



Heriot-Watt University
Research Gateway

Coal-derived unburned carbons in fly ash: A review

Citation for published version:

Hower, JC, Groppo, JG, Graham, UM, Ward, CR, Kostova, IJ, Maroto-Valer, MM & Dai, S 2017, 'Coal-derived unburned carbons in fly ash: A review', *International Journal of Coal Geology*, vol. 179, pp. 11–27. <https://doi.org/10.1016/j.coal.2017.05.007>

Digital Object Identifier (DOI):

[10.1016/j.coal.2017.05.007](https://doi.org/10.1016/j.coal.2017.05.007)

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Peer reviewed version

Published In:

International Journal of Coal Geology

Publisher Rights Statement:

© 2017 Elsevier B.V.

General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Accepted Manuscript

Coal-derived unburned carbons in fly ash: A review

James C. Hower, John G. Groppo, Uschi M. Graham, Colin R. Ward, Irena J. Kostova, Mercedes M. Maroto-Valer, Shifeng Dai



PII: S0166-5162(17)30210-0
DOI: doi: [10.1016/j.coal.2017.05.007](https://doi.org/10.1016/j.coal.2017.05.007)
Reference: COGEL 2834

To appear in: *International Journal of Coal Geology*

Received date: 15 March 2017
Revised date: 10 May 2017
Accepted date: 12 May 2017

Please cite this article as: James C. Hower, John G. Groppo, Uschi M. Graham, Colin R. Ward, Irena J. Kostova, Mercedes M. Maroto-Valer, Shifeng Dai , Coal-derived unburned carbons in fly ash: A review. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. *Cogel*(2017), doi: [10.1016/j.coal.2017.05.007](https://doi.org/10.1016/j.coal.2017.05.007)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Coal-derived Unburned Carbons in Fly Ash: A review

James C. Hower^a, John G. Groppo^a, Uschi M. Graham^a, Colin R. Ward^b, Irena J. Kostova^c,
Mercedes M. Maroto-Valer^d, Shifeng Dai^{e,f*}

^a *University of Kentucky Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511 USA*

^b *School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney, NSW 2052, Australia*

^c *Sofia University "St. Kliment Ohridski", 15, Tzar Osvoboditel Blvd., 1000 Sofia, Bulgaria*

^d *School of Engineering & Physical Sciences; Mechanical, Process & Energy Engineering, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom*

^e *State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology, China*

^f *Scholar of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116, China*

^{*}, Corresponding author: daishifeng@gmail.com

Abstract

Unburned carbon (UC) in fly ash indicates inefficiency in combustion and may be an impediment to the beneficial use of fly ash or ash products in a variety of applications. The characteristics of the coal-derived UC are a function of the rank and type of the coal, as well as the size of the feed coal and the combustion conditions. At any coal rank, inertinite macerals are inherently more difficult to combust than the associated vitrinite, and some will have a tendency to appear in the fly ash more or less unchanged from their appearance in the feed coal. The nature of UCs resulting from vitrinite is dependent upon the coal rank. Low-rank huminite/vitrinite will tend to form an isotropic char; bituminous vitrinite will appear as isotropic

and anisotropic cokes; and anthracite vitrinite, naturally anisotropic, is observed as partially combusted vitrinite fragments in the ash.

The absorption of air entraining agents by UCs limits the use of high-UC fly ashes as a Portland cement substitute, with both standards organizations and regulatory bodies imposing limits on the acceptable UC concentrations. UC in fly ash can be used to adsorb organic compounds (such as phenols, dyes, herbicides, polychlorinated biphenyls, and petroleum constituents) and to capture trace elements (particularly Hg) from flue gas. UCs can also be used as sources of activated carbons, manufacture of graphite, and cokes in the metallurgical industry, as well as a source of carbon to feed back into the boiler.

Beneficiation of fly ash to segregate relatively UC-free or UC-rich splits for beneficial re-use can be done by size classification, electrostatic separation, and froth flotation, as well as density separation, acid digestion, and incipient fluidization. Thermal processing may also be used to burn off the UC, leaving a relatively UC-free fly ash as the product.

Keywords: Unburned carbon; Coal-derived fly ash; Coal combustion products; ash utilization

Contents

1. Introduction

2. Determination of unburned carbon (UC) in fly ash (FA)

3. Factors for amount of UC in FA

4. Petrographic nomenclature and classification of UC in FA

5. Variation in UC forms with coal rank

5.1. Low-rank-coal-derived UCs

5.2. Bituminous-coal-derived UCs

5.3. Anthracite-derived UCs

6. Adsorption properties of UCs in FA

6.1. Specific surface area (SSA) and pore size distribution (PSD) of UC

6.1.1. Methods of determination

6.1.2. Factors affecting SSA and PSD of UCs in FA

6.2. Air-entraining agents

6.3. Organic compounds

6.4. Capture of mercury and other trace elements by UC in FA

6.5. Other uses of coal-derived UC

7. Removal of UC from FA

7.1. Size classification

7.2. Electrostatic separation

7.3. Thermal processing

7.4. Froth flotation and oil agglomeration

7.5. Other techniques

8. Summary

Acknowledgments

References

Abbreviations: BA, bottom ash. BET, Brunauer-Emmett-Teller. CAER, University of Kentucky Center for Applied Energy Research. CBO, carbon burnout. CCPs, coal combustion products. ESP, electrostatic precipitator. FA, fly ash. FBC, fluidized-bed combustion. FGT, flue-gas temperature. LOI, loss-on-ignition. PAHs, polycyclic aromatic hydrocarbons. PC, pulverized coal. PCC, pulverized coal combustion. PFC, pulverized fuel combustion. PRB, Powder River Basin. PSD, particle size distribution. R_r , huminite/vitrinite random reflectance. SSA, specific surface area. TGA, thermogravimetric analysis. UC, unburned carbon.

1. Introduction

Coal combustion products (CCPs) are a waste residue derived from the burning of coal in thermoelectric power plants, and include fly ash (FA), bottom ash (BA), boiler slag, and flue gas desulfurization materials. Fly ash, generally recovered by electrostatic precipitation or mechanical filtration, usually makes up the dominant proportion of the total CCP stream, especially in pulverized-fuel combustion plants. From a chemical point of view, FA is mainly composed of oxides of Si, Al, Fe, Ca, and other inorganic elements. Its mineralogical composition is typically represented by amorphous material or “glass” and crystalline or “true” mineral components, as well as unburned or partially burned carbon residues (Dai et al., 2010).

Unburned carbon (UC) in FA can be an indicator of inefficiencies in the combustion process, and an excessive proportion of UC in the FA means a significant loss of energy in (say) power production (Styszko-Grochowiak et al., 2004). UC may also be valuable as an inexpensive source of activated carbon (Batra et al., 2011; Bartoňová et al., 2011), a product of beneficiation processes (e.g., size classification, electrostatic separation, or froth flotation), or a source of carbon to feed back into the boiler. However, it may also be an obstacle to utilization or beneficial use of FA, particularly in cement and concrete industries. UC can absorb the Air Entrainment Agent (AEA), a surfactant that is added to concrete mixes to improve the final product's properties, and thus reduce the suitability of the FA in that market application. ASTM Standard C618-15 and Australian Standard (AS3852.1-1998) respectively recommend that ash with no more than 6% and 4% loss-on-ignition (LOI; as a proxy for UC analysis) should be allowed to be used in concrete.

UC in FA is not a uniform, monotone entity. In practice, the UC is not always even derived from coal; that notwithstanding, our emphasis here is on the coal-derived UCs rather

than the UCs from extraneous fuels such as petroleum coke or tire-derived fuel. The main purpose of this paper is to provide a review of determination of the UC content, factors affecting the proportion of UC in FA, UC nomenclature/classification, and variation in UC forms with coal rank, as well as the use of UC as an absorptive agent and the procedures for FA beneficiation.

2. Determination of unburned carbon (UC) in fly ash (FA)

The UC content of FA is conventionally measured by LOI to a high temperature (such as 950°C, ASTM Standard D7348, 2013). Some standards use LOI values as an indicator of UC content. For example, ASTM C168-15 (2015) specifies 6% LOI for Class C and F as one of chemical requirements for use in concrete. As defined by ASTM standard C618–05 (2015), Class F FA is normally produced from burning anthracite or bituminous coal, and Class C FA normally is produced from lignite or subbituminous coal.

However, the weight loss under high temperature (the LOI) is not only due to destruction of the UC present, but also to breakdown of mineral phases (e.g., decomposition of carbonates, oxidation of sulfides, release of structure water from clay minerals, and dehydration of lime) and to water physically adsorbed on measured samples (e.g., CaO that is rich in fluidized-bed combustion (FBC) ashes). For this reason, the UC content may be overestimated by the LOI value. When assessing the suitability of a particular FA for use as a cementitious material, the overestimated UC content implied by LOI data could lead to a FA being classed as unsuitable, even though the actual total or UC content might suggest otherwise.

The UC content of FA can be more precisely determined by elemental analysis techniques (Bartoňová et al., 2011; Kostova et al., 2016) or by thermogravimetric analysis (TGA) (Mohebbi et al., 2015). However, the total carbon content of FA derived from elemental analysis techniques may not only represent the proportion of UC, but may also include any inorganic carbons that may be present as carbonates (Brown and Dykstra, 1995), although the proportion of such inorganic carbon in FA is usually low (Dai et al., 2010). Hence, it is suggested that any carbonate minerals in the ash should be removed prior to measurement of UC using elemental techniques. ASTM D6316-09be1 (2009) covers the determination of total, combustible, and carbonate carbon remaining in the solid byproducts of combustion from boiler furnaces and similar reactors, including FA, char, slag, and similar materials; this method applies to the determination of total carbon remaining in a material after acidification with strong acid to evolve carbonate carbon. Bartoňová et al. (2011) used HCl (1:1) to leach FA samples in order to dissolve carbonates, which could otherwise misrepresent the results.

TGA is another method that is widely used for the laboratory determination of UC in ash. The key point of this method is the separation between UC oxidation and carbonate decomposition (Straka et al., 2014; Bartoňová, 2015). Mohebbi et al. (2015) designed a two-atmosphere TGA instrument coupled to a mass spectrometry system to measure organic carbon in a class F fly ash, and found that this analysis can effectively separate oxidation of organic carbon from dehydration and decomposition of minerals. Combining inert and oxidizing atmospheres, Payá et al. (1998) designed a thermogravimetric method to determine hydrated lime, calcium carbonate, and UC contents for several fly ashes.

On-line monitoring analytical methods and techniques have been developed to avoid time consuming contact with the sample or special sample preparations. The key point for any on-line method analytical methods is to make the samples analyzed representative of the vast majority of the ash leaving the boiler (Bartoňová, 2015). Some on-line methods have also been developed for real-time monitoring of the UC concentration and the boiler working status. These methods include photoacoustic absorption spectroscopy (Brown and Dona, 1990), microwave absorption (Terice, 1987; Cutmore, 1993; Smith et al. 2009; Liu et al., 2010), optical dispersion/reflection (Styszko-Grochowiak et al., 2004), laser-induced breakdown spectroscopy (Kurihara et al., 2003; Ctvrtnickova et al., 2009; Zhang et al., 2011; Yao et al., 2012), infrared emissions (Kempste, 1987; Bonanno et al., 1995), image processing methods (Yan et al., 2004), and gamma ray scattering. Owing to the associated radioactivity, the use of the gamma ray scattering technique is quite restricted. Due to their short wavelengths, photoacoustic, infrared, and optical techniques are able to provide better accuracy in determining the UC content of the pulverized-fuel system (Liu et al., 2010). The mineral content of the coal and the coal rank are the major factors that strongly affect the accuracies of these on-line methods (Bonanno et al., 1995; Zhang et al., 2011; Yao et al., 2012; Liu et al., 2013), and Liu et al. (2013) described a char/ash particle cluster spectral emittance method for on-line measurement of UC concentration, which was less influenced by mineral content or coal rank.

Waller and Brown (1996) have investigated a photoacoustic technique, which directly detects the amount of UC in a sample, to determine UC in FA. Although the photoacoustic technique has attracted less attention than conventional methods, efforts have also been made to develop it into a commercial technique. The major problem of UC determination by this technique is the small amount of sample, usually a few μg , used for the analysis, and thus grinding of at least

a few grams followed by proper homogenization prior to determination is advised (Waller and Brown, 1996; Fan and Brown, 2001; Bartoňová, 2015). Fan and Brown (2001) investigated the factors that influence precision and accuracy of photoacoustic measurements of FA, and found that the important factors include protocols for sampling and sample pretreatment (e.g., grinding), the ambient conditions at which photoacoustic determination is performed, and the wavelength of the excitation source. Dykstra and Brown (1995) compared optically- and microwave-excited photoacoustic detection of UC-entrained FA. The comparison showed that optical radiation has the advantage of relatively large absorption coefficients for carbon particles in FA, but that the absorption coefficient is also dependent on particle size. The absorption coefficient for microwave excitation is independent of particle size, but is weaker than that for optical excitation. Based on the concept that the polarization ratio resulting from the backscattering of linearly polarized incident light by FA particles is indicative of the carbon content, Ouazzane et al. (2002) designed an optical instrument to measure the carbon content of FA, and the work showed that if the mineral content of the ashes is not known, the carbon content can be determined to within $\pm 1\%$, and otherwise, the use of neural network analysis can reduce this to $\pm 0.5\%$.

Because the microwave wavelength is greater than the grain size of FA, the impact of grain size on microwave measurements is relatively small (American Society for Nondestructive Testing, 1999). Combination of the microwave technique with non-extractive ash sampling could provide reliable results (Bartoňová, 2015), and it is the most common technique for the determination of UC content in FA (Liu et al., 2010; Melick et al., 2005; Weber, 1999; Letcavits et al., 2004). Most coal-fired power plants, particularly in China, use the microwave technique to measure the UC content of FA (Liu et al., 2010).

The laser-induced breakdown spectroscopy technique also seems to have attracted much attention for online carbon determination (Noda et al., 2002; Gaft et al., 2008), due to its speed (~1 min) and low cost, as well as the lack of a requirement for vacuum or special atmosphere (Bartoňová, 2015) and the limited, if any, need for sample preparation (Ctvrtnickova et al., 2009). However, caution is required for sampling because only a small amount of material (~0.1 g) is used for analysis (Bartoňová, 2015).

3. Factors affecting the amount of UC in FA

The individual particles of UC in FA have an entirely different morphology to the other ash components. The glass cenospheres, magnetic particles, and fine Al-Si glass ash that make up most of the ash are primarily spherical in nature (Blissett and Rowson, 2012); in contrast the UC is a relatively porous material and has a more irregular shape, in some cases, retaining the intact maceral structures of the original feed coal (Fig. 1). This difference is largely explained by the FA formation mechanism, which is comprehensively reviewed by Blissett and Rowson (2012).

The UC content of FA usually ranges from 2 to 12%, but in some cases it can be higher than 20% (Ahmaruzzaman, 2010; Senneca, 2008) and even up to ~57% (Dai et al., 2014a). A number of factors influence the amount of carbon in FA, among which are the nature of the coal (e.g., coal rank, particle size, moisture, maceral composition, mineral matter, calorific value, and volatile matter) relative to the design and efficiency of the power plant (e.g., residence time available for combustion in furnace, boiler temperature and pressure, oxygen feed, and coal/air ratio, furnace heating loading, and heat flow rates, and flame patterns) (Yan and Li, 2009; Bahadori and Vuthaluru, 2010; Dindarloo and Hower, 2015; Bartoňová, 2015). In the 1990s, larger US power plants were converted to combustion under low-NO_x emission (low-oxygen and low-temperature combustion) conditions, resulting in a general increase in the proportion of

carbon in FA from pulverized-fuel (Hower et al., 1996, 1997a, 1997b) and circulating fluidized-bed combustion (Kobyłecki, 2011). However, in the same coal combustion system, the UC content is usually higher in the FA than in the BA, regardless of the nature of the coal, and the design and efficiency of the power plant (Bartoňová, 2015). It has been reported that UC contents tend to be enriched in the latter rows of electrostatic precipitator (ESP) (Mardon and Hower, 2004; Ahn and Lee, 2006; Suárez-Ruiz et al., 2007; Senneca, 2008).

Using data from Hao et al. (2004), Dindarloo and Hower (2015) determined that the proportion of UC could be modeled using three coal quality variables (ash, heating value, and volatile matter) and two plant operational variables (over-fire air and oxygen concentration in the flue gas). Bilen et al. (2015) examined the effects of moisture content and particle size distribution (PSD) of coal on UC in bottom ash. It appears that the PSD of the pulverized coal (PC) is closely related to the UC content of the FA (Bilen and Kizgut, 2016; Ganguli and Bandopadhyay, 2012). In one case studied by Hower et al. (1997b), overhaul (maintenance and repair) of the pulverizers during a plant outage resulted in a lowering of the UC content in FA, due to the decreased particle size of the pulverized feed coal and the probable improvement in plant efficiency. The proportion of UC in FA is also size dependent. The coarser FA fractions generally have a higher UC content (Dai et al., 2014b, Liu et al., 2017). Gao et al. (2013) found that particles larger than 140 μm contribute 70% of the total UC, even though such particles make up only around 20% of the feed coal. A study by Xue and Wang (2013) showed that the coarse fraction of 110–480 μm plays a significant role in high-efficiency burnout in PC power plant boilers. Atas et al. (2014) showed that fineness of coal particle size directly reduces the UC in FA.

The nature and relative proportions of the macerals in the feed coals can significantly affect the UC content of FA. The UC content is largely dependent on coal rank, as reviewed by Craig (2013). A number of studies have shown that inertinite-group macerals, primarily the higher reflecting forms (e.g., fusinite and secretinite), but also including other inertinite macerals, are more resistant to combustion than the vitrinite-group macerals, especially in PFC systems (Nandi et al., 1977; Shibaoka, 1985; Vleeskens et al., 1993). Shibaoka (1986) reported that a FA derived from a high inertinite coal contains 25.3% UC. Dai et al. (2014a) investigated Ge-rich FA derived from three giant coal-hosted Ge deposits, Lincang (Yunnan of southwestern China), Wulantuga (Inner Mongolia of northern China), and Spetzugli (Primorye, Russian Far East). The coals from the three Ge deposits have a similar rank (lignite to sub-bituminous coal). For example, huminite/vitrinite random reflectance (R_r) is 0.45% for the Wulantuga coal (Dai et al., 2012), 0.48% for the Lincang coal (Dai et al., 2014a), and 0.39% for the Spetzugli coals (Medvedev et al., 1997). Dai et al. (2014) found that, owing to high proportion of inertinite-group macerals in the feed coals (Dai et al. 2012, 2015a,b), the Wulantuga fly ashes have a higher UC content and a higher LOI (57.3-57.7%) than the Lincang (LOI, 16.3%) and Spetzugli (LOI, 8.8-15.4%) fly ashes (Dai et al. 2014a).

