Coal-derived unburned carbons in fly ash: A review

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

Published in:
International Journal of Coal Geology

DOI:
10.1016/j.coal.2017.05.007

Publication date:
2017

Document Version
Peer reviewed version

Link to publication in Heriot-Watt University Research Portal

Citation for published version (APA):
Accepted Manuscript

Coal-derived unburned carbons in fly ash: A review


PII: S0166-5162(17)30210-0
DOI: doi: 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

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

\textsuperscript{a} University of Kentucky Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511 USA

\textsuperscript{b} School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney, NSW 2052, Australia

\textsuperscript{c} Sofia University “St. Kliment Ohridski”, 15, Tzar Osvoboditel Blvd., 1000 Sofia, Bulgaria

\textsuperscript{d} School of Engineering & Physical Sciences; Mechanical, Process & Energy Engineering, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

\textsuperscript{e} State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology, China

\textsuperscript{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. Rs, huminitie/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 (Trerice, 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 ±1%, and otherwise, the use of neural network analysis can reduce this to ±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 (~0.1g) 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; Bartoňovr, 2015). In the 1990s, larger US power plants were converted to combustion under low-NOx 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 (Kobylecki, 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
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-m thick; crassi-) and thin-walled (<5-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 (Hover el at., 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 Hover, 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 → tar → 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 \textit{in situ}.

5.2. \textit{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 SO$_2$ 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. 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 C\textsubscript{60}, C\textsubscript{70}, and C\textsubscript{80} fullerenes as the major species, with other species from C\textsubscript{56} to C\textsubscript{78} corresponding to the loss of C\textsubscript{2} 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

\footnote{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, 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\textsubscript{2} gas as an adsorptive at the boiling point temperature of liquid N\textsubscript{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\textsubscript{2} is often used as the adsorptive gas, at a temperature of 273 K. Before the analysis with N\textsubscript{2} or with CO\textsubscript{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\textsuperscript{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\textsuperscript{2}/g to 400 m\textsuperscript{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\textsuperscript{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 1$^{st}$ and 3$^{rd}$ 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,
Experiments using a commercial DDBS (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., Kūlaots 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 devolatization 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 SO$_2$ (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., Cabielles 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 (~1.8 g/cm³) and other ash particles (~2.5 g/cm³), 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 (Keppler, 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 Keppler (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 metasilicate (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 through 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


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).

<table>
<thead>
<tr>
<th>Fly ash constituent - Genetic classification</th>
<th>Figure number</th>
</tr>
</thead>
<tbody>
<tr>
<td>isotropic carbon/char (from vitrinite or inertinite)</td>
<td>3A &amp; B, 4 all, 7 all, 8C</td>
</tr>
<tr>
<td>anisotropic carbon/char (from vitrinite or inertinite)</td>
<td>8 all, 11 all</td>
</tr>
<tr>
<td>inertinite</td>
<td>1 all, 2A &amp; B, 4 B-D, 5 all, 8 all, 11D</td>
</tr>
<tr>
<td>glass</td>
<td>7B</td>
</tr>
<tr>
<td>mullite</td>
<td>not illustrated</td>
</tr>
<tr>
<td>spinel</td>
<td>not illustrated</td>
</tr>
<tr>
<td>quartz</td>
<td>not illustrated</td>
</tr>
<tr>
<td>sulfide</td>
<td>2B</td>
</tr>
<tr>
<td>sulfate</td>
<td>not illustrated</td>
</tr>
<tr>
<td>uncombusted coal</td>
<td>6 all, 10 all</td>
</tr>
<tr>
<td>non-coal organics</td>
<td>not illustrated</td>
</tr>
<tr>
<td>other minerals and non-coal inorganics</td>
<td>not illustrated</td>
</tr>
</tbody>
</table>

Textural classification of isotropic and anisotropic carbon/char and inertinite

<table>
<thead>
<tr>
<th>Textural classification of isotropic and anisotropic carbon/char and inertinite</th>
<th>Figure number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenuisphere</td>
<td>8B (upper right)</td>
</tr>
<tr>
<td>Crassisphere</td>
<td>3A (?)</td>
</tr>
<tr>
<td>Tenuinetwork</td>
<td>8B &amp; C</td>
</tr>
<tr>
<td>Crassinetwork</td>
<td>3A &amp; B, 7B</td>
</tr>
<tr>
<td>Mixed porous</td>
<td>4 B-D, 8D, 10D</td>
</tr>
<tr>
<td>Mixed dense</td>
<td>4A, 7A, 8 A &amp; D, 11 A-C</td>
</tr>
<tr>
<td>Inertoid</td>
<td>1 all, 2B, 5A, 11D</td>
</tr>
<tr>
<td>Fusinoid</td>
<td>2A, 5 B-D, 6B, 8 all</td>
</tr>
<tr>
<td>Solid</td>
<td>7A</td>
</tr>
<tr>
<td>Mineroid</td>
<td>7B (glass within carbon, with caveat that glass is not a mineral)</td>
</tr>
</tbody>
</table>
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 coaldervied 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 – liptinite, 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
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 2
Figure 3
Figure 4
Figure 5
Figure 7
Figure 8
Figure 11
Figure 13

The figure shows a scatter plot with the x-axis representing Carbon (% ultimate analysis) and the y-axis representing Hg (ppm, whole ash). The data points are differentiated by various symbols and legend entries indicating different comparisons such as 'C vs Hg (Nov Mech 1st row)', 'C vs Hg (March Mech 1st row)', etc.
Figure 14
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.