Pulverised fly ash (PFA) and furnace bottom ash (FBA) – potential sources of critical metals?

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Introduction

Global concerns surrounding security of mineral supply have led many countries to re-assess indigenous resources, particularly of the 'critical' metals (so called because of their growing economic importance and high risk of supply shortage). In addition to improving knowledge of primary mineral deposits, the potential for resource recovery from waste materials is attracting considerable attention.

Pulverised fly ash is a coal combustion waste product. In meeting domestic energy demand the United Kingdom annually produces about five million tonnes of pulverised fly ash, 35 per cent of which is sent to landfill.

Numerous metallic elements are also known to occur in PFA, in concentrations ranging from a few parts per billion up to a several weight per cent, depending on the specific composition of the feedstock coal. Recent research indicates that some coals are significantly enriched with certain critical metals (Seredin and Dai, 2011).

Existing UK-based research is heavily focussed on the environmental impacts of PFA. The potential for recovery of economic concentrations of critical metals from PFA, originating from UK power stations has received limited attention.

This poster presents the findings of a recent study into the critical metal potential of PFA and FBA from coal-fired power stations in the United Kingdom.

Methodology

Fifteen samples, four samples of FBA and 11 samples of PFA, were collected from nine UK power stations (Table 1). Samples were digested using two methods, a mixed acid digestion and an Aqua Regia (HCl, HNO_3) digestion. Both sets of digestions were analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for a suite of 67 elements including, In, Te, Se, Re, REE, Nb, Ta, W, Be, and Co.

The five most abundant in a range of the critical metals, were selected for additional X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) analysis (Table 1). These samples were also subjected to a leaching protocol in order to assess whether any of the critical metals were extractable.

The extractants included: deionised water; ammonium acetate; nitric acid; and hydrochloric acid. The resulting leachates were analysed by ICP-MS, while the filtrates were collected, washed, and dried before being subjected to XRD and SEM analysis.

Power Station	Ash Type	Coal Source	Biomass Type
Cottam	PFA	Russia	Olive cake
Cottam	FBA	Russia	Olive cake
Drax	PFA	UK (Maltby)	Unknown
Ferrybridge C	PFA	Unknown	Unknown
Fiddlers Ferry	PFA	Russia/Columbia (50:50)	Unknown
Ironbridge	FBA	Russia	Unknown
Ironbridge	PFA	Russia	Unknown
Ironbridge	FBA	UK/Russia	Unknown
Ironbridge	PFA	UK/Russia	Unknown
Lynemouth	PFA	Russia/USA	Unknown
Ratcliffe	PFA	Unknown	Unknown
Rugeley	PFA	S. Africa/Russia	Unknown
West Burton	FBA	Russia	Unknown
West Burton	PFA	Russia	Unknown
West Burton	PFA	UK (Thorsby/Hatfield)	Unknown

Table 1: *Details of samples used in this study including ash type, feedstock coal country of origin, and biomass type.*

Geochemistry

• PFA derived from the combustion of Russian and South African coals generally has higher trace element concentrations compared to PFA derived from UK produced coals (Figure 2).

• Trace element concentrations are elevated in PFA and FBA compared to average crustal abundance and average world coal concentrations.

• PFA/FBA ratios for Ironbridge and West Burton (Figure 3) show that:
1. Ga, W, Zn, Mo, In, and Sb are preferentially concentrated in PFA
2. Mn, Fe, Pd, Pt, and Ta are preferentially concentrated in FBA
3. REE, Nb, Mg, and Al are equally distributed in PFA and FBA

• Samples are generally enriched in the light rare earth elements (LREE), particularly La, Ce, and Nd, relative to the middle rare earth elements (MREE) and heavy rare earth elements (HREE).

• Several of the critical metals are present in only very minor amounts, particularly Te, Re, and Ir.