4. Petrographic nomenclature and classification of UC in FA

Although separate nomenclatures have been developed for low-rank vitrinite precursors and vitrinite in bituminous coals, the bituminous coal nomenclature (ICCP, 1998; Sýkorová et al., 2005) is followed in this discussion. Revised classifications for inertinite and liptinite have also been published (ICCP, 2001; Pickel et al., 2017). Commission III of the International Committee for Coal and Organic Petrology (ICCP) is engaged in establishing a classification of UC and inorganic fractions of FA (<http://www.iccop.org/commissions/commission-iii/>). In 2007, a

proposal was made to set up an inter-laboratory classification exercise (Suárez-Ruiz et al., 2008), and the fly ashes selected for this investigation were from pulverized coal combustion (PCC) and the feed coals consisted of single coals and coal blends ranging from lignite to anthracite A (Suárez-Ruiz et al., 2008). For classification of the UCs, the parameters used included optical texture (isotropic/anisotropic), character (fused/unfused), structure (dense/massive, porous/vesiculated), and origin (coal, coke) (Suárez-Ruiz et al., 2008). An atlas for petrographic classification of FA components, including those of organic UC, has been compiled since 2006 by the Fly Ash Working Group (Commission III) of ICCP (Suárez-Ruiz and Valentim, 2015). This atlas identifies and classifies the components that can be found in FA derived from coal combustion, co-combustion, and biomass combustion processes under different operating conditions for PCC, FBC, and other processes.

The present paper follows nomenclature used by Hower et al. (1995) and Hower (2012), with some modifications by Hower and Mastalerz (2001) and Hower et al. (2005), the latter two being combinations of the Bailey et al. (1990), Lester et al. (1996), and Alvarez et al. (1997) char texture classifications with the broader scheme of Hower et al. (1995). Basically, the textural classification broadens the “isotropic” and “anisotropic” classification of Hower et al. (1995) into thick-walled (>5- μ m thick; crassi-) and thin-walled (<5- μ m thick; tenui-) spheres and networks, mixed porous and dense forms, and fusinite- and general inertinite-derived forms. The nomenclature, as modified after Hower et al. (2005), is shown on Table 1.

5. Variation in UC forms with coal rank

The discussion in this section outlines the origin of UCs in FA broadly as a product of the rank of the feed coal, and then considers the coal macerals and their fates in combustion. In

examining variations of UC in FA within power generating units, it is important to collect multiple samples from the same row of ash-collection systems wherever possible, as there is variation between bins (Hower et al., 2001a). In the collections by the University of Kentucky Center for Applied Energy Research (CAER), a deliberate effort has been made to make successive collection from the same bins at the individual generating units. However, in addition to engineering modifications that have eliminated entire banks of ash-collection bins, for various reasons it has not always been possible to be consistent through successive collections from the same combustion system.

As noted below, just within the coal-derived constituents there are significant rank-dependent differences. While it is outside of the scope of this review, we note that significant differences may also exist in the inorganics, depending upon the mineralogy and chemistry of the feed coals.

5.1. Low-rank-coal-derived UCs

In contrast to bituminous coals, lignite- and subbituminous-rank coals are not caking coals and, thus, do not pass through a plastic state upon heating (Berkowitz, 1979). Just as the inertinites of bituminous- and anthracite-rank coals generally survive combustion and pass on to the FA, we can observe intact fusinite (Fig. 2A), and mixtures of inertinite and vitrinite-derived UCs (Fig. 2B), in the FA from low-rank coal combustion (after Goodarzi and Hower, 2008; Kostova et al., 2011, 2013). Isotropic UCs are also noted among the UC components in FA (Fig. 3). The latter can be directly derived from vitrinite but, given the general lack of thermoplastic properties among the low-rank coals, it is perhaps more likely that isotropic carbons are derived from a vitrinite \rightarrow tar \rightarrow isotropic carbon pathway. The most common form of vitrinite-derived carbon in fly ashes from the combustion of low-rank coals is an isotropic char (Fig. 4). In

contrast to the isotropic carbon (Fig. 3), the char does not appear to have melted and repolymerized; rather, it has the appearance of having devolatilized *in situ*.

5.2. Bituminous-coal-derived UCs

As with fly ashes from lower rank coals, inertinite macerals will generally pass through to FA more or less in the same form as in the coal (Fig. 5). Coal fragments in FA are rare, but can include all coal macerals, albeit with varying degrees of alteration (Fig. 6). As seen on Fig. 6A, vitrinite has devolatilization vacuoles and oxidation rims on the edge of the particle and long cracks within the coal fragment. Inertinite can show signs of devolatilization, although this is a rare feature in fly ashes (Fig. 6B).

With some exceptions, United States power plants to the east of the Mississippi River were designed to burn bituminous coals. As the original coal supply was depleted, the coal sources and the coal rank became more diverse. For example, in a western Pennsylvania power plant, Hower et al. (1999a) noted a high volatile B through low volatile bituminous rank range in the coal feed to a single generating unit. Through the 1980s and beyond, Powder River Basin (PRB: Wyoming and Montana) subbituminous coals were increasingly used in order to lower flue gas SO₂ emissions, thus keeping the generating units within US Environmental Protection Agency rules in force at that time. One western Kentucky power plant burned a blend of PRB coal and the locally-mined high volatile C bituminous coal, while another burned a blend of PRB coal and Colorado and Utah high volatile C bituminous coal; the units at both plants were designed to burn high-S, high volatile bituminous Illinois Basin coal. Further complicating matters is the use of petroleum coke and tire-derived fuel (Hower et al., 2001b) as supplements to the coal supply.

Just dealing with bituminous coals, coal rank is a factor in the distribution of UC types. Caking properties of bituminous coals (specifically, the vitrinite), expressed, for example, as the free-swelling index (FSI) or the Geiseler fluidity, vary through the bituminous-rank range, peaking in the medium volatile bituminous range (Jasienko, 1978; Berkowitz, 1979; van Krevelen, 1993). Both the swelling and fluid properties of bituminous coals are fundamental to the behavior of the vitrinite in combustion. The predominance of isotropic versus anisotropic coke in FA is related to the rank of the parent coal, with anisotropic forms becoming more dominant as feed-coal rank increases as noted by Hower et al. (1995, 2005) and Hower and Mastalerz (2001), in turn based on studies of metallurgical coke by Gray and DeVanney (1986) with considerations of the inorganic phases based in part on Hulett et al. (1981). Further discussion of the properties of individual UC forms are found in Maroto-Valer et al (1999, 2001). Aside from the predominance of one type of the neo-formed carbon based solely on coal rank, within the cokes there is a continuum of forms. The lowest-rank anisotropic carbons have a sub-micron anisotropic mosaic structure which, using optical microscopy, is basically indistinguishable from that of isotropic coke. The “isotropic” coke shown on Fig. 7 is an example of this dilemma; the variation of colors in the coke hints at anisotropy but, at this scale, there is no texture definitively confirming anisotropy. The anisotropic cokes seen on Fig. 8 leave nothing to the imagination; all show clear anisotropy. For all of the particles, it appears as if the anisotropic coke/inertinite juxtaposition mimics that of the original vitrinite/inertinite assemblage; the anisotropic coke is simply the melted and repolymerized vitrinite, still attached to the inertinite.

Basically, all of the carbon forms discussed to this point can be observed with conventional optical petrography.¹ Bituminous-coal-derived (but, apparently not subbituminous-derived (Wilcox et al., 2015)) fly ashes also have amorphous and crystalline carbons attached to and binding together other FA particles (Chen et al., 2004, 2005a, 2005b, 2006; Linak et al., 2007; Lu et al., 2007; Hower et al., 2008; Silva et al., 2010; Wilcox et al., 2015). These carbons require high-resolution transmission electron microscopy (HRTEM) for proper identification. Examples of the carbon are seen on Figures 9A-B, where the carbon is attached to an Al-Si glass. Hower et al. (2008) and Silva et al. (2010) identified fullerene structures among the carbons (Fig. 9C-D). Using time of flight secondary ion mass spectrometry (TOF-SIMS), Silva et al. (2010) further identified C₆₀, C₇₀, and C₈₀ fullerenes as the major species, with other species from C₅₆ to C₇₈ corresponding to the loss of C₂ units from the major fullerenes. Fine (<3 nm) Fe-, As-, Hg-, V-, Cr-, Pb-, and Se-bearing particles are encased within the carbons (Hower et al., 2008; Silva et al., 2010). In the analysis of the bulk chemistry of the stoker FA studied by Silva et al. (2010), Mardon et al. (2008) found high levels of Mn, As, and Pb (up to 3300 ppm, 8870 ppm, and 2250 ppm, respectively). Rare earth element-bearing nano-scale particles have been noted in the amorphous UCs in FA derived from eastern Kentucky bituminous coals (Hood et al., 2017; Hower et al., 2017b).

5.3. Anthracite-derived UCs

¹ As an example, in the University of Kentucky's Center for Applied Energy Research Applied Petrology Laboratory "conventional optical petrography" implies the examination of polished epoxy-bound particulate pellets using reflected-light, oil-immersion optics. The default magnification would be a 50x oil-immersion objective and 10x-magnification eye pieces, but other objectives are used for certain purposes. Polarized light is the default illumination. Sudan Black dye is used in the epoxy in order to minimize subsurface reflections.

Unlike subbituminous coals, anthracites will not char, and will not produce tar and significant hydrocarbon emissions. Unlike bituminous coals, anthracites will not generally pass through a thermoplastic stage and repolymerize as a coke. Instead, anthracite will combust, but not as easily as do lower-rank coals,² and the UCs in FA will have a greater resemblance to the source-coal macerals. Consequently, the petrographer is faced with subtle differences across the spectrum of coal → FA (Silva et al., 2012; Hower et al, 2017a).

Unaltered anthracite fragments are seen in stoker-fired ash (Fig. 10A). The seeming lack of heat-induced alteration may be a function of the need to crush the ash to a size appropriate for petrographic examination; nevertheless, the anthracite was not combusted, whether we are looking at the interior or exterior of the original grain. In contrast, the fragment seen on Fig. 10B shows darkened vitrinite on the margin of the grain and surrounding fractures within the grain. The grains in Fig. 10 C and D have apparent devolatilization pores. The common theme through the Fig. 11 images is the anisotropy of the UC. The anthracite-derived UC shown on Fig. 11A seems to be basically unaltered. Fig. 11B-D show varying degrees of alteration, with some evidence for minor coking (Fig. 11B) and possible softening of the vitrinite-derived bands in Fig. 11C. Fig. 11D shows inertinite with thermally-degraded vitrinite.

6. Adsorption properties of UCs of FA

UC of FA is known to have both deleterious and positive effects on the adsorption of inorganic elements and organic molecules. Because of the abundant porosity, the UC has a higher surface area than the inorganic matter contained in the FA. A study by Pedersen et al. (2008) showed that the surface area of UC is 45-400 m²/g, much higher than that of the mineral

² “My father procured a lump of Lehigh coal [note: Southern Anthracite Field, Pennsylvania] about as large as his two fists, and tried it on his wood fire in an open Franklin stove. After two days he concluded that if the world should take fire, the Lehigh coal mine would be the safest retreat, the last place to burn.” (attributed to Abijah Hill [ca. 1824] by Hill, 1890)

matter (0.7-0.8 m²/g) contained in the FA. This is the major reason for the enhanced adsorption capacity of UC. The surface area of the UC in FA is a critical factor in controlling the ability of the UC to adsorb gases (Hg in gaseous state: Rubio et al., 2007) or liquids (air-entraining agents: Kulaots et al., 2004; Jolicoeur et al., 2009; organic contaminants: Akgerman and Zardkoohi, 1996; Konstantinou and Albanis, 2000; Janos et al., 2003; Nollet et al., 2003; Demirkan et al., 2006, 2011).

The form of the UC is also important, with coals of different ranks and maceral assemblages producing very different UCs. Just as important is the carbon-inorganic association; a carbon partially or totally encased by inorganics will contribute to the total carbon analyzed but will contribute little, if anything, to the absorptive properties of the FA.

6.1. Specific surface area (SSA) and pore size distribution (PSD) of UC

6.1.1. Methods of determination

The most widely used method for the determination of the Brunauer–Emmet–Teller (BET) surface area is by N₂ adsorption. Although N₂ adsorption (77 K) is very useful in the characterization of UC surface area, micropore and mesopore volume, CO₂ adsorption (273 K) is very useful in the determination of very narrow microporosity (Davis et al., 1995; Hurt et al., 1995). Two complementary tests, physical N₂ adsorption in combination with the CO₂ adsorption Dubinin-Astakhov test (CO₂ D-A test) are usually applied to determine the specific surface area (SSA) and pore size distribution (PSD) of UC. In the framework of these analyses the following parameters, BET and Langmuir specific surface area (SSA), Barrett–Joyner–Halenda (BJH) mesopore volumes, micropore surface area, monolayer capacity, and micropore volumes can be determined. These parameters may fully characterize the porous texture and UC size distribution. The BET SSA, Langmuir SSA, BJH adsorption mesopore volume, and PSD analyses

are generally carried out using N_2 gas as an adsorptive at the boiling point temperature of liquid N_2 (77 K) over a pressure range of 0- to 800-mm Hg, the standard conditions used to measure mesopore surface area and volume. For mesopore volume determination, the adsorption branch of the isotherm is generally used. For micropore volume (Dubinin-Astakov test), micropore SSA and monolayer capacity (Dubinin-Radushkevich test) determination CO_2 is often used as the adsorptive gas, at a temperature of 273 K. Before the analysis with N_2 or with CO_2 , the samples are degassed in a vacuum in order to remove adsorbed moisture and atmospheric gases. Detailed information about these techniques and interpretation of the data are given in Gregg and Sing (1982).

6.1.2. Factors affecting SSA and PSD of UCs in FA

Some factors may influence the SSA and PSD of UC in FA, including the nature of the coal (e.g., coal rank, maceral composition, and morphology; Maroto-Valer et al., 2001; Kostova et al. 2013; Bartoňová, 2015; Maroto-Valer et al., 2001) and the combustion conditions of the power plant; reported data on SSA and PSD are also, to some extent, dependent on the determination method and on methods used for separation of UC from the fly ashes (Bartoňová, 2015). However, the coal rank is the most significant factor affecting the SSA and PSD of UC in fly ashes. Both the SSA and pore volumes generally decrease with increasing coal-rank. The SSA of UC derived from high-rank coals usually ranges from 10 to 80 m^2/g (Sharonova et al., 2008; Lu et al., 2007; Yeboah et al., 2014; Goodarzi and Hower, 2008; Hower et al., 2010; Maroto-Valer et al., 2001; Külaots et al., 2002), much lower than that derived from low-rank coals with a general range of 200 m^2/g to 400 m^2/g (Sharonova et al., 2008; Gao et al., 2002; Külaots et al., 2002, 2004; Goodarzi and Hower, 2008; Hower et al., 2010). Wagner et al. (2008) have reported the SSA values in the range of 80–200 m^2/g for the UC in coarse gasification ash

derived from inertinite-rich subbituminous coals. Total pore volume (N_2) for anthracite-derived FAs (calculated on a C basis) range from 0.08 to 0.040 cm^3/g , which is lower than the values given above for carbons derived from lignites and bituminous coals (Wagner and Tlotleng, 2012).

Kostova et al. (2013) have investigated the SSA and PSD of UCs in two fly ashes collected at the first and third ESP rows in a Bulgarian thermoelectric power plant. The analyses showed that the desorption cumulative mesopore volumes of the UC derived from lignite in the 1st and 3rd rows were 0.016 cm^3/g and 0.089 cm^3/g ; the mesopore surface areas were 5 m^2/g and 96 m^2/g ; and micropore surface areas were 1 and 68 m^2/g , respectively. It was reported that Hg adsorbs on both the mesopores and micropores of the UC particles and by volume filling of the pores for the lignite-derived UC in the fly ashes. In contrast, adsorption mainly on the micropores of the UC particles and subordinate volume filling of the UC micropores were identified as preferable Hg adsorption mechanisms for bituminous-derived fly ash UC particles. Figure 12 shows the porous structure of UC in the fly ashes. Consequently, it can be concluded that the preferable location of Hg is in the micro-meso pores of lignite-derived UC fly ashes and the concentration of Hg is in the micropores of the bituminous-derived fly ash UC particles.

6.2. Air-entraining agents

Perhaps most notably, UC is a negative factor in the use of FA in many construction applications, including its use in concrete (Hemalatha and Ramaswamy, 2017); the UC will adsorb air entraining agents, degrading the quality of the concrete (Külaots et al., 2004; Jolicoeur et al., 2009). ASTM (2015) and AASHTO (2011) have published recommended limits on the LOI in FA used for concrete in highway construction; in general, U.S. Department of Transportation specifies lower LOI standards than ASTM and AASHTO. For example, Kentucky specifies a maximum of 3% LOI for FA substituting for Portland cement (Waddle,

2012). Experiments using a commercial DDDBS (dodecylbenzylsulfonate)- based air entraining agent, carbon tetrachloride, and acetone with fly ashes having similar BET specific surface areas demonstrated that the form of the UC in FA provided a better understanding of the adsorption than did the LOI (Hill et al., 1997, 1998). Specifically, there was an inverse relationship between air entraining performance and the isotropic carbon/anisotropic carbon ratio.

6.3. Organic compounds

High-UC FA has been used to adsorb phenols, dyes, herbicides, polychlorinated biphenyls, and petroleum constituents (Akgerman and Zardkoohi, 1996; Konstantinou and Albanis, 2000; Janos et al., 2003; Nollet et al., 2003; Demirkan et al., 2006). Demirkan et al. (2006) demonstrated that the addition of 5-10% (wt.) FA to contaminated soil decreased the aqueous concentrations of naphthalene and o-xylene by 90-95%. In a study of seven fly ashes from Maryland power plants, Demirkan et al. (2011) demonstrated that naphthalene and o-xylene adsorption had significant positive correlations to both LOI and the sum of the isotropic and anisotropic carbons.

In addition to capture of Hg and other trace elements as described below, capture of toxic organic compounds by UC has also been investigated (e.g., Low and Batley, 1986; Stephens et al., 1994; Liu, et al., 2000; Sun et al., 2005; Wang et al., 2013). Although other controlling factors are also important for polycyclic aromatic hydrocarbons (PAHs) capture (such as porosity, Low and Batley, 1986; vapor pressures, Eiceman and Vandiver, 1983), several studies (e.g., Low and Batley, 1986; Sun et al., 2005; Wang et al., 2013) have revealed that the capture capacity of PAHs on FA increases with the increasing UC content.

