed as for ashes of coal [6,7]. The wide variety of fuels for biomass power
46 plants, including forestry and agricultural crops and residues, animal residues, industrial residues, food
47 wastes, sewage sludge, etc., as well as their use in different energy-from-waste systems [8], influence
48 ash elemental and mineralogical composition [5,6], and therefore solubility, leachability and biological
49 availability of its components.

50 The aim of this work was comprehensive characterization, including bulk and trace element
51 composition, mineralogical and microstructural investigation and water-leaching of bottom and APC
52 residues from combustion of three types of waste biomass: (i) poultry litter, (ii) meat and bone meal
53 and (iii) straw, in UK biomass power plants. In a context of potential utilization of these residues for
54 soil nutrition, the emphasis was on determining the speciation, and solubility of nutrients and
55 pollutants. This knowledge is essential for development of appropriate, environmentally friendly and
56 economically rational biomass ash management.

57 **2. Background**

58 **2.1. Residues from biomass combustion**

59 An important body of work on biomass ash, including an excellent review of the information
60 available in the literature on biomass ash properties, has been recently carried out by Vassilev and his
61 co-authors, which obviates the need for a full review and only key points are summarised here. Vassilev
62 et al. [5] defined biomass as “a complex heterogeneous mixture of organic matter and, to a lesser
63 extent, inorganic matter, containing various intimately associated solid and fluid phases with different
64 contents and origins”. Vassilev et al. [6] proposed the following classification for biomass used as a
65 renewable energy source, with average ash chemical compositions shown in Figure 1: 1) Wood and
66 woody biomass (WWB); 2) Herbaceous and agricultural biomass (HAB; 2.1. - Grasses and flowers; 2.2.
67 – Straws, HAS; 2.3. – Other residues); 3) Aquatic biomass; 4) Animal and human biomass wastes (AB);
68 5) Contaminated biomass and industrial biomass wastes (CB); and 6) Mixed biomass (MB). Poultry litter
69 ash can be considered as part of group 6 (MB), whereas meat and bone meal falls into group 4 (AB),
70 and straw into group 2 (HAB); further information for these ashes studied in the present work was not
71 collected by Vassilev.

72 Also, according to Vassilev et al. [6], the ash yield after combustion of organic matter at 550–800°C for
73 86 varieties of biomass ranges from 0.1–46% (average - 6.8%). The ash yield from biomass, which is
74 lower than that from coal, follows the sequence: animal > aquatic > contaminated > herbaceous and

75 agricultural > wood and woody. Biomass fuels are commonly contaminated with soil and other
76 materials, which have become mixed with the fuel during collection, harvesting, handling, storage and
77 processing of the fuel [11], and may affect the ash content. In any case, ash yield at an industrial power
78 plant highly depends on the combustion conditions, including the temperature, which varies between
79 800 and 1600°C. There are three types of biomass ashes: 1) bottom ash, which mainly contains bigger
80 particles that fall through the grate during combustion; 2) fly ash, which contains fine particles that are
81 carried over by the combustion gases and fall out in various parts of the boiler and the flue gas cleaning
82 system; 3) air pollution control residue (APCr), which is the mixture of fly ash and reagents (e.g., lime
83 and active carbon) injected to remove pollutants in flue gas cleaning system. Classification of biomass
84 ashes according to the European Waste Catalogue [12] is required before making a decision for further
85 application of that waste. The following waste codes may be considered for biomass ash classification:
86 1) 10 01 01 - bottom ash, slag and boiler dust (excluding boiler dust mentioned in 10 01 04); 2) 10 01
87 03 - fly ash from peat and untreated wood; 3) 10 01 05 - calcium-based reaction wastes from flue-gas
88 desulphurisation in solid form; 4) 10 01 07 - calcium-based reaction wastes from flue-gas
89 desulphurisation in sludge form; 5) 10 01 18* - wastes from gas cleaning containing hazardous
90 substances; 6) 10 01 19 - wastes from gas cleaning other than those mentioned in 10 01 05, 10 01 07
91 and 10 01 18; 7) 19 01 07* - solid wastes from gas treatment; 8) 19 01 13* - fly ash containing hazardous
92 substances; 9) 19 01 14 - fly ash other than those mentioned in 19 01 13.

93 **2.2. Elemental composition**

94 The elemental composition of biomass ashes depends on the biomass resource (plant or animal,
95 plant species or part of plants, growing processes and conditions, age of the plants, fertilizer and
96 pesticide doses used, harvesting time, collection technique, transport, storage, pollution, processing,
97 etc.), the biomass combustion conditions (fuel preparation, combustion technology and conditions,
98 collection and cleaning equipment), and the transport and storage of the biomass ash [6]. Livingston
99 [11] proposed three types of biomass ashes that were described in [5]: “1) high Si/high K/low Ca ashes

100 with low fusion temperatures, including many agricultural residues; 2) low Si/low K/high Ca ashes with
101 high fusion temperatures, including mainly woody materials; and 3) high Ca/high P ashes with low
102 fusion temperatures, mainly from manures, poultry litters and animal wastes". Vassilev et al. [6]
103 collected information about concentrations of major (>1.0%, including Ca, K, P, S, Mg, Al, and Si), minor
104 (0.1–1.0% including Mn) and trace (<0.1%, including Cu, Zn, Cr, and Ni) elements. The potential
105 environmental contaminants Hg, Cd, Sb, Se, V, Br, Cr, Pb, Zn and As, as well as Cl and the nutrients S, K
106 and Na, have the highest volatilization potential and are enriched in the fly ash rather than in the
107 bottom ash [5,13-19]. Some biomass ashes, for example, from meat and bone meal (MBM), poultry
108 litter, olive processing and sewage sludge, can contain considerable amounts of P [20], which tends to
109 accumulate in bottom ash rather than fly ash.

110 **2.3. Phase composition**

111 Vassiliev et al. [5,21] found that 291 minerals and phases have been previously identified in different
112 biomass ashes, in comparison with 188 in coal ashes. They specified the common phases that present
113 in biomass ashes: 1) inorganic phases (e.g., silicates, oxides and hydroxides, sulphates, phosphates,
114 carbonates, chlorides, nitrates, glass, amorphous (non-glass) phases); 2) organic phases (e.g., cellulose,
115 hemicellulose, lignin, char, other organic phases and minerals). The common phases (e.g., glass, char,
116 quartz, calcite, sylvite, lime, arcanite, anhydrite, portlandite, apatite, halite, clay minerals, gypsum,
117 amorphous (non-glass) material, etc.) identified in biomass ashes were summarized by Vassilev et al.
118 [21]. The phase-mineral composition of biomass ashes is highly variable and strongly depends on the
119 type of biomass fuel, combustion conditions, transport and storage of biomass ashes [21]. Vassiliev et
120 al. [21] proposed a classification of the phases and minerals in biomass ashes by origin: 1) primary (e.g.,
121 refractory silicates, oxyhydroxides and phosphates); 2) secondary (e.g., species from all mineral classes,
122 glass, char); 3) tertiary (e.g., carbonates, hydroxides). The phase-mineral transformations of organic
123 and inorganic matter during biomass combustion were discussed in detail by Vassiliev et al. [21]. Also,
124 Vassiliev et al. [5] proposed a classification of the mineral phase composition of biomass ashes. On a

125 ternary diagram (shown as Figure 1 to include the results of the present work), the upper corner
126 (Si+Al+Fe+Na+Ti oxides) mostly represents the occurrence of glass, silicates and oxyhydroxides of these
127 elements in the biomass ashes, the left corner (Ca+Mg+Mn oxides) mainly includes carbonates,
128 oxyhydroxides, glass, silicates and some phosphates of these elements, and the right corner (K+P+S+Cl
129 oxides) represents phosphates, sulphates, chlorides, glass, some silicates, and carbonates of these
130 elements [5,6,9,10,13,21,22]. Four chemical biomass ash types (S, C, K, and CK) are further specified
131 into seven sub-types (with high (HA), medium (MA), and low acid (LA) tendencies) [21,22].

132 **2.4. Water-leaching of biomass ashes**

133 Literature data collected by Vassilev et al. [5,13,22,23] indicate that biomass ashes can be up to 70%
134 soluble in water, resulting in a pH of 4.5 to 13.4. Water can leach the following phases from biomass
135 ashes [5,22]: highly soluble chlorides (sylvite, halite), sulphates (arcanite, syngenite, ettringite, gypsum,
136 bassanite, anhydrite, hexahydrate, alunite, jarosite, szomolnokite, kieserite, polyhalite), nitrates, some
137 oxides (lime), some hydroxides (portlandite), some carbonates (calcite, dolomite, ankerite), organic
138 minerals (calcium oxalates), a portion of phosphates (phosphorites) and silicates (calcium silicates,
139 opal, zeolite, feldspars). The classification of biomass ashes proposed by Vassilev et al. [5] is very
140 important in order to differentiate biomass ashes to high (e.g., K-LA, CK-LA, and C-LA sub-types),
141 medium (e.g., S-MA, C-MA, and K-MA sub-types), and less (e.g., S-HA sub-type) water-soluble BAs
142 categories [22]. This classification can help to assess potential environmental issues for further BAs
143 application, and choose appropriate or potential utilization of BAs. Significant proportions (10-100%)
144 of elements such as Ca, Cd, Cl, Co, Cr, Cu, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sr and Zn can be
145 leached by water from biomass ashes [5,22]. Also, Vassilev et al. [23] indicated that the nutrients and
146 some potential pollutants can associate with the water-soluble fraction of BAs.

