



**coal combustion and
gasification products**

Coal Combustion and Gasification Products is an international, peer-reviewed on-line journal that provides free access to full-text papers, research communications and supplementary data. Submission details and contact information are available at the web site.

© 2016 The University of Kentucky Center for Applied Energy Research and the American Coal Ash Association

Web: www.coalcgp-journal.org

ISSN# 1946-0198

Volume# 8 (2016)

Editor-in-chief: Dr. Jim Hower, University of Kentucky Center for Applied Energy Research

CCGP Journal is collaboratively published by the University of Kentucky Center for Applied Energy Research (UK CAER) and the American Coal Ash Association (ACAA). All rights reserved.



The electronic PDF version of this paper is the official archival record for the CCGP journal.

The PDF version of the paper may be printed, photocopied, and/or archived for educational, personal, and/or non-commercial use. Any attempt to circumvent the PDF security is prohibited. Written prior consent must be obtained to use any portion of the paper's content in other publications, databases, websites, online archives, or similar uses.

Suggested Citation format for this article:

Hower, James C., Dai, Shifeng, Eskenazy, Greta, 2016, Distribution of Uranium and Other Radionuclides in Coal and Coal Combustion Products, with Discussion of Occurrences of Combustion Products in Kentucky Power Plants. *Coal Combustion and Gasification Products* 8, 44-53, doi: 10.4177/CCGP-D-16-00002.1

Distribution of Uranium and Other Radionuclides in Coal and Coal Combustion Products, with Discussion of Occurrences of Combustion Products in Kentucky Power Plants

James C. Hower^{1,*}, Shifeng Dai², Greta Eskenazy³

¹ University of Kentucky Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, USA

² State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology (Beijing), Beijing 100083, China

³ Sofia University St. Kliment Ohridski, Department of Geology, Sofia, Bulgaria

ABSTRACT

Uranium and thorium are part of the mineral assemblages within coals. Uranium can also occur in organic associations, particularly in low-rank coals. While the average U concentration in coals is 2.9 ppm for low-rank coals and 1.9 ppm for bituminous and higher rank coals, high concentrations are known from certain low-rank and thin coals and from coals in areas associated with U mineralization. No high-U coals are mined for power production in the United States. Uranium and Th in coal combustion products are found in amounts more or less in proportion to their concentrations in the feed coal. Not being volatile elements, both U and Th are concentrated in the fly ash and bottom ash with, in most cases, little indication of partitioning relative to particle size or point of ash collection.

© 2016 The University of Kentucky Center for Applied Energy Research and the American Coal Ash Association
All rights reserved.

ARTICLE INFO

Article history: Received 7 April 2016; Received in revised form 3 June 2016; Accepted 4 June 2016

Keywords: radionuclides; organic association; coal; fly ash

1. Introduction

It is unwise to categorize elements as toxic per se because toxicity depends on several factors, including concentration, chemical structure, and availability.

Swaine, 1990, p. 78

Dal Swaine devoted a long career to the study of trace elements in coal and was not one to dismiss the hazards associated with any single element or suite of elements lightly. Rather, as summarized in the above quote, he emphasized examination of the element within the total context in which it is found (Swaine, 1990). Certain elements in coal have attracted attention in proportion to potential local and regional environmental and health impacts; sulfur and mercury are good examples, and in some cases, As and F,

particularly in China (Dai et al., 2012b). With complications from radioactivity and varying environmental paths of daughter radionuclides, the concentrations of U, Th, and other radionuclides in coal and coal combustion products (CCPs) have also gotten attention (Lauer et al., 2015). On the other hand, when U concentrates in coal to the level comparable to conventional ore deposits (such as sandstone-hosted roll-type U deposits), the coal has potential economic significance as U raw sources (Seredin and Finkelman, 2008; Seredin et al., 2013; Dai et al., 2015b,d).

In this contribution, we review the occurrence of U and Th in coal and CCPs, specifically fly ash and bottom ash, with emphasis on Kentucky and other U.S. examples. The intent is not to produce a toxicology study but, rather, to provide a framework for understanding the factors involved in the geologic concentration of these elements and the nature of their redistribution in coal combustion and ash collection.

* Corresponding author. Tel.: 1-859-257-0261. E-mail: james.hower@uky.edu

2. Notes on Reporting Concentrations

For both coals and CCPs, concentrations of radionuclides are reported both as the direct concentration (ppm or mg/kg) of the element, with all isotopes considered to be part of the whole, and as the activity (in becquerels [one disintegration per second] per kilogram [Bq/kg]; 1 curie = 37×10^9 Bq = 37 GBq) of isotopes and daughter products. Based on the fly ash results presented by Lauer et al. (2015), the correlation between concentration of U in fly ash, as reported in parts per million or micrograms per gram, against the ^{238}U activity is plotted on Figure 1. The linear regression r^2 is 0.90, with much of the scatter being attributable to both the different attributes measured and to the noise in the data. When comparing trace element data, caution must be used in assessing whether coal and CCP concentrations are being reported on a whole-sample basis or on an ash basis; this is not always clear, particularly in the older literature.

In comparing CCPs to the parent coal, in many cases, particularly for bituminous and higher rank coals in which organic association is not a major factor, the *whole-ash* U or Th concentration will increase in proportion to the amount of mineral matter in the coal. Therefore, for a typical fly ash derived from an eastern U.S. bituminous coal with $\pm 10\%$ (wt) ash yield, the fly ash will have about 10 times the concentration of U and Th as did the whole-coal feed.

3. U and Th in Coal

The concentrations and modes of occurrence of U and Th in coals have been summarized in a number of coal geochemistry books and papers, notably Bouška (1981), Valković (1983), Swaine (1990), and Yudovich and Ketris (2005, 2006). Regional or broad-based reviews of trace elements and minerals in coals have been written by Raask (1985), Finkelman (1993), Huggins (2002), Ward (2002), Seredin and Finkelman (2008), and Dai et al. (2012b).

3.1. Thorium

Thorium occurrences in coal are generally linked to assemblages of detrital minerals (Eskenazy, 1992) (e.g., zircon, rare earth-bearing phosphates, and monazite [Swaine, 1990; Arbutov et al., 2012] accompanied by TiO_2 minerals) and clay minerals (Finkelman, 1995; Dai et al., 2012a). In many cases, such assemblages are found in the basal lithotype of coals (Hower and Bland, 1989; Hower and Pollock, 1989; Andrews et al., 1994; Hower et al., 1994a,b, 1996; Mardon and Hower, 2004; Dai et al., 2015a,c).

3.2. Uranium

Uranium can have both organic and inorganic associations in coal. The origins of U in coal follow three paths (after Denson, 1959; Denson et al., 1959):

1. Syngenetic—concentration or deposition from surface waters by living plants or in dead organic matter in swamps before coalification.
2. Diagenetic—introduction into the coal during coalification.
3. Epigenetic—introduction into the coal after coalification by groundwater-derived U from hydrothermal sources or from volcanic rocks.

Two enrichment types of U in coal have been identified (Seredin and Finkelman, 2008; Dai et al., 2015b–d, 2017): an epigenetic

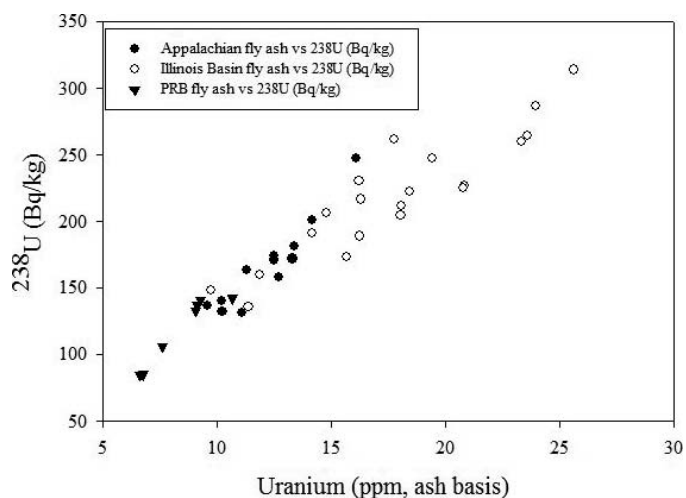


Fig. 1. Uranium concentration in fly ash (ppm or $\mu\text{g/g}$) vs. activity of the radionuclide ^{238}U in becquerels per kilogram (Bq/kg) (after Lauer et al., 2015).

infiltration type (type I) and a syngenetic or early diagenetic exfiltration type (type II). Type I is usually connected with sandstone-hosted roll-type U deposits. The coal deposits in this case were surrounded by igneous rocks, which are enriched in U and have provided U sources for coal during the epigenetic infiltration process. Type II can be divided into two subtypes (subtypes 1 and 2). Subtype 1 is usually interlayered between impermeable clays (Seredin and Finkelman, 2008; Dai et al., 2017) or limestones (Dai et al., 2015d). Subtype 2 is characterized by enrichment of Ge and U (Seredin et al., 2013; Dai et al., 2015c), although other elements, including V, Cr, Mo, and Se, are depleted in the coals, unlike type I and subtype 1. Associated U- and Ge-rich granites, which have served as both the basement for the coal-bearing sequences and as the sediment source materials (Dai et al., 2015c), have provided the sources of U during the peat accumulation stage.