6.4. Capture of mercury and other trace elements by UC in FA

Mercury capture by UC in FA is a function of the temperature of the flue gas, the proportion of UC in the FA, and the type of UC (Senior et al., 2000a,b,c; Hower et al., 2010). The mechanism of mercury capture by UC has been extensively reviewed by Hower et al. (2010) and Bartoňová (2015). Rows within an ash-collection array more or less correspond to flue-gas temperature (FGT) zones; given similar C contents, there is an increase in Hg capture with a decrease in FGT from the boiler side of the ash-collection array to the gas-exit side (Hower et al., 2000a). Within a single row of an ESP or baghouse, the mercury concentration in FA can be correlated with the amount of UC (Hower et al. 1999b, 2000a, 2006, 2016; Sakulpitakphon et al 2000, 2003; Mardon and Hower, 2004; Suárez-Ruiz et al., 2007). Plots showing the relation between Hg and UC in FA for arrays with different FGTs can be seen on Fig. 13 (after Mardon and Hower, 2004, and Hower et al., 2006). Of the variables investigated by Li et al. (2007), the strongest correlation was between UC and Hg, albeit somewhat overlooked because they did not consider the temperature difference between rows to be a variable in their study. Once adsorbed by the UC of FA, Hg is relatively thermally stable, not being driven off until the 300-400°C range (Rubel et al., 2006).

With respect to Hg capture from flue gas, some studies (e.g., Külaots et al., 2004; Goodarzi, 2005, 2006; Goodarzi et al., 2008; Goodarzi and Hower, 2008; and Kostova et al. 2011, 2013) noted the enhanced efficiency of low-rank-coal-derived char compared to carbons derived from the combustion of bituminous coals (Fig. 14 after Kostova et al., 2011). Hower et al. (2000b) and Maroto-Valer et al. (1999, 2001) examined density-gradient fractions of carbon from high volatile A bituminous coal-derived FA. While no fractions contained pure carbon forms, fractions dominated by anisotropic coke had the highest BET surface area and, generally, the highest Hg content of the fractions investigated. The ranking with respect to Hg capture was in a

decreasing order of anisotropic coke, isotropic coke, and inertinite. In a study of anthracite-derived fly ashes, Suárez-Ruiz et al (2007) and Suárez-Ruiz and Parra (2007) found a positive correlation between Hg capture and both the proportion of anisotropic carbon and the BET surface area. López-Antón et al. (2009) noted that BET surface area per unit carbon (carbon expressed as the LOI) decreased in an order of the subbituminous-derived FA, bituminous-derived FA, and anthracite-derived FA. In contrast to Kostova et al. (2011), Lopez-Anton et al. (2009) found that Hg retention, expressed as mg Hg/g sorbent (versus Hg/C), was highest in the bituminous-derived FA and lowest in the subbituminous-derived FA.

Studies dealing with the possible capture of other trace elements on UC are not as common as those of Hg and rather rare (Bartoňová et al., 2007; Vassilev et al., 2000); also, results on Se capture by UC in FA are inconsistent (Suárez-Ruiz et al. 2007; López-Antón et al., 2007; Bartoňová et al., 2007, 2012). Suárez-Ruiz et al. (2007) have not found a distinct relation between Se concentration and different UC forms, but found an association of Se with the inorganic fraction and temperature in the bulk PFC FAs derived from anthracite/metantracite blends. Distinct relations between Se concentrations and LOI values for FA fractions of three PFC FAs have not been observed either by López-Antón et al. (2007). However, Bartoňová (2007, 2012) has observed a positive relation between Se and UC contents in FA fractions collected from three FBC power stations. Additionally, Bartoňová et al. (2012) showed that UC particles can help in the retention of S, Cl, Br, As, Se, Cu, Ni, Zn, Ga, Ge, Rb, and Pb from flue gas during coal combustion at a fluidized-bed power station where the coal was combusted along with limestone, suggesting that the UC is a promising material in terms of flue gas cleaning.

In addition to toxic trace elements, UC in FA may also capture valuable trace elements. Three types of UC have been identified in Ge-rich fly ashes by Dai et al. (2014a), namely,

fusinite and secretinite with well-preserved maceral structures, isotropic and anisotropic carbon, and fine-grained secondary char. These UCs contain more abundant Ge (up to 18.7 wt.%) than the feed coals, suggesting that the enrichment of Ge in UC may be attributed to sorption by organic matter of Ge from an external condensed vapor phase, and hence that such carbon may be of value in the processing of Ge (Dai et al., 2014a).

6.4. Other uses of coal-derived UC

In addition to uses of UC as mentioned above based on its adsorption properties, other aspects of UC utilization have also attracted much attention. Coal-derived UC is a promising material that can advantageously be used for the preparation of activated carbons. Because UC has already been subjected to devolatilization during the combustion process, only one step, activation, is required to enhance its adsorption properties, making it more profitable relative to the conventional two-step activation procedures (Maroto-Valer et al., 2001, 2008; Izquierdo and Rubio, 2008).

Various methods have been developed for such activation, and these have been comprehensively reviewed by Bartoňová (2015). For example, the use of steam in a fluidised bed (Rubio et al., 2007; Izquierdo and Rubio, 2008) or in a horizontal furnace for steam activation (Maroto-Valer et al., 2005; Lu et al., 2010), and preparation from UC in bottom ash with KOH activation for liquid-phase adsorption (Wu et al., 2010). Activated carbon produced from UC has various applications, including removal of SO₂ (Davini, 2002; Izquierdo and Rubio, 2008) and the retention of NO_x (Davini, 2002; Izquierdo and Rubio, 2007) in flue gases.

Some studies (e.g., Cabiellas et al., 2008a,b; Cameán et al., 2011) have also investigated its suitability in the manufacture of graphite and have found that the physical properties and performance of graphite materials produced from coal-derived UC are similar to those of

graphite in lithium-ion batteries. Another potential use of UC from FA is as a coke in the metallurgical industry, although the P content should be reduced to <20 ppm for such applications (Blissett and Rowson, 2012; Yang and Halvacek, 1999).

7. Removal of UC from FA

UC, particularly when present in significant proportions, often limits or precludes the use of FA as a substitute for Portland cement in concrete. The actual proportion that restricts use varies among regulating agencies, but, in general, most limit the proportion of unburned carbon to a maximum of 3% by weight. The principle technical reason is to provide consistency in air entrainment; however, other aspects, such as compressive strength and color, are considerations as well. Nevertheless, FA containing excessive proportions of UC cannot be used in many applications, and this presents a need to employ some form of selective carbon reduction technology. On the other hand, the collected UC can be used for preparation of activated carbon, graphite-like materials, or as a source of carbon to feed back into the boiler. There are essentially four such technologies that are suitable for commercial scale applications: size classification, electrostatic separation, thermal processing, and froth flotation. Other techniques including density separation (sink-float technique), acid digestion, and incipient fluidization, have also been investigated for separation of UC from FA.

7.1. Size classification

Many high-UC fly ashes contain a disproportionate amount of coarse (i.e. >150 μm) carbon particles. While this coarse size fraction often represents as little as 10% of the total mass, it frequently contains as much as 50% of the total carbon present. The efficiency of this separation is largely dependent on particle-size distribution of the UC in the fly ash. As such, size classification can be an effective means of selectively removing carbon, particularly when large

amounts of coarse carbon are present. However, there will be a low efficiency separation if the UC grains are distributed evenly within certain particle-size fractions. Dry screening at such a fine size is not practical for large scale applications; however, due to its simplicity without a requirement for liquid media, this technique can be an effective option for removing coarse carbon particles while simultaneously improving ash fineness.

A typical cyclone classifier uses centrifugal force to separate coarse particles from the air stream as a mixture of particles dispersed in air enters a cylindrical chamber. Coarse particles move to the cylinder wall under centrifugal forces, slide down the cylinder wall, and exit from the bottom, while lower-mass finer particles partition to an inner vortex and exit with air from the inner core. Commercial air classifiers vary considerably in the feed arrangement employed, but most use some means of effectively dispersing the feed across the cyclone profile. Since air classification is based on the density difference between carbon ($\sim 1.8 \text{ g/cm}^3$) and other ash particles ($\sim 2.5 \text{ g/cm}^3$), it is not particularly effective for removing fine carbon. Coarse, low-density carbon particles may be rejected with coarse ash particles, but since the density of carbon particles is lower than that of ash particles, carbon may actually be concentrated with fine ash in the vortex exit stream (Groppo et al., 1996).

7.2. *Electrostatic separation*

Electrostatic separation is accomplished by exploiting the differences in electrical properties between carbon and other ash particles. Particles are charged by inter-particle contact, where charges are transferred between particles by differences in electron affinity. Since UC particles have a lower electron affinity, electrons are lost and carbon particles become positively charged, while the other ash particles gain electrons and become negatively charged. This differential charge is the basis for electrostatic separation.

Electrostatic separation techniques have been studied by a number of investigators (e.g., Ban et al., 1997; Gray et al., 2002; Soong et al., 2002; Cangialosi et al., 2009) and have been commercially adopted. The primary difference between the electrostatic separation techniques is the mechanical device that is used to achieve the separation between the oppositely charged particles. The first commercial application was reported by Separation Technologies, Inc. and works by feeding ash into a thin gap (0.635-1.9 cm) between two parallel plane electrodes (Bittner and Gasiorowski, 2001). The particles are then swept by a moving open mesh belt and conveyed in opposite directions, depending on their charge. Similar approaches have been proposed using different separation devices (Ban et al., 1997; Kim et al., 2000, 2001; Soong et al., 2002). Although undesirable behavior caused by the exposure of the ash to moisture can be overcome by the addition of Na, Ca or borate ions (Baltrus et al., 2002), it is required that the FA should be sufficiently dried prior to separation; otherwise the separation efficiency would be significantly diminished (Cangialosi et al., 2009). Electrostatic separation has also been used to remove Fe-rich particles from FA for ceramic and refractory applications (Rao et al., 1999).

7.3. Thermal processing

Perhaps the most effective means of removing UC from FA is simply to burn the carbon using thermal processes. Given the low proportion of carbon in FA (typically 4 to 10 wt. %), conventional combustion approaches are not suitable without the use of supplemental fuel. However, thermal decomposition of carbon can be achieved with a fluidized bed, which has been commercially applied. Fluidized-bed combustors are capable of treating a continuous stream of FA using a thermal process designed to burn out the residual carbon, which has been proved to be a robust technique. For example, it has been commercially used at the Wateree Station of South Carolina Electric and Gas since 1999, and can process 180,000 tonnes of ash per year

(Blissett and Rowson, 2012). In another case the technique was applied at the Winyah Station of Santee Cooper in 2002, and can process 200,000 tonnes FA per year (Kepler, 2001). Cammarota et al. (2008) reported use of a conical fluidized-bed reactor not only to burn the residual carbon and but also to separate the remaining FA into two narrow size groups.

As described by Kepler (2001), the Carbon Burnout (CBO) process uses start-up fuel to heat FA to 460°C, the auto-ignition temperature for residual carbon. Once the ash is heated and the desired level of carbon reduction is achieved, low-carbon ash is removed from the bed, cooled, and stored for use as a pozzolan. Heated ash that is not removed from the process is recycled back to the bed to maintain bed temperature. Once the auto-ignition temperature is achieved, no additional fuel is required to maintain bed temperature, provided there is sufficient UC in the fresh ash introduced to the process. For this reason, CBO is particularly well suited for treating ash with higher proportions of carbon. An additional benefit is realized when fine ash particles entrained in carbon particles are liberated as the carbon decomposes, resulting in improved overall ash fineness. Another important advantage of thermal processing is that it is suitable for use on both freshly produced FA and previously disposed coal ash reclaimed from ponds (Knowles and Fedorka, 2015).

7.4. Froth flotation and oil agglomeration

Use of froth and column flotation to remove carbon from FA has been the subject of numerous investigations (Hemmings and Berry, 1986; Gruenwald and Ostettler, 1989; Gray et al., 2001; Hwang et al 2002; Cao et al., 2012; Li et al., 2015) and patents (Hurst and Styron, 1978; Hwang, 1991), and is among the most promising methods for liberating UC from FA. Froth flotation has also been commercialized in the US, with carbon grade recovery as high as 70% (Baltrus et al., 2001). The froth flotation method is based on the ability of air bubbles to

selectively adhere to the surface of a particular particle surface. In this manner, carbon particles are selectively removed from an agitated tank by attachment to air bubbles, while hydrophilic ash particles remain in suspension. Reagents that are generally used in column flotation include kerosene or Orfom (as collector), methyl isobutyl carbinol or pine oil (as frother), sodium meta silicate (as dispersant/depressant) and butanol (as promoter used to enhance floatability of carbonaceous particles) (Demir et al., 2008; Yamik and Dogruoz, 2008; Ucurum et al., 2011).

A significant disadvantage of froth flotation is that it requires thermal drying of the processed low-carbon ash when the ash is to be used as a pozzolan. However, several advantages are offered. One is that it is applicable to ash stored in ponds and landfills. The other is that it provides the opportunity to separate the ash into a variety of marketable products, thereby offering the potential for total utilization (Groppo et al., 2004). Some techniques combining froth flotation with other methods have been attempted to achieve high UC recoveries. For example, a combination of sieving and froth flotation has been investigated to achieve high carbon yields and grades (Vassilev et al., 2004). Hwang et al. (2002) have efficiently separated the UCs from clean ash using combined separation technologies including gravity separation, electrostatic separation, and froth flotation. They separated UC from the coarse portion using gravity separation, followed by electrostatic separation, and the fine portion was fed into flotation circuit for carbon separation.

The mechanism of oil agglomeration is similar to that of froth flotation. The oil agglomeration technique is based on the preferential wetting of oleophilic/hydrophobic particles by oil that is added to an aqueous slurry. The process allows the UC particles to be wetted by the oil and the mineral particles of ash to remain in suspension. During agitation, the UC particles coated with oil would collide with each other and form agglomerates, which have a lesser density

than the mineral particles remaining in suspension. Oil/UC agglomerates would rise to the top of the aqueous slurry system and separation of UC from the ash would be achieved (Mehrotra et al., 1983). Using the oil agglomeration method allows not only high-purity UC (66-71% C; Rubio et al., 2008; Gray et al., 2001) to be obtained, but also high recoveries of UC (e.g., 55-57% recoveries; Gray et al., 2001). A recycling process was designed by Sung et al. (2016) to remove and recover UC from FA using kerosene extraction, and under an optimum combination of shaking time, pulp density, temperature, shaking speed, and organic to suspension ratio, the content of UC was decreased successfully to less than 3%.

7.5. Other techniques

Other techniques, including density separation (sink-float technique), acid digestion, and incipient fluidization, have also been subjected to investigations, but have not been utilized as widely as above-mentioned techniques. The mineral-matter ash fractions usually have higher density than those of UC particles (e.g., bulk density refers to the volume of pores and intra-particle space; envelope density includes the volume of skeleton and pores; and skeletal density only refers to the volume of skeleton). A certain liquid medium (e.g., tungstate; Maroto-Valer et al., 1999, 2001) could be used to separate them, the former present in “sink” fraction and the latter occurring in “float” fraction. It has been reported that the values densities of UCs increase in order of bulk density (0.257-0.279 g/cm³), envelope density (0.26-0.87 g/cm³), and skeletal density (2-3 g/cm³) (Baltrus et al., 2001). Although acid digestion can effectively remove mineral matter in FA and consequently concentrate UC, some insoluble or poorly soluble minerals (e.g., chromite) in some cases could remain in the UC residues, the UC characteristics could be changed (producing new functional groups), or the sample could be contaminated (Bartoňová, 2015). For incipient fluidization, the ash sample is put at the bottom of a tube, a flow

of gas (usually He) is pulsed upward through the ash sample, and the dense mineral matter particles then settle at the bottom while the UC are floated at the top. Not only could UC of high purity be obtained (e.g., 75%, Hurt et al., 1995), but also contamination and UC property changes could be avoided (Bartoňová, 2015) because no chemical reagents are used.

8. Summary and future investigations

Unburned carbon in FA is an indicator of inefficiency in combustion and an impediment to the beneficial reuse of FA, but also has a potential as a value-added product in its own right after beneficiation of the FA. Factors affecting the nature of the UC, including coal rank and type, and the behavior of different maceral groups during combustion, have been addressed in many research programs, and the petrological characteristics, absorptive properties and techniques for UC separation have been extensively studied. However, a number of beneficial results may still be expected after further investigations on some aspects of UC properties as well as processes for UC utilization, and this would make UC a valuable commodity with a range of applications. These potential investigations include the mechanism for capture of toxic and valuable trace elements by UC, the inorganic and organic compositions of UC, formation process of isotropic and anisotropic chars/cokes derived from coal macerals, the survival mechanism of some different inertinite macerals during coal combustion, techniques for elevating UC purity and high-recovery efficiency from FA. Additional aspects that have not been discussed in this review paper but are worthy of consideration include engineering factors affecting the proportion of UC, the nature of UC in gasification products, development of multi-walled carbon nanotubes, the use of UC in retention of dyes or other pollutants from wastewaters, and graphite production from UC as a raw material source.

Acknowledgements: Many thanks are given to the anonymous reviewer who has provided extremely thorough and careful comments, which greatly improved the quality of the paper. This work was in part supported by the National Natural Science Foundation of China (No. 41420104001), which is an international cooperative project between China University of Mining and Technology (Beijing) and University of Kentucky Center for Applied Energy Research.

References

- AASHTO (American Association of State Highway and Transportation Officials), 2011. Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. AASHTO M 295.
- Ahmaruzzaman, M., 2010. A review on the utilization of fly ash. *Prog. Energy Combust. Sci.* 36, 327–363.
- Ahn, Y.C., Lee, J.K., 2006. Physical, chemical, and electrical analysis of aerosol particles generated from industrial plants. *J. Aerosol Sci.* 37, 187–202.
- Akgerman, A., Zardkoohi, M., 1996. Adsorption of phenolic compounds on fly ash. *J. Chem. Eng. Data* 41, 185–187.
- Alvarez, D., Borrego, A.G., Menéndez, R., 1997. Unbiased methods for the morphological description of char structures. *Fuel* 76, 1241-1248.
- American Society for Nondestructive Testing. 1999. Handbook of American non-destructive testing (Electromagnetic volume). Shanghai, Shanghai World Book Publishing Co., p. 699–767.
- ASTM C618-15, 2015. Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. ASTM International, West Conshohocken, PA. www.astm.org.
- ASTM D6316-09be1, 2009. Standard Test Method for Determination of Total, Combustible and Carbonate Carbon in Solid Residues from Coal and Coke, ASTM International, West Conshohocken, PA. www.astm.org
- ASTM D7348-13, 2013. Standard Test Methods for Loss on Ignition (LOI) of Solid Combustion Residues. ASTM International, West Conshohocken, PA. www.astm.org.
- Atas, S., Tekir, U., Paksoy, M.A., Çelik, A., Çam, M., Sevgel, T., 2014. Numerical and experimental analysis of pulverized coal mill classifier performance in the Soma B Power Plant. *Fuel Process. Technol.* 126, 441–452.
- Australian Standard AS3582.1, 1998. Supplementary Cementitious Materials for Use with Portland and Blended Cement – Part 1: Fly Ash, ISBN 0 7337 1688 1, Standards Australia International.
- Bahadori, A., Vuthaluru, H.B., 2010. Estimation of potential savings from reducing unburned combustible losses in coal-fired systems. *Appl. Energy* 87, 3792–3799.
- Bailey, J.G., Tate, A., Diessel, C.F.K., Wall, T.F., 1990. A char morphology system with applications to coal combustion. *Fuel* 69, 225-239.

