Speciation of Trace Elements in Fossil Fuels and Combustion Byproducts

INTRODUCTION

There is much interest in various trace elements in fossil fuels, their behavior during fossil fuel utilization, especially combustion for electrical power generation, and the hazards that such elements may pose to human health as a result of their release to the environment. The elements of prime concern are listed as potential hazardous air pollutants (HAPs) in Title III of the 1990 Clean Air Act Amendments and include such species as chromium, nickel, arsenic, mercury, etc. Issues of concern include acid-mine drainage, the aqueous leachability of specific trace elements in ash disposal strategies, the formation of aerosol-sized toxic compounds (e.g. nickel subsulfide, Cr(VI) compounds, arsenites, etc.) in airborne particulate matter (PM), the contribution of fossil-fuel derived mercury to the aquatic food chain, and so on.

To understand fully the health or environmental hazard posed by a specific trace element, it is not enough to measure the concentration of the element in the ash or other material of interest, although such information is clearly of importance. Often, more specific information is needed regarding how the element actually occurs or in what species the element is found in the material of interest. Analysis for this type of information is now generally referred to as speciation analysis. For coal, the term, mode of occurrence, is a closely related concept for describing elemental occurrences or species. Information that may be of importance to the speciation of an element includes how it is associated with different major components in the material, its distribution among such components, its chemical forms or species, the oxidation state of the element, etc. Such information complements concentration data and is often more significant for health hazard assessment as different forms of an element are known to differ widely in their toxicity towards humans. In this article, a discussion of speciation analysis of trace elements in coal and ash is presented.

Many of the methods suggested for speciation analysis are indirect and involve simple physical tests that divide the coal or ash into different fractions, followed by determining the concentration of the elements of concern in the different fractions. The method developed in the 1960’s by Zubovic of determining the organic affinity of an element in coal from how it was distributed between different float/sink fractions was one of the first systematic efforts to obtain speciation information about elements in coal. More recently, sequential chemical leaching methods have become popular for speciation analysis of elements in coal because specific stages in the chemical leaching protocol can be associated with a particular type of elemental occurrence (Figure 1). For example, the fraction of an element that dissolves in dilute hydrochloric acid can be assumed to be associated with carbonates or simple monosulfides (ZnS, Fe₉S₈, etc.), whereas those fractions of an element dissolved by hydrofluoric acid or nitric acid can be assumed to be associated with silicates or pyrite.

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The combination of XAFS spectroscopy and leaching protocols is providing detailed information regarding the occurrences of key trace elements in coal and combustion products. Such information is needed to assess most precisely the hazards posed to human health by the release to the environment of HAPs elements in fly-ash products, especially those that are emitted to the ambient atmosphere in ultrafine aerosols.
Speciation of Trace Elements, (cont.)

There is therefore interest in developing more direct methods of determining elemental occurrences, and various electron, X-ray and laser microbeam analysis methods have been used to obtain information to supplement results from indirect methods. Although such methods are very useful for establishing elemental associations and therefore can confirm or refute the importance of specific occurrences, it is often difficult to obtain quantitative information about the speciation with such methods. An alternative method for directly determining elemental speciation is provided by X-ray absorption fine-structure (XAFS) spectroscopy and its derivative technique of X-ray absorption near-edge structure (XANES) spectroscopy. In this method, the XAFS spectrum of a specific element in coal or ash is measured and analyzed to determine the speciation of the element. There are two major drawbacks with this method: (i) the spectrum obtained is the weighted sum of all the different species of the element in the coal or ash; and (ii) the method requires an intense X-ray source, such as a synchrotron, which limits its availability. The combination of the XAFS spectroscopic method with an indirect method readily circumvents the first drawback as variation of the XAFS spectrum with the float/sink or leached fractions of the ash or coal provides more information than the single spectrum of the bulk material. An example is shown in Figure 2. In this figure, four arsenic XANES spectra are shown after each stage in the U.S. Geological Survey’s leaching protocol applied to an Ohio coal. As can be seen, there are two major peaks in the arsenic XANES spectra, one representing arsenic associated with pyrite, the other representing arsenic in the form of arsenate. By applying a least-squares fitting scheme and a calibration procedure, it is possible to quantify the areas under the two peaks and relate them to the percentage of arsenic present in the different forms. Then by knowing the arsenic content of each residue, one can calculate the concentration of arsenic associated with each form. Results for the Ohio bituminous coal are summarized in Table 1.