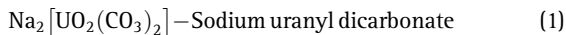
3.2.1. Inorganic associations of U in coal

Inorganic associations can include carnotite $[\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}]$, uraninite (UO_2), coffinite $[\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4+x}]$, autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 11\text{H}_2\text{O}]$, torbernite $[\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}]$, zeunerite $[\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 10(\text{H}_2\text{O})]$, becquerelite $[\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8(\text{H}_2\text{O})]$, pitchblende $(\text{U}^{4+}, \text{U}^{6+})\text{O}_2$, brannerite (UTi_2O_6) , zircon [ideal formula is ZrSiO_4 , but it can broaden to $(\text{Zr}_{1-y}\text{REE}_y)(\text{SiO}_4)_{1-x}(\text{OH})_{4+x-y}$, including trace amounts of U], U-bearing sulfates, and rare earth element (REE)-bearing phosphates (Berthoud, 1875; Denson, 1959; Finkelman, 1981; Swaine, 1990; Mohan et al., 1991; Dai et al., 2015b–d; Wang et al., 2015). The phosphates can include ningyuite $[\text{CaU}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ or $(\text{U}_{1-x}\text{Ca}_{1-x}\text{REE}_x)(\text{PO}_4)_2 \cdot 1-2\text{H}_2\text{O}]$ (Havelcová et al., 2014). Jacob and Isrusch (1988) noted zippeite $[\text{K}_4(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot 4(\text{H}_2\text{O})]$ in a Swedish coal. Similar cases have also been observed in other areas, such as coals from the Fusui Coalfield, Guangxi Province (Dai et al., 2013), and the Songzao Coalfield, Chongqing (Zhao et al. 2015), China.

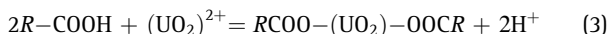
3.2.2. Organic associations of U in coal

Discussions of organic associations can be found in Breger et al. (1955a,b), Andreyev and Chumachenko (1964), Zubovic (1966), Manskaya and Drozdova (1968), Szalay and Szilágyi (1969), Breger (1974), Bouška (1981), Disnar (1981), Disnar and Trichet (1983), Valković (1983), Nakashima et al. (1984, 1987), Raask (1985), Zielinski (1985), Disnar and Sureau (1990), Meunier et al. (1990), Swaine (1990), Mohan et al. (1991), Tomschey (1995), Landais

(1996), and Liu et al. (2015). Weathering of U-bearing rocks oxidizes U^{4+} to U^{2+} , increasing the ability for U to be transported (Eskenazy, 1992). The uranyl ion is transported as a uranyl carbonate in an alkaline solution (Moore, 1954; Szalay, 1954; Breger, 1974):

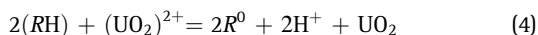


Contact of the solution with the acidic organic matter decomposes the complexes, releasing the uranyl ion which, in turn, would be absorbed by the organics, as follows (after Landais, 1996):



The formation of uranyl humates was established in the extraction of U from coals with 2% NaOH and 10% $(NH_4)_2CO_3$ and sorption of U on humic acids (Voskresenskaya, 1960a,b; Swanson et al., 1966). Peat can adsorb 100% of the available U at pH 6–7.2 (Lopatkina, 1967). Sorption of $(UO_2)^{2+}$ is the result of ion exchange processes with the carboxylic groups of humic acids (Borovec et al., 1979; Yudovich and Ketris, 2005). If uranium is present as $[UO_2(SO_4)_3]^{4-}$, the formation of uranyl humates is optimal in the pH 4–5 range, whereas binding with fulvic acids is optimal at pH 7–7.5 (Manskaya and Drozdova, 1964). In solutions containing $[UO_2(CO_3)_3]^{4-}$, pH 6.6 is optimal for both humic and fulvic acids (Manskaya and Drozdova, 1964). Van der Weiden et al. (1985) studied the pH-dependant sorption of uranyl on peat.

Further reduction could make the uranium available to form minerals such as uraninite or coffinite (after Landais, 1996):



Szalay (1964; see also Szalay and Szilágyi, 1969) used organic matter in the experimental sorption of $(UO_2)^{2+}$, noting that the “lignite powder or peat sample sorbed U so quickly that even from very dilute aqueous solutions that it virtually disappeared from the water within one minute.” Their “Geochemical enrichment factor,” the ratio of the concentration of $(UO_2)^{2+}$ in the peat to the concentration in water, was on the order of 10^4 , similar to the enrichment factors for Fe^{3+} , La^{3+} (as a proxy for the rare earth series), and VO^{2+} . Zubovic (1966), while mainly discussing Ge and V chelation, did note that complete degradation of lignin to phenylpropane (as per Manskaya and Kodina, 1963) was not necessary to produce the sites for the chelation of Ge, V, and U.

As inferred above, peats and low-rank coals are more likely to adsorb and retain U than bituminous and higher rank coals. The functional groups responsible for the chelation are progressively lost with the increase in coal rank (Given, 1984; Hatcher and Clifford, 1996), making it difficult for the higher rank coals to retain the elements picked up at lower levels of organic maturation. Öztürk and Özdoğan (2000) found that Turkish lignites had significantly higher concentrations of ^{238}U (expressed in Bq/kg) than higher rank coals. Similar results were reported for Greek (Manolopoulou and Papastefanou, 1992) and Hungarian (Rausch et al., 1995) lignites and brown coals. For the Hungarian brown coals, the ^{238}U , at 568 ± 67 Bq/kg, was two or three orders of magnitude higher than the concentrations in bituminous coals. In contrast, Wang et al. (2015) found that one lignite studied fell within the 17.7–92.3 Bq/kg

^{238}U activity range of the bituminous and anthracite-rank coals from eastern Yunnan, China. Tsikritzis et al. (2008) found western Macedonia, Greece, lignites to have an average ^{238}U of 106 ± 9.4 Bq/kg compared with brown coals with 58 ± 13 Bq/kg. Coals feeding the Kolubara and Kostolac power plants in Serbia had ^{238}U concentrations in the 27–71 Bq/kg range, with the resulting fly ash in the 100–174 Bq/kg ^{238}U range at Kolubara and Kostolac, with fly ash averaging 75 ± 16 Bq/kg ^{238}U (Životic et al., 2008). The Yili coals from Xijiang Province of southwestern China are of high volatile C/B bituminous rank (0.51–0.59% vitrinite reflectance) and are significantly enriched in U, up to 7207 ppm (Dai et al., 2015d). The latter coals, preserved within carbonate successions and with coal rank from high, through medium, to low-volatile bituminous, have elevated concentrations of U, varying from several tens of microgram per gram to ~ 200 ppm (Dai et al., 2015b), which is much higher than the average values for world low-rank coals (2.9 ppm) and world hard coals (1.9 ppm) reported by Ketris and Yudovich (2009).