- Baltrus, J.P., Diehl, J.R., Soong, Y., Sands, W., 2002. Triboelectrostatic separation of fly ash and charge reversal. *Fuel* 81, 757 – 762.
- Baltrus, J.P., Wells, A.W., Fauth, D.J., Diehl, J.R., White, C.M., 2001. Characterization of carbon concentrates from coal-combustion fly ash. *Energy Fuels* 15, 455 – 462.
- Ban, H., Li, T.X., Hower, J. C., Schaefer, J.L., Stencel, J.M., 1997. Dry triboelectric beneficiation of fly ash. *Fuel* 76, 801-805.
- Bartoňová, L., 2015. Unburned carbon from coal combustion ash: An overview. *Fuel Process. Technol.* 134, 136 – 158.
- Bartoňová, L., Cech, B., Ruppenthalova, L., Majvelderova, V., Juchelkova, D., Klika, Z., 2012. Effect of unburned carbon content in fly ash on the retention of 12 elements out of coal-combustion flue gas. *J. Environ. Sci.* 24, 1624–1629.
- Bartoňová, L., Juchelková, D., Klika, Z., Cech, B., 2011. On Unburned Carbon in Coal Ash from Various Combustion Units. *Int. J. Chem., Mol. Nucl. Mater. Metall. Eng.* 5(4), scholar.waset.org/1999.2/4929
- Bartoňová, L., Klika, Z., Spears, A.D., 2007. Characterization of unburned carbon from ash after bituminous coal and lignite combustion in CFBs. *Fuel* 86, 455–463.
- Batra, V.S., Varghese, A.R., Vashisht, P., Balakrishnan, M., 2011. Value-added products from unburned carbon in bagasse fly ash. *Asia-Pac. J. Chem. Eng.* 6, 787–793.
- Berkowitz, N., 1979. *An Introduction to Coal Technology*. New York, Academic Press, 345 p.
- Bilen, M., Kizgut, S., 2016. Modeling of unburned carbon in fly ash and importance of size parameters. *Fuel Process. Technol.* 143, 7-17.
- Bilen, M., Kizgut, S., Akkaya B., 2015. Prediction of unburned carbon in BA in terms of moisture content and sieve analysis of coal. *Fuel Process. Technol.* 138, 236 – 242.
- Bittner, J.D., Gasiorowski, S.A., 2001. STI's Six Years of Commercial Experience in Electrostatic Beneficiation of Fly Ash. 2001 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, Paper #16. Available at <http://www.flyash.info/2001/benef1/16bitn.pdf>, accessed 10 May 2017.
- Blissett, R.S., Rowson, N.A., 2012. A review of the multi-component utilisation of coal fly ash. *Fuel* 97, 1-23.
- Bonanno, A.S., Knight, K.S., Kinsella, K., Serio, M.A., Solomon, P.R., 1995. In-situ measurement of residual carbon content in fly ash. *Proc. SPIE* 2367, 194–201
- Brown, R.C., Dona, A.R., 1990. On-line determination of unburned carbon in airborne fly ash. *J. Eng. Gas Turb. Power*, 112, 597-601.
- Brown, R.C., Dykstra, J., 1995. Systematic errors in the use of loss-on-ignition to measure unburned carbon in fly ash. *Fuel* 74, 570-574.
- Cabiellas, M., Montes-Morán, M.A., Garcia, A.B., 2008a. Structural study of graphite materials prepared by HTT of unburned carbon concentrates from coal combustion fly ashes. *Energy Fuels* 22, 1239–1243.
- Cabiellas, M., Rouzaud, J.-N., Garcia, A.B., 2008b. High-resolution transmission electron microscopy studies of graphite materials prepared by high-temperature treatment of unburned carbon concentrates from combustion fly ashes. *Energy Fuels* 23, 942–950.
- Cameán, I., Garcia, A.B., 2011. Graphite materials prepared by HTT of unburned carbon from coal combustion fly ashes: performance as anodes in lithium-ion batteries. *J. Power Sour.* 196, 4816–4820.

- Cammarota, A., Chirone, R., Solimene, R., Urciuolo, M., 2008. Beneficiation of pulverized coal combustion fly ash in fluidised bed reactors. *Exp. Therm. Fluid Sci.* 32, 1324–1333.
- Cangialosi, F., Notarnicola, M., Liberti, L., Stencel, J., 2009. The role of weathering on fly ash charge distribution during triboelectrostatic beneficiation. *J. Hazard. Mater.* 164, 683–688.
- Cao, Y., Li, G., Liu, J., Zhang, H., Zhai, X., 2012. Removal of unburned carbon from fly ash using a cyclonic-static microbubble flotation column. *J. S. Afr. I. Min. Metall.* 112, 891–896.
- Chen, Y., Shah, N., Huggins, F.E., Huffman, G.P., 2004. Investigation of the microcharacteristics of PM_{2.5} in residual oil fly ash by analytical transmission electron microscopy. *Environ. Sci. Technol.* 38, 6553–6560.
- Chen, Y., Shah, N., Huggins, F.E., Huffman, G.P., 2005a. Transmission electron microscopy investigation of ultrafine coal fly ash particles. *Environ. Sci. Technol.* 39, 1144–1151.
- Chen, Y., Shah, N., Huggins, F.E., Huffman, G.P., Dozier, A., 2005b. Characterization of ultrafine coal fly ash particles by energy-filtered TEM. *J. Microsc.* 217, 225–234.
- Chen, Y., Shah, N., Huggins, F.E., Huffman, G.P., 2006. Microanalysis of ambient particles from Lexington, KY, by electron microscopy. *Atmos. Environ.* 40, 651–663.
- Ctvrtnickova, T., Mateo, M.-P., Yañez, A., Nicolas, G., 2009. Characterization of coal fly ash components by laser-induced breakdown spectroscopy. *Spectrochimica Acta B.* 64, 1093–1097.
- Cutmore, N.G., 1993. Determination of carbon in fly ash from microwave attenuation and phase shift. US Patent No. 5,177,444.
- Dai, S., Liu, J., Ward, C.R., Hower, J.C., Xie, P., Jiang, Y., Hood, M.M., O’Keefe, J.M.K., Song, H., 2015a. Petrological, geochemical, and mineralogical compositions of the low-Ge coals from the Shengli Coalfield, China: A comparative study with Ge-rich coals and a formation model for coal-hosted Ge ore deposit. *Ore Geol. Rev.* 71, 318–349.
- Dai, S., Seredin, V.V., Ward, C.R., Jiang, J., Hower, J.C., Song, X., Jiang, Y., Wang, X., Gornostaeva, T., Li, X., Liu, H., Zhao, L., Zhao, C., 2014a. Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals. *Int. J. Coal Geol.* 121, 79–97.
- Dai, S., Wang, X., Seredin, V.V., Hower, J.C., Ward, C.R., O’Keefe, J.M.K., Huang, W., Li, T., Li, X., Liu, H., Xue, W., Zhao, L., 2012. Petrology, mineralogy, and geochemistry of the Ge-rich coal from the Wulantuga Ge ore deposit, Inner Mongolia, China: New data and genetic implications. *Int. J. Coal Geol.* 90, 72–99.
- Dai, S., Wang, P., Ward, C.R., Tang, Y., Song, X., Jiang, J., Hower, J.C., Li, T., Seredin, V.V., Wagner, N.J., Jiang, Y., Wang, X., Liu, J., 2015b. Elemental and mineralogical anomalies in the coal-hosted Ge ore deposit of Lincang, Yunnan, southwestern China: Key role of N₂–CO₂-mixed hydrothermal solutions. *Int. J. Coal Geol.* 152, 19–46.
- Dai, S., Zhao, L., Hower, J.C., Johnston, M.N., Song, W., Wang, P., Zhang, S., 2014b. Petrology, mineralogy, and chemistry of size-fractionated fly ash from the Jungar Power Plant, Inner Mongolia, China, with emphasis on the distribution of rare earth elements. *Energy Fuels* 28, 1502–1514.
- Dai, S., Zhao, L., Peng, S., Chou, C.-L., Wang, X., Zhang, Y., Li, D., Sun, Y., 2010. Abundances and distribution of minerals and elements in high-alumina coal fly ash from the Jungar Power Plant, Inner Mongolia, China. *Int. J. Coal Geol.* 81, 320–332.

- Davini, P., 2002. Flue gas treatment by activated carbon obtained from oil-fired fly ash. *Carbon* 40, 1973 - 1979.
- Davis, K.A., Hurt, R.H., Yang, N.Y.C., Headley, T.J., 1995. Evolution of char chemistry, crystallinity, and ultrafine structure during pulverized-coal combustion. *Combust. Flame* 100, 31 - 40.
- Demir, U., Yamik, A., Kelebek, S., Oteyaka, B., Ucar, A., Sahbaz, O., 2008. Characterization and column flotation of bottom ashes from Tuncbilek power plant. *Fuel* 87, 666 - 672.
- Demirkan, M.M., Aydılek, A.H., Seagren, E.A., Hower, J.C., 2011. Naphthalene and *O*-xylene Adsorption onto High Carbon Fly Ash. *J. Environ. Eng.-ASCE* 137, 377-387.
- Demirkan, M.M., Seagren, E. A., Aydılek, A. H., 2006. Reuse of fly ash amended petroleum contaminated soils in highway embankments. *Transportation Research Record* 1975, Transportation Research Board, Washington, DC, 104-111 (<http://terpconnect.umd.edu/~aydilek/papers/PCS.pdf>, accessed 9 May 2017)
- Dindarloo, S.R., Hower, J.C., 2015. Prediction of the unburned carbon content of fly ash in coal-fired power plants. *Coal Combust. Gasification Prod.* 7, 19-29.
- Dykstra, J.R., Brown, R.C., 1995. Comparison of optically and microwave excited photoacoustic detection of unburned carbon in entrained fly ash. *Fuel* 74, 368-373.
- Eiceman, G.A., Vandiver, V.J., 1983. Adsorption of polycyclic aromatic hydrocarbons on fly ash from a municipal incinerator and a coal-fired power plant. *Atmos. Environ.* 17, 461-465
- Fan, M., Brown, R.C., 2001. Precision and accuracy of photoacoustic measurements of unburned carbon in fly ash. *Fuel* 80, 1545-1554.
- Gaft, M., Dvir, E., Modiano, H., Schone, U., 2008. Laser induced breakdown spectroscopy machine for online ash analyses in coal. *Spectrochimica Acta B*, 63, 1177-1182.
- Gao, Y., Külaots, I., Chen, X., Suuberg, E.M., Hurt, R.H., Veranth, J.M., 2002. The effect of solid fuel type and combustion conditions on residual carbon properties and fly ash quality. *Proceedings of the Combustion Institute* 90, 475 - 483.
- Ganguli, R., Bandopadhyay, S., 2012. Relationship between Particle Size Distribution of Low-Rank Pulverized Coal and Power Plant Performance. *J. Combust.* Article ID 786920, 7 pages. DOI: 10.1155/2012/786920.
- Gao, H., Majeski, A.J., Runstedtler, A., 2013. A method to target and correct sources of unburned carbon in coal-fired utility boilers. *Fuel* 108, 484-489.
- Goodarzi, F., 2005. Petrology of subbituminous feed coal as a guide to the capture of mercury by fly ash - influence of depositional environment. *Int. J. Coal Geol.* 61, 1-12.
- Goodarzi, F., 2006. Characteristics and composition of fly ash from Canadian coal-fired power plants. *Fuel* 85, 1418-27.
- Goodarzi, F., Hower, J.C., 2008. Classification of carbon in Canadian fly ashes and their implications in the capture of mercury. *Fuel* 7, 1949-1957.
- Goodarzi, F., Huggins, F.E., Sanei, H., 2008. Assessment of elements, speciation of As, Cr, Ni and emitted Hg for a Canadian power plant burning bituminous coal. *Int. J. Coal Geol.* 74, 1-12.

- Gray, M.L., Champagne, K.J., Soong, Y., Finseth, D.H., 2001. Parametric study of the column oil agglomeration of fly ash. *Fuel* 80, 867-871.
- Gray, M.L., Champagne, K.J., Soong, Y., Killmeyer, R.P., Maroto-Valer, M.M., Andrésen, J.M., Ciocco, M.V., Zandhuis, P.H., 2002. Physical cleaning of high carbon fly ash. *Fuel Process. Technol.* 76, 11-21.
- Gray, R.J., DeVanney, K.F., 1986. Coke carbon forms: Microscopic classification and industrial applications. *Int. J. Coal Geol.* 6, 277-297.
- Gregg, S.J., Sing, K.S.W., 1982. Adsorption, Surface Area and Porosity, 2nd ed. Harcourt Brace Javanovich, London, U.K. pp. 303.
- Groppo, J.G, Robl, T., Hower, J.C., 2004. The beneficiation of coal combustion ash. In: Gieré, R., Stille, P. (eds), *Energy, Waste, and the Environment: a Geochemical Perspective*. Geological Society, London, Special Publications 236, 247-262.
- Groppo, J.G., Robl, T.L., Graham, U.M., McCormick, C.J., 1996. Selective beneficiation for high loss-on-ignition fly ash. *Min. Eng.* 48, 51-53.
- Gruenwald, K., Ostettler, H., 1989. Investigations into the beneficiation of fly ash from power plants using flotation. *Bundesministerium für Bildung, Wissenschaft und Kultur.* 42, 61-63.
- Hao, Z., Qian, X., Cen, K., Fan, J., 2004. Optimizing pulverized coal combustion performance based on ANN and GA. *Fuel Process. Technol.* 85, 113-124.
- Hemalatha, T., Ramaswamy, A., 2017. A review on fly ash characteristics – Towards promoting high volume utilization in developing sustainable concrete. *J. Clean. Prod.* 147, 546-559.
- Hemmings, R.T., Berry, E.E., 1986. Evaluations of plastic filler applications for leached fly ash. *Electric Power Research Institute Report No. CS4765*.
- Hill, R.L., Rathbone, R.F., Hower, J.C., 1998. Investigation of fly ash carbon by thermal analysis and optical microscopy. *Cem. Concr. Res.* 28, 1479-1488.
- Hill, R.L., Sarkar, S.L., Rathbone, R.F., Hower, J.C., 1997. An examination of fly ash carbon and its interactions with air entraining agents. *Cem. Concr. Res.* 27, 193-204.
- Hill, T., 1890. A journey on horseback from New Brunswick, New Jersey, to Lycoming County, Pennsylvania, in 1799. *Penn. Mag. Hist. Biog.* 14, 189-198.
- Hood, M.M., Taggart, R.K., Smith, R.C., Hsu-Kim, H., Henke, K.R., Graham, U.M., Groppo, J.G., Unrine, J.M., Hower, J.C., 2017. Rare earth element distribution in fly ash derived from the Fire Clay coal, Kentucky. *Coal Combust Gasification Prod.* DOI:10.4177/CCGP-D-17-00002.1.
- Hower, J.C., 2012. Petrographic examination of coal-combustion fly ash. *Int. J. Coal Geol.* 92, 90-97.
- Hower, J.C., Clack, H.C., Hood, M.M., Hopps, S.G., Thomas, G.H., 2016. Impact of coal source changes on mercury content in fly ash: Examples from a Kentucky power plant. *Int. J. Coal Geol.* 170, 2-6.
- Hower, J.C., Finkelman, R.B., Rathbone, R.F., Goodman, J., 2000a. Intra- and Inter-unit Variation in Fly Ash Petrography and Mercury Adsorption: Examples from a Western Kentucky Power Station. *Energy Fuels* 14, 212-216.
- Hower, J.C., Graham, U.M., Dozier, A., Tseng, M.T., Khatri, R.A., 2008. Association of sites of heavy metals with nanoscale carbon in a Kentucky electrostatic precipitator fly ash. *Environ. Sci. Technol.* 42, 8471-8477.

- Hower, J.C., Groppo, J.G., Henke, K.R., Graham, U.M., Hood, M.M., Joshi, P., Preda, D.V., 2017b. Pondered and landfilled fly ash as a source of rare earth elements from a Kentucky power plant. *Coal Combust. Gasification Prod.* DOI: 10.4177/CCGP-D-17-00003.1.
- Hower, J.C., Hood, M.M., Taggart, R.K., Hsu-Kim, H., 2017a. Chemistry and petrology of paired feed coal and combustion ash from anthracite-burning stoker boilers. *Fuel* 199, 438-446
- Hower, J.C., Maroto-Valer, M.M., Taulbee, D.N., Sakulpitakphon, T., 2000b. Mercury Capture by Distinct Fly Ash Carbon Forms. *Energy Fuels* 14, 224-226.
- Hower, J.C., Mastalerz, M., 2001. An Approach Towards a Combined Scheme for the Petrographic Classification of Fly Ash. *Energy Fuels* 15, 1319-1321.
- Hower, J.C., Rathbone, R.F., Graham, U.M., Groppo, J.G., Brooks, S.M., Robl, T.L., Medina, S.S., 1995. Approaches to the petrographic characterization of fly ash. *International Coal Testing Conference*, 11th, Lexington, KY, May 10-12, 1995, p. 49-54. (<https://www.osti.gov/scitech/biblio/83299>)
- Hower, J.C., Rathbone, R.F., Robl, T.L., Thomas, G.A., Haeberlin, B.O., Trimble, A.S., 1997a. Case study of the conversion of tangential- and wall-fired units to low-NO_x combustion: Impact on fly ash quality. *Waste Manage.* 17, 219-229.
- Hower, J.C., Robertson, J.D., Roberts, J.M., 2001b. Combustion by-products from the co-combustion of coal, tire-derived fuel, and petroleum coke at a Western Kentucky cyclone-fired unit. *Fuel Process. Technol.* 74, 125-142.
- Hower, J.C., Robl, T.L., Rathbone, R.F., Groppo, J.G., Graham, U.M., Taulbee, D.N., 1996. Case studies of the impact of conversion to low-NO_x combustion on fly ash petrology and mineralogy. *Australian Coal Science Conference*, 7th, Dec. 2-4, 1996, Gippsland, Victoria, Australia, p. 347-354. ISBN, 0958694907.
- Hower, J.C., Robl, T.L., Rathbone, R.F., Schram, W.H., Thomas, G.A., 1997b. Characterization of Pre- and Post-NO_x Conversion Fly Ash from the Tennessee Valley Authority's John Sevier Fossil Plant. *Proceedings, 12th International Symposium on Coal Combustion By-Product (CCB) Management and Use*, January 26-30, 1997, Orlando, FL, published by Electric Power Research Institute, EPRI TR-107055-V2, p. 39-1 - 39-13.
- Hower, J.C., Sakulpitakphon, T., Trimble, A.S., Thomas, G.A., Schram, W.H., 2006. Major and Minor Element Distribution in Fly Ash from a Coal-fired Utility Boiler in Kentucky. *Energy Sources* 28, 79-95.
- Hower, J.C., Senior, C.L., Suuberg, E.M., Hurt, R.H., Wilcox, J.L., Olson, E.S., 2010. Mercury capture by native fly ash carbons in coal-fired power plants. *Prog. Energy Combust. Sci.* 36, 510-529.
- Hower, J.C., Suárez-Ruiz, I., Mastalerz, M., 2005. An approach toward a combined scheme for the petrographic classification of fly ash: Revision and clarification. *Energy Fuels* 19, 653-655.
- Hower, J.C., Trecice, D.R., Rathbone, R.F., Thomas, G.A., Hobbs, A.D., 1999a. Short-term variation in fly ash petrology and mineralogy: Examples from a western Pennsylvania power station. *13th International Symposium on Use and Management of Coal Combustion Products (CCPs)*, American Coal Ash Association, 11-15 Jan 1999, Orlando, FL, EPRI TR-111829-V1, p. 28-1 - 28-28-10.
- Hower, J.C., Trimble, A.S., Eble, C.F., 2001a. Temporal and spatial variations in fly ash quality. *Fuel Process. Technol.* 73, 37-58.
- Hower, J.C., Trimble, A.S., Eble, C.F., Palmer, C., Kolker, A., 1999b. Characterization of Fly Ash from Low-sulfur and High-sulfur Coal Sources: Partitioning of carbon and trace elements with particle size. *Energy Sources* 21, 511-525.

