The internal microstructure and fibrous mineralogy of fly-ash from coal-burning power stations

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Abstract

Coal fly-ash (CFA) is a significant environmental pollutant that presents a respiratory hazard when airborne. Although previous studies have identified the mineral components of CFA, there is a paucity of information on the structural habits of these minerals. Samples from UK, Polish and Chinese power stations were studied to further our understanding of the factors that affect CFA geochemistry and mineralogy. ICP-MS, FE-SEM/EDX, XRD, and laser diffraction were used to study physicochemical characteristics. Analysis revealed important differences in the elemental compositions and particle size distributions of samples between sites. Microscopy of HF acid-etched CFA revealed the mullite present possesses a fibrous habit; fibres ranged in length between 1–10μm. Respirable particles (<10μm) were frequently observed to contain fibrous mullite. We propose that the biopersistence of these refractory fibres in the lung environment could be contributing towards chronic lung diseases seen in communities and individuals continually exposed to high levels of CFA.

Capsule: Chinese CFA possessed a greater crystalline mineral content and smaller particle size than UK and Polish CFA, the fibrous mullite present displayed a high aspect-ratio and thus is likely to be a respiratory hazard in vivo.

Keywords: Coal Fly Ash; Mineralogy; Geochemistry; Microstructure; Fibrous Mullite

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Background

Over 60% of global electricity is generated by coal-fired power stations, resulting in vast quantities of coal fly ash (CFA) being produced annually Worldwide; approximately 600 million tons (Johnson, 2009). During coal combustion in a modern power station furnace, minerals contained within the raw pulverised feed coal are melted to 'glass'; the amount of incombustible matter contained within raw coal differs largely depending on source and quality, ranging from between 2-50 wt%. Subsequently, fine liquid droplets are released and lifted by the flue gases, where they undergo rapid solidification forming small glassy spheres, known as CFA. In addition, a small amount of particles also form through nucleation, a sublimation reaction of gaseous phases present in the flue gases (Seames, 2003). The five main elemental constituents of CFA are Si, Al, Fe, Ca and O. The Si, Al and O combine together to form an amorphous aluminosilicate glass matrix ($Si_xAl_yO_z$); Fe can be substituted into this matrix in place of Al. The $SiO_2:Al_2O_3$ ratio is commonly close to 2:1, and is governed by the mineral content of the feed coal; which is a function of the local geology, extraction and cleaning methods. The concentration of metals in CFA is highly dependent on the coal; with an enrichment factor usually between 10 - 15 times the levels found in the coal (Vassilev and Vassileva, 2007). Trace elements commonly found in CFA include Ni, V, As, Be, Cd, Cu, Zn, Pb, Hg, Se, Rn and Mo (Donaldson, 2005; Jones and BéruBé, 2006). CFA often possesses a surface layer, nm-μm in thickness, formed from the readily-leachable material deposited whilst cooling (Ugurlu, 2004). CFA also contains recrystallized minerals, such as quartz (SiO_2) and mullite ($Al_{4+2x}Si_{2-2x}O_{10-x}$), which are derived from the elements in the minerals originally present in the feed coal. Crystalline silicates, most notably the SiO_2 polymorph minerals

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68 quartz and cristobalite, are of great concern to respiratory health (Fubini et al, 2007).

69 However, little is known about the respiratory hazards of mullite, although one study

70 cited chronic bronchitis, silicotuberculosis and pneumoconiosis (mullitosis) in workers

71 exposed to highly aluminiferous clay (Artamonova et al, 2000).

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73 Despite CFA not being classified as a toxic waste hazard, there are concerns with the

74 current methods of storage, given that CFA is known to contain a range of metals and

75 other elements of environmental concern, such as Cd, Hg, Pb, As, and Se. Commonly,

76 CFA is stock-piled in ash mounds for storage, where it can be re-suspended by winds and

77 contribute to ambient particulate air pollution. Numerous epidemiological studies have

78 associated exposure to small particles, such as combustion-generated fine particles, with

79 lung cancer, heart disease, asthma and/or increased mortality (Zanobetti and Schwartz,

80 2007; Knox, 2008). It is noted that strictly speaking CFA is not a combustion particle, but

81 more precisely a 'melt' particle. This study examines CFA samples from the UK, Poland

82 and China. The main objective was to further detail our current understanding of the

83 geochemistry and structure of CFA, with special attention paid to the crystalline mineral

84 component. This paper considers the various factors that can influence CFA composition,

85 structure and morphology by comparing CFA sourced from power stations that differ in

86 their operational procedures, including the quality and source of the feed coal.

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Methods

Fly Ash Sources

The two UK-sourced CFA samples were obtained (anonymous donation) from a coastally-located coal-burning power station; UK1 was taken from the top of a compacted fly-ash pile (~50m high) formed from CFA that had been 'conditioned' (sprayed) with local seawater, whilst UK2 was taken directly from the electrostatic precipitators (ESP). The power station burned a mixture of UK and overseas-sourced bituminous coal, which was supplemented with biomass from Scandinavia (5-10 wt%, wood chippings/sawdust). The two Polish CFA samples were collected from power stations located in the Małopolska district. The first sample, PL1, was taken from the main ESP unit of an old 590MW coal-fired power station. The second sample, PL2, was collected from the final filter of a three-stage ESP unit that served a combined electricity (460MW) and heat (1236MW) power station. The stations both co-fired biomass (10-15 wt%) in a 60:40 split of sawdust and crops (corn/sunflower seeds) with bituminous coal from numerous sources, the majority coming from the nearby open-cast mines of Katowice. The Chinese CFA samples were obtained from power stations that used locally-sourced coal that is found inter-bedded in late Permian limestones ($CaCO_3$). Both were collected from the power station's ESP units. The first sample, CH1, was collected from a very small, relatively new power station (50MW) located in the Henan province of China. The second Chinese sample, CH2, was obtained from a significantly older and larger (1260MW) coal-fired power station located in the Shandong province. The stations burn locally-sourced sub-bituminous coal known for having a high sulphur content, approximately 1.8 – 4.5%, and high overall ash content, 35 – 39% (Shao et al, 2003).