3.3.3. Concentrations of U in coal

As noted, the average concentrations of U for world low-rank and hard coals are 2.9 and 1.9 ppm, respectively (Ketris and Yudovich, 2009). Extreme concentrations of U and other elements, such as Ge and V (Yudovich, 2003), can occur in coals (Breger et al., 1955a,b; Breger and Schopf, 1955; Szalay and Szilágyi, 1969), with concentrations exceeding 0.1% U (ash basis) in Colorado and South Dakota lignites (Berthoud, 1875; Breger et al., 1955b). The Late Permian coals preserved within carbonate successions in southwestern China have a highly elevated concentrations of U (e.g., 950 ppm U in coal ash from Guiding coalfield of Guizhou Province and 556 ppm U in coal ash from Yanshan coalfield of Yunnan Province) (Dai et al., 2015d). Up to 1.62% U (ash basis; or 7207 ppm whole coal) was detected in one sample from Yili coals in Xijiang Province of southwestern China (Dai et al., 2015d). Up to 0.45% U (ash basis) was noted in North Dakota lignite (Moore et al., 1959). In their study of Devonian shales, Breger and Schopf (1955) found 2.58% U in the ash from coal in the Chattanooga shale (Tennessee) and 0.50% U in the ash from coal in the Cleveland shale (Ohio). Both Ge (4.5%) and V (2.90%) were also enriched in the Chattanooga coal ash. Up to 2% U was reported in coal with hydrothermal carnotite mineralization at the Old Leyden coal mine in Jefferson County, Colorado (Berthoud, 1875). Vassilev et al. (1995) reported 1.19% U in the ash (phosphates and zircon associations) and up to 0.19% (wt) organic-associated¹ U from a vitrain lens in the Vulche Pole coal, Bulgaria. Havelcová et al. (2014) noted Czech coals with >6% U on a whole-coal basis. Meunier et al. (1990) found fragments of coaly material within the Middle Eocene Coutras uranium deposit (France), one sample having 15.5% U (29.2% ash; basis of reporting of U was not given in paper). Caution must be used in interpreting such high concentrations because they are not representative of the usual deposition environments and elemental concentrations. No such high-U coals are currently mined or have been mined for many decades in the United States (Finkelman, 2006).

Zielinski (1985) and Crowley et al. (1989) observed U enrichment in coal below tonsteins in Wyoming and Utah coals, suggesting epigenetic leaching from the overlying volcanic deposit. Hower et al. (1999) reported the highest U in the top and bottom lithotypes and in the lithotypes immediately adjacent to a tonstein in the Fire

¹ Analysis by electron microprobe of particles with no minerals >0.01 μm in size.

Clay coal, Leslie County, Kentucky. Uranium is enriched in the bottom four Fire Clay–correlative lithotypes influenced by a volcanic ash fall, up to 60 ppm U in the basal bench compared with an average of 13–14 ppm U in the top three lithotypes (Mardon and Hower, 2004).

Bragg et al. (1998) summarized coal analyses for >7000 U.S. coals collected by or for the U.S. Geological Survey. The sampling and analyses are generally restricted in time; for example, the sampling in eastern Kentucky largely ranged from 1979 to 1983. For eastern Kentucky, those years represent a peak in coal production; therefore, they also represent a wide distribution of mines and coal seams. In contrast, sampling in the 1970s and 1980s in the Pennsylvania Anthracite fields was >60 years after the peak production years during World War I. The ash, moisture, U, and Th data for several major U.S. coal fields is summarized in Table 1 (after Bragg et al., 1998), with the complete data tables in Appendix A. The average Th content is quite variable, from 10 ppm (dry, ash-free basis) for the Hams Fork coalfield to 46 ppm for the Pennsylvania Anthracite fields. The average U content is not as variable, ranging from 10 ppm for the Denver and Powder River basins to 21 ppm for the Eastern Interior (Illinois) basin and 27 ppm for the Western Interior basin.

4. U, Th, and Daughter Elements in CCPs

The amount of an element in fly ash is fundamentally related to the coal source; if the feed coal is enriched or depleted in an element, the resulting fly ash, bottom ash, or both is likely to be similarly enriched or depleted. Both enrichment and depletion have been demonstrated for other elements, such as the rare earths, As, and Hg (Sakulpitakphon et al., 2000, 2003, 2004; Mardon and Hower, 2004; Dai et al., 2012b). Within the ash collection system, the rare earths are distributed relatively uniformly through the bottom ash and the mechanical collection and electrostatic precipitator (ESP) rows (Mardon and Hower, 2004; Hower et al., 2013, 2015). Arsenic is volatile; the concentrations in ash increase with a drop in flue gas temperature and a decrease in particle size (Sakulpitakphon et al., 2000, 2003, 2004; Mardon and Hower, 2004). Mercury is also volatile, but its behavior is more complex than that of other volatile elements. In general, Hg, while having a dependency on temperature decrease, adsorbs onto fly ash carbons (Sakulpitakphon et al., 2000, 2003, 2004; Mardon and Hower, 2004; Hower et al., 2008, 2010; Silva et al., 2010; Wilcox et al., 2015).

Moreover, for those elements that are not among the most volatile in combustion, most, if not all of the element, should be captured in the fly ash, bottom ash, and flue gas desulfurization product. Therefore, in general, the mass of U and Th in the combustion products should equal the mass in the feed coal. As noted above, in many cases, particularly for bituminous and higher rank coals, the concentration of the radionuclides in the combustion products will increase in proportion to the amount of ash in the feed coal. Combustion neither decreases nor increases the absolute amount of the U and Th in the CCPs relative to the feed coal.

Studies of radionuclides in fly ash and bottom ash include power plants in Serbia (Kisić et al., 2013); Turkey (Ayçık and Ercan, 1997); Greece (Papastefanou and Charalambous, 1982; Manolopoulou and Papastefanou, 1992; Karangelos et al., 2004); Tennessee and Alabama (McBride et al., 1978; Sutton et al., 2001), Indiana (Brownfield et al., 2005; Mastalerz and Drobnik, 2007), and various other U.S.

sites (Affolter et al., 2011); Brazil (Flues et al., 2006, 2007); and the Philippines (Parami et al., 2010). McBride et al. (1978) investigated airborne emissions at two Tennessee Valley Authority power plants. In their model, 23 g U/a/MW and 46 g Th/a/MW would be emitted. Their assumptions are dated because particulate emissions are more strictly regulated than at the time of their study. Similarly, Gabbard (1993, 1995) exaggerated radionuclide emissions from coal combustion by underestimating the efficiency of particulate collection in modern power plants.

Karamdoust et al. (1988, 1991) found that Rn exhalation from fly ash was less than from the parent coal or from soil. They alluded to the question of permeability of fly ash compared with coal and soil but did not really present it as the reason for the lower permeability. It is reasonable, though, that a fly ash glass would not emit the same amount of a gas as would more permeable materials.

Ayçık and Ercan (1997) conducted a study at a Turkish power plant based on a radioactivity alarm in February 1993. The alarm was false, but they continued the study at two plants with 3 × 210 MW and 210 MW capacity (840 MW total capacity) burning about 20 kt lignite/day. With an overall ESP capture efficiency of 99.2%, 120 t/day of fly ash escapes. Based on the Papastefanou and Charalambous (1982) study of Greek lignite-burning power plants, they assumed that ²³⁸U and ²²⁶Ra concentrations should not exceed 0.48 Bq/g. Turkish plants show a range of 0.085–0.52 Bq/g for just ²²⁶Ra. The best-case scenario (2000 kcal/kg lignite, 15% ash, and 99% ESP efficiency, based on an average of 0.30 Bq/g) for the 3 × 210 MW plant is a ²²⁶Ra discharge of 3.7 × 10⁹ Bq/yr. This is different from Kentucky because of the lower rank of coal and probable greater concentration of U in the Turkish coals.

Tadmor (1986) demonstrated an enrichment of ²³⁸U, ²²⁶Ra, and ²¹⁰Pb in a <10-μm fly ash fraction. The lowest enrichment among the radionuclides studied was for ²³²Th, and the highest was for ²¹⁰Pb; the latter is known to be a highly volatile element in combustion. In the plant studied by Karangelos et al. (2004), the ²³⁸U/²²⁶Ra ratio increased in the smaller particles collected at the cooler end of the ESP array from 0.9 in the hotter ESPs to 1.4 in the cooler rows. The latter investigation is notable in being one of the more detailed studies, with six weekly samples of the feed lignite, fly ash, and bottom ash and the collection of the fly ash at 10 points, including four hoppers on both sides of the ESP array. Sahu et al. (2014) found that ²³²Th had the least size partitioning and ²¹⁰Po the greatest, with ²³⁸U and ²²⁶Ra being intermediate. Some partitioning of ²³⁸U can be attributed to the mineral association, with ²³⁸U in coffinite reported in the bottom ash (Manolopoulou and Papastefanou, 1992). Although the feed coal radionuclides are in secular equilibrium, the bottom ash and fly ash are not, owing to the slight increase in ²³⁸U, the aforementioned increase in ²³⁸U/²²⁶Ra, and the increase in ²¹⁰Pb toward the back (cooler) end of the ESP array (Karangelos et al., 2004). The fly ash with the highest amount of radionuclides was collected from the fourth ESP row (Karangelos et al., 2004), which we note is the row with the least amount of fly ash.