- Hulett, L.D., Weinberger, A.K., Ferguson, N.M., Northcutt, K.J., Lyon, W.S., 1981. Trace element and phase relations in fly ash. Electric Power Research Institute EA-1822, Research Project 1061, 63 p. Available at <https://www.osti.gov/scitech/biblio/6184448>, accessed 9 May 2017.
- Hurst, V.J., Styron, R.W., 1978. Fly ash beneficiation process. US Patent No. 4,121,945.
- Hurt, R.H., Davis, K.A., Yang, N.Y.C., Headley, T.J., Mitchell, G.D., 1995. Residual carbon from pulverized-coal-fired boilers. 2. Morphology and physicochemical properties. *Fuel* 74, 1297 – 1306.
- Hwang, J.Y., 1991. Wet process for fly ash beneficiation. US Patent No. 5,047,145.
- Hwang, J.Y., Sun, X., Li, Z., 2002. Unburned Carbon from Fly Ash for Mercury Adsorption: I. Separation and Characterization of Unburned Carbon. *J. Miner. Mater. Charact. Eng.* 1, 39-60.
- International Committee for Coal and Organic Petrography (ICCP), 1998. The new vitrinite classification (ICCP System 1994). *Fuel* 77, 349-358.
- International Committee for Coal and Organic Petrology (ICCP), 2001. New inertinite classification (ICCP system 1994). *Fuel* 80, 459-471.
- Izquierdo, M.T., Rubio, B., 2008. Carbon-enriched coal fly ash as a precursor of activated carbons for SO₂ removal. *J. Hazard. Mater.* 155, 199–205.
- Janos, P., Buchtová, H., Ryznarová, M., 2003. Sorption of dyes from aqueous solutions onto fly ash. *Water Res.* 37, 4938–4944.
- Jasienko, S., 1978. The nature of coking coals. *Fuel* 57, 131-146.
- Jiménez, S., Ballester, J., 2007. Study of the evolution of particle size distributions and its effects on the oxidation of pulverized coal. *Combust. Flame* 151, 482–494.
- Jolicoeur, C., To, T.C., Benoit, E., Hill, R., Zhang, Z., Pagé, M., 2009. Fly Ash Carbon Effects on Concrete Air Entrainment: Fundamental Studies on Their Origin and Chemical Mitigation. *World of Coal Ash*, Lexington, KY, 4-7 May 2009 (<http://www.flyash.info/>, accessed 22 December 2016).
- Kempster RD, Crosse PAE. 1987. Apparatus for monitoring the carbon content of boiler fly ash. European Patent, Appl. No. 86,307,677,4, Publication number EP 0217677 A2.
- Kepler, J., 2001. Carbon burnout, an update on commercial applications. Proceedings: 2001 International Ash Utilization Symposium, 20-24 October 2001, Lexington, KY, cd-rom. (also see <http://www.flyash.info/2001/benef1/61kepperl.pdf>, accessed 9 May 2017).
- Kim, J.-K., Cho, H.-C., Kim, S.-C., 2001. Removal of unburned carbon from coal fly ash using a pneumatic triboelectric separator. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 36, 1709-1724.
- Kim, J.-K., Cho, H.-C., Kim, S.-C., Chun, H.-S., 2000. Electrostatic beneficiation of fly ash using an ejector-tribocharger. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 35, 357-377.
- Knowles, J. C., Fedorka, B., 2015. A new solution for a long-standing dilemma. *Ash at Work: Applications, Science, and Sustainability of Coal Ash*, American Coal Ash Association, Issue 2, 6-9, (Available at <https://www.aaaa-usa.org/Portals/9/Files/PDFs/ASH02-2015.pdf>, Accessed 3 January 2017).
- Kobylecki, R., 2011. Unburned carbon in the circulating fluidized bed boiler fly ash. *Chem. Process Eng.* 32, 255-266.
- Konstantinou, I.K., Albanis, T.A., 2000. Adsorption-desorption studies of selected herbicides in soil-fly ash mixtures. *J. Agric. Food Chem.* 48, 4780–4790.

- Kostova, I.J., Hower, J.C., Mastalerz, M., Vassilev, S.V., 2011. Mercury capture by selected Bulgarian fly ashes: Influence of coal rank and fly ash carbon pore structure on carbon efficiency. *Appl. Geochem.* 26, 18-27.
- Kostova, I., Vassileva, C., Dai, S., Hower, J.C., 2016. Mineralogy, geochemistry and mercury content characterization of fly ashes from the Maritza 3 and Varna thermoelectric power plants, Bulgaria. *Fuel* 186, 674-684.
- Kostova, I., Vassileva, C., Dai, S., Hower, J.C., Apostolova, D., 2013. Influence of surface area properties on mercury capture behavior of coal fly ashes from some Bulgarian power plants. *Int. J. Coal Geol.* 116-117, 227-235.
- Külaots, I., Hurt, R.H., Suuberg, E.M., 2004. Size distribution of unburned carbon in coal fly ash and its implications. *Fuel* 83, 223-230.
- Külaots, I., Aarna, I., Callejo, M., Hurt, R.H., Suuberg, E.M. 2002. Development of porosity during coal char combustion. *Proceedings of the Combustion Institute* 29, 495 - 501.
- Kurihara, M., Ikeda, K., Izawa, Y., Deguchi, Y., Tarui, H., 2003. Optimal boiler control through real-time monitoring of unburned carbon in fly ash by laser-induced breakdown spectroscopy. *Appl. Optics* 42, 6159-6165.
- Lester, E., Cloke, M., Allen, M., 1996. Char Characterization Using Image Analysis Techniques. *Energy Fuels* 10, 696-703.
- Letcavits, J.J., Conrads, H. Shelton, E., Sommer, T., 2004. Finally—a reliable, on-line carbon-in-ash analyzer, *Proceedings of ASME POWER 2004*, March 30–April 1, Baltimore, Maryland, USA, 2004, p. 199–2004. ISBN: 0-7918-4162-6 (Available at <http://proceedings.asmedigitalcollection.asme.org/proceeding.aspx?articleid=1633941>, accessed 9 May 2017).
- Li, G., Deng, L., Liu, J., Cao, Y., Zhang, H., Ran, J., 2015. A new technique for removing unburned carbon from coal fly ash at an industrial scale. *Int. J. Coal Prep. Util.* 35, 273-279.
- Li, S., Cheng, C.-M., Chen, B., Cao, Y., Vervynckt, J., Adebambo, A., Pan, W-P., 2007. Investigation of the relationship between particulate-bound mercury and properties of fly ash in a full-scale 100 MWe pulverized coal combustion boiler. *Energy Fuels* 21, 3292-3299.
- Linak, W.P., Yoo, J.I., Wasson, S.J., Zhu, W., Wendt, J.O.L., Huggins F.E., Chen Y., Shah N., Huffman G.P., 2007. Ultrafine ash aerosols from coal combustion: Characterization and health effects. *Proc. Combust. Inst.* 31, 1929-1937.
- Liu, D., Duan, Y.-Y., Yang, Z., Yu, H.-T., 2013. A New Route for Unburned Carbon Concentration Measurements Eliminating Mineral Content and Coal Rank Effects. *Scientific Report* 4: 4567; DOI: 10.1038/srep04567.
- Liu, H.Y., Tan, H.Z., Gao, Q., Wang, X.B., Xu, T.M. 2010. Microwave attenuation characteristics of unburned carbon in fly ash. *Fuel* 89, 3352-3357.
- Liu, J., Dai, S., He, X., Hower, J.C., Sakulpitakphon, T., 2017. Size-Dependent Variations in Fly Ash Trace Element Chemistry: Examples from a Kentucky Power Plant and with Emphasis on Rare Earth Elements. *Energy Fuels* 31, 438-447.
- Liu, K., Xie, W., Zhao, Z.-B., Pan, W.-P., Riley, J.T., 2000. Investigation of polycyclic aromatic hydrocarbons in fly ash from fluidised bed combustion systems, *Environ. Sci. Technol.* 34, 2273-2279.

- López-Antón, M.A., Abad-Valle, P., Díaz-Somoano, M., Suárez, I., Martínez-Tarazona, M.R., 2009. The influence of carbon particle type in fly ashes on mercury adsorption. *Fuel* 88, 1194-1200.
- López-Antón, M.A., Díaz-Somoano, M., Abad-Valle, P., Martínez-Tarazona, M.R., 2007. Mercury and selenium retention in fly ashes: Influence of unburned particle content. *Fuel* 86, 2064–2070.
- Low, G.K.C., Batley, G.E., 1986. Use of liquid chromatography for the measurement of adsorption isotherms for polycyclic aromatic hydrocarbons on coal fly ashes. *J. Chromatogr. A* 355, 177–191.
- Lu, Y., Rostam-Abadi, M., Chang, R., Richardson, C., Paradis, J., 2007. Characteristics of fly ashes from full-scale coal-fired power plants and their relationship to mercury adsorption. *Energy Fuels* 21, 2112-2120.
- Lu, Z., Maroto-Valer, M.M., Schobert, H.H., 2010. Catalytic effects of inorganic compounds on the development of surface areas of fly ash carbon during steam activation. *Fuel* 89, 3436-3441.
- Mardon, S.M., Hower, J.C., 2004. Impact of coal properties on coal combustion by-product quality: Examples from a Kentucky power plant. *Int. J. Coal Geol.* 59, 153-169.
- Mardon, S.M., Hower, J.C., O’Keefe, J.M.K., Marks, M.N., Hedges, D.H., 2008. Coal combustion by-product quality at two stoker boilers: Coal source versus fly ash collection system design. *Int. J. Coal Geol.* 75, 248-254.
- Maroto-Valer, M.M. Lu, Z., Zhang, Y., Tang, Z., 2008. Sorbents for CO₂ capture from high carbon fly ashes. *Waste Manage.* 28, 2320 - 2328.
- Maroto-Valer, M.M., Taulbee, D.N., Hower, J.C., 1999. Novel separation of the differing forms of unburned carbon present in fly ash using density gradient centrifugation. *Energy Fuels* 13, 947-953.
- Maroto-Valer, M.M., Taulbee, D.N., Hower, J.C., 2001. Characterization of the carbon types present in fly ash separated by density gradient centrifugation. *Fuel* 80, 795-800.
- Maroto-Valer, M.M., Zhang, Y., Granite, E.J., Tang, Z., Pennline, H.W., 2005. Effect of porous structure and surface functionality on the mercury capacity of a fly ash carbon and its activated sample. *Fuel* 84, 105 - 108.
- Maroto-Valer, M.M., Zhang, Y., Lu, Z., Andrésen, J.M., Schobert, H.H., 2002. Development of Value-Added Products from Fly Ash Carbons, in: Maroto-Valer, M.M., Song, C., Soong, Y. (Eds.), *Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century*. Springer US, Boston, MA, pp. 431-444. ISBN: 978-1-4613-5232-7 (Print) 978-1-4615-0773-4 (Online).
- Medvedev, Ya.V., Sedykh, A.K., Chelpanov, V.A., 1997. Pavlovsk deposit. *Coal Resources of Russia, V-I*. Geoinformmark, Moscow, pp. 175–194 (in Russian).
- Mehrotra, V.P., Sastry, K.V.S., Morey, B.W., 1983. Review of oil agglomeration techniques for processing of fine coals. *Int. J. Miner. Process.* 11, 175-201.
- Melick, T., Sommer, T., Conrads, H., 2002. Real-time monitoring of unburned carbon on utility fly ash, *Proceedings of World of Coal Ash/DOE UBC Conference 2005, April 11–15, 2005* (Lexington, Kentucky, USA, 11 pp.). (Available at <http://infohouse.p2ric.org/ref/45/44684.pdf>, accessed 9 May 2017).
- Mohebbi, M., Rajabipour, F., Scheetz, B.E., 2015. Reliability of loss on ignition (LOI) test for determining the unburned carbon content in fly ash. 2015 World of Coal Ash (WOCA) Conference in Nashville, TN – May 5-7, 2015 (Available at <http://www.flyash.info/2015/141-mohebbi-2015.pdf>, accessed 9 May 2017)
- Nandi, B.N., Brown, T.D., Lee, G.K., 1977. Inert coal macerals in combustion. *Fuel* 56, 125-130.

- Noda, M., Deguchi, Y., Iwasaki, S., Yoshikawa, N., 2002. Detection of carbon content in a high-temperature and high pressure environment using laser-induced breakdown spectroscopy. *Spectrochim. Acta Part B*, 57, 701-709.
- Nollet, H., Roels, M., Lutgen, P., Van der Meeren, P., Verstraete, W., 2003. Removal of PCBs from wastewater using fly ash. *Chemosphere* 53, 655–665.
- Ouazzane, A.K., Castagner, J.L., Jones, A.R., Ellahi, S., 2002. Design of an optical instrument to measure the carbon content of fly ash. *Fuel* 81, 1907-1911.
- Pandhija, S., Rai, N.K., Singh, A.K., Rai, A.K., Gopal, R., 2006. Development of photoacoustic spectroscopic technique for the study of materials. *Prog. Cryst. Growth. Charact. Mater.* 52, 53–60.
- Payá, J., Monzó, J., Borrachero, M.V., Perris, E., Amahjour, F., 1998. Thermogravimetric methods for determining carbon content in fly ashes. *Cement Concrete Res.* 28, 675-686.
- Pedersen, K.H., Jensen, A.D., Skjøth-Rasmussen, M.S., Dam-Johansen, K., 2008. A review of the interference of carbon containing fly ash with air entrainment in concrete. *Prog. Energy Combust. Sci.* 34, 135-154.
- Pickel, W., Kus, J., Flores, D., Kalaizidis, S., Christanis, K., Cardott, B.J., Misz-Kennan, M., Rodrigues, S., Hentschel, A., Hamor-Vido, M., Crosdale, P., Wagner, N., ICCP, 2017. Classification of liptinite – ICCP System 1994. *Int. J. Coal Geol.* 169, 40-61.
- Rao, R.B., Chattopadhyay, P., Banerjee, G.N., 1999. Removal of iron from fly ash for ceramic and refractory applications. *Magnetic and Electrical Separation* 10, 21-27.
- Rubel, A.M., Hower, J.C., Mardon, S.M., Zimmerer, M.J., 2006. Thermal Stability of Mercury Captured by Ash. *Fuel* 85, 2509-2515.
- Rubio, B., Izquierdo, M.T., 2010. Coal fly ash based carbons for SO₂ removal from flue gases. *Waste Manage.* 30, 1341 – 1347.
- Rubio, B., Izquierdo, M.T., Mayoral, M.C., Bona, M.T., Andres, J.M., 2007. Unburnt carbon from coal fly ashes as a precursor of activated carbon for nitric oxide removal. *J. Hazard. Mater.* 143, 561-566.
- Rubio, B., Izquierdo, M.T., Mayoral, M.C., Bona, M.T., Martinez-Tarazona, R.M., 2008. Preparation and characterization of carbon-enriched coal fly ash. *J. Environ. Manage.* 88, 1562-1570.
- Sakulpitakphon, T., Hower, J.C., Trimble, A.S., Schram, W.H., Thomas, G.A., 2000. Mercury capture by fly ash: Study of the combustion of a high-mercury coal at a utility boiler. *Energy Fuels* 14, 727-733.
- Sakulpitakphon, T., Hower, J.C., Trimble, A.S., Thomas, G.A., Schram, W.H., 2003. Arsenic and Mercury Partitioning in Fly Ash at a Kentucky Power Plant. *Energy Fuels* 17, 1028-1033.
- Schneider, A., Chabicoovsky, R., Aumüller, A., 1997. Verfahren und vorrichtung zur bestimmung des kohlegehalts in asche. Austrian Patent No. AT 402571 B; Int.Cl. G01N. 21/47.
- Schneider, A., Chabicoovsky, R., Aumüller, A., 1998. Optical sensor system for the on-line measurement of carbon in fly-ash. *Sens. Actuators A Phys.* 67, 24-31.
- Senior, C.L., Bool III, L.E., Morency, J.R., 2000a. Laboratory study of trace element vaporization from combustion of pulverized coal. *Fuel Process. Technol.* 63, 109-24.
- Senior, C.L., Helble, J.J., Sarofim, A.F., 2000c. Emissions of mercury, trace elements, and fine particles from stationary combustion sources. *Fuel Process. Technol.* 65, 263-88.
- Senior, C.L., Sarofim, A.F., Zeng, T., Helble, J.J., Mamani-Paco, R., 2000b. Gas-phase transformations of mercury in coal-fired power plants. *Fuel Process. Technol.* 63, 197-213.