Examination of Figure 2 and Table 1 clearly reveals the changes brought about on the arsenic speciation in the Ohio coal by the different leaching solutions. Most of the arsenate is removed by HCl leaching, while HF leaching has only a minimal effect on both forms. The peak due to As/pyrite remains unchanged, as does the concentration of As as As/pyrite,
Figure 2. Arsenic XANES spectra of residues after successive sequential leaching in ammonium acetate, 3N HCl acid, conc. HF acid, and 2N HNO₃. The zero point of energy corresponds to the K absorption edge in As₂O₅, which, by definition, is assumed to occur at 11,867 eV.

Figure 3. Ni XANES spectra of coarse and fine PM fractions obtained from combustion of Low Sulfur #6 residual oil showing the variation in the spectra as a result of aqueous leaching. Note the difference in the spectra of the residues after leaching: the spectrum of the leached fine PM₂.₅ fraction derives from Ni ferrite (NiFe₂O₄), whereas the predominant phase in the leached coarse fraction is nickel sulfide (Ni₁⁺S). Zero-point for nickel is assumed to occur at 8,333 eV.

Figure 4. Cr XANES spectra of original and leached PM₂.₅ samples derived from combustion of Montana lignite. The small sharp peaks at about 4 eV are used to determine the Cr(VI) content of the PM sample. In this case, the unleached sample contains about 22 percent of the Cr as Cr(VI) in chromate form. The Cr(VI) content is reduced to 16 percent by aqueous leaching and completely removed by acid leaching. Zero point of energy for chromium is assumed to occur at 5,989 eV.

through the ammonium acetate, 3N HCl and conc. HF leaching stages. Only when nitric acid is applied as the leaching agent is the As/pyrite removed, and then completely so. In this way, the direct speciation method of XAFS spectroscopy provides a valuable check on the assumptions with respect to arsenic made by the indirect leaching method. Further, it clearly demonstrates that the arsenic form associated with HCl leaching is arsenate that is formed by oxidation of the arsenic associated with pyrite.

Similar combined leaching and XAFS investigations have been applied to determine the speciation of trace elements in ash byproducts from coal and residual oil combustion. For fine particulate matter (PM₂.₅), not only does leaching provide sample variation for improved XAFS analysis, but also the aqueous soluble species are the ones most likely to be of concern for health-effect studies, whereas the acid insoluble forms are most likely to be used for source apportionment studies.

XAFS examination of fine aerosol emissions, derived from residual oil fly-ash (ROFA) and separated by a cyclone separator into fine (PM₂.₅) and coarse (PM₁₀) fractions, indicated that the trace metals of concern (V, Ni, Zn, etc.) are present largely as sulfates. However, such sulfates are readily dissolved by aqueous solutions, leaving a residue of various oxide and sulfide phases, including nickel sulfides, (Figure 3) which are known to have highly toxic and
carcinogenic properties. The sulfide phases are the next most abundant phases after sulfates in the coarser PM$_{2.5}$ fractions, but are minor or absent from the finer PM$_{2.5}$ fractions, as the oxide phases are almost entirely associated with the PM$_{2.5}$ fraction.

XANES studies of trace element behavior in coal combustion reveal a difference in chromium speciation between fly-ash and PM$_{2.5}$ byproducts from combustion of western U.S., high Ca, low S subbituminous coals and lignites compared with those from eastern U.S. bituminous coals. Whereas Cr in the eastern ash products is entirely Cr$^{3+}$, up to 40 percent of the Cr in western ash products may be present as Cr(VI) in chromate (Figure 4). As is well known, Cr(VI) is the much more hazardous form of chromium, being both carcinogenic and toxic. Combined leaching and XAFS studies show that acid leaching readily dissolves the Cr(VI) species (Figure 4). The same combined methods also reveal that certain coal-based fly-ash materials may contain a very minor fraction of As(III), the much more toxic oxidation state of arsenic. Such identification is extremely important because even 5 percent of the total arsenic, if identified as As(III) with the balance as As(V), will approximately triple the toxicological threat posed by arsenic.

CONCLUSIONS

The combination of XAFS spectroscopy and leaching protocols to examine trace element occurrences in coal and in ash byproducts from coal and residual oil combustion provides the most detailed speciation information about elements of concern to human health. Such information is necessary for accurate assessment of the hazards to human health posed by fugitive emissions and other releases of coal and oil fly-ash species to the environment.