147 **3. Materials & Methods**

148 **3.1. Materials**

149 This research was conducted with eight UK biomass ashes (approximately 5 kg of each samples),
150 including three bottom ashes and five APC residues, obtained from five UK power plants that combust
151 waste biomass. Table 1 shows the sample identification codes, which are based on the fuel type (S
152 indicates straw, PL indicates poultry litter, i.e., a mixture of wood shavings, straw and poultry
153 droppings, and MBM indicates meat and bone meal) and ash type (bottom ash, BA and air pollution
154 control residue, APCr), and combustion history. Since biomass ashes can contain hygroscopic phases,
155 the samples were stored in air-tight containers. Representative subsamples for testing were obtained
156 for each of the UK biomass ashes by coning and quartering. The subsamples were ground for analysis
157 using a micronizing mill.

158 Figure 2 shows the appearance of the biomass ashes. The colour of these samples ranged from light
159 grey and brown to black. Darker coloured biomass ashes generally contain char, indicating poor
160 combustion efficiency. They include a fine sandy sample (MBM-BA), dusty fine-grained powders (S-
161 APCr, MBM-APCr, PL1-APCr, and PL3-APCr), and mixtures of fine sandy and dusty fine-grained
162 materials (PL2-BA, PL2-APCR, and PL3-BA). Some biomass ashes had friable agglomerated chunks with
163 spots of black, grey, blue, brown and/or white particles.

164 **3.2. Methods**

165 The moisture content of each biomass ash sample was determined using standard method BS EN
166 12880:2000 [24] conducted in triplicate, and the results were averaged. The organic matter content in
167 biomass ash was estimated by loss on ignition (LOI) at 550°C for 2 h.

168 An energy dispersive X-ray fluorescence (EDXRF) spectrometer Spectro XLAB2000, equipped with a
169 400W Rh end window X- ray tube and a Si(Li) detector with a resolution of 148 eV (1000 cps Mn Ka),
170 was used for element analysis of a representative subsample (2-4 g of powder) of each of the

171 homogenized biomass ashes. The accuracy and precision of the XRF analysis were determined by
172 running two certified reference materials.

173 XRD was used to characterize the crystalline phases present in the biomass ashes. Each sample was
174 ground with a mortar and pestle and side-loaded against a ground-glass surface into a glass-backed
175 sample holder. XRD analyses were carried out using a high-resolution PANalytical X'pert PRO powder
176 diffractometer. This diffractometer is equipped with a Co anode X-ray tube and an incident beam Ge
177 monochromator, which produces a single CoK-alpha 1 line, leading to very sharp diffraction maxima.
178 The software available includes search-match access to the International Centre for Diffraction Data
179 (ICDD) database for phase identification. Phases in the APC residues were identified on the basis of a
180 match for at least three main peaks with phases in the ICDD database.

181 The morphologies of the biomass ash particles were investigated by scanning electron microscopy
182 (SEM) at different magnifications on a JEOL JSM-6480LV high-performance, variable-pressure analytical
183 scanning electron microscope with secondary electron imaging (SEI) and backscattered electron
184 imaging (BEI) detectors. More than a hundred spot-analyses were performed.

185 A representative subsample of each biomass ash was tested according to BS EN 12457-2:2002 [25]
186 to characterise and assess the constituents that can be leached by water at a liquid-to-solid (L/S) ratio
187 of 10 L/kg without pH adjustment. This is a regulatory test for granular waste in the UK, and the
188 leaching results can therefore be compared with waste acceptance criteria (WAC) for landfill [26]. This
189 test was also used to assess the solubility of K and P in relation to possible direct application of biomass
190 ash to land as a fertilizer. The pH value was measured before filtration of the leachate and analysis for
191 the parameters of interest. The leachates were filtered using a 0.45 µm membrane filter. Subsamples
192 of the filtered leachates were acidified to pH 2 using concentrated ultra-pure HNO₃ prior to elemental
193 analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES). A second subsample,
194 which was not acidified, was used for ion analysis by ion chromatography (IC).

195 The temperature, pH, Eh, major anion and cation concentrations, and trace element concentrations
196 measured in the water leachates from the biomass ashes were used for geochemical equilibrium
197 modelling. Equilibrium calculations were performed using the WATERQ4F computer program [27],
198 1991), applying the thermodynamic database from that software to calculate the solution speciation
199 of major and selected trace elements, and the saturation indices (SI) for selected minerals that might
200 be controlling element concentrations in the leachates. The SI gives information about whether the
201 water was saturated ($SI = 0$), undersaturated ($SI < 0$), or supersaturated ($SI > 0$) with respect to a given
202 mineral. Minerals with SIs from -1 to +1 were considered to be the potential solubility controlling
203 minerals.

204 **4. Results and Discussion**

205 **4.1. Total element composition**

206 The biomass ash moisture contents varied from 0.2 to 4.2% wet mass (Table 2). The moisture
207 contents of the bottom ashes were usually higher than the moisture contents of the APC residues. The
208 biomass ash organic matter content varied from 0.04 to 5.4% (Table 2).

209 The total concentrations of the 24 elements measured in the biomass ashes by XRF are presented
210 in Table 2. All biomass ashes contained high concentrations of Ca (3.4-37%), P (2.2-9.0%) and K (0.93-
211 14%). Also, the Mg concentrations were considerable in two bottom ashes (3.7% in PL2-BA and 4.9%
212 in PL3-BA). The Ca and P, and other lithophile element (Al, Si, Ti, Ba) concentrations were higher in the
213 bottom ashes than in the APC residues, whereas K and other more volatile elements (Cl, S, Zn) were
214 found to be significantly enriched in the APC residues compared to the bottom ashes. The high Ca and
215 P content is characteristic of animal biomass residues, particularly poultry litter, and meat and bone
216 meal. According to Vassilev et al. [6], the extremely high K content is characteristic of the HAB group
217 and this agrees with our data for the straw ash.

218 The element concentrations measured in the biomass ashes can be compared with the average
219 crustal abundances of these elements [28] and coal ash Clarke for some elements [29]. Major elements

220 such as Ca, P, and K significantly exceed the average crustal abundance almost for all samples. The
221 concentrations of potential pollutants, especially Zn, Cd, Mo, Pb, and Cu, were also enriched in the
222 biomass ashes. For example, Zn exceeded the average crustal abundance by 2.1-83 times, Cd by 6-43
223 times, Mo by 27-44 times (excluding MBM-BA), Pb by 1.4-34 times (excluding PL1-FA), Cu by 1.1-14
224 times (excluding S-FA), and As by 1.2-3.9 times (for several samples). Also, P, Cl, Zn, Cd, Cu, Mn and Pb
225 concentrations exceeded the respective coal ash Clarke values for almost all investigated biomass
226 ashes.

227 For potential application of biomass ashes as a fertilizer or soil improver, comparison of element
228 concentrations in biomass ash with limits for land application of poultry litter ash (PLA) (Table 2; [30]),
229 the non-waste comparators such as manufactured fertiliser and/or liming agents as soil improvers
230 (Table 2; [31,32]) may be very helpful to assist with making end-of-waste decisions. The concentration
231 of trace elements in the poultry litter bottom ashes did not exceeded the PLA limits, excluding Cu, Mn,
232 and Ni for PL3-BA. However, the concentrations of Cd, Co, Mo, Pb (only for PL2-APCr), Zn (only for PL1-
233 APCr and PL3-APCr) in the APC residues exceeded the PLA limits. The bottom ashes have similar levels
234 of Ca with liming agents as soil improvers but concentrations of most other elements are higher than
235 for the comparator (Table 2). The concentration of most of elements in the APC residues exceeded the
236 liming agent comparator. The APC residues have similar levels of K with manufactured fertilisers but
237 concentrations of K in bottom ashes and P in both types of ashes are different from that comparator.
238 Therefore, the effect of application rate should be taken into account. Regarding potential pollutants,
239 Cu and Co exceeded the fertiliser comparator almost for all biomass ashes; Pb – for MBM-APCr and
240 PL2.

241 Based on Vassilev's chemical classification for biomass ashes (2.3), all biomass bottom ashes
242 investigated belong to the basic CK type with low acid tendency (CK-LA sub-type) and are comparable
243 to other animal biomass ashes (Figure 1). All APC residues from the HAB and MB groups are type K with

244 low acid tendency (K-LA sub-type). Moreover, there is an obvious difference between biomass bottom
245 ashes and APC residues where-by the latter drift to the right corner compared with the former.

246 **4.2. X-ray diffraction**

247 The results from XRD to identify the crystalline phases in the biomass ashes are summarised in
248 Table 3. The bulk crystalline phases in the bottom ashes included apatite, portlandite, and quartz. Lime
249 and disodium tricalcium silicate were identified in the bottom ash from combustion of meat and bone
250 meal (MBM-BA). Crystalline arcanite, periclase and potassium hydrogen phosphate were found in the
251 bottom ashes from co-combustion of poultry litter with wood and horse bedding (PL2-BA and PL3-BA).
252 Additionally, albite was present in PL2-BA.