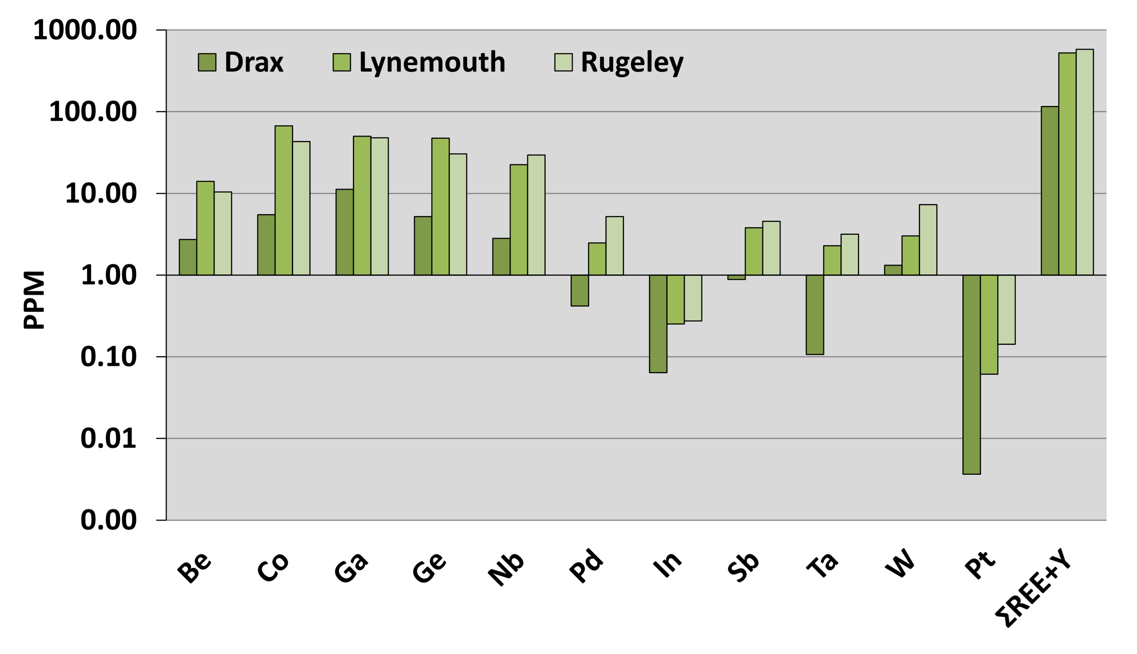

Figure 2: *Trace element variation in PFA from Drax (UK coal); Lynemouth (Russian-USA coal); and Rugeley (South African-Russian coal). ΣREE+Y = Total REE (La-Lu) + yttrium (Y)*