- Senneca, O., 2008. Burning and physico-chemical characteristics of carbon in ash from a coal fired power plant. *Fuel* 87, 1207–1216.
- Sharonova, O.M., Anshits, N.N., Yumashev, V.V., Anshits, A.G., 2008. Composition and morphology of char particles of fly ashes from industrial burning of high-ash coals with different reactivity. *Fuel* 87, 1989 – 1997.
- Shibaoka, M., 1985. Microscopic investigation of unburnt char in fly ash. *Fuel* 64, 263-269.
- Silva, L.F.O., DaBoit, K., Serra, C., Mardon, S.M., Hower, J.C., 2010. Fullerenes and metallofullerenes in coal-fired stoker fly ash. *Coal Combust. Gasification Prod.* 2, 66-79.
- Silva, L.F.O., Jasper, A., Andrade, M.L., Sampaio, C.H., Dai, S., Li, X., Li, T., Chen, W., Wang, X., Liu, H., Zhao, L., Hopps, S.G., Jewell, R.F., Hower, J.C., 2012. Applied investigation on the interaction of hazardous elements binding on ultrafine and nanoparticles in Chinese anthracite-derived fly ash. *Sci. Total Environ.* 419, 250-264.
- Smith, K., Dixon, T., Taylor, J. 2009. On-line monitoring of carbon in fly ash for boiler control. World of Coal Ash (WOCA) Conference. May 4-7, 2009, Lexington, KY, USA. 10 pages. Available at <http://www.flyash.info/2009/055-smith2009.pdf>, accessed 9 May 2017.
- Soong, Y., Schoffstall, M.R., Gray, M.L., Knoer, J.P., Champagne, K.J., Jones, R.J., Fauth, D.J., 2002. Dry beneficiation of high loss-on-ignition fly ash. *Sep. Purif. Technol.* 26, 177-184.
- Soong, Y., Schoffstall, M.R., Link, T.A., 2001. Triboelectric beneficiation of fly ash. *Fuel* 80, 879-884.
- Stephens, D.L., McFadden, T., Heath, O.D., Mauldin, R.F., 1994. The effect of sonication on the recovery of polycyclic aromatic hydrocarbons from coal stack ash surfaces. *Chemosphere* 28, 1741–1747.
- Straka, P., Náhunková, J., Žaloudková, M., 2014. Analysis of unburned carbon in industrial ashes from biomass combustion by thermogravimetric method using Boudouard reaction. *Thermochimica Acta* 575, 188–194.
- Styszko-Grochowiak, K., Gołaś, J., Jankowski, H., Kozinski, S., 2004. Characterization of the coal fly ash for the purpose of improvement of industrial on-line measurement of unburned carbon content. *Fuel* 83, 1847–1853.
- Suárez-Ruiz, I., Hower, J.C., Thomas, G.A., 2007. Hg and Se Capture and Fly Ash Carbons from Combustion of Complex Pulverized Feed Blends Mainly of Anthracitic Coal Rank in Spanish Power Plants. *Energy Fuels* 21, 59-70.
- Suárez-Ruiz, I., Parra, J.B., 2007. Relationship between textural properties, fly ash carbons, and Hg capture in fly ashes derived from the combustion of anthracitic pulverized feed blends. *Energy Fuels* 21, 1915-23.
- Suárez-Ruiz, I., Valentim, B. (Eds.), 2015. Atlas of Fly Ash Occurrences: Identification and Petrographic Classification of Fly Ash Components Working Group, Commission III – ICCP. ISBN: 978-84-608-1416-0. 203 pp. (Available at <http://www.iccop.org/documents/atlas-of-fly-ash-occurrences.pdf>, accessed 13 March 2017).
- Suárez-Ruiz, I., Valentim, B., Borrego, A.G., Bouzinos, A., Flores, D., Kalaitzidis, S., Malinconico, M.L., Marques, M., Misz-Kennan, M., Montes, J.R., Predeanu, G., Siavalas, G., Wagner, N., 2008. Towards an ICCP classification of Fly Ash components. Preliminary results. *The Society For Organic Petrology Newsletter* 25 (3), 10-13. ISSN 0743-3816. Available at http://www.tsop.org/newsletters/25_3.pdf, accessed 15 May 2010).

- Sun, P., Taerakul, P., Weavers, L.K., Walker, H.W., 2005. Distribution of polycyclic aromatic hydrocarbons in lime spray dryer ash. *Energy Fuels* 19, 1911–1918.
- Sung, H., Yoo, K., Lee, S.-H., 2016. The removal of unburned carbon from fly ash by kerosene extraction. *Geosyst. Eng.* 19, 96-99.
- Sýkorová, I., Pickel, W., Christanis, K., Wolf, M., Taylor, G.H., Flores, D., 2005. Classification of huminite—ICCP System 1994. *Int. J. Coal Geol.* 62, 85-106.
- Trerice, D.N., 1987. Method and apparatus for measurement of carbon content in fly ash. US Patent No. 4,705,409.
- Ucurum, M., Toraman, O.Y., Depci, T., 2011. A study on characterization and use of flotation to separate unburned carbon in bottom ash from Cayiran power plant. *Energ. Source. Part A* 33, 562–574.
- van Krevelen, D.W., 1993. *Coal: Typology – Physics – Chemistry – Constitution* (3rd edition). Amsterdam, Elsevier, 979 p.
- Vassilev, S.V., Eskenazy, G.M., Vassileva, C.G., 2000. Contents, modes of occurrence and behaviour of chlorine and bromine in combustion wastes from coal-fired power station. *Fuel* 79, 923–937.
- Vassilev, S.V., Menendez, R., Borrego, A.G., Diaz-Somoano, M., Rosa Martinez-Tarazona, M., 2004. Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 3. Characterization of magnetic and char concentrates. *Fuel* 83, 1563–1583.
- Vleeskens, J.M., Menendez, R.M., Roos, C.M., Thomas, C.G., 1993. Combustion in the burnout stage: the fate of inertinite. *Fuel Process. Technol.* 36, 91-99.
- Waddle, S.K., 2012. Standard specifications for road and bridge construction. Commonwealth of Kentucky Transportation Cabinet, Frankfort, Kentucky, various pagination: 668 pages total. (Available at <http://transportation.ky.gov/Construction/Standard%20amd%20Supplemental%20Specifications/Complete%20KYTC%20Standard%20Specifications-2012.pdf>, accessed 10 May 2017).
- Wagner, N.J., Matjie, R.H., Slaghuis, J.H., van Heerden J.H.P., 2008. Characterization of unburned carbon present in coarse gasification ash. *Fuel* 87, 683 - 691.
- Waller, D.J., Brown, R.C., 1996. Photoacoustic response of unburnt carbon in fly ash to infrared radiation. *Fuel* 75, 1568-1574.
- Wagner, N.J., Tlotleng, M.T., 2012. Distribution of selected trace elements in density fractionated Waterberg coals from South Africa. *Int. J. Coal Geol.* 94, 225 - 237.
- Wang, R., Zhang, J., Liu, J., Liu, G., 2013. Levels and patterns of polycyclic aromatic hydrocarbons in coal-fired power plant bottom ash and fly ash from Huainan, China. *Arch. Environ. Contam. Toxicol.* 65, 193 - 202.
- Weber, J.M., 1999. Unburnt carbon content determination in fly ash using microwave transmission measurement. *Bulk Solids Handling* 19, 394 - 395.
- Wilcox, J., Wang, B., Rupp, E., Taggart, R., Hsu-Kim, H., Oliveira, M.L.S., Cutruneo, C.M.N.L., Taffarel, S., Silva, L.F.O., Hopps, S.D., Thomas, G.A., Hower, J.C., 2015. Observations and assessment of fly ashes from high-sulfur bituminous coals and blends of high-sulfur bituminous and subbituminous coals: Environmental processes recorded at the macro and nanometer scale. *Energy Fuels* 29, 7168-7177.
- Wu, F., Wu, P., Tseng, R., Juang, R., 2010. Preparation of activated carbons from unburnt coal in bottom ash with KOH activation for liquid-phase adsorption. *J. Environ. Manage.* 91, 1097-1102.

- Xue, X., Wang, Y., 2013. Particle size distribution as a nonindependent variable affecting pulverized-coal burnout in coal-fired power-plant boilers energy. *Energy Fuels* 27, 4930–4934.
- Yamik, A., Dogruoz, A., 2008. Recovery of unburned carbon by conventional flotation of bottom ashes from Tuncbilek Thermal power plant. *J. S. Afr. I. Min. Metall.* 108, 171–177.
- Yan, W., Li, J., 2009. Modeling of the unburned carbon in fly ash. *Energy Power Eng.* 2009, 90-93.
- Yan, W.-P., Li, J.-H., Ye, X.-M., Gao, Z.-Y., 2004. Apparatus for on-line monitoring carbon content of coal-fired boiler and stove. China Patent, No. CN2655241. (in Chinese).
- Yang, F., Hlavacek, V., 1999. Recycling of carbon-enriched coal fly ash. *Powder Technol.* 104, 190 – 195.
- Yang, Y.B., Sharifi, V.N., Swithenbank, J., Ma, L., Darvell, L.I., 2008. Combustion of a single particle of biomass. *Energy Fuels* 22, 306–316.
- Yao, S.C., Lu, J.D., Zheng, J.P., Dong, M.R., 2012. Analyzing unburned carbon in fly ash using laser-induced breakdown spectroscopy with multivariate calibration method. *J. Anal. At. Spectrom.* 27, 473–478.
- Yeboah, N.N.N., Shearer, Ch.R., Burns, S.E., Kurtis, K.E., 2014. Characterization of biomass and high carbon content coal ash for productive reuse applications. *Fuel* 116, 438 – 447.
- Zhang, L., Ma, W., Dong, L., Yan, X., Hu, Z., Li, Z., Zhang, Y., Wang, L., Yin, W., Jia, S., 2011. Development of an apparatus for on-line analysis of unburned carbon in fly ash using laser-induced breakdown spectroscopy (LIBS). *Appl. Spectrosc.* 65, 790–796.

Table 1. Genetic and textural classifications of fly ash constituents modified after Hower et al. (2005), as based on Hower et al. (1995), Hower and Mastalerz (2001) and the char texture classifications of Bailey et al. (1990), Lester et al. (1996), and Alvarez et al. (1997).

Fly ash constituent - Genetic classification	Figure number
isotropic carbon/char (from vitrinite or inertinite)	3A & B, 4 all, 7 all, 8C
anisotropic carbon/char (from vitrinite or inertinite)	8 all, 11 all
inertinite	1 all, 2A & B, 4 B-D, 5 all, 8 all, 11D
glass	7B
mullite	not illustrated
spinel	not illustrated
quartz	not illustrated
sulfide	2B
sulfate	not illustrated
uncombusted coal	6 all, 10 all
non-coal organics	not illustrated
other minerals and non-coal inorganics	not illustrated
Textural classification of isotropic and anisotropic carbon/char and inertinite	
Tenuisphere	8B (upper right)
Crassisphere	3A (?)
Tenuinetwork	8B & C
Crassinetwork	3A & B, 7B
Mixed porous	4 B-D, 8D, 10D
Mixed dense	4A, 7A, 8 A & D, 11 A-C
Inertoid	1 all, 2B, 5A, 11D
Fusinoid	2A, 5 B-D, 6B, 8 all
Solid	7A
Mineroid	7B (glass within carbon, with caveat that glass is not a mineral)

Figure Captions

Figure 1. SEM back-scattered electron images of unburned carbon in FA with intact inertinite structures (Source: Wulantuga, China).

Figure 2. Unburned carbon derived from inertinite in low-rank coals (optical microscope photos under reflected light and oil immersion; Source: Bulgaria). (A), well-preserved fusinite; Image MW3 04 (Image plus number in all the figures are a CAER bank). (B), relatively massive inertinite with sulfides; Image MW2 01.

Figure 3. Low-rank isotropic coke/char (optical microscope photos under reflected light and oil immersion); Source: Bulgaria. (A), massive to porous isotropic coke/char; Image BD 8III 18. (B), porous isotropic coke/char; Image Rep 61 05.

Figure 4. Low-rank char (optical microscope photos under reflected light and oil immersion). (A), massive to porous char; Source: Cretaceous subbituminous coal-derived FA, San Juan Basin, New Mexico; Image 93922 04. (B), massive to porous char with inertinite (center); Image BD 8I 13. (C), char with inertinite (top); Image MW2 12. (D), char with inertinite (lower right); Image MW2 13. (B)-(D), Sources: Bulgaria.

Figure 5. Bituminous-derived inertinite (optical microscope photos under reflected light and oil immersion). (A), massive inertinite; Source: Illinois Basin bituminous coal-derived FA; Image 93670 03. (B), bogen-structure inertinite; Source: Central Appalachian bituminous coal-derived FA; Image 93685 08.

Figure 6. Bituminous-derived coal fragments (optical microscope photos under reflected light and oil immersion). (A), central Appalachian bituminous coal-derived FA; Key: ox – oxidation rim, lip – lipinitite, v – vitrinite; Sample MA 45593/+100 mesh; Image 351 33; Scale ca. 330 μm on long axis. (B), inertinite from Central Appalachian bituminous coal-derived FA; Sample PR 2-20; Image 385 6; Scale ca. 330 μm on long axis.

Figure 7. Bituminous-derived isotropic coke (optical microscope photos under reflected light and oil immersion). (A), source: Illinois Basin bituminous coal-derived FA; Key: i – inertinite, c – coke; Image 93705 07. (B), isotropic coke surrounding glass; Source: Central Appalachian bituminous coal-derived FA; Image 94016 05.

Figure 8. Bituminous-derived anisotropic coke (optical microscope photos under reflected light and oil immersion). Key for all: i – inertinite. Source for all: Central Appalachian bituminous coal-derived FA. (A), massive anisotropic coke with inertinite; Sample PR 2-13; Image 387 7; Scale ca. 330 μm on long axis. (B), inertinite with anisotropic coke; Anisotropic coke

tenuisphere at upper right; Image 93701 08. (C), anisotropic and isotropic coke with inertinite; Image 93701 09. (D), massive to porous anisotropic coke with inertinite; Image 93701 15.

Figure 9. HRTEM images for fly ash (all images from Hower et al., 2008; Source: Central Appalachian bituminous coal-derived FA; Sample 92804). (A), carbon surrounding spherical Al-Si glass grain; Scale = 50 nm. (B), magnified view of part of (A); Scale = 20 nm. (C), soot-like carbon with fullerenes (arrows); Scale = 10 nm. (D), fullerene-like nanocarbon with double shells; Scale = 5 nm.

Figure 10. Anthracite-derived coal fragments (optical microscope photos under reflected light and oil immersion). (A), relatively unaltered coal fragment in stoker-fired ash; Image 94001 03. (B), signs of heating along edges of coal fragment in stoker-fired ash; Image 94007 05. (C), subtle indications of devolatilization pores in coal fragment; Image Yunnan 2 02. (D), subtle indications of devolatilization pores in coal fragment; Image Yunnan 4 06. (A) and (B), Sources: Source: Pennsylvanian, Pennsylvania. (C) and (D), Source: Permian, China; from Silva et al. (2012).

Figure 11. Anthracite-derived anisotropic carbon (optical microscope photos under reflected light and oil immersion). (A), Pennsylvanian anthracite-derived circulating fluidized bed ash; Source: Pennsylvania Anthracite Fields; Image 93976 05. (B), anisotropic carbon; Image Yunnan 1 09. (C), anisotropic carbon; Image Yunnan 1 06. (D), inertinite- (i) and vitrinite-derived (v) carbons; Image Yunnan 1 08. (B)- (D), Source: Permian, China, from Silva et al. (2012).

Figure 12. SEM secondary electron images of typical UC fly ash particles, which show its porous structure. (a) and (b), UC fly ash particles derived from lignite, Maritza 3 TPP, Bulgaria; (c) and (d), UC fly ash particles derived from bituminous coal, Varna TPP, Bulgaria. (a) and (c), general view of UC fly ash particles, (b) and (d), details of the surface area.

Figure 13. Mercury versus ESP and mechanical collection unburned carbon in FA for March and November 2001 samplings of the same 200-MW pulverized coal unit. Note that the two mechanical collection rows are plotted below the break in y axis (Hg). Also, note that the scale of the y axis changes at the break. Data from Mardon and Hower (2004) and Hower et al. (2006).

Figure 14. Comparison of Hg capture relative to the amount of unburned carbon (Hg/C) versus ESP row for two Kentucky power plants (H, I) and the Republica (Rep) power plant, Bulgaria. Flue gas temperature decreases from the 1st through the 3rd and 4th ESP rows (after Kostova et al., 2011).