Affolter et al. (2011) presented data for feed coal, pulverized coals, pulverizer rejects, fly ash, and bottom ash for five U.S. power plants (Appendix A). Not all sample sites were available at each power plant. Individual samples were taken daily for 10–17 days; the results shown in Table 2 represent averages of the feed coal or pulverized coal, the fly ash, and, where sampled, the bottom ash. Overall, none of the Th or U values for the fly ashes are as high as the

Table 1

Moisture (Mois, as received [ar] basis), ash (as received and dry basis), and Th and U (whole-coal [wc] and dry, ash-free basis [daf]) averages, standard deviations (SD), and number of samples for U.S. coal fields and regions (summary after Bragg et al., 1998)

Coal field and region	Parameter	Mois (ar)	Ash (ar)	Ash (dry)	Th (wc)	U (wc)	Th (daf)	U (daf)
Appalachian								
Northern	Avg	3.44	12.43	12.85	2.7	1.7	20.7	13.9
	SD	2.44	5.38	5.50	1.7	2.2	9.2	18.0
	Count	1528	1528	1528	1528	1528	1528	1528
Pennsylvania Anthracite	Avg	2.39	13.45	13.78	5.9	2.3	46.4	16.8
	SD	2.74	6.48	6.59	3.6	3.8	27.4	18.8
	Count	40	40	40	40	40	40	40
Central	Avg	3.39	8.98	9.30	2.7	1.5	28.9	17.2
	SD	2.50	5.38	5.57	2.2	1.1	15.4	10.8
	Count	1678	1678	1678	1678	1678	1678	1678
Southern	Avg	2.89	11.96	12.31	2.9	1.7	23.6	14.2
	SD	2.91	6.39	6.57	1.9	3.5	9.4	21.1
	Count	981	981	981	981	981	981	981
Eastern Interior (Illinois Basin)	Avg	8.54	10.86	11.83	1.9	2.5	16.2	20.8
	SD	3.18	4.52	4.78	1.6	3.2	11.0	21.7
	Count	264	264	264	264	264	264	264
Western Interior	Avg	7.71	13.76	14.97	2.7	3.9	15.5	27.1
	SD	5.84	5.96	6.44	7.4	6.7	39.9	44.9
	Count	286	286	286	286	286	286	286
Rocky Mountains								
Denver	Avg	21.47	11.20	14.63	3.5	2.0	20.1	10.3
	SD	8.35	5.85	8.42	3.6	3.5	14.2	11.1
	Count	41	41	41	41	41	41	41
Green River	Avg	15.47	10.79	12.72	2.8	2.1	21.0	15.6
	SD	6.58	6.93	7.92	2.8	3.0	16.5	19.0
	Count	289	289	289	289	289	289	289
Hams Fork	Avg	12.13	10.10	11.12	1.5	1.4	10.3	12.1
	SD	6.65	6.45	6.55	1.7	1.1	12.1	6.3
	Count	25	25	25	25	25	25	25
Raton Mesa	Avg	2.14	15.45	15.77	5.0	2.0	33.1	12.5
	SD	1.38	7.28	7.40	3.0	1.2	17.4	3.9
	Count	34	34	34	34	34	34	34
San Juan	Avg	12.42	16.39	18.86	5.3	2.5	28.3	14.1
	SD	5.64	6.65	7.86	3.4	1.3	17.2	6.8
	Count	174	174	174	174	174	174	174
Southwestern Utah	Avg	16.98	12.37	14.78	3.4	2.3	22.2	13.6
	SD	4.96	6.14	7.01	3.2	2.5	17.0	10.8
	Count	42	42	42	42	42	42	42
Uinta	Avg	10.88	10.34	11.75	2.5	1.7	20.3	13.5
	SD	10.53	5.25	5.93	2.1	2.9	15.0	15.2
	Count	226	226	226	226	226	226	226
Wind River	Avg	16.80	10.99	13.15	2.0	1.4	14.9	11.4
	SD	6.04	5.21	5.95	1.1	0.9	6.4	4.6
	Count	42	42	42	42	42	42	42
Northern Great Plains								
Fort Union	Avg	36.92	9.22	14.41	1.9	1.8	12.8	12.2
	SD	6.54	4.61	6.22	2.0	2.1	15.3	12.8
	Count	277	277	277	277	277	277	277
Powder River	Avg	28.09	7.59	10.56	1.9	1.2	17.2	9.9
	SD	5.13	4.30	5.80	2.4	1.3	18.6	6.6
	Count	493	493	493	493	493	493	493
Gulf Coast								
Mississippi	Avg	47.11	12.50	23.18	4.6	3.0	21.1	13.9
	SD	4.08	5.81	9.89	4.5	3.4	25.9	14.6
	Count	21	21	21	21	21	21	21
Texas, Arkansas, and Louisiana	Avg	32.10	12.82	19.04	4.7	2.2	23.0	11.7
	SD	9.68	5.26	7.62	4.3	1.4	18.3	6.0
	Count	89	89	89	89	89	89	89

basin coal averages noted in section 3 above, with Th ranging from 14 ppm in the Powder River Basin to 28 ppm in the San Juan Basin power plant fly ash and U ranging from 8 ppm in the northern Appalachian coal-source fly ash to 13 ppm in the San Juan Basin

power plant fly ash. The slag derived from high-U (52.5 ppm on average, whole-coal basis) and high-Ge coals from Lincang, Yunnan Province of southwestern China, is significantly enriched in U (377 ppm) (Dai et al., 2015c).

Table 2

Pulverized coal moisture (Mois, as received [ar] basis), ash (dry basis), and Th and U (ppm ash); Th and U fly ash (ppm ash); and Th and U bottom ash (ppm ash) for five U.S. power plants (summary after Affolter et al., 2011)

Job	State	Coal source	Parameter	Pulverized coal				Fly ash (ppm)		Bottom ash (ppm)	
				Mois (ar)	Ash (dry)	Th (ppm ash)	U (ppm ash)	Th	U	Th	U
7017	Wyoming	Powder River Basin	Avg	19.28	9.01	18.0	13.9	14.0	8.7	17.9	9.0
			SD	0.83	0.20	1.7	4.8	1.5	1.1	0.8	0.4
			Count	15	15	15	15	15	15	15	15
7018	Ohio	Northern Appalachian	Avg	0.09	9.64	22.7	9.7	18.2	7.7	16.1	5.8
			SD	0.04	0.50	1.2	0.9	3.3	1.5	0.5	0.4
			Count	15	15	15	15	13	13	15	15
7019	Indiana	Eastern Interior (Illinois Basin)	Avg	3.03	8.66	19.6	6.0	27.2	8.7		
			SD	0.20	0.32	2.1	0.5	22.6	7.7		
			Count	11	11	10	10	13	13		
E0709002	New Mexico	San Juan Basin	Avg	2.91	25.35	25.6	11.2	28.0	12.7	25.3	9.7
			SD	0.39	0.81	1.5	0.7	0.7	0.4	1.4	0.6
			Count	17	17	17	17	16	16	17	17
E0901001	Alaska	Cook Inlet–Susitna	Avg	2.51	10.84	14.3	6.2	14.6	6.9	14.9	0.9
			SD	0.52	1.08	2.0	1.1	1.0	0.6	2.1	0.1
			Count	12	12	12	12	16	16	16	16

5. U and Th Distribution in Fly Ash from Kentucky Power Plants by Coal Source and by Ash Collection Site

Over the period represented by our studies, generally from 1992 to 2015, the coal feed at individual Kentucky power plants has been from the central (generally Kentucky, West Virginia, and Tennessee) and northern Appalachian (Ohio), the Illinois, and the Powder River and Uinta basins, with occasional use of more distant coal sources (e.g., Poland) (Kentucky Public Service Commission, 2002). In some cases, coal is blended with small amounts of tire-derived fuel (2–3% of blend), petroleum coke (up to 30% or more), or both (Hower et al., 2001, 2005). As will be discussed below, we did not include non-Appalachian or non-Illinois Basin coal sources in our summaries.

Zielinski and Budahn (1998) studied fly ashes from two of four units of 4 × 550 MW Kentucky plant. One of the studied units had a central Appalachian coal source, and the other unit had an Illinois Basin coal source. Although Ra isotopes are not found to be fractionated from parent ^{238}U and ^{232}Th , ^{210}Pb is enriched in fly ash and depleted in bottom ash compared with ^{238}U . This is not a surprise because Pb is highly volatile and is not expected to have a high concentration in bottom ash under ordinary collection conditions.

In the feed coal, the ^{210}Pb is in secular equilibrium with the parent ^{238}U and with the preceding nuclide ^{226}Ra . That is not the case for the fly ash, because Pb is volatile in combustion and the Pb concentration in ESP rows partitions with respect to the flue gas temperature. Lauer et al. (2015, fig. S2), in a study of fly ash samples from two Kentucky power plants, reported an increase in ^{210}Pb (plotted as $^{210}\text{Pb}/^{226}\text{Ra}$), a daughter product of ^{238}U , from the first to the last ESP rows in two Kentucky power plants. Radium, expressed as $^{228}\text{Ra}/^{226}\text{Ra}$, does not vary significantly between rows (Lauer et al., 2015, fig. S3). In addition to the expected increase in concentration of Pb from the first to the last ESP row, there is differentiation in the isotopes (also noted by Coles et al., 1978).