253 The biomass APC residues contained mainly sylvite, arcanite, and halite. The biomass APC
254 residues from straw combustion (S-APCr) also contained portlandite and anhydrite. Lime was identified
255 in MBM-APCr and PL2-APCr. Potassium sodium calcium phosphate was found in the APC residues from
256 combustion of poultry litter (PL1-APCr, PL2-APCr and PL3-APCr). The biomass APC residues from straw
257 combustion also contains portlandite and calcium sulphate hydrate. Periclase was present in PL2-BA,
258 PL2-APCr, and PL3-BA as well as disodium tricalcium silicate - in MBM-BA. A trace of calcite was found
259 in some bottom and APC residues (Table 3). The XRD diffractograms also show the presence of some
260 amorphous material in biomass ashes as indicated by the background around 30-40° Two-Theta and a
261 lack of sharp diffraction peaks.

262 **4.3. Microstructure and local chemical composition of the bottom ashes by scanning electron**
263 **microscopy with energy dispersive x-ray Spectroscopy**

264 **4.3.1. Biomass bottom ashes**

265 The three biomass bottom ashes examined (MBM-BA, PL2-BA, and PL3-BA) mainly contained
266 unshaped particles (up to 1 mm), aggregates and fine materials (Figure 3). Some spherical particles
267 were also identified.

268 The unshaped sub-smooth particles, which were abundantly present in the biomass bottom
269 ashes, consisted of calcium phosphate (probably apatite) with impurities of Na, Mg, K, Si, Al, S and Cl
270 (Figure 4a, point and spectrum 1). Fine phases on the surfaces of the unshaped particles had a similar
271 composition (Figure 4b, point and spectrum 2).

272 Cubic and unshaped aggregates had a similar composition to the unshaped sub-smooth particles,
273 including also Fe (Figure 5a, point and spectrum 1, and point and spectrum 2). A monodisperse
274 aggregate contained fine particles that consisted of Ca and O (probably CaO or Ca(OH)₂) with impurities
275 of Mg and P (Figure 5b, point and spectrum 3).

276 Spherical particles (50-150 μm) again seemed to be mainly calcium phosphate (Figure 6a,
277 spectrum 1). The fine phases on the surface of the spherical particle were (Ca, Mg) phosphates, NaCl,
278 and K₂SO₄ (Figure 6b and c, spectrum 2, 3, and 4).

279 **4.3.2. Biomass APC residues**

280 The morphologies of the five different biomass APC residues examined (S-APCr, PL1-APCr, MBM-
281 APCr, PL2-APCr, and PL3-APCr) were quite different (Figure 7), and may depend on the biomass type,
282 combustion technology and conditions, and air pollution control systems.

283 S-APCr mainly contained fine phases (<1 μm) and unburnt straw residues (200-300 μm) with a
284 few glassy particles. Unburnt straw residue consisted of C, K, Ca, Cl, P and Si as major elements, with
285 impurities of Na, Mg, Al, Cu and S. This biomass ash contained a lot of very fine-grained material, mainly
286 composed of K, Ca, Cl and P.

287 The APC residue from poultry litter combustion (PL1-APCr) contained unshaped and spherical (up
288 to 150 μm) particles, aggregates and fine phases (Figure 7). The unshaped and spherical particles were
289 covered by fine phases of KCl and K_2SO_4 (Figure 8, points and spectra 1 and 2). This particular sample
290 contained many fine spherical particles (about 20-35 μm), which are potassium, calcium phosphates.
291 These spherical particles are covered and/or cemented by NaCl and K_2SO_4 .

292 MBM-APCr (Figure 9) includes unshaped particles (up to 300 μm), aggregates, sub-spheres and
293 fine materials. The sub-spherical particles are calcium phosphate, decorated by fine phases of NaCl and
294 potassium (sodium) sulphates. Also, open-work crusts mainly consist of Na, P, Cl, and O (probably Na
295 phosphate chloride) (Figure 9, point and spectrum 2).

296 PL2-APCr was full of spherical particles (50-250 μm), unshaped and slaggy phases (50-400 μm).
297 Smooth spherical particles mainly contained K, Ca, Mg, P, Si, and O (Figure 10, point and spectrum 1).
298 Another spherical particle seemed to be an empty aggregate, with a "puzzle" surface structure. Pieces
299 of the puzzle have different shapes and colour tones in backscattering mode. Bright and dark parts of
300 the surface reflect variability in composition. For example, some puzzle pieces consist of potassium
301 (calcium, magnesium) phosphates with different impurities, some with Na and Cl (Figure 10, point and
302 spectrum 2), others with S and/or Si. Some quartz particles (100-200 μm) with smooth, angular and
303 conchoidal fractures were found in this sample. Unshaped and porous particles varying in size from
304 20 to 300 μm are mostly likely calcium, potassium phosphate.

305 PL3-APCr mainly contained unshaped particles (20-150 μm) and fine phases (Figure 7). The
306 unshaped (rounded, oblong, sub-smooth with dirt-like decoration) particles mainly consisted of K, Ca,
307 Na, Mg, P and S. A variety of fine phases with different morphologies and compositions were observed.
308 For instance, 2-5 μm fine-grained phases consisted mainly of K, Na, Cl, S, P, and O (Figure 11, point 1).
309 1 μm rounded plate-like fine particles form a foam structure and were consisted mainly of K, Na, Cl,
310 and P (Figure 11, point 2). Prismatic crystals consisted of Na, Cl, and P were found throughout the fine
311 material (Figure 11, point 3).

312 **4.4. Leachability of biomass ashes in water**

313 The pH of the water-based leachates according to BS EN 12457-2:2002 was high due to the CaO
314 or Ca(OH)₂ in these samples (identified by XRD, Table 3) and varied from 11.32 to 12.78 (Table 4). It
315 should be noted that a saturated solution of Ca(OH)₂ has a pH of about 12.4. The low pH value was
316 associated with sample PL3-APCr, which showed neither Ca(OH)₂ and CaO by XRD and had the lowest
317 Ca value of all the samples (Table 2). The presence of alkali oxides/hydroxides may increase the pH,
318 but XRD showed the alkalis to be speciated predominantly as neutral salts.

319 Element concentrations leached from the biomass ashes are shown together with the Waste
320 Acceptance Criteria (WAC) for landfilling of inert waste in Table 4. Values that exceed the WAC have
321 been shaded. The water-leached concentrations of Cl and SO₄²⁻ exceed the WAC for inert waste for all
322 of the biomass ashes. However, Cl concentrations of the water leachates from the biomass APC
323 residues also exceed the WAC for hazardous waste (Cl > 2.5 wt.%). It can be seen that all the Mo
324 leachate concentrations, and all the Pb leachate concentrations except S-APCr, exceed the WAC for
325 inert waste, as do all the Zn leachate concentrations from the APC residues. Cu concentrations also
326 exceed the WAC for inert waste for some biomass ashes (see Table 4).

327 The water-soluble fractions from the biomass bottom ashes varied from 1.0 to 8.4%. However,
328 the water-soluble fractions from the biomass APC residues were quite high and ranged from 33.8 to
329 36.7%. It can be seen that a higher proportion of Cl could be leached by water at L/S=10 from the APC
330 residues (up to 74%) than from the bottom ashes (up to 51%). Cl solubility in water may be limited by
331 its uptake in some phases, such as apatite, which was shown as to be a dominant phase in the bottom
332 ashes. S is leached relatively easily from biomass ashes (38-55%), which is consistent with identification
333 of soluble arcanite as a dominant phase by XRD in most biomass ashes. In contrast to the biomass
334 bottom ashes, almost all Na (up to 96%) and high proportions of K (up to 84%) could be leached from
335 the biomass APC residues by water. A lower proportion of K than Na leached suggests that K is
336 substituted in mineral phases with lower solubility (probably phosphate phases and aluminosilicates).

337 The water-soluble fractions of P, Ca, and Mg are very low and range from 0.004 to 1.4% for P, from
338 0.01 to 2.7% for Ca, and from 0.01 to 3.7% for Mg. However, the higher concentration of P was leached
339 from APC residues from poultry litter incineration due to presence of mineral phases with higher
340 solubility (probably potassium sodium calcium phosphate and potassium hydrogen phosphate).

341 **4.5. Element speciation in water-leachates of biomass ashes**

342 Table 5 presents the calculated distributions of selected aqueous element species (%), and Table
343 6 the saturation indices (SI) for hydroxyapatite and $\text{Pb}(\text{OH})_2$, for the water leachates from the biomass
344 ashes.

345 Table 5 shows that sodium and potassium are mainly present as free ions (Na^+ , K^+), and less than
346 1.1% of sulphate is complexed, in the water leachates of all the biomass ashes. Fe and Al prevail as
347 anionic hydroxide complexes ($\text{Fe}(\text{OH})_4^-$, $\text{Al}(\text{OH})_4^-$). Ca speciation in the leachates varies; the simple
348 aqua-ion (Ca^{2+}) dominates, but significant proportions are complexed with phosphate and/or sulphate
349 (CaPO_4^- , CaSO_4^0). Magnesium is mainly present as the cationic hydroxide complex (MgOH^+) and
350 percentages of the simple ion (Mg^{2+}) and anionic phosphate (MgPO_4^-) are also significant.

351 As a consequence of the alkaline pH, geochemical modelling shows the amphoteric contaminants
352 Zn, Pb and Cu to prevail in the form of neutral and anionic hydroxide complexes (Table 5). In fact, Cu
353 may be complexed with dissolved organic matter [33], which was not taken into account in the
354 modelling.