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Fly Ash Preparation

All samples were dried in a Heraeus oven at 50°C for 24 hours. For each sample, the 'respirable' PM_{10} fraction was dry separated from the bulk via a rotating drum with a HEPA-filtered air flow of 30 L/min. The PM_{10} fraction was then collected on a 0.67μm polycarbonate filter in a NEGRETTI collection head (BéruBé et al, 2006).

Fly Ash Heating Experiments

Heat-treated samples were prepared for the UK and Polish CFA in order to identify the relative thermostability of each sample's mineral content via X-ray diffraction (XRD). The rationale behind the heating experiments was to mimick conditions possibly experienced by particles collected on ESP plates, but still being exposed to hot flue gases. Samples were weighed into ceramic crucibles and placed into a muffle furnace at 400°C for 7 days, on removal samples were left to cool naturally at room temperature and pressure.

Laser Diffraction Particle Sizing

Laser diffraction was used to establish a particle-size distribution profile for both bulk and PM_{10} fractions of each sample. An approximate dry mass of 200mg of each sample was analysed using a Scirocco 2000 Mastersizer (Malvern Instruments); all measurements were made on the same day under the same conditions. A refractive index (RI) of 1.60 with an adsorption of 0.001 was used; as recommended by the manufacturer for use with CFA samples. Median mass diameter (MMD) and specific surface area (SSA) values for each sample were calculated from the distribution data; a reference

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136   particle density value of 2.46 g/cm^3 was used when calculating MMD values (Gurupira et

137   al, 2001).

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139   **Scanning Electron Microscopy**

140   Particle morphology and microstructure was studied via Field Emission-Scanning

141   Electron Microscopy (FE-SEM). Samples were mounted on standard aluminium SEM

142   stubs using sticky carbon tabs before being gold/palladium coated to a thickness of 20nm

143   using a BIO-RAD Microscience Division SC500 sputter coater. The samples were

144   analysed using a Phillips XL30 FE-SEM, equipped with an Oxford Instruments INCA

145   ENERGY Energy Dispersive X-ray analyser (EDX). The working distance was 10mm,

146   beam voltage 20.0Kv, aperture 4 and spot size 5. The images were captured via

147   secondary electron detection. All images were saved as *.TIF files. INCA ENERGY

148   analysis package was used to determine the composition of specific sites of interest; spot

149   analysis was used for verifying the composition of individual items of interest.

150

151   **Resin-Embedded Polished Blocks**

152   The UK and Polish CFA was embedded and polished in resin blocks using standard coal

153   petrology techniques (Jones and Rowe, 1999). A portion of dry sample (~5g) was mixed

154   with low viscosity epoxy resin in a 5cm diameter circular mould. The blocks were then

155   set in a vacuumed oven to minimise trapped air bubbles in the resin. The blocks were

156   polished following the British Standard guidelines for preparation for coal petrology,

157   finishing with a diamond paste abrasive to achieve a high polish (Jones and Rowe, 1999).

158   This revealed the cross-sections of individual CFA spheres and agglomerates. Acetone

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159 was used to clean the surface of the blocks, which were carbon-coated to a thickness of

160 15nm using an EMITECH K450 sputter coater prior to analysis. The resin blocks were

161 examined under SEM using back scatter detection, with site-specific composition

162 determined by EDX.

163

164 **Hydrofluoric Acid Etching Experiments**

165 In order to study the structural habits of CFA mineral components in detail, the

166 amorphous glass matrix must first be removed by an etching process. Bulk CFA samples

167 were placed on 0.45μm Whatman cellulose nitrate membrane filters (47mm diameter)

168 inside a separable Millipore filter unit attached to a syringe. The samples were then

169 suspended in 40% hydrofluoric acid (HF) for 30 seconds, enough time to allow the acid

170 to etch away a layer of the amorphous aluminosilicate glass matrix. Following

171 completion of the etching time, each sample was flushed with de-ionised water to ensure

172 removal of surface HF acid. The resin-embedded polished blocks were also subjected to

173 the same etching process for cross-sectional comparison of the spheres; the resin is

174 unaffected by the acid.

175

176 **X-Ray Diffraction**

177 Sample mineralogy was determined by XRD analysis carried out using a Philips PW1710

178 diffractometer with Co-Kα radiation (from a Cobalt tube) generated at 35kV and 40mA.

179 All samples were packed into a cell using double-sided tape and measurements were

180 taken between 2 and 70 2θ at a scan speed of 0.040 °2θ/sec with a count time of 0.5

181 sec/step with a total of 3400 steps.

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182   **Inductively Coupled Plasma-Mass Spectrometry**

183   The major and selective trace elemental compositions of bulk and PM_{10} CFA samples

184   were determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The

185   Claisse Fluxy fusion system was used to prepare samples for analysis. 1g (+/- 1%) of

186   each sample was weighed and placed into a platinum crucible. In each crucible, 0.6g of

187   50% lithium metaborate and 50% lithium tetraborate flux was added; 6-9 drops of lithium

188   iodide were also added to each crucible as a wetting agent. The crucibles were then

189   heated to between 800°C – 1000°C. The resulting flux was then tipped into a beaker

190   containing diluted nitric acid and 1ml of 100ppm rhodium solution (internal standard).