Figure 1

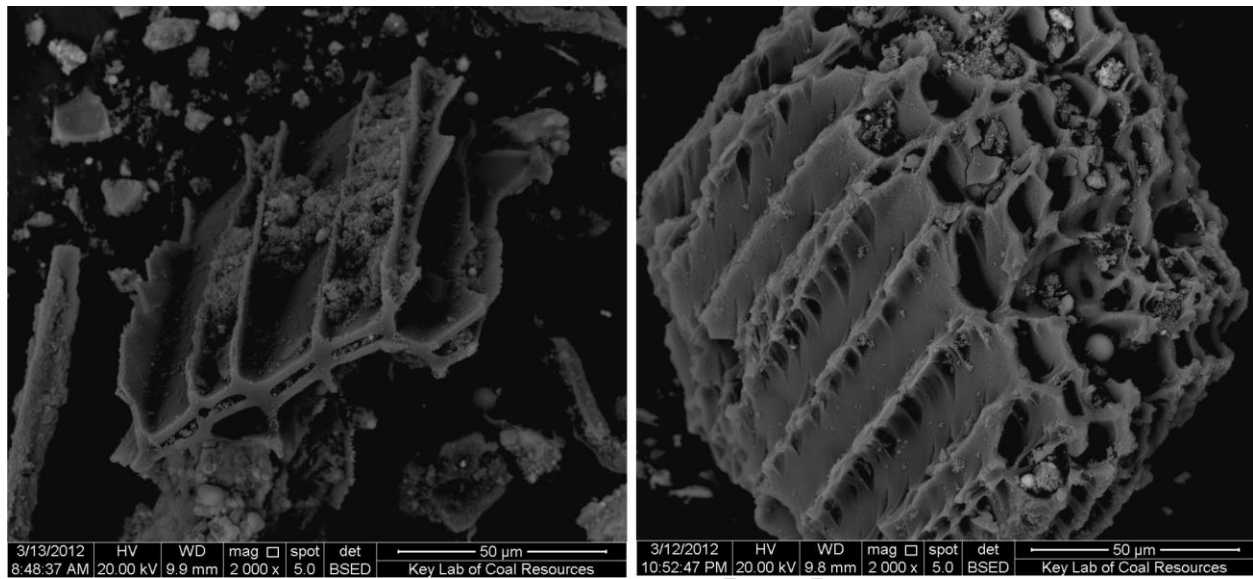
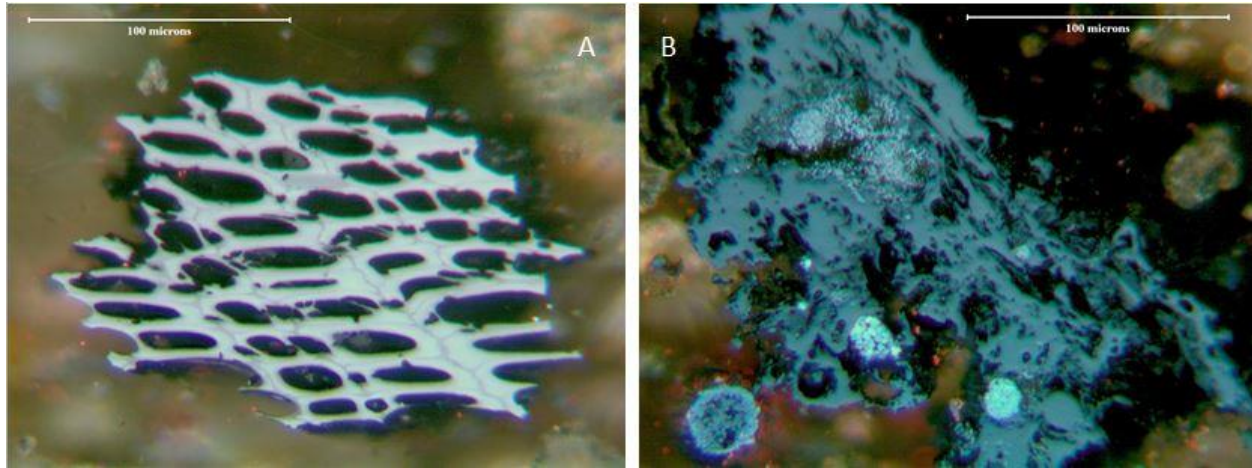
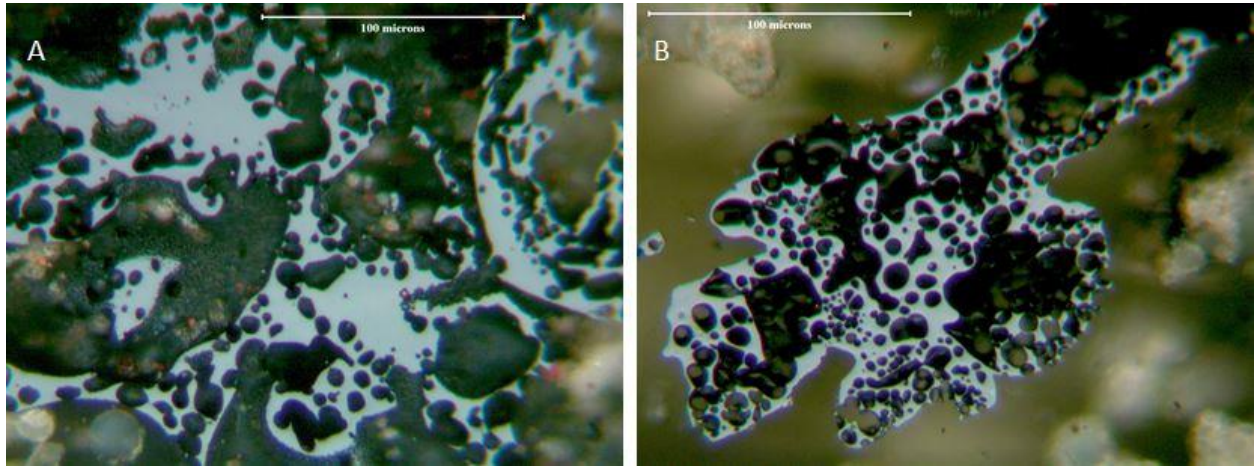


Figure 2



ACCEPTED MANUSCRIPT

Figure 3



ACCEPTED MANUSCRIPT

Figure 4

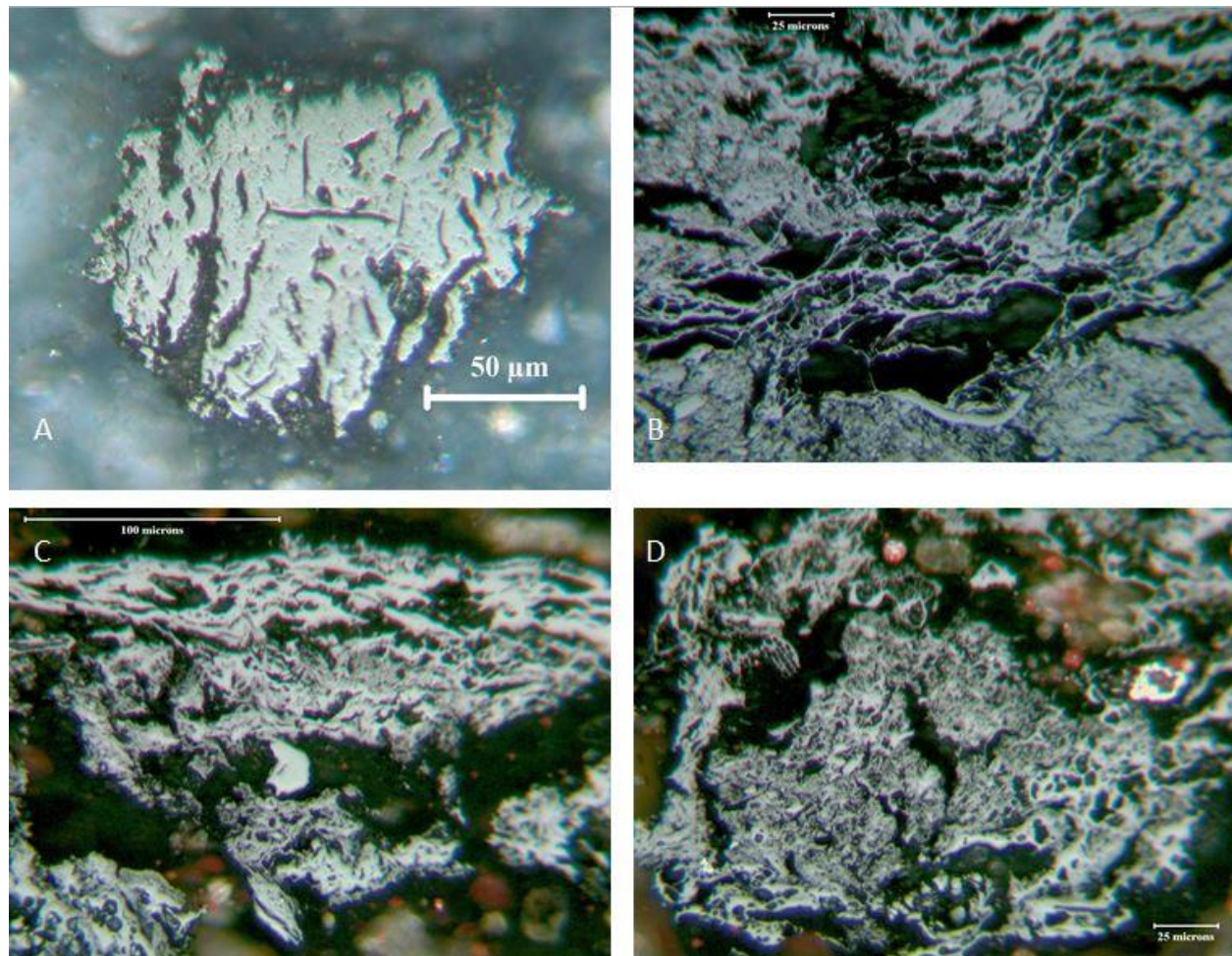


Figure 5

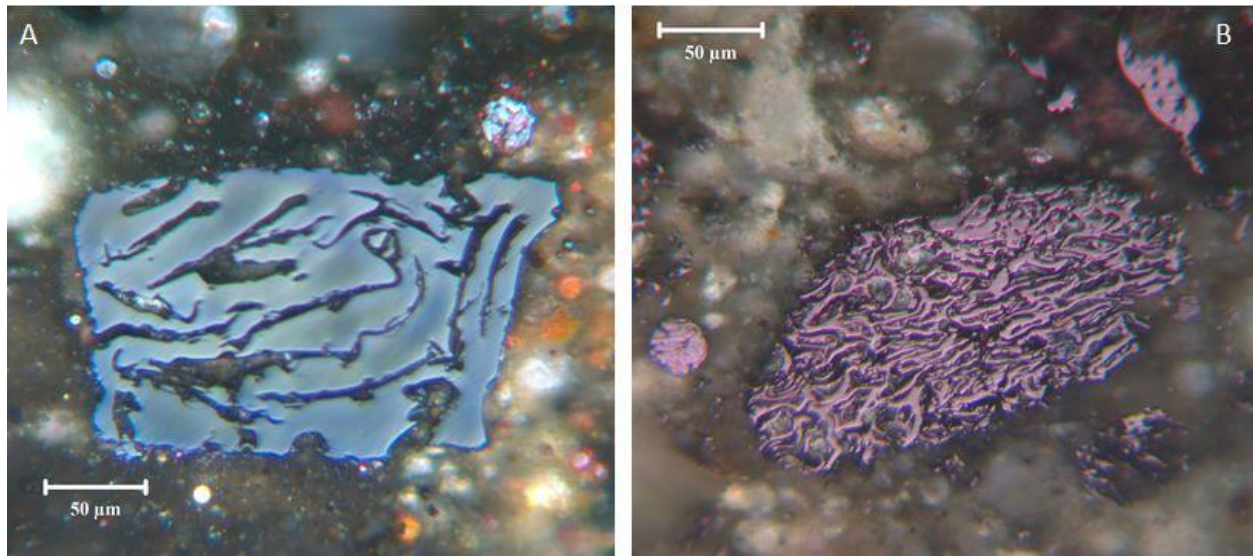


Figure 6

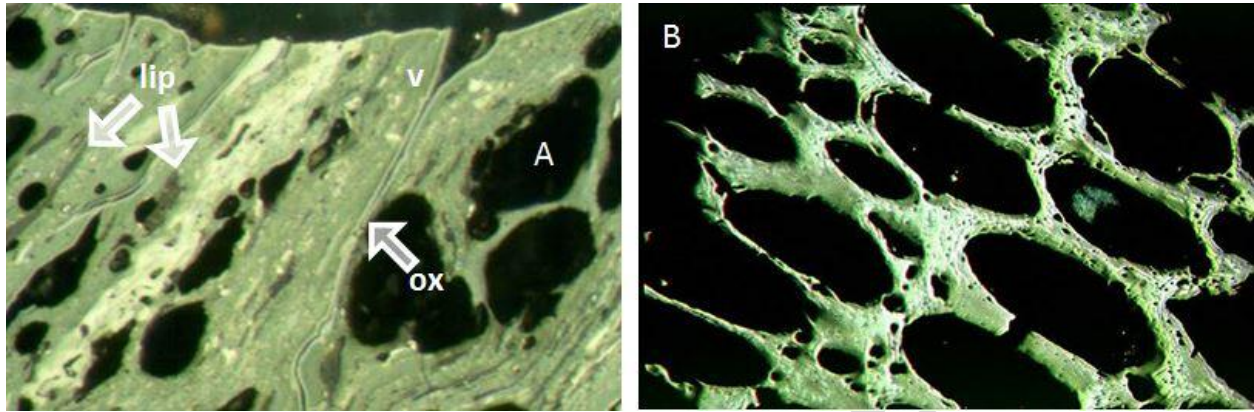


Figure 7

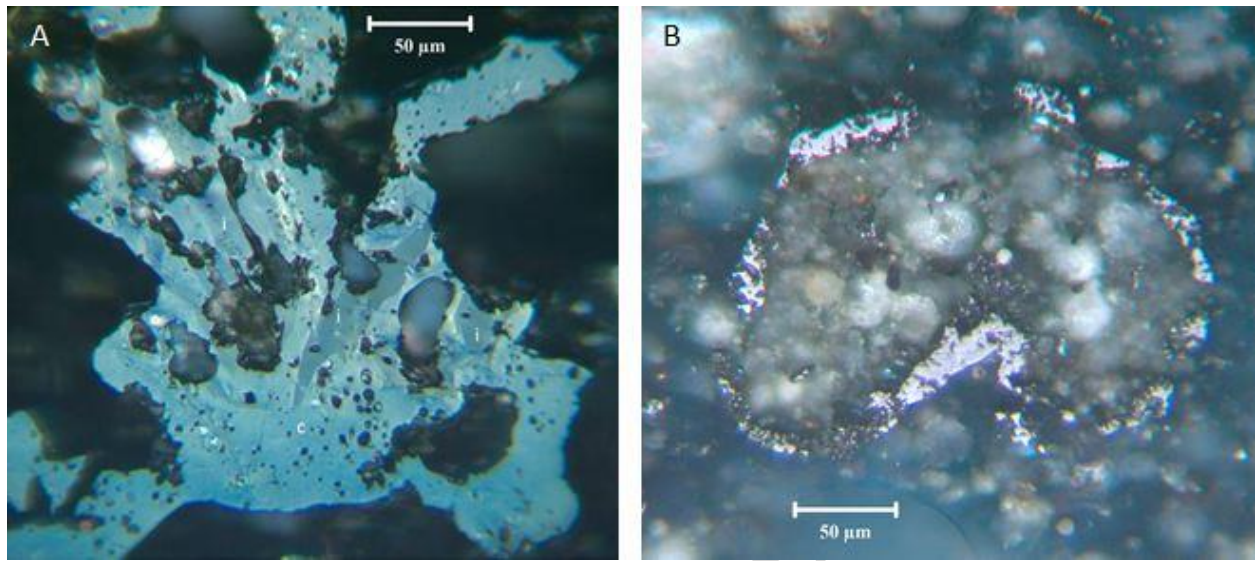
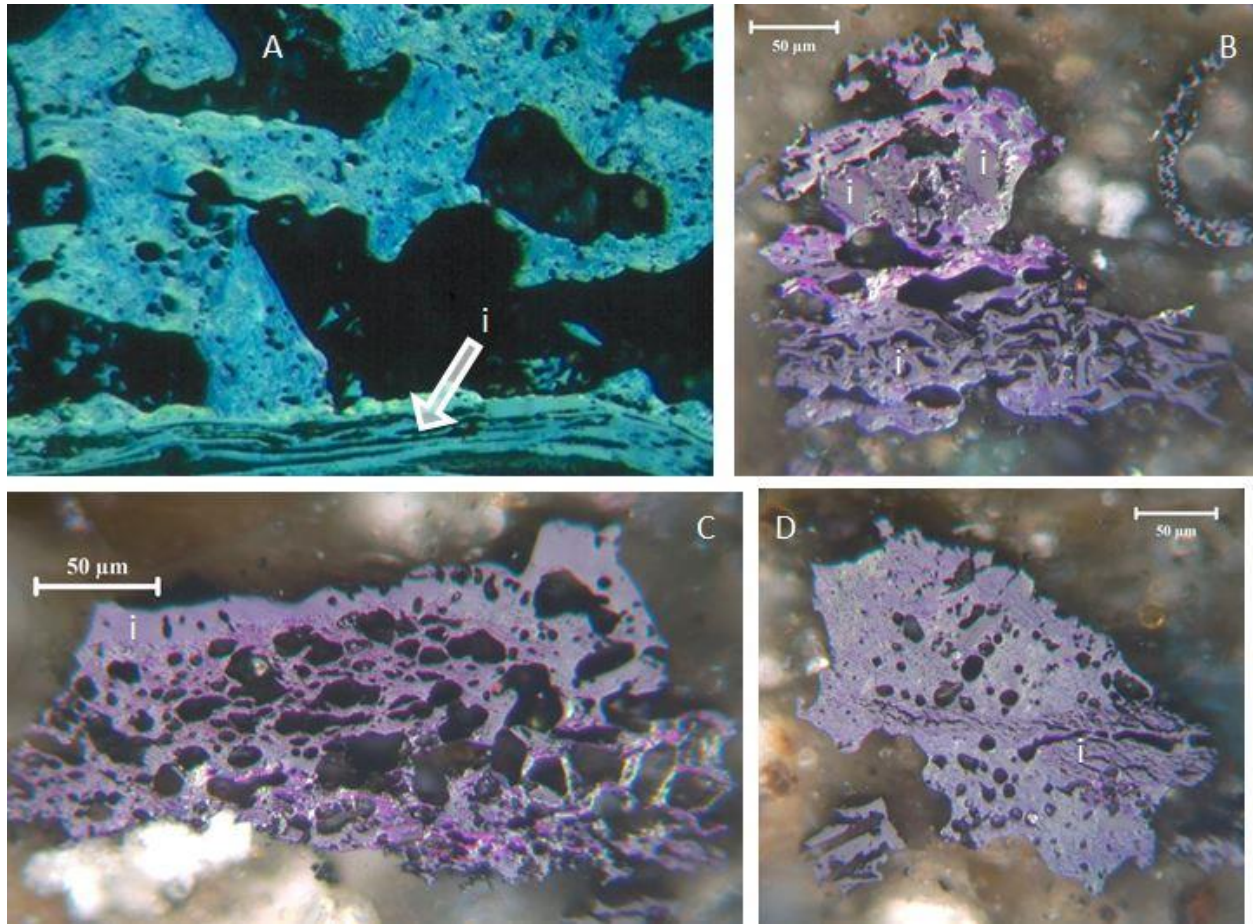