355 The toxicity and bioavailability of an element are strictly related to the chemical forms in which
356 it occurs [34]. The most toxic and bioavailable chemical forms of elements such as Zn, Pb, Cu, Cd, and
357 Ni are aqua-ions (Me^{2+}) and simple complexes with inorganic anions [35].

358 The saturation indices in Table 6 suggest that hydroxyapatite may control solubility of P, and lead
359 hydroxide may control leachate concentrations of Pb, for most of the biomass ashes. Brucite ($\text{Mg}(\text{OH})_2$)
360 altered from periclase identified in the ashes by XRD can be considered as the potential solubility
361 controlling mineral for Mg. Copper and zinc were undersaturated with respect to their

362 oxides/hydroxides, and substitution of elements into the bulk mineral phases may control the leachate
363 concentrations of these and other elements, but it is difficult to take this into account in the modelling.

364 **5. Conclusions**

365 All the UK biomass ashes investigated, whether from combustion of poultry litter, meat and bone
366 meal, and straw, were alkaline and contained high concentrations of P, K, and Ca. Mg concentrations
367 were also considerable in the poultry litter bottom ashes. The biomass bottom ashes belong to the CK
368 type with low acid tendency. All APC residues belonging to HAB and MB groups are K type with low
369 acid tendency. The biomass APC residues were enriched in the more volatile elements, such as Cl, S, K
370 and Zn, and contained less lithophile elements, such as Al, Ca, P, Mg, Si, Ti, and Ba, compared to the
371 bottom ashes. The concentrations of potential pollutants, especially Zn, Cd, Mo, Pb, and Cu were
372 enriched in all the biomass ashes, especially in the APC residues compared to average crustal
373 abundance and coal ash Clarkes.

374 The mineral phase composition of the investigated biomass ashes was complex. The bulk
375 crystalline phases in the bottom biomass ashes included quartz, portlandite, apatite (all bottom ashes),
376 and other phosphates (potassium hydrogen phosphate and potassium iron phosphate in the bottom
377 ashes from combustion of poultry litter). Biomass APC residues contained mainly sylvite, arcanite,
378 halite and lime. Potassium sodium calcium phosphate was identified in the APC residues from
379 combustion of poultry litter. The XRD patterns suggested the presence of amorphous phases which can
380 influence to element leachability.

381 In general, all the UK biomass bottom ashes were found to have a similar morphology, being
382 composed of unshaped particles (up to 1 mm), aggregates and fine materials with minor amounts of
383 spherical particles. However, the biomass APC residues were found to have different morphologies,
384 which may depend on the type of biomass, combustion and residue collection technology and
385 conditions, and particularly cleaning process.

386 Almost all Na and high proportions of K, Cl, and S were easily leached by water from the biomass
387 APC residues, which had high water-soluble fractions compared to the biomass bottom ashes.
388 However, water leaching of P, Ca, and Mg was very low, with leaching of P possibly controlled by
389 hydroxyapatite. Leaching of Cl, S, Pb, Cu, Co, Mo and Zn in water exceeded the WAC for landfilling as
390 inert waste. Aqueous Zn, Cu and Pb appear to prevail in the form of neutral and anionic hydroxide
391 complexes, which are toxic and easily accessible chemical forms for live organisms.

392 6. Recommendations and further investigation

393 As all biomass ashes investigated contain significant quantities of valuable potassium and
394 phosphorus, it is not sustainable or rational to deposit them in landfills. Application of the poultry litter
395 bottom ashes as a PK fertiliser in agriculture is appropriate. However, direct application of APC residues
396 to agricultural fields is not appropriate because of the significant concentrations of potentially harmful
397 elements and water-soluble Cl-bearing phases (can cause soil salination), which exceed levels in
398 Environment Agency Material Comparators for fertilizers and soil improvers. Also, the availability of
399 phosphorus from biomass ashes to plants is known to be low [36]. Therefore, recovery of K and P from
400 the biomass ashes should be considered.

401 Whereas significant amounts of K can be simply extracted by water with L/S 10 from the biomass
402 APC residues, water-leachability of P from the biomass bottom ashes is very low (<1.4 wt.%). Therefore,
403 development of a process for P extraction or increasing its phytoavailability (for some biomass ashes
404 with low potential toxic element concentrations) is recommended.

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509 **Table 1. UK biomass ashes used in this work**

Sample Code	Combustion system	Combustion Temperature (°C)	Bottom ash discharge technology	Flue gas cleaning technology	Biomass group based on Vassilev et al. [5]
PL1-APCr	FBI	850		DS	AB
PL2-BA	GI	850	DD		MB
PL2-APCr				DS	MB
PL3-BA	GI	850	DD		MB
PL3-APCr				DS	MB
MBM-BA	GI	850	DD		AB
MBM-APCr				DS	AB
S-APCr	GI	850		DS	HAB

510 FBI – fluidized bed incinerator; GI – grate incinerator; DD – dry discharge; DS – dry scrubbing

511

512 **Table 2. Compositions of UK biomass bottom ashes (BA) and air pollution control residue (APCr) determined by X-ray Fluorescence (mg/kg dry mass,**
 513 **unless otherwise indicated; NA indicates that a parameter was not available; >1% - major; 0.1-1% - minor; <0.1 – trace element)**

Element	S-APCr	PL1-APCr	MBM		PL2		PL3		Average crustal abundance [28]	Coal ash Clarke [29]	Upper limit for PLA used as a fertiliser [30]	manufactured fertilisers [31]	soil improver (liming materials) [32]
			BA	APCr	BA	APCr	BA	APCr					
Al, %	0.04	0.096	0.3	0.095	0.16	0.11	0.32	0.046	8.23	-	-	-	-
As	1.3	1.8	<0.6	2.2	3.8	5.9	<0.8	2.7	1.5	47	17	8.6-18.6	1.0-16
Ba	24	170	180	120	400	180	210	60	425	940	-	-	-
Ca, %	13	8.5	37	13	19	8.4	18	3.4	4.15	-	-	-	21-41
Cd	3.3	5.0	8.5	4.5	1.3	2.0	1.2	6.3	0.2	1.2	3.0	13.6-30.6	0.2-4.0
Co	2.5	22	16	15	7.2	26	11	12	<u>25</u>	32	11	0.5-9.4	0.22-2.0
Cu	43	540	61	130	530	500	770	450	55	92	596	25-56	1.3-20
Cr	12	<7.0	34	55	<7.0	<7.0	<7.0	<7.0	<u>35</u>	100	31	115-360	0.62-11
Fe, %	0.021	0.37	0.37	0.34	0.8	0.39	0.65	0.22	0.563	-	-	-	0.06-1.3
K, %	14	13	0.93	8.3	5.7	11	6.1	13	2.09	-	-	11-20	0.014-0.13
Mg, %	0.17	1.6	0.4	0.26	3.7	1.5	4.9	0.66	2.33	-	-	-	0.11-13
Mn, %	0.015	0.24	0.016	0.017	0.35	0.21	0.43	0.14	0.095	0.049	0.35	-	0.011-0.23

Mo	40	49	-	-	44	51	66	54	1.5	14	45	-	1.0-20
Na, %	0.051	1.03	0.35	2.4	0.29	0.69	0.33	0.74	2.36	-	-	-	0.0057-0.043
Ni	1.8	19	8.8	6.5	20	12	31	12	<u>75</u>	76	24	36-56	1.6-10
P, %	2.2	3.7	8.8	2.9	8.1	2.9	9.0	1.7	0.105	0.14	-	15-47	0.0019-0.73
Pb	28	10	17	150	100	420	35	26	12.5	47	244	5.7-35	1.0-59
Si, %	2.2	0.75	0.44	0.38	5.3	0.88	4.6	0.31	28.2	-	-	-	-
Sr	160	200	260	160	280	180	290	120	375	740	-	-	-
Ti	30	130	370	180	2200	650	600	100	5700	4700	-	-	-
Zn	490	2200	150	940	1300	3800	910	5800	70	140	2063	260-640	11-58
U	26	77	64	40	71	43	83	64	2.7	-	-	-	-
Cl, %	22	3.9	0.57	12	0.68	8.8	0.35	10	NA	0.14	-	-	0.0011-0.034
S, %	0.69	7.4	0.14	5.2	1.1	7.3	1.7	9.6	NA	-	-	-	-
Moisture content, %	3.2	2.7	1.1	0.2	4.2	2.2	4.1	0.6					
Organic matter, %	5.4	2.5	0.37	0.04	2.5	1.2	2.5	1.1					

514

515 **Table 3. Mineral phases identified in UK biomass ashes**

Chemical formula	
NaAlSi ₃ O ₈	
Ca ₅ (PO ₄) ₃ O(Cl, OH, CO ₃)	
K ₂ SO ₄	
CaCO ₃	
CaSO ₄ ·H ₂ O	
Na ₂ Ca ₃ Si ₃ O ₁₀	
NaCl	
CaO	
Ca(OH) ₂	
K ₈ H ₂ P ₄ O ₁₅	
MgO	
KFe ₂ (PO ₄) ₂	
KNaCa ₂ (PO ₄) ₂	
SiO ₂	
KCl	

Mineral phase	Albite	Apatite	Arcanite	Calcite	Calcium sulfate hydrate	Disodium tricalcium silicate	Halite	Lime	Portlandite	Potassium hydrogen phosphate	Periclase	Potassium iron phosphate	Potassium sodium calcium phosphate	Quartz	Sylvite
Sample	al	ap	ar	ca	cs	ds	h	l	p	ph	pr	pi	ps	q	s
S-APCr			+		+				+						+
PL1-APCr		+	+	+					+				+		+
MBM-BA		+		+		+		+	+					+	
MBM-APCr		+		+		+	+	+	+						
PL2-BA	+	+	+	+					+	+	+			+	
PL2-APCr			+				+	+			+		+		+
PL3-BA		+	+	+					+	+	+			+	
PL3-APCr			+				+						+		+