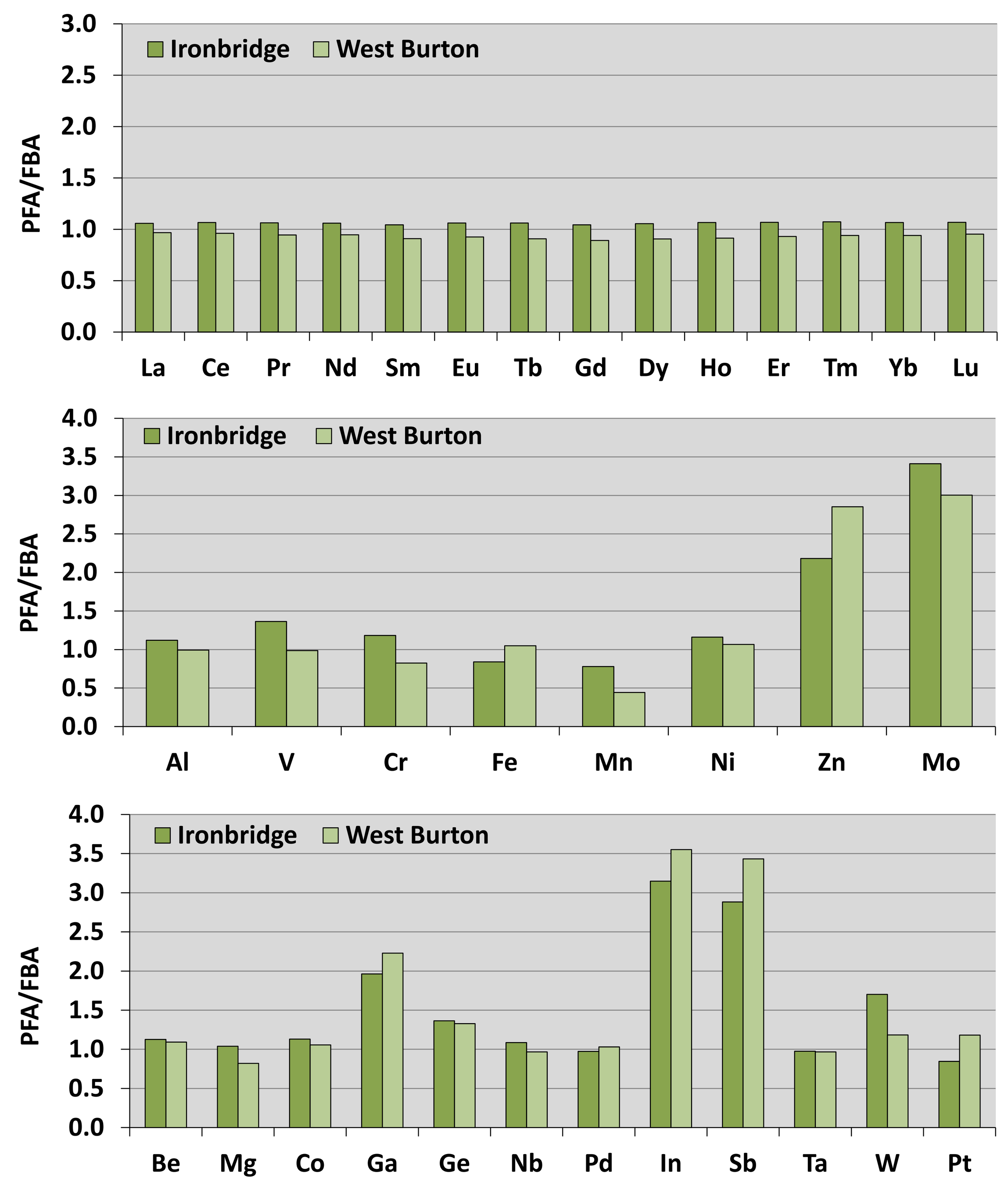

Figure 3: *PFA/FBA ratios are used to show the degree of element enrichment in the two different ash types (Depoi et al., 2008). For example: a ratio value of 1 indicates that elements are equally distributed between PFA and FBA; a ratio of <1 would indicate that an element was more enriched in FBA; while a ratio of >1 would indicate that an element is preferentially concentrated in PFA.*

Mineralogy

• The bulk mineralogy of both PFA and FBA is dominated by quartz with minor amounts of mullite [$Al_6Si_2O_{13}$].

• Other probable phases identified include: haematite [Fe_2O_3], magnetite [Fe_3O_4]; spinel [$MgAl_2O_4$]; fairchildite [$K_2Ca(CO_3)_2$]; and svanbergite [$SrAl_3(PO_4)(SO_4)(OH)_6$] .

• Discrete accessory mineral phases (e.g. monazite, xenotime, apatite, and zircon) were not identified by XRD.

Morphology

PFA and FBA are largely composed of vesicular cenospheres that are typically in the range of <1 to 200 µm across. Cenospheres form welded aggregates or they may become nested within larger, hollow plerospheres (Figure 4c and 4d). In addition to well-formed spheres, irregular elongate particles also occur in PFA and FBA (Figure 4a). The morphology of particles and the formation of vesicles is controlled by: differences in density and chemistry; residence time in the furnace; and escape of gases from molten particles during combustion (Glasser, 2004; Goodarzi and Sanei, 2009).