191   This was automatically mixed until all the flux had dissolved. The resulting solution was

192   made up to 100ml with deionised (>18ΩM) H_2O and analysed using a ThermoElemental

193   X-series ICP-MS equipped with a Cetac AS-500 autosampler. Raw data was corrected for

194   blanks, controls and dilutions. The international standards, JB 1a, Japanese basalt, and

195   MRG-1, a rock standard, were run in duplicate as external controls.

196   # Results

197   **Particle Size Distribution**

198   The values obtained represent equivalent spherical diameter (ESD); although the majority

199   of CFA particles are spheres, irregular shaped particles are also common. The median

200   mass diameter (MMD, μm) and specific surface area (SSA, m^2g^{-1}) values were

201   determined for each sample (Table 1). The bulk sample represents the full size-

202   distribution of the sample, including spheres, composites/aggregates and large

203   agglomerates, or grains, whereas the PM_{10} fraction is composed almost exclusively of

204   individual spheres. The separation of the PM_{10} fraction from the bulk was successful,

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205   with the average sphere size of the respirable fractions ranging from between 1.98 –

206   5.64μm. The Chinese PM_{10} samples displayed both smaller particle size and greater SSA

207   values than the European PM_{10} samples, at $1.98μm/3.01m^2g^{-1}$ (CH1) and

208   $2.42μm/2.96m^2g^{-1}$ (CH2), compared to the European samples particle size range of

209   3.50μm – 5.64μm and SSA range of $1.72 – 2.20m^2g^{-1}$. The bulk samples showed greater

210   variation, most notably the Chinese samples, which revealed a dramatic increase in

211   particle size between the PM_{10} and bulk samples; conversely, the PL2 sample displayed

212   little difference between samples.

213   Insert Table 1

214   **Morphology**

215   The FE-SEM analysis revealed a variety of particle morphologies, although the vast

216   majority of particles were spherical. These spheres were present as solid or hollow

217   spheres (cenospheres); fragments of spheres were also present. In addition, some spheres

218   were seen to house other much smaller sub-micron sized particles, these structures are

219   known as plerospheres. Another common feature observed was the aggregation of

220   smaller spheres to form larger masses; smaller spheres were also adhering to the surfaces

221   of other larger spheres or agglomerates. The FE-SEM images (Figures 1a-1h) illustrate

222   some of the key features observed during morphological analysis. The UK1 PM_{10} sample

223   (Figure 1a) consisted of spheres that were highly uniform in shape and surface texture,

224   their size ranging between 3μm – 5μm in diameter (laser diffraction MMD value of

225   3.50μm); with the exception of a few larger spheres up to 15μm. Plerospheres were

226   frequently observed during analysis (Figure 1b). The spheres in the UK2 sample (Figure

227   1c) had notably rougher surface textures than those of the UK1 sample (conditioned

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228   CFA). An uncommon chain-like structure was found in the UK2 PM_{10} sample, where

229   three adjoining spheres, fairly uniform in size (~2μm), appeared to have fused together;

230   their surface textures varied from very rough to quite smooth (Figure 1d). The overall

231   morphology of the PL1 PM_{10} sample was comparable to that of the UK1 PM_{10} sample;

232   however, the spheres possessed a rougher surface texture by comparison. An unusual

233   particle was found in the PL2 sample, its morphology suggests extremely rapid

234   solidification during movement-derived deformation (Figure 1e). FE-SEM images of the

235   HF etched bulk samples revealed that mullite fibres form a three dimensional mesh cage

236   integral to the particles overall morphology (Figures 1f – 1h); as such the recrystallized

237   sphere is a pseudomorph of the original wholly glass sphere. Fibres were observed to

238   differ in both length and width, with some spheres possessing thick fibres (Figure 1f) and

239   others much finer fibres (Figure 1g). It was also noted that the fibres were not restricted

240   to spherical structures, as a number of irregular shaped particles also exhibited a fibrous

241   scaffold (Figure 1h).

242   Insert Figure 1

243   **Microstructure**

244   The following features highlighted in this section apply to all six samples; however,

245   resin-embedded blocks were only made from the UK and Polish samples. FE-SEM

246   images of the resin-embedded polished blocks were taken in back scatter mode (Figures

247   2a-h). The cross-sectional analysis revealed the majority of particles were small solid

248   spheres, however both large and small cenospheres were also observed, as well as a

249   distribution of spheres possessing complex internal crystalline structures (Figure 2a;

250   UK1). The internal structures observed belong to ferrospheres, although few exhibit such

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251   complex structures at the surface (Figure 2b; PL1). These dendritic structures varied in

252   branch size and complexity (Figure 2c; UK1). The voids and pockets seen in larger

253   spheres were associated with particle degassing (Figure 2d; UK2). Ferrospheres were

254   often found residing in larger plerospheres, along with many other smaller solid spheres

255   (Figure 2e; PL2). The microscopy of the HF-etched polished blocks (Figures 2f – 2h)

256   revealed very clearly that a fibrous component was present in nearly all particles,

257   although to a varying degree. This fibrous mineral component was found in plerospheres

258   (Figure 2f; PL1), where fibres were typically 5µm in length (Figure 2g; UK1), along with

259   smaller and larger spheres (Figure 2h; UK2).