516

517 **Table 4. Element concentrations leached from UK biomass ashes with water according to BS EN 12457-2:2002 and UK criteria for acceptance of granular**
518 **waste (WAC) to inert landfill (mg leached/kg of dry solid)**

Element	S-APCr	PL1-APCr	MBM		PL2		PL3		WAC for granular waste to inert landfill [26]
			BA	APCr	BA	APCr	BA	APCr	
pH	12.68	11.54	12.22	12.4	12.78	12.27	12.59	11.32	-
Al	1.6	6.0	0.4	68	10	60	4.7	1.4	-
Ba	1.4	<0.01	5.3	5.0	0.3	0.1	0.01	<0.01	20
Ca	13	12	220	280	150	20	20	80	20
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04
Co	0.48	<0.01	<0.01	0.6	<0.01	<0.01	<0.01	<0.01	0.04
Cu	1.6	2.1	2.1	3.1	1.0	2.3	1.5	0.24	2.0
Fe	1.2	1.3	2.0	5.8	100	75	7.0	4.0	-

K, %	11.2	5.5	0.084	1.2	2.3	8.5	2.1	10.9	-
Mg	54	12	1.3	2.0	950	560	57	78	-
Mn	0.003	<0.01	<0.01	<0.01	<0.01	<0.01	0.2	0.01	-
Mo	28	35	0.7	2.4	31	28	56	37	0.5
Na, %	0.037	0.79	0.026	2.3	0.053	0.54	0.049	0.6	-
Ni	<0.01	1.3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.4
P	21	520	3.9	54	310	320	200	280	-
Pb	0.3	3.0	3.5	6.0	3.0	4.3	1.7	2.3	0.5
Si	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-
Sr	43	1.7	15	6.5	2.7	3.0	0.1	1.4	-
Ti	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-
Zn	5.0	8.0	1.0	39	0.4	17	0.9	2.0	4.0
Cl ⁻ , %	13	2.9	0.2	6.5	0.33	5.8	0.18	5.1	0.08
SO ₄ ²⁻ , %	0.32	4.0	0.053	3.0	0.6	3.6	0.73	4.3	0.033
NO ₃ ⁻ , %	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-
Total	35.1	33.8	1.0	34.6	8.4	35.6	7.5	36.7	-
Dissolved									
Solids, %									

>1% - major; 0.1-1% - minor; <0.1 – trace element

Failure of inert WAC

Table 5. Element species (%) for water leachates from UK biomass ashes.

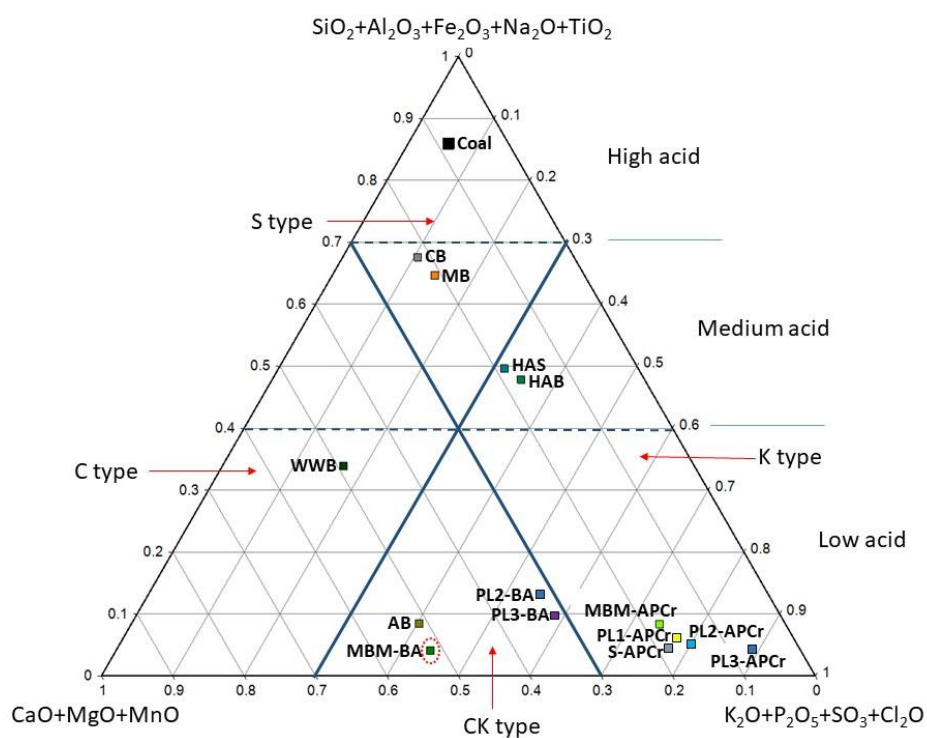
Element species	S- APCr	PL1- APCr	MBM		PL2		PL3	
			BA	APCr	TA	APCr	BA	APCr
Na ⁺	99.95	99.21	99.99	99.87	99.99	99.32	99.94	99.64
NaSO ₄ ⁻	0.05	0.79	0.01	0.13	0.01	0.68	0.06	0.36
K ⁺	99.93	98.90	99.98	99.82	99.99	99.06	99.91	99.5
KSO ₄ ⁻	0.07	1.10	0.02	0.18	0.01	0.94	0.09	0.5
Ca ²⁺	64.87	50.12	82.69	71.76	61.98	72.11	46.91	71.51
CaOH ⁺	31.94	2.21	16.97	20.59	37.8	15.33	19.95	1.95
CaPO ₄ ⁻	2.46	36.65	0.02	5.40	0.13	0.81	32.49	19.18
CaHPO ₄ ⁰	0	0.04	0	0	0	0	0	0.04
CaSO ₄ ⁰	0.72	10.99	0.32	2.25	0.11	11.75	0.65	7.35
Mg ²⁺	8.31	31.06	18.11	13.36	6.85	16.92	8.78	47.97
MgOH ⁺	91.14	30.07	81.81	84.77	93.12	79.54	82.76	28.77
MgHPO ₄ ⁰	0	0.03	0	0	0	0	0	0.03
MgPO ₄ ⁻	0.43	30.80	0	1.37	0.02	0.26	8.31	17.43
MgSO ₄ ⁰	0.11	8.04	0.08	0.5	0.01	3.27	0.14	5.82
Cl ⁻	100	100	100	100	100	100	100	100
SO ₄ ²⁻	98.95	99.19	0	99.54	99.64	99.00	99.78	98.47
PO ₄ ³⁻	44.10	13.97	0.56	21.71	12.34	19.73	65.22	8.44
HPO ₄ ²⁻	8.76	56.15	0.45	9.96	1.89	12.19	17.81	59.3
Fe(OH) ₃ ⁰	0.02	0.29	0.06	0.04	0.02	0.05	0.02	0.48
Fe(OH) ₄ ⁻	99.98	99.71	99.94	99.96	99.98	99.95	99.98	99.52
Al(OH) ₄ ⁻	100	100	100	100	100	100	100	100
ZnOH ⁺	0	0.01	0	0	0	0	0	0.03
Zn(OH) ₂ ⁰	2.39	43.61	11.23	6.47	1.65	9.36	3.44	57.16
Zn(OH) ₃ ⁻	43.20	52.56	65.40	58.84	37.64	63.06	49.31	41.07
Zn(OH) ₄ ²⁻	54.41	3.82	23.37	34.69	60.72	27.58	47.25	1.74
Cu(OH) ₂ ⁰	52.94	97.55	86.14	76.82	43.09	83.40	62.42	98.58
Cu(OH) ₃ ⁻	18.20	2.24	9.56	13.30	18.78	10.71	17.03	1.35
Cu(OH) ₄ ²⁻	28.86	0.2	4.3	9.87	38.13	5.90	20.54	0.07
PbOH ⁺	0	0.08	0	0	0	0	0	0.26
Pb(OH) ₂ ⁰	0.08	10.02	0.76	0.32	0.05	0.56	0.13	19.15
Pb(OH) ₃ ⁻	5.20	43.86	16.09	10.47	4.11	13.58	6.73	49.96
Pb(OH) ₄ ²⁻	94.72	46.03	83.14	89.21	95.84	85.86	93.15	30.63

525 **Table 6. Saturation Indices (SI) for water leachates from UK biomass ashes.**

Element species	S-APCr	PL1-APCr	MBM		PL2		PL3	
			BA	APCr	BA	APCr	BA	APCr
Brucite (Mg(OH) ₂)	2.5	0.3	0.4	-0.8	2.9	2.1	1.4	-0.2
Cupric Ferrite (CuFe ₂ O ₄)	2.3	5.0	4.0	4.7	5.6	7.3	4.1	6.1
Goethite (FeOOH)	2.2	3.4	2.9	3.2	4.0	4.5	3.1	11
Hematite (Fe ₂ O ₃)	6.4	8.7	7.8	8.3	10	11	8.1	4.3
Hydroxyapatite (Ca ₅ (PO ₄) ₃ (OH))	-4.7	-2.3	3.3	3.0	0.98	-5.3	-0.64	1.1
Pb(OH) ₂	-3.0	0.13	-0.92	-1.1	-2.2	-0.97	-2.0	0.30
Cu(OH) ₂	-2.8	-2.5	-2.5	-2.5	-3.1	-2.5	-2.8	-3.4
Tenorite (CuO)	-1.8	-1.4	-1.5	-1.4	-2.1	-1.5	-1.8	-2.4
Zn(OH) ₂	-3.3	-1.9	-3.4	-2.0	-4.6	-2.2	-3.9	-2.4
ZnO	-3.1	-1.7	-3.2	-1.8	-4.4	-2.0	-3.7	-2.2