The distribution of U and Th in first and second rows of mechanical and ESP hoppers is shown in Table 3. (Appendix A contains the long version of this table and the data used to calculate the summary table.) In all cases, the original data was from Kentucky

utility-scale pulverized-fuel boilers burning single-source coal or blends of Appalachian or Illinois Basin coals. Blends of more than one basin, such as Illinois Basin plus Powder River Basin coals, were excluded. We also excluded blends of coal with non-coal fuels, such as petroleum coke or tire-derived fuel. The use of just first- and second-row ESP data is due to the lesser amount of data from the third and higher rows. In contrast to the daily sampling conducted by Affolter et al. (2011), the University of Kentucky Center for Applied Energy Research sampling was done as single (1-day) samples from individual fly ash hoppers. Where possible, multiple hoppers per ESP row were sampled. Additionally, while not all sampling years are represented in the data here, as best as possible, samples from individual plants in the 2001, 2002, 2004, 2007, 2012, and later samplings are from the same hoppers.

As noted above, certain trace elements can have notably different behavior in coal combustion and capture of the fly ash. Uranium, in general, is not a volatile element and, as such, it does not show much variation between mechanical collection and ESP rows. An exception was the combustion of the Fire Clay correlative coal in the November 2001 suite studied by Mardon and Hower (2004). They found U concentrations of 23–27 ppm in the mechanical collection fly ash and of 51–69 ppm in the ESP fly ashes, with a slight increase by row. In a 2007 collection, the other unit at the same plant showed an increase from 10 to 12 ppm U in the mechanical collection to 21 to 25 ppm U in the ESP rows. A September 2007 collection at another Kentucky plant had an increase from 12 to 13 ppm U in the first ESP row to 27 to 28 ppm U in the fourth row. After a switch from central Appalachian coal to Illinois Basin coal by the time of a December 2011 collection at the same unit, no such increase was observed. Why are we seeing exceptions to the expected lack of partitioning? The first rows of the ash collection array will preferentially collect coarser particles than the later rows, so it is possible that the coarser particles are relatively depleted in U compared with the particles remaining in the last ESP rows. This can be demonstrated in the sized fly ashes from the study by Sakulpitakphon et al. (2000; U data generated in 2016 by Shifeng Dai), in which there is a particle size-dependent trend toward higher U in finer sizes in both the mechanical hopper 6 fly ash and in the second-row ESP fly ash. The mechanical fly ashes are coarser than

Table 3

Fly ash moisture (as determined [det.] basis), ash (dry basis), carbon (dry, ash-free [daf] basis), and Th and U (ppm ash) for first- and second-row mechanical (mech) separation (cyclone) hoppers and first- and second-row electrostatic precipitator (ESP) hoppers for Kentucky utility power plants burning either central Appalachian (App) or Illinois Basin source coals

Hopper	Parameter	Moisture			Ash (ppm)	
		(as det.)	Ash (dry)	C (daf)	Th	U
App mech 1st row	Avg	0.23	84.85	14.35	90	16
	SD	0.13	8.55	8.28	3	8
	Count	10	10	10	4	10
App mech 2nd row	Avg	0.14	85.89	12.44	82	24
	SD	0.02	3.65	2.69	3	1
	Count	4	4	4	4	4
App ESP 1st row	Avg	0.23	92.99	6.05	110	15
	SD	0.19	4.57	4.20	45	10
	Count	33	33	33	17	33
App ESP 2nd row	Avg	0.72	91.20	6.99	110	18
	SD	1.77	5.42	5.07	46	11
	Count	30	30	30	16	29
IL Basin ESP 1st row	Avg	0.33	95.61	3.86	54	16
	SD	0.37	5.03	4.56	32	4
	Count	33	33	29	18	33
IL Basin ESP 2nd row	Avg	0.42	93.62	5.30	52	18
	SD	0.34	6.74	6.17	33	4
	Count	29	29	28	20	29

the ESP fly ashes, 14.2% vs. 96% for <500 mesh, respectively, so a larger percentage of coarse ash would tend to lower the overall concentration of U. Similarly, Dai et al. (2014) found a slight increase, from <7 ppm U to nearly 13 ppm U, from the >120-mesh fraction to the <500-mesh fraction of the fly ash from the Jungar power plant, Inner Mongolia, China. In contrast, Eskenazy (unpublished data) did not see any U partitioning among size fractions of bottom ash from the Pernik, Bulgaria, power plant.

6. Summary

Thorium in coal is generally associated with detrital minerals such as zircon, REE-bearing phosphates, and monazite. The highest reported coal-based U concentrations tend to be in low-rank thin coals, coaly inclusions, and coals subjected to hydrothermal mineralization. Uranium occurs in both organic and inorganic associations. Organic associations are particularly prevalent in low-rank coals, where humic acids and other organics can chelate the U. Such associations should generally be lost with an increase in coal rank and the consequent loss of functional groups. Inorganic associations include zircon and REE-bearing phosphates and a wide variety of other minerals. Uranium can be leached from the surrounding sediments; thus, the highest U concentrations tend to be found in the basal and uppermost coal lithotypes. In a Kentucky coal with a volcanic ash parting, high U concentrations were also noted in lithotypes immediately adjacent to the tonstein (Hower et al., 1999).

The concentration of Th and U in fly ash and bottom ash is generally in proportion to their concentrations in the coal source; if the latter is enriched or depleted in an element, the fly ash and bottom ash is likely to be similarly enriched or depleted. Neither are particularly volatile elements; therefore, the Th and U released in combustion will be retained in the CCPs. Some partitioning between fly ash and bottom ash may occur owing to mineral associations; in

general, though, the concentrations among the latter CCPs should be similar.

Variation in U concentration between ESP rows is not common, but could be attributable to interrow variations in the fly ash constituents (carbon, glass, magnetite and other spinels, other neo-formed minerals, minerals inherited from the coal, etc.), which will contain varying amounts of U and Th.

In general, the concentrations of U and Th in coals and fly ashes are not high. As noted by Zielinski and Finkelman (1997), the levels of radionuclides in coal and CCPs are generally in the range of many rocks and soils, The Appalachian-derived ESP fly ashes had 110 ppm Th, twice the concentration in the Illinois Basin-derived ESP fly ashes. The ESP fly ashes from coals from both basins fell in the 15–18 ppm U range. Based on Figure 1 (after Lauer et al., 2015), such a U concentration translates to a ^{238}U activity of about 175–250 Bq/kg. In contrast to some of the power plants studied in past decades, U.S. power plants meeting current emission standards should have virtually no fly ash, U, Th, and other radionuclide emissions. The particulate control system, ESPs or fabric filters, should be capturing well over 95% of the particles. Particulates not captured in the latter systems should be caught in the flue gas desulfurization process, required for SO_2 control in all of the larger plants in the eastern United States.

Acknowledgments

We thank Tom Adams (American Coal Ash Association), Ken Ladwig (Electric Power Research Association), Rodney Andrews and Tom Robl (University of Kentucky Center for Applied Energy Research), and Lisa Bradley (Haley & Aldrich) for their guidance in this project. We also thank our reviewers, Maria Mastalerz and Bob Finkelman, and editor, Anne Oberlink, for their roles in shaping the manuscript.

