

Ultrafine Ash Aerosols from Coal Combustion: Characterization and Health Effects

William P. Linak, Jong-Ik Yoo, Shirley J. Wasson
National Risk Management Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711 USA

Weiyan Zhu
Center for Environmental Medicine, Asthma, and Lung Biology
University of North Carolina
Chapel Hill, NC 27514 USA

Jost O.L. Wendt
Department of Chemical Engineering
University of Utah
Salt Lake City, UT 84112 USA

Frank E. Huggins, Yuanzhi Chen, Naresh Shah, Gerald P. Huffman
Consortium for Fossil Fuel Science
Department of Chemical and Materials Engineering
University of Kentucky
Lexington, KY 40506 USA

M. Ian Gilmour
National Health and Environmental Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711 USA

Prepared for presentation at:
31st International Symposium on Combustion
University of Heidelberg
Heidelberg, Germany
August 6-11, 2006

Colloquium: 6. Heterogeneous Combustion

Word Count:

Abstract:	297
Text:	3670
24 References (M1):	454
7 Figs (M1): $187+224+348+196+220+337+162=$	1673
Total (less abstract):	5797

Corresponding author:

William Linak
U.S. EPA, NRMRL/APPCD, E305-01
Research Triangle Park, NC 27711 USA
Tel: 919-541-5792, Fax: 919-541-0554, Email: linak.bill@epa.gov

Abstract

Ultrafine coal fly-ash particles, defined here as those with diameters less than 0.5 μ m, typically comprise less than 1% of the total fly-ash mass. These particles are formed primarily through ash vaporization, nucleation, and coagulation/condensation mechanisms, which lead to compositions notably different compared to other fine or coarse particle fractions formed by fragmentation. Whereas previous studies have focused on health effects of particulate matter with aerodynamic diameters less than 2.5 μ m (PM_{2.5}) (including both vaporization and fragmentation modes), this paper reports results of interdisciplinary research focused on both characterization and health effects of primary ultrafine coal ash aerosols alone. Ultrafine, fine, and coarse ash particles were segregated and collected from a coal burned in a 20kW laboratory combustor and two additional coals burned in an externally heated drop tube furnace. Extracted samples from both combustors were characterized by transmission electron microscopy (TEM), wavelength dispersive X-ray fluorescence (WD-XRF) spectroscopy, and X-ray absorption fine structure (XAFS) spectroscopy. Pulmonary inflammation was characterized by albumin concentrations in mouse lung lavage fluid after instillation of collected particles in saline solutions and a single direct inhalation exposure. Results indicate that coal ultrafine ash sometimes, but not always, contain significant amounts of carbon, probably soot originating from coal tar volatiles, depending on coal type and combustion device. Surprisingly, XAFS results revealed the presence of chromium and thiophenic sulfur in the ultrafine ash particles. Although the single direct inhalation study failed to reveal significant health effects, the instillation results suggested potential lung injury, the severity of which could be correlated with the carbon (soot) content of the ultrafines. Further, this increased toxicity is consistent with theories in which the presence of carbon mediates transition metal (i.e., Fe) complexes, as revealed in this work by TEM and XAFS spectroscopy, promoting reactive oxygen species, oxidation-reduction cycling, and oxidative stress.

Keywords: Coal, Fly-ash, Ultrafine particles, Emissions, Health effects

1. Introduction

Pulverized coal fly-ash aerosol size distributions appear to possess three distinct modes[1]. These include a coarse fragmentation mode with particle diameters greater than $5\mu\text{m}$, a fine fragmentation mode with diameters between 0.5 and $5\mu\text{m}$, and an ultrafine vaporization mode defined here as particles with diameters less than $0.5\mu\text{m}$. Ambient fine particulate matter (PM) concentrations are regulated as $\text{PM}_{2.5}$ denoting PM with aerodynamic diameters less than $2.5\mu\text{m}$. Yet for primary particles emitted from pulverized coal combustors, $\text{PM}_{2.5}$ is dominated by the fine fragmentation mode which contains particles with essentially the same composition as those in the coarse mode[1]. The ultrafine ash aerosol mode, which comprises only a small portion of the mass of coal fly-ash primary particles less than $2.5\mu\text{m}$, contains particles of different composition formed primarily by the vaporization, nucleation, condensation, and growth of volatile and semi-volatile metals and other elements. Earlier experiments based on instillation of size segregated fly-ash particles in mice[2], showed that ash aerosols from the ultrafine mode were on a mass basis, more toxic than those from either the fine or coarse fragmentation modes.

That ultrafine particles might have adverse toxicological effects different than those of larger fine particles is consistent with recent toxicological results[3,4]. The relative importance of composition and size in determining the health effects of ultrafine particles is not clear. There is, therefore, a need to focus solely on the ultrafine aerosol from important emission sources including coal combustion, without the confounding complications caused by dilution with the more abundant fine fragmentation mode that results when $\text{PM}_{2.5}$ is considered as a whole. This paper follows on the previous work of Linak et al.[1] and Gilmour et al.[2]. It is directed solely towards the ultrafine vaporization mode of coal combustion aerosol, for which a more detailed characterization in terms of particle morphology, speciation, and the consequent health effects is desired. To this end, ultrafine particles were produced both in a 20kW down-fired furnace, and in a 1g/h drop tube furnace. From the former device, ultrafine particles were sampled, size-

segregated, and collected on impactor substrates for detailed analysis and subsequent animal instillation. From the latter device the ultrafine particles were segregated by an in-line five-stage cascade cyclone system, and delivered in real-time to an exposure chamber for direct inhalation studies, or were collected by impaction for parallel instillation experiments. Also of interest is whether ultrafine particle composition depends not only on coal type but also on combustion configuration, and if so, how these differences influence health effects, and what guidance does this provide for the combustion system to provide the most realistic prototype particle for animal exposure studies.