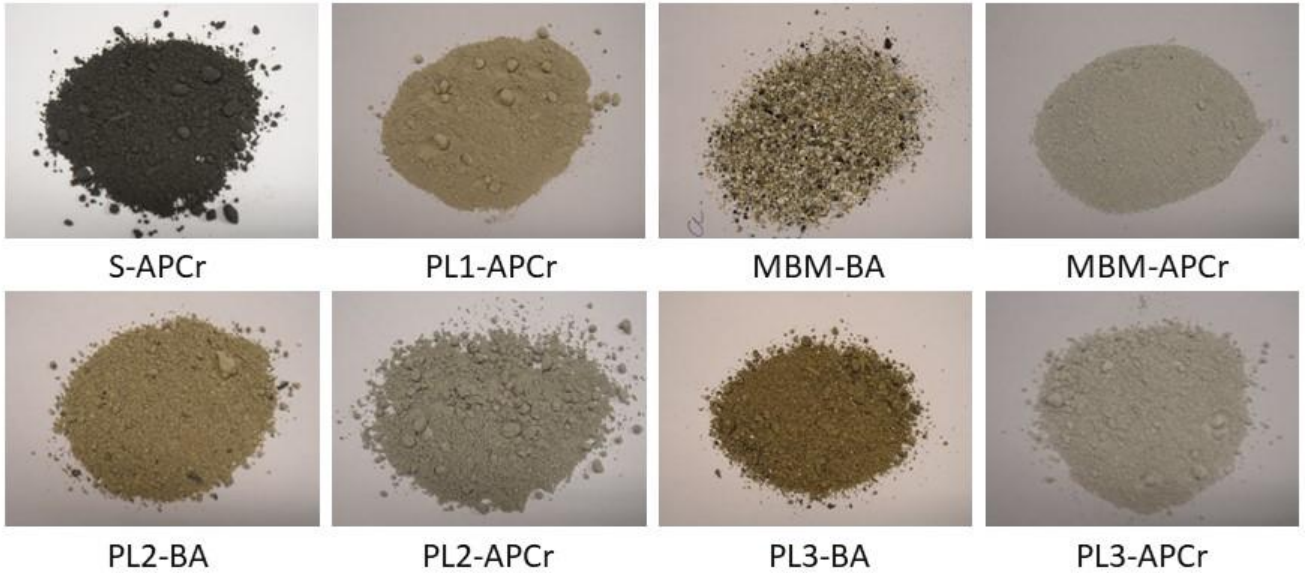
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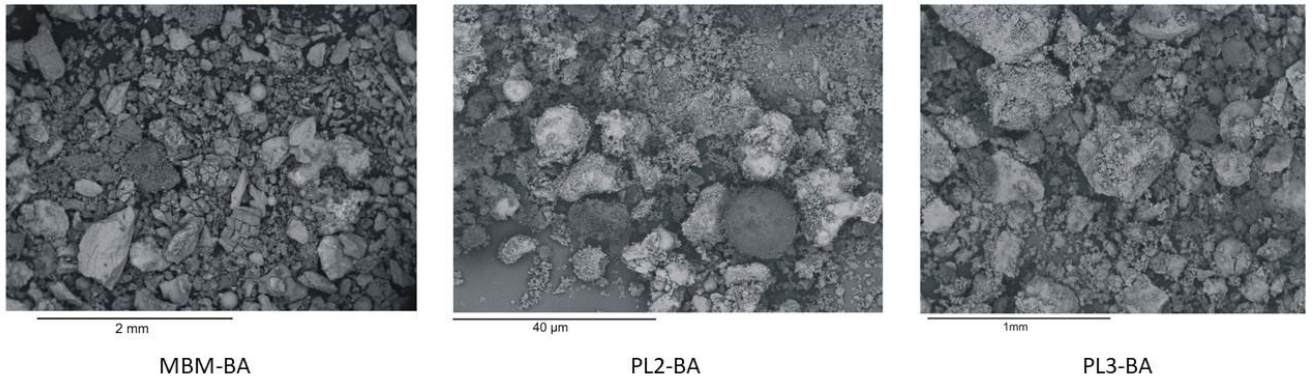
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529 **Figure 1. Positions of the eight UK biomass ashes compared with other biomass ashes and fossil fuels**
 530 **in the chemical classification system of biomass ashes based on [5,6,9,10]. Abbreviations: C – coal;**
 531 **WWB – wood and woody biomass; HAB – herbaceous and agricultural biomass; HAS - herbaceous**
 532 **and agricultural straw; AB – animal biomass; MB – mixture of biomass; CB – contaminated biomass.**
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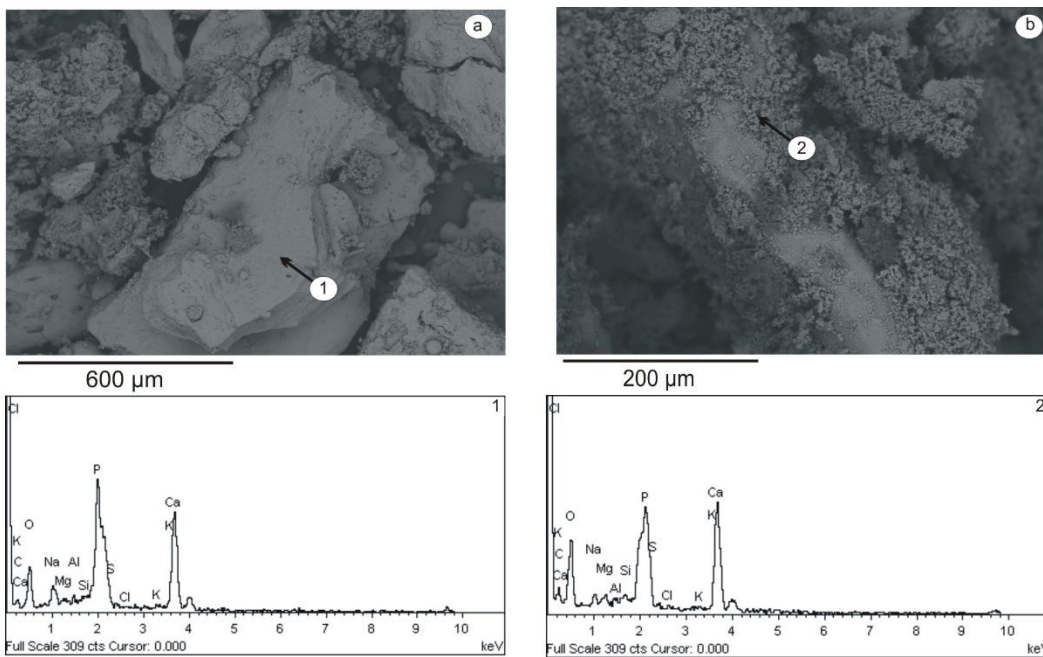
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Figure 2. Visual observation of UK biomass ashes.



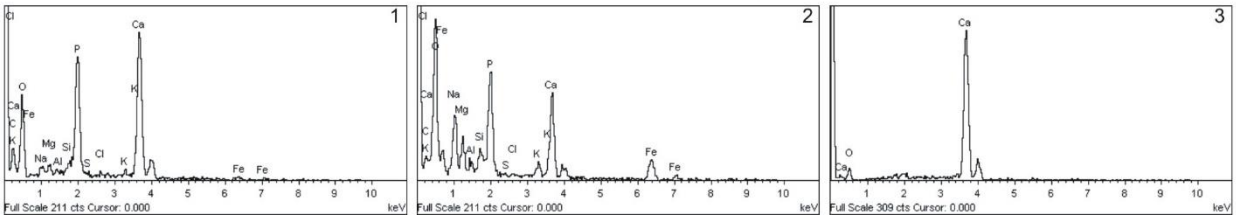
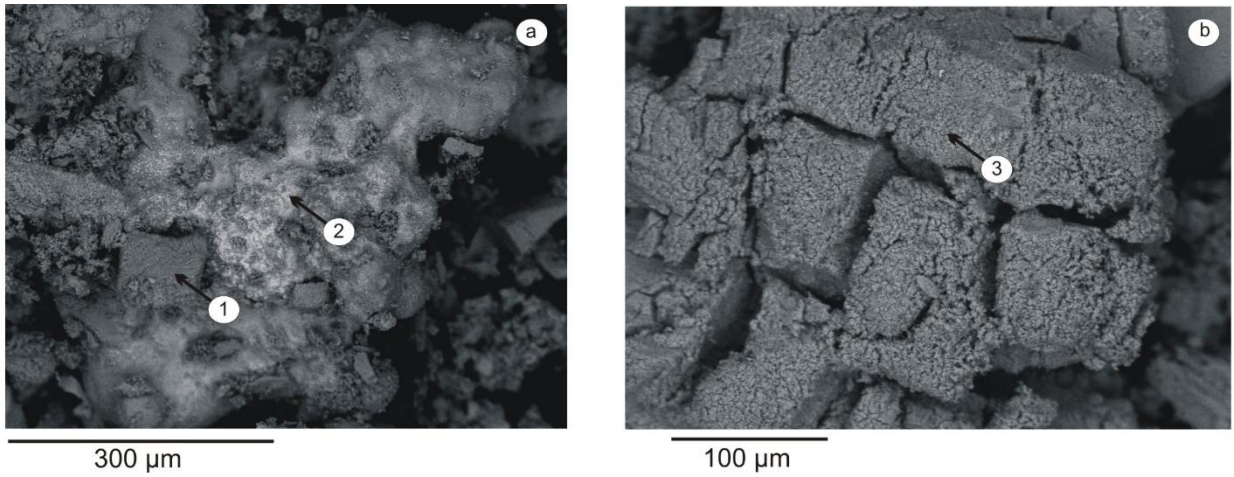
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Fig 3. Scanning electron microscope images of the biomass bottom ashes.