References

- Affolter, R.H., Groves, S., Betterton, W.J., Benzel, W., Conrad, K.L., Swanson, S.M., Ruppert, L.F., Clough, J.G., Belkin, H.E., Kolker, A., Hower, J.C., 2011. Geochemical Database of Feed Coal and Coal Combustion Products (CCPs) from Five Power Plants in the United States. U.S. Geological Survey Data Series 635, pamphlet, 19 pp.
- Andrews, W.M., Jr., Hower, J.C., Hiatt, J.K., 1994. Investigations of the Fire Clay coal bed, southeastern Kentucky, in the vicinity of sandstone washouts. *International Journal of Coal Geology* 26, 95–115.
- Andreyev, P.F., Chumachenko, A.P., 1964. Reduction of uranium by natural organic substances. *Geochemistry International* 1, 3–7.
- Arbuzov, S.I., Maslov, S.G., Volostnov, A.V., Il'enok, S.S., Arkhipov, V.S., 2012. Modes of occurrence of uranium and thorium in coals and peats of northern Asia. *Solid Fuel Chemistry* 46, 52–66.
- Ayçik, G.A., Ercan, A., 1997. Radioactivity measurements of coals and ashes from coal-fired power plants in the southwestern part of Turkey. *Journal of Environmental Radioactivity* 35, 23–35.
- Berthoud, E.L., 1875. On the occurrence of uranium, silver, iron, etc., in the Tertiary formation of Colorado Territory. *Proceedings of the Academy of Natural Sciences of Philadelphia* 27, 363–365.
- Borovec, Z., Kribek, B., Tolar, V., 1979. Sorption of uranyl by humic acids. *Chemical Geology* 27, 39–46.
- Bouška, V., 1981. *Geochemistry of Coal—Coal Science and Technology* 1. Elsevier, Amsterdam, The Netherlands, 284 pp.
- Bragg, L.J., Oman, J.K., Tewalt, S.J., Oman, C.L., Rega, N.H., Washington, P.M., Finkelman, R.B., 1998. U.S. Geological Survey Coal Quality (COALQUAL) Database: Version 2.0. U.S. Geological Survey Open-File Report 97-134. (CD-ROM.)
- Breger, I.A., 1974. The role of organic matter in the accumulation of uranium. In: *Proceedings of a Symposium on Formation of Uranium Ore Deposits*, Athens, Greece, 6–10 May 1974. International Atomic Energy Agency, Vienna, Austria, pp. 99–124.

- Breger, I.A., Deul, M., Meyrowitz, R., 1955a. Geochemistry and mineralogy of a uraniumiferous subbituminous coal (Wyoming). *Economic Geology* 50, 610–624.
- Breger, I.A., Deul, M., Rubenstein, S., 1955b. Geochemistry and mineralogy of a uraniumiferous lignite (South Dakota). *Economic Geology* 50, 206–226.
- Breger, I.A., Schopf, J.M., 1955. Germanium and uranium in coalified wood from Upper Devonian black shale. *Geochimica et Cosmochimica Acta* 7, 287–293.
- Brownfield, M.E., Cathcart, J.D., Affolter, R.H., Brownfield, L.K., Rice, C.A., O'Connor, J.T., Zielinski, R.A., Bullock, J.H., Jr., Hower, J.C., Meeker, G.P., 2005. Characterization and Modes of Occurrence of Elements in Feed Coal and Coal Combustion Products from a Power Plant Utilizing Low-Sulfur Coal from the Powder River Basin, Wyoming. U.S. Geological Survey Scientific Investigations Report 2004-5271, 36 pp. <http://pubs.usgs.gov/sir/2004/5271/>, accessed 23 June 2016.
- Coles, D.G., Ragaini, R.C., Ondov, J.M., 1978. Behavior of natural radionuclides in western coal-fired power plants. *Environmental Science & Technology* 12, 442–446.
- Crowley, S.S., Stanton, R.W., Ryer, T.A., 1989. The effects of volcanic ash on the maceral and chemical composition of the C coal bed, Emery Coal Field, Utah. *Organic Geochemistry* 14, 315–331.
- Dai, S., Hower, J.C., Ward, C.R., Guo, W., Song, H., O'Keefe, J.M.K., Xie, P., Hood, M.M., Yan, X., 2015a. Elements and phosphorus minerals in the middle Jurassic inertinite-rich coals of the Muli Coalfield on the Tibetan Plateau. *International Journal of Coal Geology* 144–145, 23–47.
- Dai, S., Jiang, Y., Ward, C.R., Gu, L., Seredin, V.V., Liu, H., Zhou, D., Wang, X., Sun, Y., Zou, J., Ren, D., 2012a. Mineralogical and geochemical compositions of the coal in the Guanbanwusu Mine, Inner Mongolia, China: further evidence for the existence of an Al (Ga and REE) ore deposit in the Jungar Coalfield. *International Journal of Coal Geology* 98, 10–40.
- Dai, S., Ren, D., Chou, C.-L., Finkelman, R.F., Seredin, V.V., Zhou, Y., 2012b. Geochemistry of trace elements in Chinese coals: a review of abundances, genetic types, impacts on human health, and industrial utilization. *International Journal of Coal Geology* 94, 3–21.
- Dai, S., Seredin, V.V., Ward, C.R., Hower, J.C., Xing, Y., Zhang, W., Song, W., Wang, P., 2015b. Enrichment of U–Se–Mo–Re–V in coals preserved within marine carbonate successions: geochemical and mineralogical data from the Guiding Coalfield, Guizhou, China. *Mineralium Deposita* 50, 159–186.
- 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., 2015c. Elemental and mineralogical anomalies in the coal-hosted Ge ore deposit of Lincang, Yunnan, southwestern China: key role of N₂-CO₂-mixed hydrothermal solutions. *International Journal of Coal Geology* 152, 19–46.
- Dai, S., Xie, P., Jia, S., Ward, C.R., Hower, J.C., Yan, X., French, D., 2017. Enrichment of U–Re–V–Cr–Se and rare earth elements in the Late Permian coals of the Moxinpo Coalfield, Chongqing, China: genetic implications from geochemical and mineralogical data. *Ore Geology Reviews* 80, 1–17. <http://dx.doi.org/10.1016/j.oregeorev.2016.06.015>
- Dai, S., Yang, J., Ward, C.R., Hower, J.C., Liu, H., Garrison, T.M., French, D., O'Keefe, J.M.K., 2015d. Geochemical and mineralogical evidence for the coal-hosted uranium deposit from the Yili Basin, Xinjiang, northwestern China. *Ore Geology Reviews* 70, 1–30.
- Dai, S., Zhang, W., Ward, C.R., Seredin, V.V., Hower, J.C., Li, X., Song, W., Kang, H., Zheng, L., Zhou, D., 2013. Mineralogical and geochemical anomalies of Late Permian coals from the Fusui Coalfield, Guangxi Province, southern China: influences of terrigenous materials and hydrothermal fluids. *International Journal of Coal Geology* 105, 60–84.
- Dai, S., Zhao, L., Hower, J.C., Johnston, M.N., Song, W., Wang, P., Zhang, S., 2014. 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.
- Denson, N.M., 1959. Uranium in Coal in the Western United States: Introduction. U.S. Geological Survey Bulletin 1055-A, pp. 1–10.
- Denson, N.M., Bachman, G.O., Zeller, H.D., 1959. Uranium-bearing lignite in northwestern South Dakota and adjacent states. U.S. Geological Survey Bulletin 1055-B, pp. 11–57.
- Disnar, J.R., 1981. Etude expérimentale de la fixation de métaux par un matériau sédimentaire actuel d'origine algale—II. Fixation “*in vitro*” de UO₂²⁺, Cu²⁺, Ni²⁺, Zn²⁺, Pb²⁺, Co²⁺, Mn²⁺, ainsi que de VO₃⁻, MoO₄²⁻ et GeO₃²⁻. *Geochimica et Cosmochimica Acta* 45, 363–379.
- Disnar, J.R., Sureau, J.F., 1990. Organic matter in ore genesis: progress and perspectives. *Organic Geochemistry* 16, 577–599.
- Disnar, J.R., Trichet, J., 1983. Pyrolyse de complexes organo-métalliques formés entre un matériau organique actuel d'origine algale et divers cations métalliques divalents (UO₂²⁺, Cu²⁺, Pb²⁺, Ni²⁺, Mn²⁺, Zn²⁺, et Co²⁺). *Chemical Geology* 46, 203–223.
- Eskenazy, G., 1992. Geochemistry of Thorium and Uranium in Bulgarian Coals. *Annuaire de l'Université de Sofia “St. Kliment Ohridski” Faculté de Géologie et Géographie, Livre 1—Géologie* 83, 43–70.
- Finkelman, R.B., 1981. Modes of Occurrence of Trace Elements in Coal. U.S. Geological Survey Open-File Report OFR-81-99, 301 pp.
- Finkelman, R.B., 1993. Trace and minor elements in coal. In: *Organic Geochemistry* (Engel, M.H., Masko, S.A., eds.). Plenum Press, New York, pp. 593–607.
- Finkelman, R.B., 1995. Modes of occurrence of environmentally sensitive trace elements in coal. In: *Environmental Aspects of Trace Elements in Coal* (Swaine, D.J., Goodarzi, F., eds.). Kluwer Academic Publishing, Dordrecht, The Netherlands, pp. 24–50.
- Finkelman, R.B., 2006. Health impacts of coal: facts and fallacies. *Ambio* 36, 103–106.
- Flues, M., Camargo, I.M.C., Figueiredo Filho, P.M., Silva, P.S.C., Mazzilli, B.P., 2007. Evaluation of radionuclides concentration in Brazilian coals. *Fuel* 86, 807–812.
- Flues, M., Camargo, I.M.C., Silva, P.S.C., Mazzilli, B.P., 2006. Radioactivity of coal and ashes from Figueira coal power plant in Brazil. *Journal of Radioanalytical and Nuclear Chemistry* 270, 597–602.
- Gabbard, A., 1993. Coal Combustion: Nuclear Resource or Danger. Oak Ridge National Laboratory Review 26. <http://www.nrc.gov/docs/ML0932/ML093280447.pdf>, accessed 23 June 2016.
- Gabbard, A., 1995. Can coal combustion breed Pu in the sky? *Physics Today* 48(5), 88–90.
- Given, P.H., 1984. An essay on the organic geochemistry of coal. *Coal Science* 3, 163–251, 339–34.
- Hatcher, P.G., Clifford, D.J., 1996. The organic geochemistry of coal: from plant materials to coal. *Organic Geochemistry* 27, 251–274.
- Havelcová, M., Machovič, V., Mizera, J., Šýkrová, I., Borecká, L., Kopecký, L., 2014. A multi-instrumental geochemical study of anomalous uranium enrichment in coal. *Journal of Environmental Radioactivity* 137, 52–63.
- Hower, J.C., Andrews, W.M., Jr., Wild, G.D., Eble, C.F., Dulong, F.T., Salter, T.L., 1994a. Coal quality trends for the Fire Clay coal bed, southeastern Kentucky. *Journal of Coal Quality* 13, 13–26.
- Hower, J.C., Bland A.E., 1989. Geochemistry of the Pond Creek coal bed, eastern Kentucky coalfield. *International Journal of Coal Geology* 11, 205–226.
- Hower, J.C., Dai, S., Seredin, V.V., Zhao, L., Kostova, I.J., Silva, L.F.O., Mardon, S.M., Gurdal, G., 2013. A note on the occurrence of yttrium and rare earth elements in coal combustion products. *Coal Combustion and Gasification Products* 5, 39–47.
- 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. *Environmental Science & Technology* 42, 8471–8477.
- Hower, J.C., Groppo, J.G., Henke, K.R., Hood, M.M., Eble, C.F., Honaker, R.Q., Zhang, W., Qian, D., 2015. Notes on the potential for the concentration of rare earth elements and yttrium in coal combustion fly ash. *Minerals* 5, 356–366. doi:10.3390/min5020356
- Hower, J.C., Hiatt, J.K., Wild, G.D., Eble, C.F., 1994b. Coal resources, production, and quality in the eastern Kentucky coalfield: perspectives on the future of steam coal production. *Nonrenewable Resources* 3, 216–236.
- Hower, J.C., Pollock, J.D., 1989. Petrology of the River Gem coal bed, Whitley County, Kentucky. *International Journal of Coal Geology* 11, 227–245.
- Hower, J.C., Robertson, J.D., Roberts, J.M., 2001. Combustion by-products from the co-combustion of coal, tire-derived fuel, and petroleum coke at a western Kentucky cyclone-fired unit. *Fuel Processing Technology* 74, 125–142.
- Hower, J.C., Ruppert, L.F., Eble, C.F., 1999. Lanthanide, yttrium, and zirconium anomalies in the Fire Clay coal bed, eastern Kentucky. *International Journal of Coal Geology* 39, 141–153.
- Hower, J.C., Ruppert, L.F., Eble, C.F., Graham, U.M., 1996. Geochemical and paly-nological indicators of the paleoecology of the River Gem coal bed, Whitley County, Kentucky. *International Journal of Coal Geology* 31, 135–149.
- 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. *Progress in Energy and Combustion Science* 36, 510–529.
- Hower, J.C., Thomas, G.A., Mardon, S.M., Trimble, A.S., 2005. Impact of co-combustion of petroleum coke and coal on fly ash quality: case study of a western Kentucky power plant. *Applied Geochemistry* 20, 1309–1319.
- Huggins, F.E., 2002. Overview of analytical methods for inorganic constituents in coal. *International Journal of Coal Geology* 50, 169–214.
- Jacob, K.-H., Irsusch, R., 1988. Die Stockheimer Steinkohle und ihr umstrittenes Uranpotential. *Erzmetall. Journal for Exploration, Mining and Metallurgy* 41, 379–382.
- Karamdoust, N.A., Durrani, S.A., 1991. Determination of radon emanation power of fly ash produced in coal-combustion power stations. *Nuclear Tracks and Radiation Measurements* 19, 339–342.
- Karamdoust, N.A., Durrani, S.A., Fremlin, J.H., 1988. An investigation of radon exhalation from fly ash produced in the combustion of coal. *International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements* 15, 647–650.