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I have been fortunate to serve as Chairman of the Kentucky Public Service Commission during an extraordinarily exciting time for the utility industry. The dynamic nature of this industry has made my work incredibly interesting, but also incredibly challenging. In a time when so much emphasis is placed upon “deregulation” of utility services, regulators have to reexamine their processes, procedures, their statutory authority and responsibility. Regulators also have to reexamine their mission, their charge, and their obligation to balance the needs of consumers with those of utility companies.

The stated mission of the Kentucky Public Service Commission is “To provide safe, adequate, and reliable utility service to all Kentuckians at fair, just, and reasonable prices.” Safe. Adequate. Reliable. Fair. Just. Reasonable. It is impossible to understand the full meaning of these words until you have applied them as a test to utility rates and services provided to real people with real needs who are paying real money and expect the lights to come on without fail when they flip the switch. Just how safe is safe? Just how adequate is adequate? Just how fair, just, and reasonable is acceptable to a person whose utility bills comprise a third of their monthly income? These are all questions that we ask with nearly every case before our commission.

But the last few years have brought dramatic changes to the utility industry. While the telecommunications industry has been nationally restructured since 1996, the electricity industry is still struggling to find its way through the shifting utility paradigm. Kentucky is caught in the middle of an incredibly complex web of interests, agendas, and needs as it negotiates through this paradigm shift. In an attempt to ensure that dramatic industry changes do not negatively impact the Commonwealth, the Kentucky PSC has taken an active role on a national level as new electricity industry policy is formed.

Kentucky currently enjoys the lowest electricity rates in the nation. In fact, according to the most recent figures from the Energy Information Administration, Kentucky’s rates are 11 percent lower than the next lowest state – which is Wyoming. Our rates are 40 percent below the national average. These low rates are one of our most valuable assets in the Commonwealth’s economic development efforts. The low rates contribute to the low cost of doing business in the state, and the low cost of living we enjoy.

We used to share this privilege with states like Washington and Oregon in the Northwest that depend largely on hydropower. A massive drought in the region, coupled with the devastating effects of California’s failed electricity restructuring effort sent electricity prices in the region skyrocketing. The Kentucky PSC is working to ensure that our rates do not see the same dramatic increase from restructuring efforts taking place around us.

It is somewhat disturbing that the path national policy makers seem to be heading is toward a national averaging of rates. You may have heard of the “Standard Market Design” initiative that the Federal Energy Regulatory Commission has recently undertaken. While this initiative was born of a desire to create a vibrant wholesale electricity market, it is evolving into something much more than just wholesale market development. States like Kentucky that have maintained retail rate regulation over electricity are finding their ability to protect their electricity customers threatened on many fronts.

Arguably, some in Kentucky will benefit from a vibrant wholesale electricity market. After all, selling our cheap power at higher prices to other states could enhance revenues for power producers and provide an opportunity to sell “coal by wire,” a boost to Kentucky’s coal industry. However, the state will not benefit in the bigger picture if Kentucky’s citizens and economy are asked to subsidize the development of that market. The Kentucky PSC has worked for over 70 years in cooperation with Kentucky’s electricity companies to build an electricity infrastructure that provides reliable service to all Kentuckians at the lowest prices in the nation. We have infrastructure.
adequate to serve our needs, and our citizens and businesses should not be required to subsidize the building of additional infrastructure to accommodate bulk power transfers between Michigan and Florida that happen to flow through our state.

While the Kentucky PSC has worked for several years to make that message heard in the nation, it may be falling on deaf ears. A bill recently passed by the United States House of Representatives and one currently pending before the U.S. Senate seeks to remove the authority and protections that states like Kentucky continue to provide for our citizens. These bills include language that would bring about changes certain to cause electricity rates for Kentucky customers to increase.

Under the proposed legislation, Kentuckians would pay for upgrades to the transmission system, not to accommodate Kentucky customers, but to accommodate power transfers between out of state producers and out of state customers. Kentuckians would no longer be protected by state oversight of resource planning. Kentuckians would not even enjoy state protections against curtailment of service if the transmission grid becomes overloaded due to power transfers moving through the state. These decisions would no longer reside in the hands of the state, but would reside with a regional body far removed from the electorate, and not answerable to any voter. Customers with complaints would not be heard by coming to state decision-makers in Frankfort. Instead, their complaints will be swallowed by the vast regional body, one small voice amid countless “stakeholders.”

Serving as Chairman of the Kentucky PSC certainly has its rewards and challenges. Perhaps no challenge is greater than the struggle that the national electricity policy has become. Our agency will have served Kentucky well if we can succeed in making the voice of the Commonwealth heard in Washington, DC.