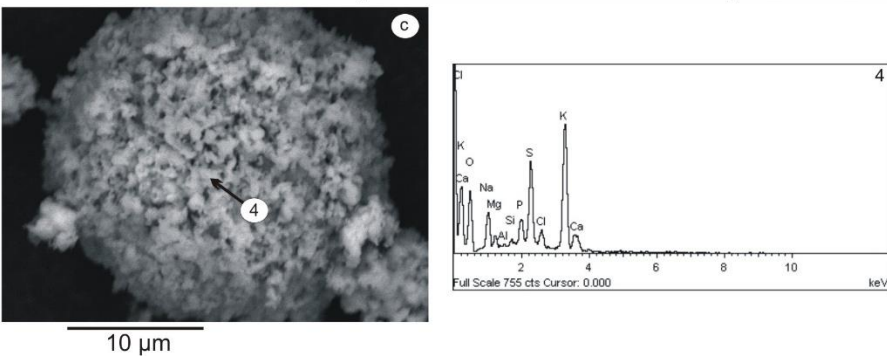
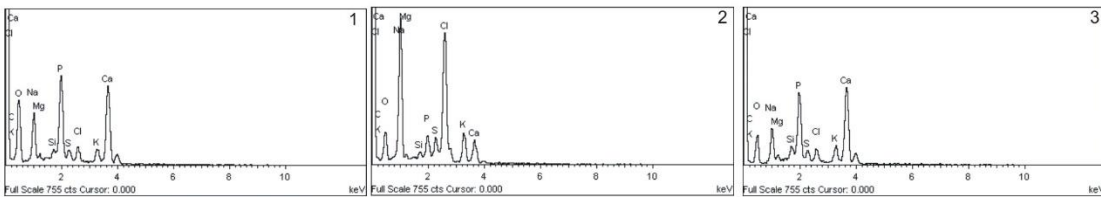
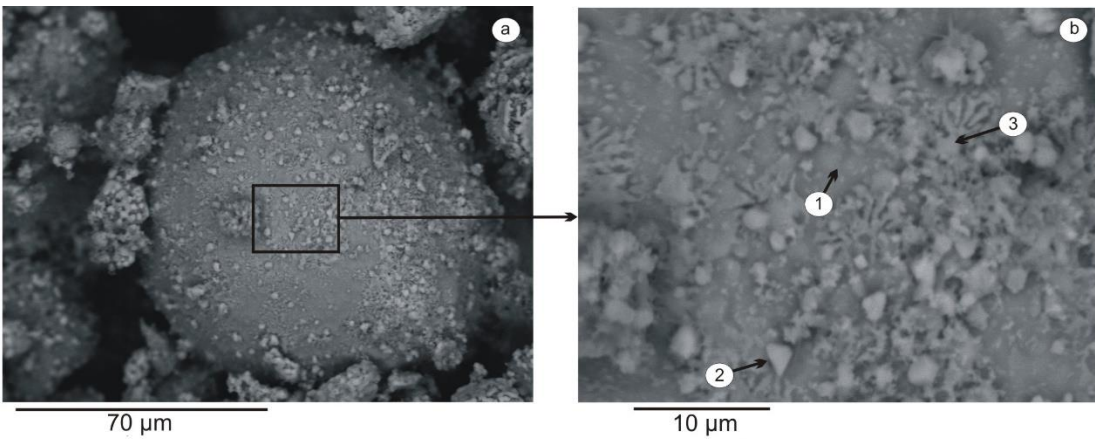


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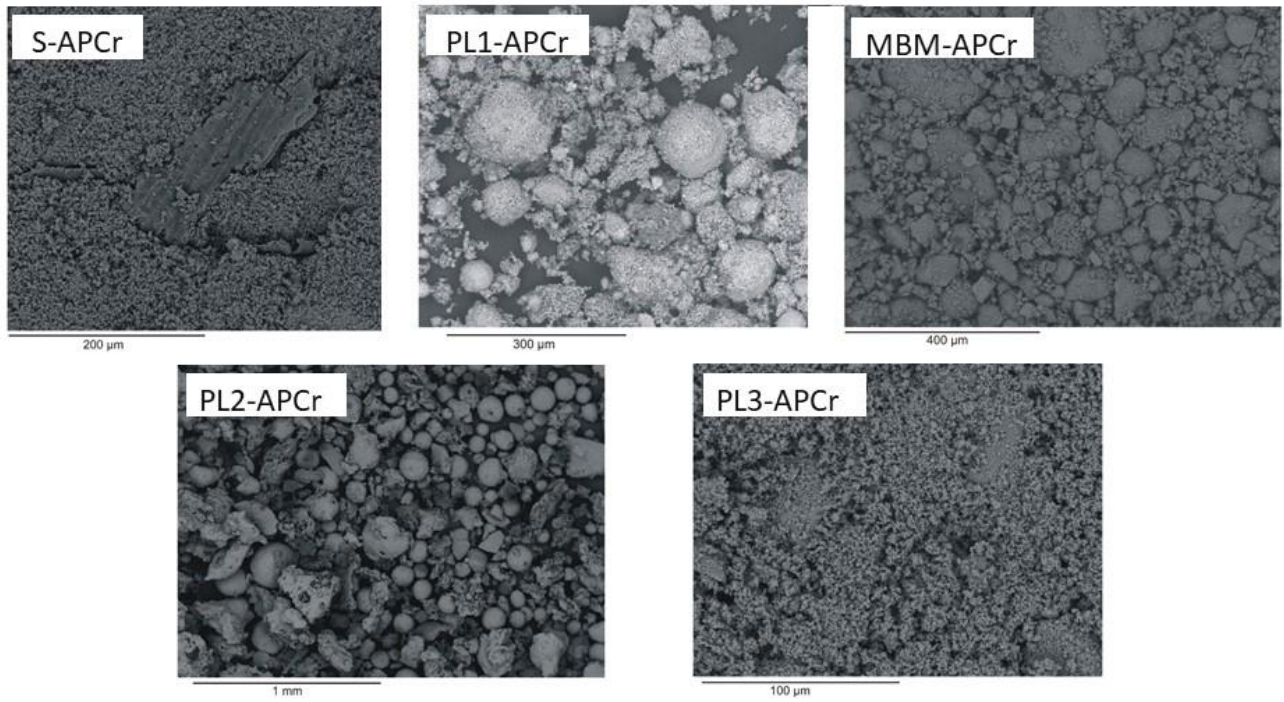
541 Figure 4. Scanning electron microscope images of unshaped particle (a) and associated fine materials
542 (b) with EDS spectra.
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545 **Figure 5. Scanning electron microscope images of unshaped particle (a) and aggregate (b) with EDS**
546 **spectra.**
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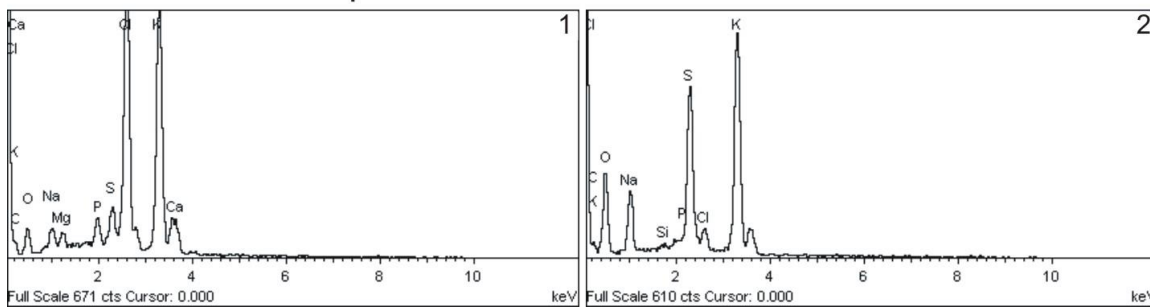
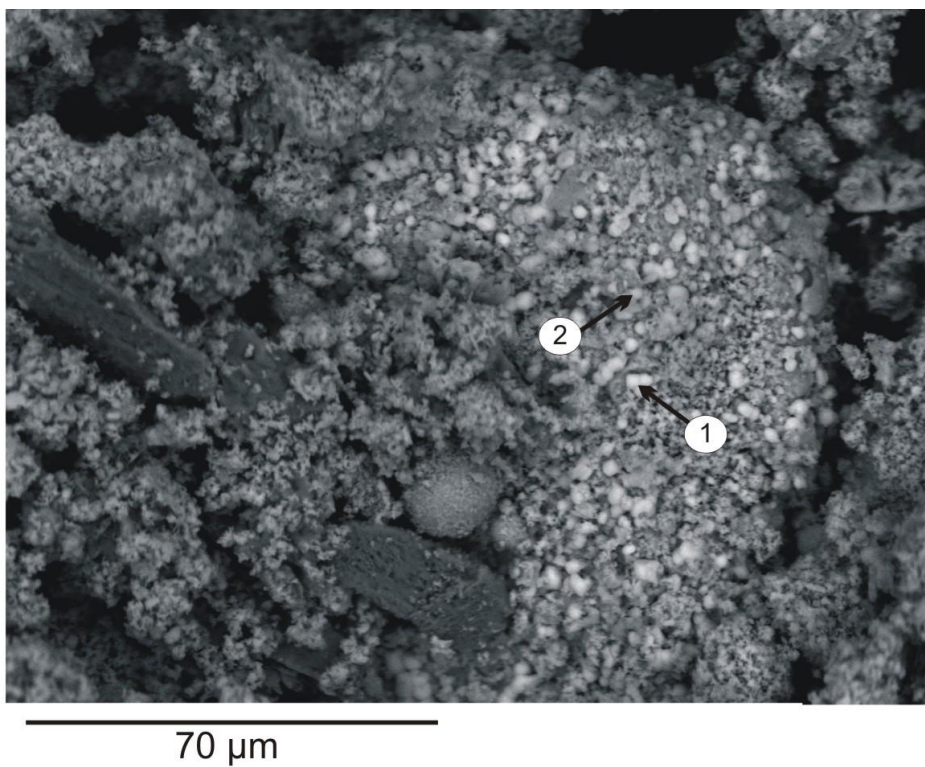