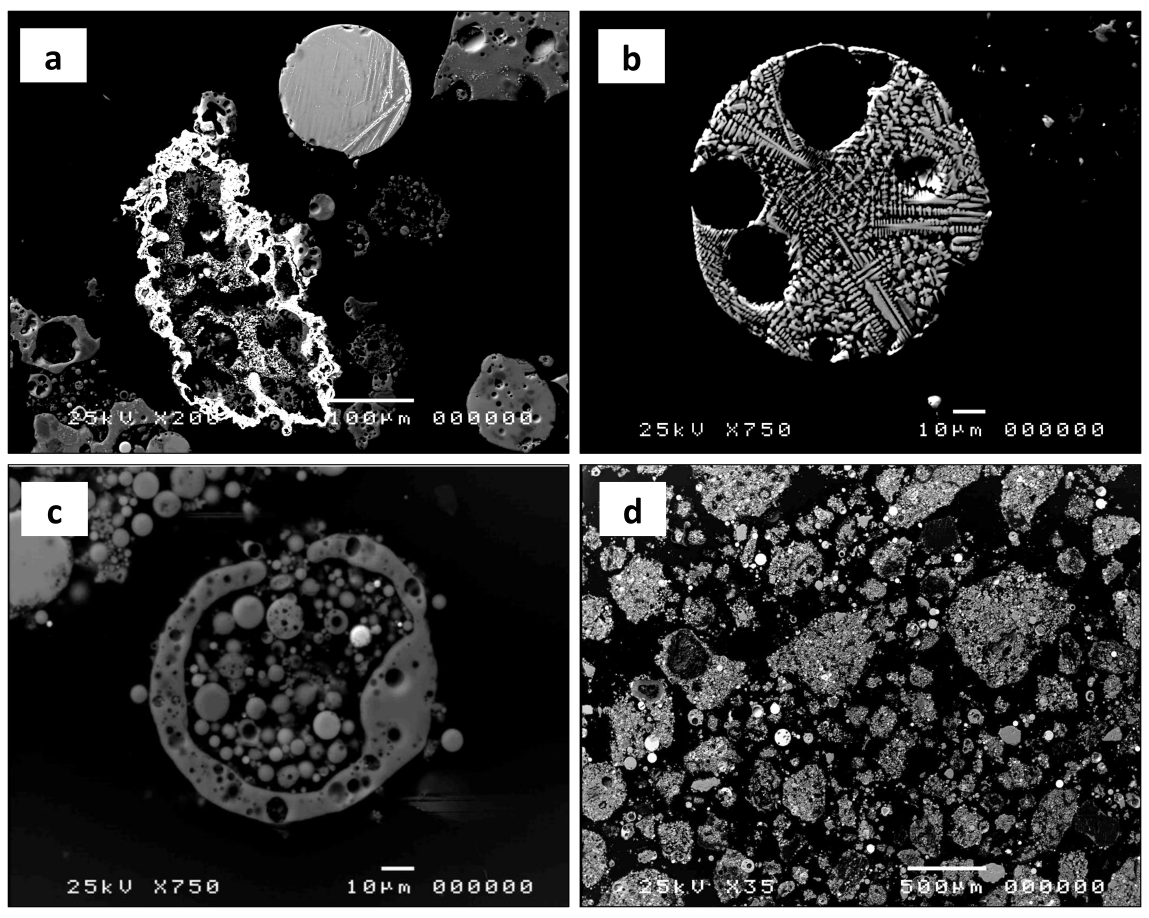

Figure 4: *Back scattered electron (BSE) images of PFA and FBA: (a) the bright white areas of this glassy particle contains Sr, Ti, Ca, Mg, Ce, La, and Nd, (b) Fe-rich dendritic quench texture , (c) a large plerospheres containing smaller cenospheres, both plerospheres and cenospheres are rich in Al, Si, and Ca, brighter cenospheres also contain Fe, (d) general morphology of PFA material comprising individual ceno- and plerospheres, and coarse aggregates of the both.*

Leaching geochemistry

• Deionised water and ammonium acetate are ineffective extractants for the critical metals in PFA and FBA.

• Concentrated HNO_3 (16 M) and HCl (12 M) are most effective at leaching a wide range of metals.

• 1.57 M HNO_3 and 1.25 M HCl are almost as effective at leaching metals as their concentrated equivalents. The effectiveness of both acids was significantly decreased at 0.157 M and 0.125 M.

• All critical metals show increased leachability in PFA compared to FBA (Figure 5a-5d).

•With the exception of REE in PFA HCl is a more effective extractant than HNO_3 (Figure 5a-5d).

• LREE (La, Ce, and Nd) are up to 46 per cent extractable using concentrated acids at room temperature and atmospheric pressure.