Figure 8



ACCEPTED

Figure 9

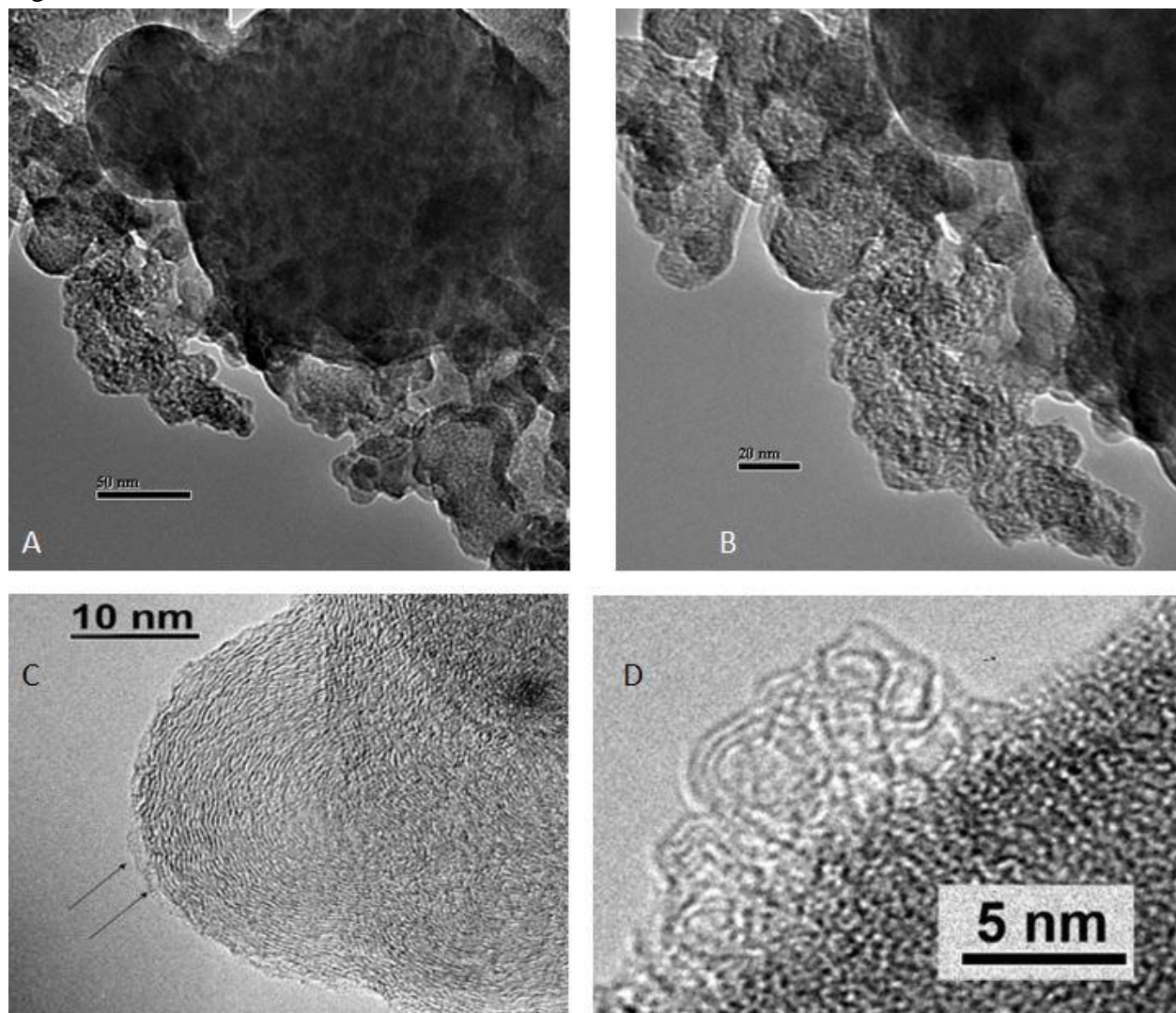


Figure 10

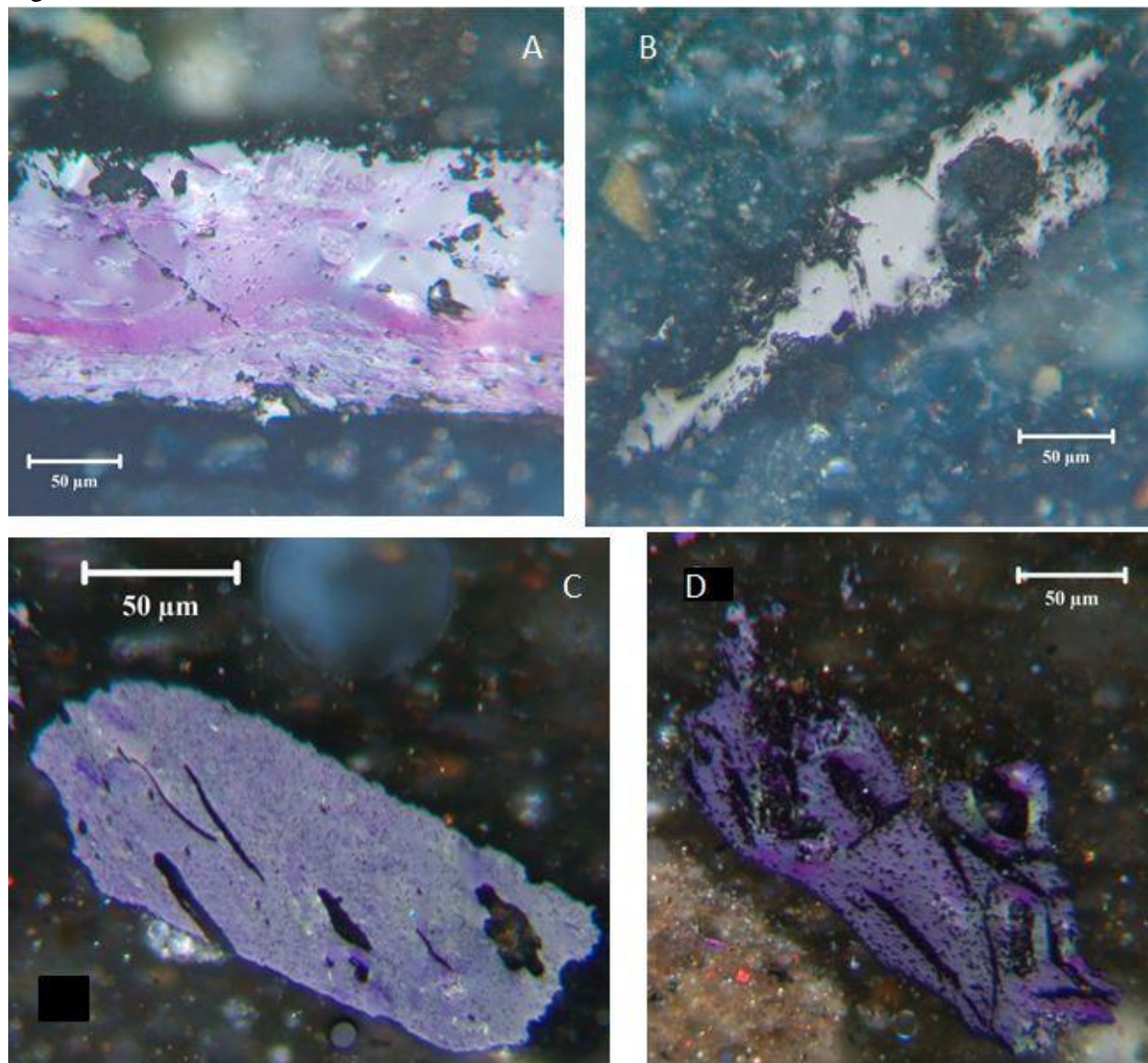


Figure 11

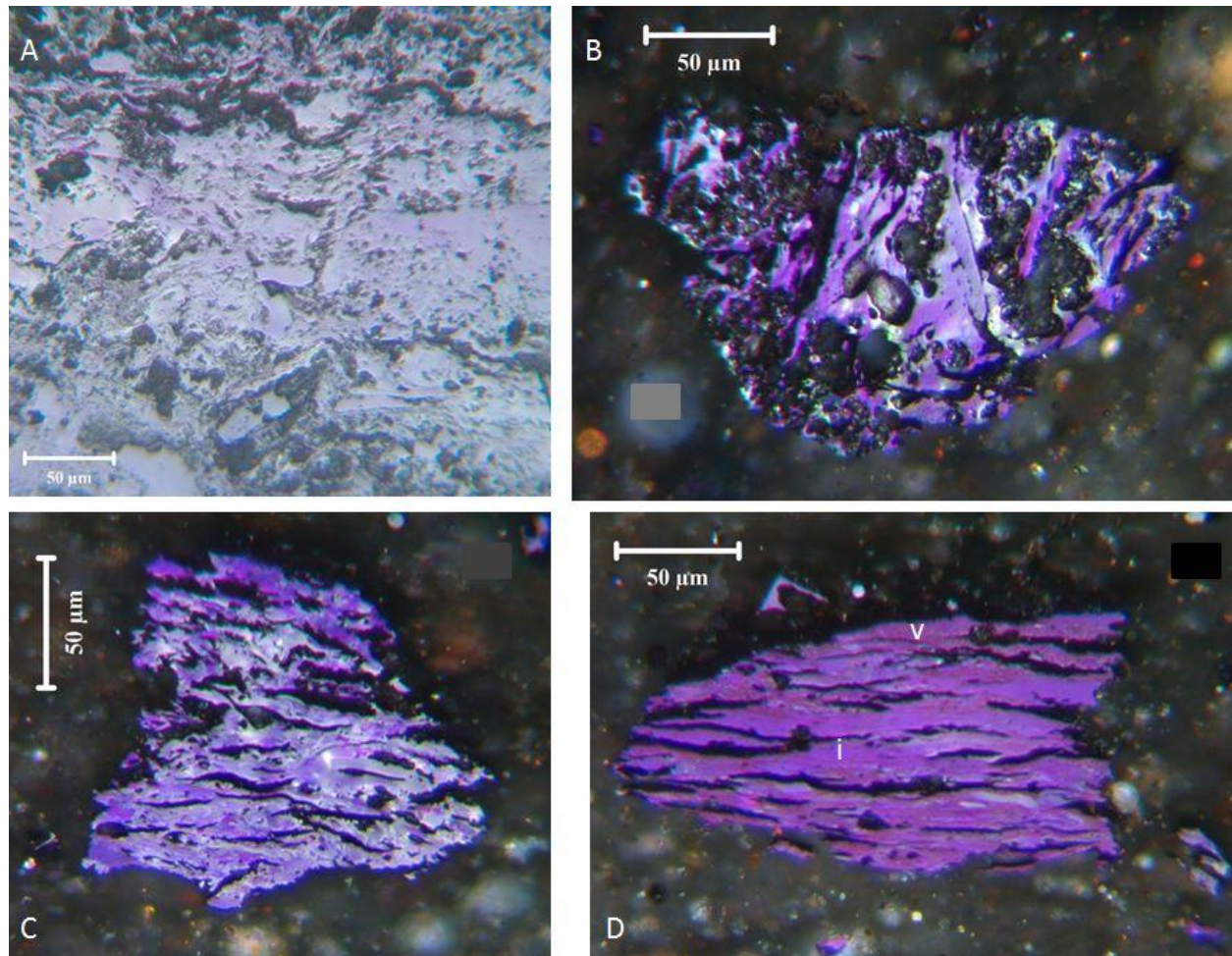


Figure 12

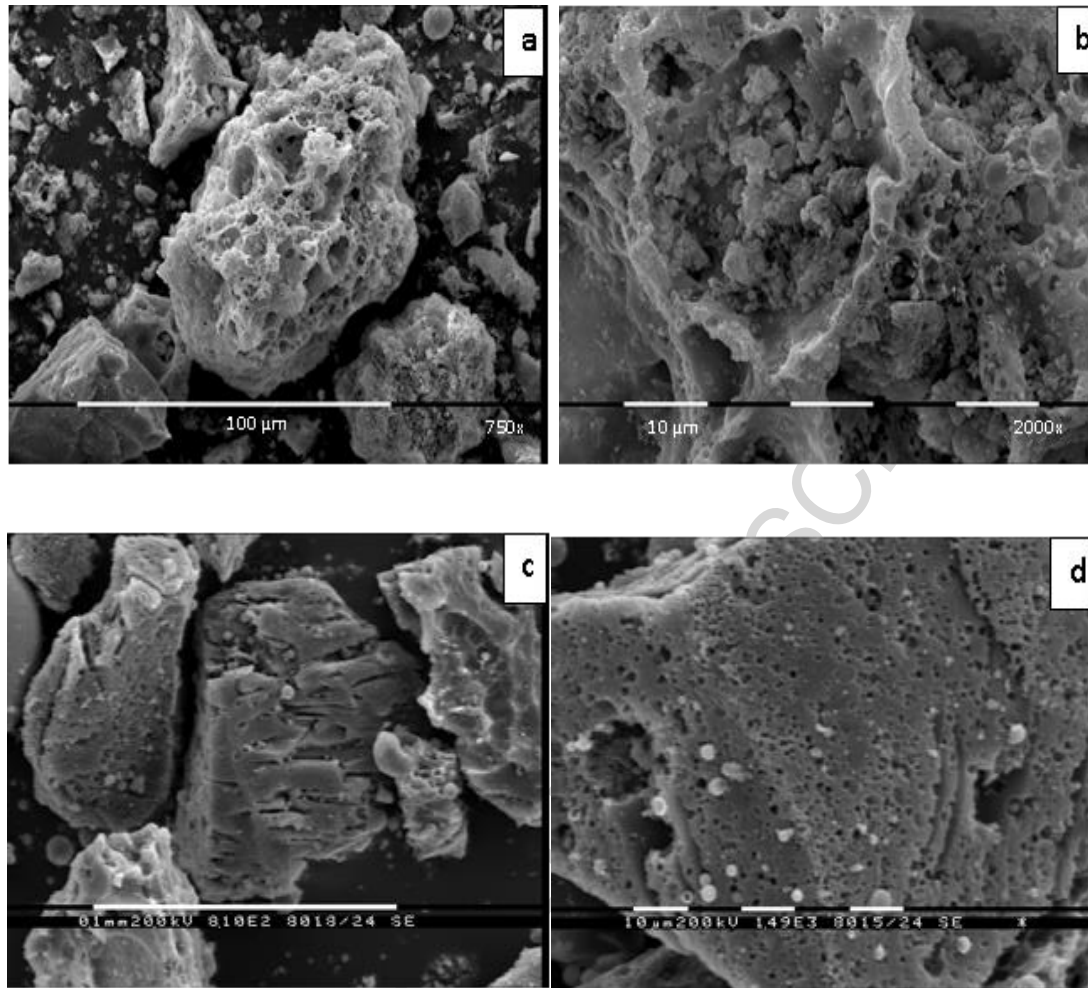


Figure 13

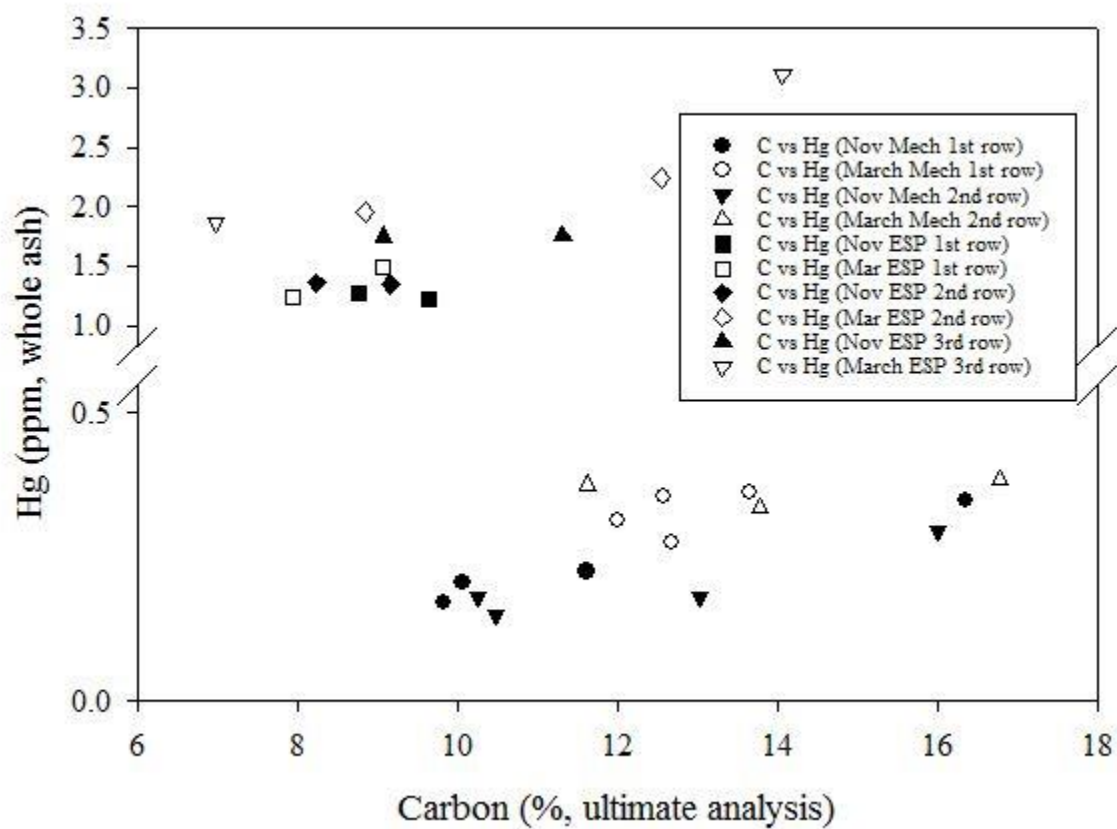
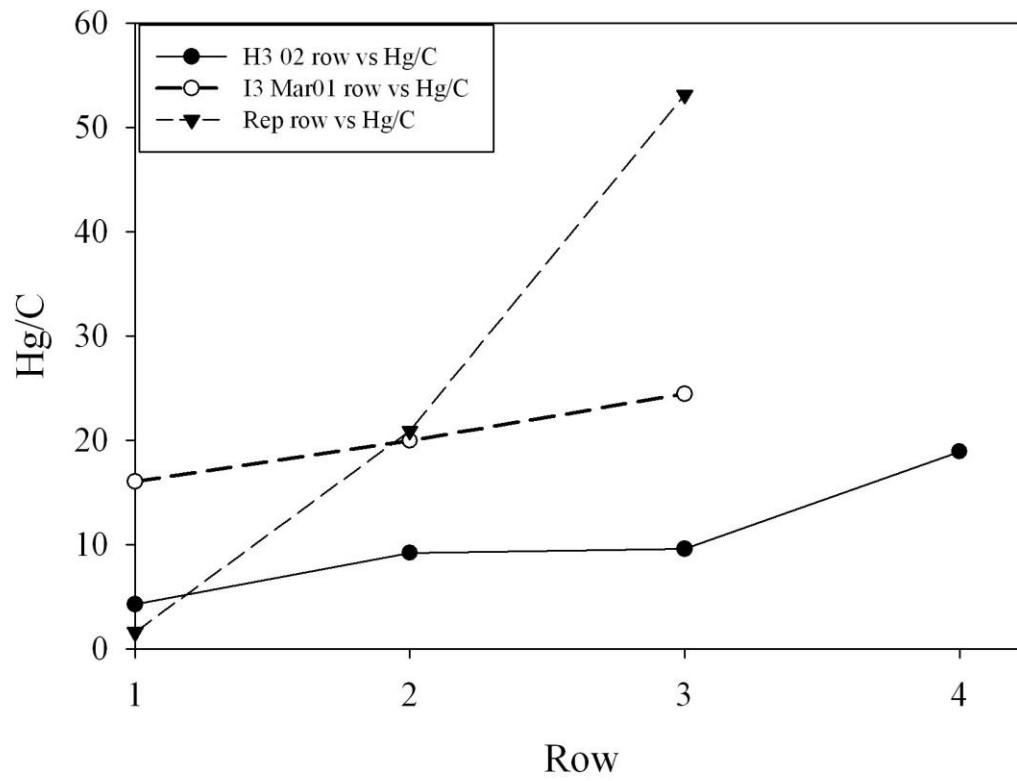


Figure 14



ACCEPTED

Highlights

- Unburned carbon (UC) in fly ash is comprehensively reviewed.
- The characteristics of UC are dependent on coal rank, the size of the feed coal and the combustion conditions.
- UC nomenclature/classification is discussed in term of petrology.
- UC can be used as an absorptive agent for various organic and inorganic matter.
- The separation of UC from FA can be done mainly by size classification, electrostatic separation, and froth flotation.