260   Insert Figure 2

261   **Mineralogy**

262   The XRD analysis (Figures 3a-3d) revealed the most abundant minerals found in CFA to

263   be quartz, mullite and hematite. The diffractogram for the UK1 sample (Figure 3a) had a

264   clearly visible baseline distortion due to the amorphous glass, which can cause peaks to

265   appear less prominent; quartz and mullite were the dominant minerals. Upon heating, the

266   diffractogram for the UK1 sample showed an increase in mullite peaks, with a decrease in

267   quartz peaks, and the emergence of a strong hematite peak. The major peaks observed

268   during analysis of the UK2 sample were quartz and mullite, with quartz being the most

269   abundant. The number of identifiable peaks dropped considerably after heating, though

270   the intensity of the peaks remaining appeared not to have been affected. The PL1 sample

271   had high counts for quartz and mullite (Figure 3b); the heating program failed to alter the

272   mineral content of the PL1 sample. The level of baseline distortion was high for the PL2

273   sample, with low counts for quartz and mullite. The PL2 sample showed some notable

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274   changes upon heating. The counts for the quartz and mullite peaks increased slightly, and

275   a number of new hematite peaks were observed. The CH1 sample displayed peaks for

276   quartz, mullite and hematite, as well as gypsum (Figure 3c). The CH2 sample also

277   displayed strong peaks for quartz, mullite and hematite. Overall, the counts for the

278   Chinese CFA crystalline mineral peaks were much higher than those seen for the

279   European CFA; in addition the baseline was flatter. Along with the CFA samples, the

280   mineral composition of PL1 pulverised feed coal was analysed, revealing peaks for quartz

281   and kaolinite, halite, illite and pyrite (Figure 3d).

282   Insert Figure 3

283   **Geochemical Composition**

284   The major elemental compositions of all six samples were determined via ICP-MS (Table

285   2a). In order to assess whether elements were disproportionally fractionated dependent on

286   particle size, the elemental compositions of four PM_{10} samples were also determined. The

287   Chinese samples had the highest Si content, CH1 at 58.49wt% and CH2 at 54.59wt%

288   (PM_{10}; 54.15wt%), considerably higher than the UK1 and UK2 samples, which were

289   44.72wt% (PM_{10}; 51.07wt%) and 44.27wt% (PM_{10}; 47.16wt%), respectively. The Al

290   content of samples was more consistent, ranging between 20.55wt% - 26.14wt%. The

291   levels of Mg and K were higher in the Polish samples, especially PL2 which had values

292   of 3.31wt% and 3.36wt% respectively, compared to CH2, whose levels were the lowest,

293   at 0.82wt% and 0.34wt%. The levels of trace elements varied between sub-samples; the

294   UK bulk samples had higher values than the PM_{10} equivalents for every element except

295   Ba and Zr (Table 2b). The Ni content ranged from 52ppm for CH1 to 541ppm for CH2.

296   The same level of variation was seen for Zn, which was present at 83ppm for CH1 and

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297   702ppm for PL2. The highest levels of Cr were found in the CH2 sample at 324ppm, with

298   the lowest levels found in the CH1 sample at 93ppm.. The PL2 bulk and PM_{10} samples

299   were very similar in major and trace composition, yet the readings for the CH2 PM_{10}

300   sample were higher than those seen in the bulk sample for every trace metal except Cr, Ni

301   and Zr. There appears to be an enrichment of Ca in the PM_{10} fraction, which was noted

302   for 3 of the 4 PM_{10} samples. The levels of Ca in the CH2 PM_{10} sample were over double

303   those seen in the bulk sample. In addition, the $SiO_2:Al_2O_3$ ratio appears to shift in the

304   PM_{10} fraction, with the exception of CH2 PM_{10}, all European samples had increased SiO_2

305   content and decreased Al_2O_3 content in the smaller size fraction. Fe content was observed

306   to decrease in the respirable fraction, with all four PM_{10} samples presenting lower values

307   than their respective bulk samples.

308   Insert Table 2a/b

309   **Particle-Specific Composition**

310   The FE-SEM/EDX analysis was performed simultaneously with the morphological

311   analysis (Figures 4a-f). The data obtained for each sample generally agreed with the

312   respective ICP-MS data; the major elements present were Si, Al, Fe, Ca and Mg.

313   Assumptions based on elemental ratios suggest that $Ca_3(PO_4)_2$ and $CaSO_4$ were present in

314   CH1, and NaCl in UK1, as well as CaO in CH2 (Figure 4a). The levels of unburned

315   carbon (LOI values) recorded for the UK samples were ~15% (Table 1a); an example of

316   carbonaceous material (92% carbon) was found in the UK2 bulk sample (Figure 4b). The

317   dendritic structures observed in the cross-sectional work (Figures 2a-h) were selected for

318   analysis by EDX. The structures were formed from iron oxides (Figure 4c); these spheres

319   are commonly referred to as ferrospheres (Sokol et al, 2002). The crystalline mineral

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320   fibres identified following the HF etching procedure proved to be an aluminosilicate

321   composite (Figure 4d). Further analysis was performed on exposed crystals that had been

322   etched, revealing whole particle scaffolds to be composed of fibrous mullite; this was

323   confirmed using both pin-point analysis and a quadrat setting (Figures 4e and 4f).