- Karangelos, D.J., Petropoulos, N.P., Anagnostakis, M.J., Hiniš, E.P., Simopoulos, S.E., 2004. Radiological characteristics and investigation of the radioactive equilibrium in the ashes produced in lignite-fired power plants. *Journal of Environmental Radioactivity* 77, 233–246.
- Kentucky Public Service Commission, 2002. An Examination by the Public Service Commission on the Application of the Fuels Adjustment Clause of Kentucky Utilities Company from May 1, 2001 to October 31, 2001: Case No. 2000-00497-B. Commonwealth of Kentucky, Kentucky Public Service Commission. https://psc.ky.gov/order_vault/Orders_2001/200000497B_122001.pdf, accessed 23 June 2016.
- Ketris, M.P., Yudovich, Ya.E., 2009. Estimations of Clarks for carbonaceous biolithes: world average for trace element contents in black shales and coals. *International Journal of Coal Geology* 78, 135–148.
- Kisić, D.M., Miletić, S.R., Radonjić, V.D., Radanović, S.B., Filipović, J.Z., Gržetić, I.A., 2013. Natural radioactivity of coal and fly ash at the Nikola Tesla B TPP [Prirodna radioaktivnost uglja i letećeg pepela u termoelektrani "Nikola Tesla B"]. *Hemijska Industrija* 67, 729–738. (In Serbian.)
- Landais, P., 1996. Organic geochemistry of sedimentary uranium ore deposits. *Ore Geology Reviews* 11, 33–51.
- Lauer, N., Hower, J.C., Hsu-Kim, H., Taggart, R.K., Vengosh, A., 2015. Naturally occurring radioactive materials in coal and coal combustion residuals in the United States. *Environmental Science & Technology* 49, 11227–11233.
- Liu, J., Yang, Z., Yan, X., Ji, D., Yang, Y., Hu, L., 2015. Modes of occurrence of highly-elevated trace elements in superhigh-organic-sulfur coals. *Fuel* 156, 190–197.
- Lopatkina, A.P., 1967. Accumulation of uranium on peat. *Geokhimiya (Geochemistry)* 6, 708–720.
- Manolopoulou, M., Papastefanou, C., 1992. Behavior of natural radionuclides in lignites and fly ashes. *Journal of Environmental Radioactivity* 16, 261–271.
- Manskaya, S.M., Drozdova, T.V., 1964. *Geochemistry of Organic Matter*. Moskva, Nauka, 315 pp. (In Russian.)
- Manskaya, S.M., Drozdova, T.V., 1968. *Geochemistry of Organic Substances (Geokhimiya Organicheskogo Veshchestva)*. Pergamon, London, U.K., 345 pp. (Translated from Russian and edited by L. Shapiro and I.A. Breger.)
- Manskaya, S.M., Kodina, L.A., 1963. Aromatic monomers of lignin in lignites and their possible role in the concentration of uranium, germanium and vanadium. *Geokhimiya* 4, 370–383.
- Mardon, S.M., Hower, J.C., 2004. Impact of coal properties on coal combustion by-product quality: examples from a Kentucky power plant. *International Journal of Coal Geology* 59, 153–169.
- Mastalerz, M., Drobnik, A., 2007. *Radiative Elements in Indiana Coals*. Indiana Geological Survey, Open-File Study 07-03, 37 pp.
- McBride, J.P., Moore, R.E., Witherspoon, J.P., Blanco, R.E., 1978. Radiological impact of airborne effluents of coal and nuclear plants. *Science* 202(4372), 1045–1050.
- Meunier, J.D., Landai, P., Pagel, M., 1990. Experimental evidence of uranite formation from diagenesis of uranium-rich organic matter. *Geochimica et Cosmochimica Acta* 54, 809–817.
- Mohan, M.S., Ilger, J.D., Zingaro, R.A., 1991. Speciation of uranium in a south Texas lignite: additional evidence for a mixed mode of occurrence. *Energy & Fuels* 5, 568–573.
- Moore, E.S., 1954. Extraction of uranium from aqueous solution by coal and some other materials. *Economic Geology* 49, 652–658.
- Moore, G.W., Melin, R.E., Kepferle, R.C., 1959. Uranium-Bearing Lignite in Southwestern North Dakota. *U.S. Geological Survey Bulletin* 1055-E, pp. 147–166.
- Nakashima, S., Disnar, J.R., Perrochet, A., Trichet, J., 1984. Experimental study of mechanisms of fixation and reduction of uranium by sedimentary organic matter under diagenetic or hydrothermal condition. *Geochimica et Cosmochimica Acta* 48, 2321–2329.
- Nakashima, S., Disnar, J.R., Perruchot, A., Trichet, J., 1987. Fixation et reduction de l'uranium par les matières organiques naturelles: mécanismes et aspects cinétiques. *Bulletin de Mineralogie* 10, 227–234.
- Öztürk, N., Özdoğan, S., 2000. Preliminary analyses of radionuclides in Afsin-Elbistan lignite samples. *Journal of Radioanalytical and Nuclear Chemistry* 245, 653–657.
- Papastefanou, C., Charalambous, S., 1982. Radioactivity in the atmosphere by coal burning. In: *Radiological Protection, Advances in Theory and Practice: Proceedings of the Third International Symposium*, vol. 1, Inverness, U.K., 6–11 June 1982. Society for Radiological Protection, Totnes, Devon, U.K., pp. 287–292.
- Parami, V.K., Sahoo, S.K., Yonehara, H., Takeda, S., Quirit, L.L., 2010. Accurate determination of naturally occurring radionuclides in Philippine coal-fired thermal power plants using inductively coupled plasma mass spectrometry and γ -spectroscopy. *Microchemical Journal* 95, 181–185.
- Raask, E., 1985. The mode of occurrence and concentration of trace elements in coal. *Progress in Energy and Combustion Science* 11, 97–118.
- Rausch, H., Sziklai, I.L., Sándor, S., Szabó, T., 1995. Analysis of toxic and radioactive components in sedimental type air particulates by INAA and XRF. *Journal of Radioanalytical and Nuclear Chemistry* 196, 25–33.
- Sahu, S.K., Tiwari, M., Bhangare, R.C., Pandit, G.G., 2014. Enrichment and particle size dependence of polonium and other naturally occurring radionuclides in coal ash. *Journal of Environmental Radioactivity* 138, 421–426.
- Sakulpitakphon, T., Hower, J.C., Schram, W.H., Ward, C.R., 2004. Tracking mercury from the mine to the power plant: geochemistry of the Manchester coal bed, Clay County, Kentucky. *International Journal of Coal Geology* 57, 127–141.
- 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.
- Seredin, V.V., Dai, S., Sun, Y., Chekryzhov, Yu.I., 2013. Coal deposits as promising sources of rare metals for alternative power and energy-efficient technologies. *Applied Geochemistry* 31, 1–11.
- Seredin, V.V., Finkelman, R.B., 2008. Metalliferous coals: a review of the main genetic and geochemical types. *International Journal of Coal Geology* 76, 253–289.
- 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 Combustion & Gasification Products* 2, 66–79.
- Sutton, M.E., Schmaltz, T., Miller, E.C., Harper, K.J., 2001. Radon emissions from a high volume coal fly ash structural fill site. *International Ash Utilization Symposium, Lexington, KY, 22–24 October 2001*. flyash.info/2001/envben2/91sutton.pdf, accessed 1 June 2016.
- Swaine, D.J., 1990. *Trace Elements in Coal*. Butterworths, London, U.K., 278 pp.
- Swanson, V.E., Frost, J.C., Rader, L.E., Huffman, C., 1966. *Metal Sorption by Northwest Florida Humate*. U.S. Geological Survey Professional Paper N550 C, pp. 174–177.
- Szalay, A., 1954. The enrichment of uranium in some brown coals in Hungary. *Acta Geologica Hungarica* 2, 299–311.
- Szalay, A., 1964. Cation exchange properties of humic acids and their importance in the geochemical enrichment of UO_2^{++} and other cations. *Geochimica et Cosmochimica Acta* 28, 1605–1614.
- Szalay, A., Szilágyi, M., 1969. Accumulation of microelements in peat humic acids and coal. In: *Advances in Organic Geochemistry 1968* (Schenck, P.A., Havenaar, I., eds.). Pergamon, Oxford, U.K.
- Tadmor, J., 1986. Radioactivity from coal-fired power plants: a review. *Journal of Environmental Radioactivity* 4, 177–204.
- Tomschey, O., 1995. Unusual enrichment of U, Mo and V in an Upper Cretaceous coal seam, Hungary. In: *European Coal Geology* (Whateley, M.K.G., Spears, D.A., eds.). The Geological Society Special Publication 82, London, U.K., pp. 299–305.
- Tsikritsis, L.I., Fotakis, M., Tzimkas, N., Kolovos, N., Tsikritzi, R., 2008. Distribution and correlation of the natural radionuclides in a coal mine of the West Macedonia Lignite Center (Greece). *Journal of Environmental Radioactivity* 99, 230–237, 567–578.
- Valković, V., 1983. *Trace Elements in Coal*, vol. 1. CRC Press, Boca Raton, FL, 210 pp.
- Van der Weiden, C.H., Van Leeuwen, M., 1985. The effect of the pH on the adsorption of uranyl onto peat. *Uranium 2(N1)*, 59–66.
- Vassilev, S.V., Eskenazy, G.M., Tarassov, M.T., Dimov, V.I., 1995. Mineralogy and geochemistry of a vitrain lens with unique trace element content from the Velche Pole coal deposit, Bulgaria. *Geologica Balcanica* 25, 111–124.
- Voskresenskaya, N.T., 1960a. On the mode of occurrence of uranium in coals. I. Extraction of uranium from coal by different solvents. *Izvestiya Akademii Nauk Kirgizkoi SSR, Natural and Technological Science* 2(5), 49–56.
- Voskresenskaya, N.T., 1960b. Calculation of uranium in coal. II. Study of the reaction of humic acid with uranyl salts. *Izvestiya Akademii Nauk Kirgizskoj SSR, Estestvoznaniya i Tekhniki Nauk* 2, 57–64.
- Wang, X., Feng, Q., Sun, R., Liu, G., 2015. Radioactivity of natural nuclides (^{40}K , ^{238}U , ^{232}Th , ^{226}Ra) in coals from eastern Yunnan, China. *Minerals* 5, 637–646.
- Ward, C.R., 2002. Analysis and significance of mineral matter in coal seams. *International Journal of Coal Geology* 50, 135–168.
- Wilcox, J., Wang, B., Rupp, E., Taggart, R., Hsu-Kim, H., Oliveira, M.L.S., Cutroneo, 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. doi: 10.1021/acs.energyfuels.5b02033
- Yudovich, Ya.E., 2003. Coal inclusions in sedimentary rocks: a geochemical phenomenon. A review. *International Journal of Coal Geology* 56, 203–222.
- Yudovich, Ya.E., Ketris, M.P., 2005. *Toxic Trace Elements in Coal*. Ekaterinburg, Russian Academy of Sciences, Ural Division, 655 pp. (In Russian.)