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549 **Figure 6. Scanning electron microscope images of spherical particle from biomass bottom ashes and**
550 **EDS spectra.**
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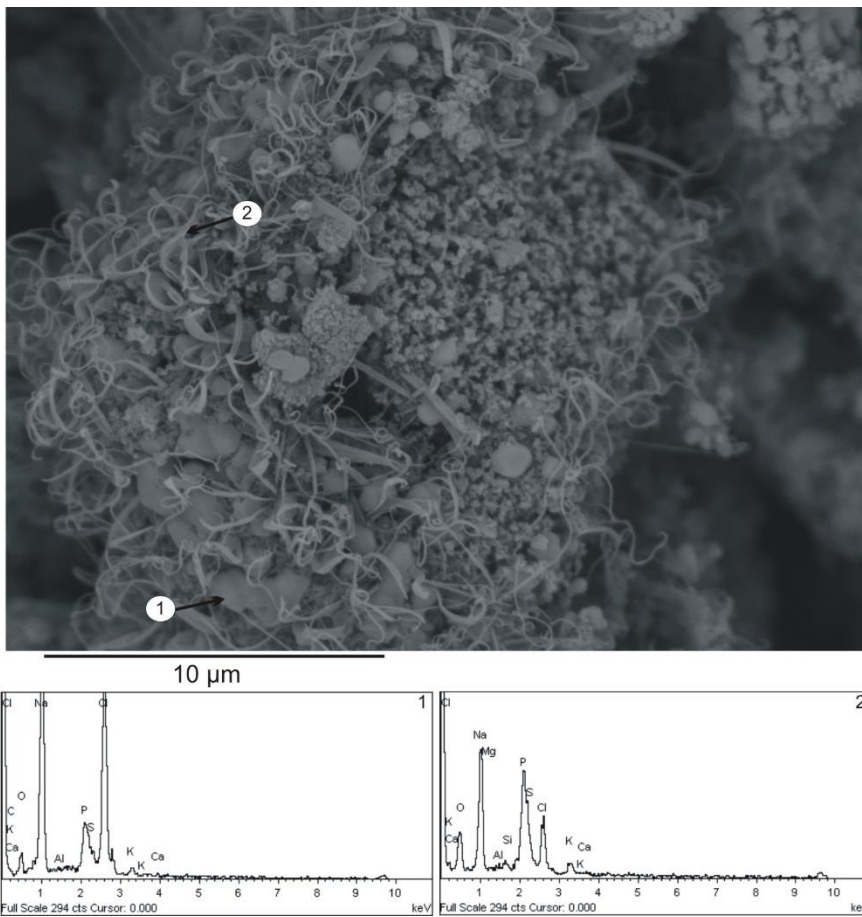
Fig 7. Scanning electron microscope images of the biomass APC residues.



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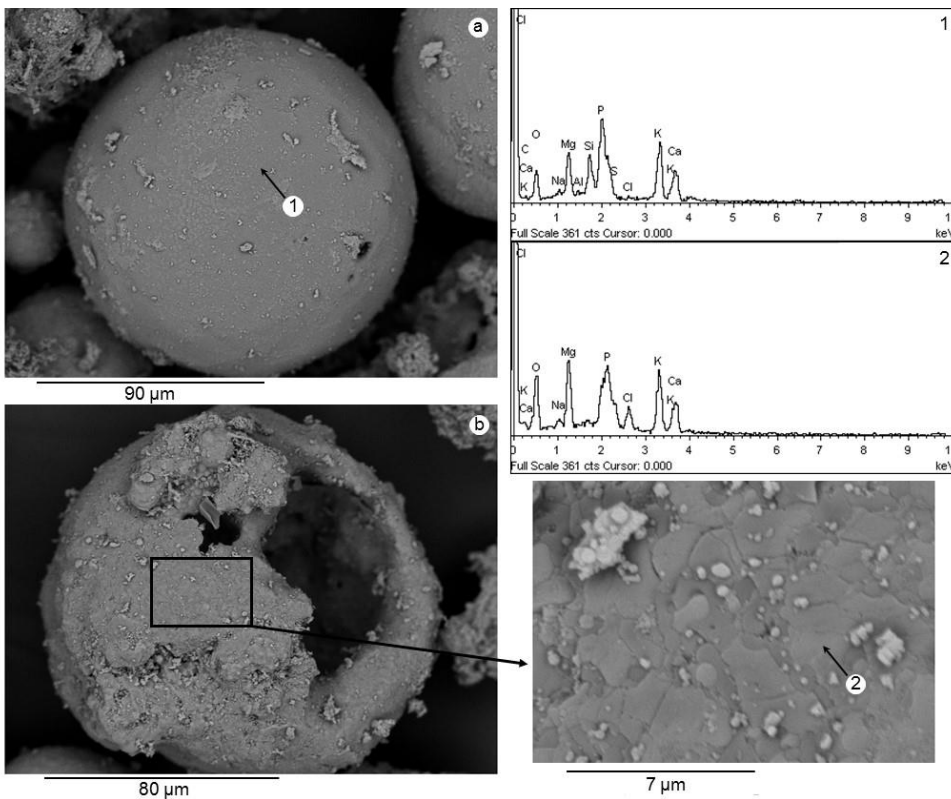
Figure 8. Scanning electron microscope image of unshaped and spherical particles covered by fine phases.

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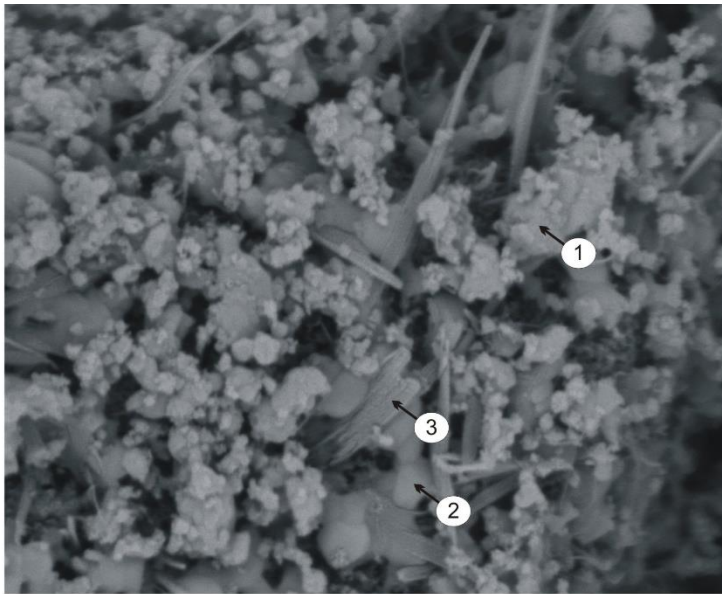
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Figure 9. Scanning electron microscope image of aggregate consisting of different fine phases.

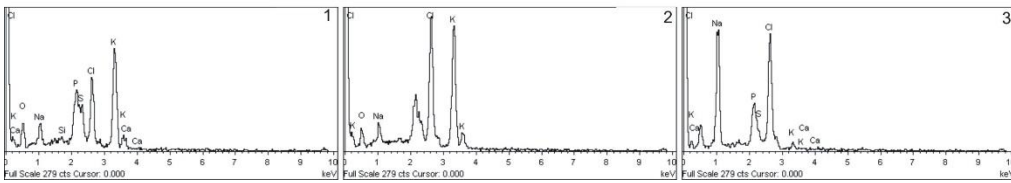


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Figure 10. Scanning electron microscope images of spherical particles from PL2-APCr.



10 μ m



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Fig 11. Scanning electron microscope image of fine phases from PL3-APCr.

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