324   Insert Figure 4

Discussion

326   **Morphology**

327   The morphology of the CFA showed only marginal differences between samples, mainly

328   in average particle size. However, the conditioning of the UK1 sample with locally-

329   sourced seawater resulted in the removal of surface condensates and water soluble

330   phases; although EDX analysis revealed these compounds were often replaced with NaCl

331   crystals. The difference in surface texture between UK1 and UK2 suggests the material

332   has adhered to the surface as opposed to protruding from the particle body. It is probable

333   that relative particle surface charge plays a key role in dictating the degree of surface

334   coating, as there does not appear to be a correlation between size and surface texture (Li

335   et al, 2011). Particles will become negatively charged on passing through the electrostatic

336   precipitators, the degree to which each particle holds this negative charge is likely

337   dependent on their individual composition. Previously, surface charge has been shown to

338   be dependent on composition in the clay mineral montmorillonite for particles ~1μm)

339   (Liu et al, 2008). Slight differences in surface charge, either during particle formation or

340   electrostatic precipitation, may influence the level of coating for each particle.

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342   The FE-SEM analysis of the polished block cross-sections (Figures 2a-h) provided

343   valuable insight into CFA microstructure that could not be determined by conventional

344   FE-SEM. The majority of particles were composed of aluminosilicate glass, often with

345   gas pockets and iron oxide inclusions (ferrospheres); these findings suggest that CFA is

346   perhaps not as homogeneous as previously thought (Goodarzi, 2006). Ferrospheres are

347   known to be derived from the decomposition and oxidation of Fe-bearing minerals

348   present in the feed coal, such as pyrite (Fe_2S) and clay minerals, during combustion (Fe^{2+}

349   $\rightarrow Fe^{3+}$) (Hubbard et al, 1984); pyrite was identified in the XRD analysis of the PL1

350   pulverised feed coal sample (Figure 4g). This suggests that the Fe from the pyrite was

351   incorporated into the aluminosilicate matrix and also present as oxidised spherules

352   (ferrospheres).

353   **Geochemistry**

354   Cho et al, (2009) suggested that enrichment of elements in the smaller particle size

355   fraction occurs while the incombustible material is molten, the sulphur and metals

356   vaporise and subsequently nucleate and combine with small droplets of fused inorganic

357   material that can be coated with condensed or reacted semi-volatile metalloids. However,

358   our ICP-MS data revealed little difference between the compositions of the bulk samples

359   and their PM_{10} fractions (Table 2a and 2b), despite notable differences in particle median

360   mass diameter as seen in the laser diffraction analysis (Table 1). It is worth noting that the

361   surface compositions of fugitive CFA re-suspended from power stations, or emitted from

362   the stack, may differ from CFA collected directly from an ESP unit, as particles readily

363   acquire new surface compounds during long-distance travel, such as polycyclic aromatic

364   hydrocarbons (Eiceman and Vandiver, 1983). The increased Ca content in the CH2 PM_{10}

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365 sample is likely to be $Ca(OH)_2$ particle surface material associated with the smaller size

366 fraction derived from contaminating limestone bedrock in the coal that was initially

367 converted to CaO, and then hydrated to $Ca(OH)_2$. This would explain the highly basic pH

368 of the Chinese CFA, which was determined during previous pH elution analysis (data not

369 shown). The analysis found all six CFA samples and their PM_{10} fractions to be alkaline,

370 with little variation between fractions over a seven day trial period. Surface $Ca(OH)_2$ has

371 been cited previously as a source of CFA alkalinity (Dutta et al, 2009). It is noted that

372 post-combustion 'conditioning' of the UK1 sample appeared to reduce CFA alkalinity

373 (pH 11.7 for UK2 reduced to 8.8 for UK1), suggesting surface material or accessible

374 soluble elements dissociated during 'wetting' of the CFA with local seawater (pH ~7.5).

375 Broncheo-alveolar lung fluid is known to have a pH ~7.3, thus it is possible the same

376 surface dissolution chemistry of soluble components would apply in the lung

377 environment. It is also observed that as the Ca content increases from bulk to PM_{10}

378 samples, the Fe content is seen to decrease, especially for CH2. This is likely to be a

379 result of the separation process causing a decrease in the number of Fe-bearing spheres

380 (ferrospheres) present in the sample. Due to their relatively large average particle size (5−

381 50μm; Xue and Lu, 2008), proportionately fewer ferrospheres will reside in the respirable

382 (<10μm) fraction. The magnetic fraction, including ferrospheres, is believed to account

383 for approximately 1.5 − 1.8wt% of bulk CFA (Hansen et al, 1981; Dai et al, 2010).

384 Interestingly, Kulkier et al (2003) found that when comparing magnetic (haematite,

385 magnetite) and non-magnetic (quartz, mullite) fractions, more elements leached out of

386 non-magnetic than magnetic fractions under alkaline conditions created by CFA.

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Mineralogy

Mullite and quartz were the two minerals most frequently identified during XRD

analysis. The coexistence of hematite, mullite and quartz in the Chinese samples could

have resulted from iron spherules becoming embedded in the amorphous-silicate matrix

(Lu et al, 2009). The counts observed for each sample differed considerably indicating

that the Chinese samples had a higher mineral content; this was also supported by the

flatter baselines seen for these samples, which is indicative of a lower amorphous silica

content (Diamond, 1984). Zhao et al (2008) reported that CFA particles become more

crystalline (quartz) and less amorphous with decreasing particle size, however, our ICP-

MS data would suggest there is little difference between bulk and PM_{10} CFA. The coal

used in the Chinese power stations was obtained from limestone and clay mineral

sedimentary sequences (Shao et al, 2003); the limestone ($CaCO_3$) accounts for the high

Ca levels measured in the CFA and the kaolinite, mica-illite and smectitic clay minerals

provided the Si, Al and O (along with other trace elements) required for the

aluminosilicate glass (McCarthy et al, 1987). When gradually heated kaolinite undergoes

several intermediary changes (kaolinite → metakaolin → aluminium silicon spinel)

before eventually forming mullite, with temperatures exceeding ~1050°C required for the

final transformation step (Zhao et al, 2010). This process mimics the natural formation of

mullite at the type location at Port Na Cloidheig, Isle of Mull, Scotland, where clay

minerals are trapped and transformed between hot volcanic lava flows (Jones et al, 2009).