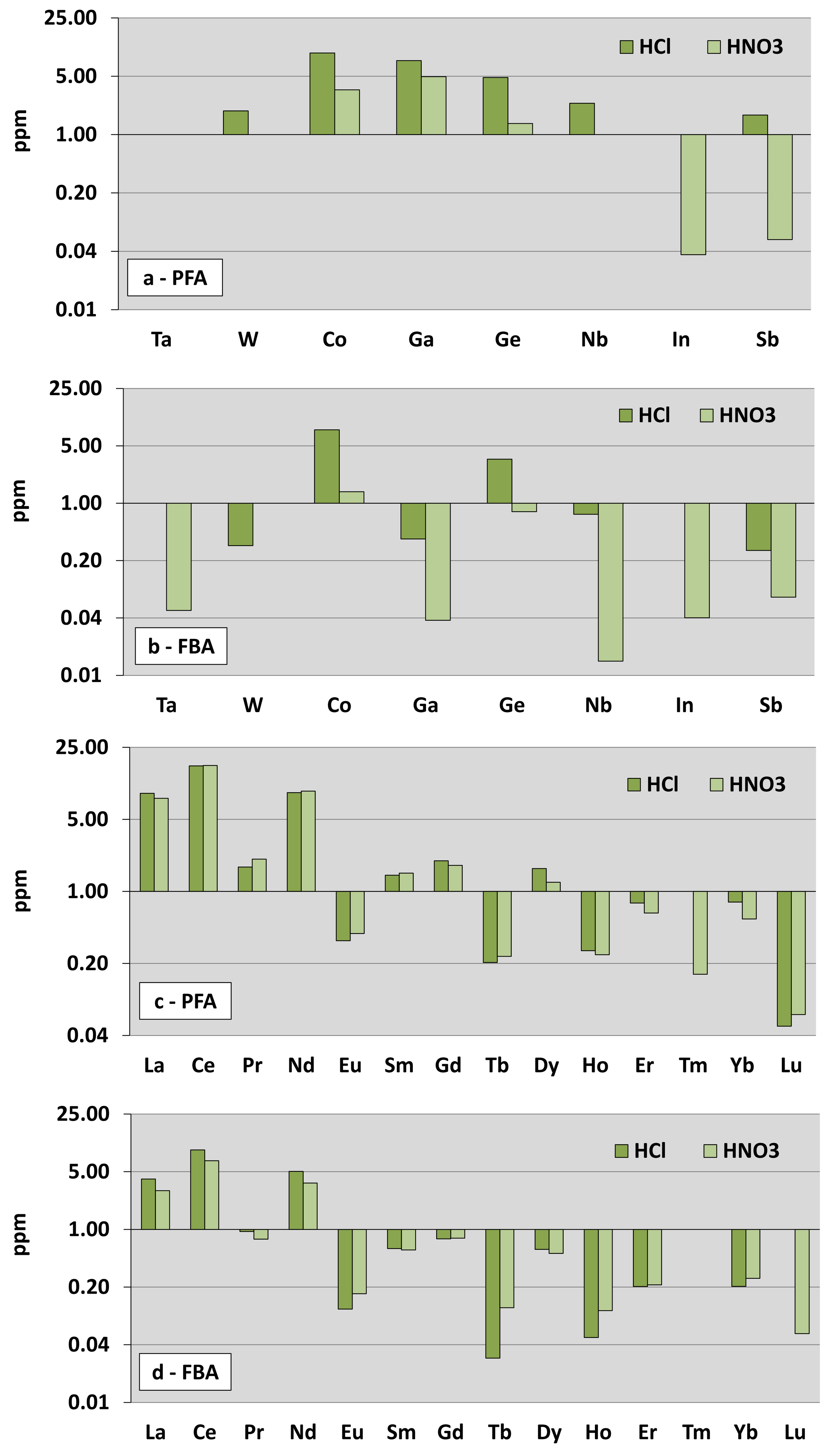

Figure 5: *Results from PFA and FBA leaching experiments using concentrated HCl and concentrated HNO_3. Generally, HCl is a more effective extractant than HNO_3 for a number of metals in both PFA and FBA. However, HNO_3 appears to be more effective at leaching REE from PFA than HCl.*

Leaching mineralogy

• The only significant change in bulk mineralogy appears to be the increased amounts of haematite, possibly as a result of the oxidation of magnetite.

• Visual differences between pre- and post-leached samples are minimal. The majority of particles appear to be more angular post-leaching.

Conclusions

• The economic potential of recovering critical metals from PFA and FBA requires further investigation.

• Coal source exerts a significant control on the metal content of ashes.

• The critical metals are extractable using concentrated acids at room temperature and atmospheric pressure, particularly from PFA.

• Uncertainty remains over the mineral phases hosting the critical metals. The presence of La, Ce, and Nd in FBA glass particles (Figure 4a) suggests these elements may be disseminated in glassy phases generally at concentrations <0.2 per cent (based on SEM detection limits).

Future work

• Sample feedstock coal, PFA and FBA to better constrain critical metal distribution and calculate a mass balance.

• Assess the value of physical beneficiation e.g. cleaning of PFA and FBA to produce a rough concentrate, prior to chemical leaching.

• Develop the leaching methodology by assessing the effects of pressure and temperature on recovery and by using other acids (H_2SO_4).

• Research alternative techniques for processing PFA and FBA materials e.g. bio-leaching or biohydrometallurgy.

References

DEPOI, F. S., POZEBON, D. & KALKREUTH, W. D. 2008. Chemical characterization of feed coals and combustion-by-products from Brazilian power plants. *International Journal of Coal Geology, 76*, 227-236.

GLASSER, F. P. 2004. Coal combustion wastes: characterization, reuse and disposal. *Geological Society, London, Special Publications*, 236, 211-222.

GOODARZI, F. & SANEI, H. 2009. Plerosphere and its role in reduction of emitted fine fly ash particles from pulverized coal-fired power plants. *Fuel*, 88, 382-386.

SEREDIN, V. V. & DAI, S. 2011. Coal deposits as potential alternative sources for lanthanides and yttrium. *International Journal of Coal Geology*.