- Yudovich, Ya.E., Ketris, M.P., 2006. Valuable Trace Elements in Coal. Ekaterinburg, Russian Academy of Sciences, Ural Division, 538 pp. (In Russian.)
- Zhao, L., Ward, C.R., French, D., Graham, I.T., 2015. Major and trace element geochemistry of coals and intra-seam claystones from the Songzao Coalfield, SW China. *Minerals* 5, 870–893.
- Zielinski, R.A., 1985. Element mobility during alteration of silicic ash to kaolinite—a study of tonstein. *Sedimentology* 32, 567–579.
- Zielinski, R.A., Budahn, J.R., 1998. Radionuclides in fly ash and bottom ash: improved characterization based on radiography and low energy gamma-ray spectrometry. *Fuel* 77, 259–267.
- Zielinski, R.A., Finkelman, R.B., 1997. Radioactive Elements in Coal and Fly Ash: Abundance, Forms, and Environmental Significance. U.S. Geological Survey Fact Sheet FS-163-97, 4 pp.
- Životic, D., Gržetić, I., Lorenz, H., Simić, V., 2008. U and Th in some brown coals of Serbia and Montenegro and their environmental impact. *Environmental Science and Pollution Research* 15, 155–161.
- Zubovic, P., 1966. Physicochemical properties of certain minor elements as controlling factors in their distribution in coal. In: *Coal Science* (Given, P.H., ed.), Advances in Chemistry Series, vol. 55. American Chemical Society, Washington, DC, pp. 221–231.