For all six CFA samples (UK, Poland, and China) in this study, we did not identify any

'original' mineral grains, as has been seen in previous CFA studies. For example, Ribeiro

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410   et al (2011) show images of CFA from a deactivated Portuguese power station that are

411   clearly original quartz grains (their Figure 3, image A1), which indicated that the furnace

412   temperatures did not reach 1,650 (+/-75)°C, the melting point of quartz. Furthermore, our

413   XRD of the Polish coal feedstock (PL1) indicates that the clay minerals in the coal

414   (kaolinite and illite) did not survive the heating. There is ambiguity in the scientific

415   literature and commercial information, but a consensus would have the melting point of

416   clays around 1,750°C. Therefore, as all our CFA appears to be derived from glass, all the

417   original minerals must have melted, and this sets a minimum furnace coal combustion

418   temperature of 1,750°C. In addition to the mineral temperature information, the spherical

419   shape of the CFA is critical in understanding the mineralogical processes. All the coal

420   minerals were melted (1,750°C+), converted into liquid glass, and formed the spherical

421   shapes. The temperature then decreased resulting in the glass solidifying (900°C-

422   1,100°C) and retaining that spherical shape, regardless of any other mineralogical

423   changes. At these lower temperatures, minerals recrystallized (devitrification) from the

424   amorphous non-crystalline glass, and the order in which they recrystallise is controlled by

425   their melting temperatures. The first mineral to start forming is mullite which has a

426   melting temperature ~1,760°C; however the recrystallization occurs at a much lower

427   temperature, 900°C and less. The mullite forms as fibrous crystals in a three-dimensional

428   framework (pseudo-morph) the same overall shape as the original glass sphere (Hulett

429   and Weinberger, 1980; Joshi et al, 1985). In the bulk glass composition the ratio of Si:Al

430   is approximately 2:1 (Table 2a), in the mullite the Si:Al ratio is reversed at approximately

431   1:2 (Figure 4d, 4e, 4f). Therefore, as the mullite fibres form, the remaining glass matrix

432   becomes progressively depleted in Al. Once depleted in Al, and at lower temperatures,

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433   the matrix will then start recrystallising a groundmass of quartz around the mullite fibres.

434   This will continue until the temperature reaches a sufficiently lower level to stop any

435   further recrystallization. The mullite content of a given CFA sample is therefore highly

436   dependent on the post-melting cooling pathway, and the Al content derived from minerals

437   in the coal (Dai et al, 2009).

438

439   The heating experiments were designed to mimic the conditions of a "hot-side" ESP unit,

440   which operate between 300-450°C upstream of the air pre-heater. We were advised that

441   this was the temperature range by the power station operators. It is possible that ash may

442   become trapped on the ESP for long periods before removal, thereby exposing it to

443   conditions capable of thermodynamically altering the mineral content. The results of the

444   heating experiments showed some evidence of changes to CFA mineralogy, though

445   mostly concerned with the appearance or increase in hematite peaks, rather than the

446   expected overall increase in crystalline material. Similar results have been reported

447   previously (Medina et al, 2010). A slight increase in mullite and decrease in quartz was

448   noted for the UK1 sample, a possible thermodynamic alteration of the SiO_2-Al_2O_3

449   system, as reported previously (Illic et al, 2003). New hematite peaks were observed in

450   two samples, UK1 and PL2, suggesting that iron present had been oxidised to hematite

451   (α-Fe_2O_3), possibly associated to the iron-rich rim found on many CFA particles (Škvára

452   et al, 2009; Smith and Baer, 1983). The decrease in the number of peaks observed for the

453   UK2 sample following the heating program is suggestive of slight differences in the

454   mineralogy of the two UK samples despite the samples having both originated from the

455   same power station.

20

Fibrous Mullite Hazard

456

457   Whilst the respiratory hazards of quartz dusts have been heavily researched (Fubini et al,

458   2004), there is a paucity of research into the risks associated with exposure to mullite.

459   When CFA is treated with HF acid, the quartz and amorphous glass matrix is rapidly

460   dissolved, whereas mullite is a more refractory material, enabling it to withstand the

461   etching process much longer. Fibre length appears to be dependent on the size of the

462   spheres, with the majority approximately 5µm in length and 0.5 – 1µm in width. Fibrous

463   minerals have been the subject of intensive research in the field of respiratory toxicology,

464   most notably asbestos, but also including man-made mineral fibres such as glass or

465   mineral wools (Dörger et al, 2001). The most dangerous known mineral is the fibrous

466   natural zeolite erionite, which is linked to mesothelioma (Dogan et al, 2008; Fach et al,

467   2003). A result of all this intense interest in fibrous minerals has been the development of

468   the 'fibre paradigm', where the shape of the mineral is believed to have a direct bearing on

469   disease initiation (Donaldson et al, 2006). It is conceivable that these mullite fibres could

470   prove to be damaging to respiratory health should they accumulate in the tracheo-

471   bronchial and broncho-alveolar regions of the lungs. The determining factor of whether

472   the mullite fibres come into direct contact with cells lining the respiratory tract is the

473   dissolution rate of the amorphous silica matrix in lung fluid. In addition, we must also

474   consider the possibility that this dissolution rate could be markedly increased if the

475   particle were in an acidic environment, for example, following phagocytosis by a

476   macrophage (intracellular pH ~4.5). Rothenberg et al (1989) recovered CFA from rat

477   lungs at 1, 3, 6 and 12 months following a 4 week exposure; particles were characterised

478   using SEM and EDX. They were able to distinguish between inhaled and control CFA,

21

479   noting that the number of Si-rich particles decreased with time. After 6 months, 1% of

480   particles had been transformed, producing numerous 'needles' associated with residues of

481   CFA particles. These 'needles' are almost certainly the mullite fibres presented in this

482   study. Furthermore, macrophages have been shown to unsuccessfully attempt

483   phagocytosis of fibres between $5 - 10\mu m$ in length, leading to the release of inflammatory

484   mediators (Tomatis et al, 2010). Mullite is a refractory material and one would expect the

485   half-life of the fibres within the lung environment would be substantial, and this level of

486   biopersistence could contribute towards a chronic lung condition (Osmond-McLeod et al,

487   2011).

488   **Conclusions**

489   The physicochemistry and potential health effects of CFA are dependent on a number of

490   factors, including feed coal geochemistry, furnace operating conditions and post-

491   combustion processing. Notable geochemical differences between the bulk and PM_{10}

492   samples studied in this paper included a shift in the SiO_2-Al_2O_3 ratio towards SiO_2 for the

493   UK samples, as well as an increased Ca and decreased Fe content in the respirable size

494   fraction of all samples. XRD analysis revealed the Chinese CFA to be more crystalline.

495   Feed coal geochemistry and furnace temperature are critical in dictating the mineralogy

496   and post-furnace recrystallization of potentially hazardous minerals from the glass matrix.

497   The fibrous mullite component present in CFA forms a crystalline framework that

498   pseudomorphs the original spherical structure of the CFA particles. CFA and its

499   constituent mineral mullite should be viewed as a potential respiratory hazard due to the

500   abundance of CFA in our environment, and the insolubility and therefore likely

501   biopersistence of mullite in the lung environment. The fibres are of significant length to

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502 cause chronic respiratory health problems should they become deposited throughout the

503 lower respiratory tract.

Acknowledgements

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Figures

685 **Figure 1.** Field Emission-Scanning Electron Microscopy of raw CFA and HF etched

686 CFA.

687 1a: FE-SEM image of UK1 PM_{10} sample consisting of spheres highly uniform in shape

688 and size, with the majority around 3μm – 5μm in diameter and smooth in appearance.

689 1b: An example of a plerosphere found in the UK1 PM_{10} sample, many smaller sub-

690 micron sized particles remain trapped inside of a hollow sphere around 8μm in diameter.

691 1c: FE-SEM image of a sphere from the UK2 sample; the sphere possesses a

692 considerably rougher surface texture in comparison to that of the spheres in Figure 1a. 1d:

693 Three connecting spheres, found in the UK2 PM_{10} sample, appear to have fused together

694 forming a chain-like structure. The spheres are fairly uniform in size, around 2μm,

695 although their surface textures are more varied.

696 1e: FE-SEM image of a particle found in the PL2 sample, which has had its shape

697 distorted whilst cooling, presenting an unusual pear-shaped morphology.

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698   1f: A sphere found in the CH2 sample, approximately 15µm in diameter, exhibiting a

699   fibrous mullite framework.

700   1g: Image highlighting a large sphere which appears to have opened up following the HF

701   etching procedure.

702   1h: A large irregular shaped agglomerate displays the same fibrous mullite framework

703   seen in Figures 3b and 3c.

704

705   **Figure 2**. Field Emission-Scanning Electron Microscopy of resin-embedded polished

706   blocks including HF etched blocks and raw material.

707   2a: A large CFA sphere with a highly crystalline structure (UK1).

708   2b: FE-SEM image of a ferrosphere found in the PL1 sample demonstrating a complex

709   surface structure formed from Fe oxides, as confirmed by EDX analysis.

710   2c: A close-up image of the dendritic structure seen in Figure 2a.

711   2d: CFA sphere with large pockets (formed by degassing) containing numerous small

712   spheres (UK2).

713   2e: A large plerosphere housing a number of smaller spheres, including one with a

714   dendritic crystalline structure (PL2).

715   2f: A cross-sectional view of fibrous mullite contained within a plerosphere (PL1).

716   2g: Fibrous mullite meshwork of a sphere approximately 20µm in diameter (UK1).

717   2h: Cross-sectional image reveals a fibrous mullite component is present in nearly all

718   spheres to a varying extent (UK2).

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720   **Figure 3**. X-Ray Diffraction Spectra for UK, Polish and Chinese coal fly ash, and one

721   pulverised feed coal sample.

722   Selected spectra of three coal fly ash samples, UK1, PL1 and CH1, and one pulverised

723   feed coal sample (PL1) are shown in Figures 3a -3d, respectively. The two UK samples

724   revealed a near identical mineral content, with quartz and mullite the only minerals to

725   register peaks. The Polish samples also had quartz and mullite as their major crystalline

726   phases. The Chinese spectra revealed the highest levels of quartz and mullite. In addition,

727   haematite and gypsum were found to be present. The overall resolution seen for the CH1

728   sample is higher, peaks are more pronounced, counts higher, and baselines flatter;

729   indicative of a greater degree of re-crystallisation. The PL1 pulverised feed coal sample

730   displays peaks for quartz, kaolinite, halite, illite and pyrite.

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732   **Figure 4**. FE-SEM/EDX analysis of coal fly ash.

733   4a: EDX-determined composition for the rough surface texture of a particle from the CH1

734   sample.

735   4b: Identification and confirmation of highly carbonaceous material found in the UK2

736   sample.

737   4c: A sphere possessing a dendritic crystalline structure formed from iron oxide, known

738   as a ferrosphere.

739   4d: Fibrous mullite identified during the cross-sectional analysis of the HF etched

740   polished resin-embedded blocks.

741   4e: Further pin-point analysis of mullite fibres confirming an aluminosilicate

742   composition.

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743   4f: EDX spectrum gathered using a quadratt setting reveals the mullite composition to be

744   consistent throughout.

Tables

746   **Table 1.** Laser diffraction analysis for UK, Polish and Chinese bulk and PM_{10} coal fly

747   ash samples. The median mass diameter (MMD, μm) and specific surface area (SSA,

748   m^2g^{-1}) values are given for all samples.

749   **Table 2**. Fluxy bulk ICP-MS values for UK, Polish and Chinese fly ash, showing the

750   major (2a: wt%) and trace (2b: ppm) elemental compositions of both the bulk CFA and

751   PM_{10} samples. The final column shows the measured values and reference values, in

752   parenthesis, for Jb1a; a Japanese basalt and MRG-1, an international rock standard.

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Table 1:
Laser Diffraction Analysis

Sample	MMD (μm)	SSA (m^2g^{-1})
UK1	21.57	0.73
UK1 *	3.50	2.20
UK2	13.09	0.61
UK2 *	5.64	1.72
PL1	15.94	1.00
PL1 *	5.16	1.92
PL2	6.80	2.20
PL2 *	4.36	2.64
CH1	28.16	0.61
CH1 *	1.98	3.01
CH2	97.58	0.27
CH2 *	2.42	2.96

* PM_{10} fraction

MMD = Median Mass Diameter

SSA = Specific Surface Area

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Table 2 2a: Major elements given as weight percentage (wt%)

Oxides wt%	UK1 Cond.FA	UK1 PM$_{10}$	UK2 ESP	UK2 PM$_{10}$	PL1 ESP	PL2 ESP	PL2 PM$_{10}$	CH1 ESP	CH2 ESP	CH2 PM$_{10}$	Standards (Ref Values) JB1a	MRG1
SiO$_2$	44.72	51.07	44.27	47.16	52.31	43.18	45.07	58.49	54.59	54.15	52.45 (52.16)	39.17 (39.12)
Al$_2$O$_3$	24.30	22.11	26.14	24.14	25.31	25.45	22.54	20.55	25.26	25.15	14.60 (14.51)	8.40 (8.47)
Fe$_2$O$_3$	6.10	6.06	6.29	5.54	6.96	8.86	7.42	8.28	7.35	3.16	8.97 (9.10)	18.31 (17.94)
CaO	1.57	2.66	1.54	2.80	3.63	5.54	5.34	3.46	4.93	11.41	9.25 (9.23)	14.65 (14.70)
MgO	1.00	1.04	1.31	1.02	2.43	3.31	3.31	1.39	0.82	0.73	7.72 (7.75)	13.43 (13.55)
K$_2$O	2.38	1.67	2.62	1.75	2.78	3.36	2.99	1.06	0.34	0.32	1.45 (1.42)	0.17 (0.18)
Na$_2$O	0.80	0.95	0.77	0.97	1.02	1.95	1.91	0.33	0.11	0.16	2.86 (2.74)	0.75 (0.74)
TiO$_2$	0.85	0.91	1.02	1.02	1.07	1.23	1.21	0.93	1.06	1.19	1.31 (1.30)	3.75 (3.77)
P$_2$O$_5$	0.72	0.51	1.03	0.88	0.43	1.98	1.81	0.24	0.14	0.34	0.25 (0.25)	0.08 (0.08)
MnO	0.07	0.12	0.09	0.12	0.11	0.14	0.17	0.06	0.06	0.09	0.15 (0.15)	0.18 (0.17)
L.O.I.	17.50	12.91	14.90	14.60	3.94	4.99	8.23	5.22	5.33	3.30	0.99 (0.78)	1.11 (0.55)
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

2b: Trace elements given as parts per million (ppm)

Elements ppm	UK1 Cond.FA	UK1 PM$_{10}$	UK2 ESP	UK2 PM$_{10}$	PL1 ESP	PL2 ESP	PL2 PM$_{10}$	CH1 ESP	CH2 ESP	CH2 PM$_{10}$	Standards (Ref Values) JB1a	MRG1
Ba	1228	1179	1385	1777	1040	2505	2090	1179	329	587	491 (494)	61 (61)
Co	60	18	82	34	35	77	67	19	16	29	38 (41)	92 (87)
Cr	99	48	176	67	138	168	166	93	324	101	405 (409)	420 (430)
Cu	89	40	202	61	75	179	177	83	73	89	55 (59)	148 (134)
Ni	154	56	536	87	77	212	198	52	541	73	125 (142)	207 (193)
Sc	32	16	50	20	25	32	31	18	15	32	28 (28)	53 (55)
Sr	806	692	1217	1034	398	985	941	1242	579	1546	453 (450)	278 (266)
V	218	103	320	143	238	455	465	120	102	203	223 (201)	534 (526)
Y	66	62	93	83	49	71	71	38	46	92	23 (24)	13 (14)
Zn	105	49	282	117	268	702	648	83	92	198	81 (85)	201 (191)
Zr	74	148	70	188	173	81	66	210	234	97	140 (139)	105 (108)