Numerous published studies summarized by Linak and Wendt[5], and more recent work by Seames and Wendt[6] show that submicron and ultrafine coal fly-ash particles typically contain a large number of alkali and alkali earth metals (Na, K, Mg, Ca) and transition metals (Ti, Mn, Fe, Co, Ni, Zn, V, Cr, Cu), and can be enriched in a number of metalloids and other trace elements including Sb, As, Se, S, and Cl. Non-volatile species such as Si are also found in the ultrafine fraction, and this is explained through a mechanism by which reduced forms of the element are volatilized during char burnout and then oxidized and condensed[7,8]. Although not typically the subject of inorganic ash characterization studies, carbon has also been reported to be enriched in submicron particles[9]. Recent work[10,11,12] suggests that ultrafine coal ash particles produced in EPA's 20kW self-sustained combustion furnace burning a Montana subbituminous coal contain significant amounts of carbon. In fact, the ultrafine fraction of this coal contained significantly more carbon than either the fine or coarse fractions. That ash sample was also the one shown by Gilmour et al.[2] to be the most toxic. The purpose of this paper is to synthesize these disparate findings on the ultrafine coal ash aerosol with new data and produce a cohesive picture of how ultrafine particles are formed, their composition, and how they alone might induce adverse health effects.

2. Experimental

2.1. Generation of ultrafine ash

Size classified pulverized coal fly-ash samples were generated, collected, and characterized from two EPA experimental systems. These include a down-fired laboratory-scale (4kg/h) combustor and a bench-scale (1g/h) drop tube furnace. Details regarding the laboratory-scale combustor are provided elsewhere[1,13]. The drop tube furnace is comprised of a 5.080cm inside diameter (ID), 152.4cm long, alumina tube externally heated by a 121.9cm long, three-zone, Lindberg furnace (Model 54679) and Eurotherm programmable controller (Model 812). All three furnace zones were maintained at 1350°C. The alumina tube combustion chamber is sealed by high temperature O-rings and supported at the top and bottom by machined stainless steel (SS) inlet and outlet transition caps attached to flexible aluminum plates designed to accommodate thermal expansion. Pulverized coal (1g/h) and transport air (0.5L/min) are introduced at the top of the furnace along the centerline through a 0.318cm ID SS tube. Additional annular air (12.0L/min) is introduced through a ceramic flow straightener around the coal and transport air. Inlet transport and annular air velocities are matched (~0.5m/s) to minimize turbulent mixing. Reynolds number and residence time within the alumina reactor are approximately 340 and 2s, respectively. At the bottom of the furnace, the conical SS transition cap directs the combustion gases and particles out through a 1.588cm ID SS tube. From the furnace exit, the combustion gases and fly-ash particles are directed to a 134L (45cm x 70cm x 43cm) SS chamber (with Plexiglas door) that can be used for whole animal exposure studies and from which samples can be collected for physical, chemical, and additional indirect toxicological analysis. Alternatively, emission samples can be collected directly from the furnace exhaust. Typically, a five-stage in-stack cascade cyclone (Thermo Electron Corp.) is positioned between the furnace exhaust and chamber inlet to remove fly-ash particles greater than approximately 0.5 μ m diameter[14]. The cyclone flow rate and temperature during this study were 12.5L/min and 80°C, respectively, to provide the proper

particle size cut and prevent water condensation. A subsequent air aspiration pump provides additional dilution and helps moderate the negative pressure and temperature within the chamber.

Pulverized coal is introduced into the drop tube furnace using a modified syringe pump feeding system based on the design of Quann et al.[15]. In brief, an agitated bed of coal particles contained within a 0.8cm ID, 46cm long, glass tube are entrained by transport air flowing over its surface and into a stationary 0.318cm ID SS tube positioned in the center of the glass tube above the coal bed. The glass tube and coal bed are moved by means of a motorized screw towards the stationary tube where the transport air maintains a fixed clearance. A range of stable coal feed rates are available by adjusting the screw speed. A number of external pneumatic vibrators maintain bed agitation and prevent the coal from settling and plugging the stationary tube between the feeder and the furnace. As designed, the feeder can operate up to 15h without supervision and, once empty, the glass tubes containing coal can be replaced within 2min making the system useful for short and long term exposure studies.

2.2. Physico-chemical characterization of ultrafine ash

Emissions from both the laboratory-scale and bench-scale combustors were characterized using a number of extractive measurements. Particle size distributions were determined using a Scanning Mobility Particle Sizer/Aerodynamic Particle Sizer (SMPS/APS, TSI Inc.) system. A 10-stage, 30L/min Micro-Orifice Uniform Deposition Impactor (MOUDI, MSP Inc.) or an 11-stage Berner design low pressure impactor (LPI) were used in conjunction with the cascade cyclone system to separate and collect the fly-ash emissions from three coals into coarse ($>2.5\mu\text{m}$), fine ($>0.5\mu\text{m}$ and $<2.5\mu\text{m}$), and ultrafine ($<0.5\mu\text{m}$) fractions. These fractions were then examined chemically as well as toxicologically using animal instillation techniques. Gas concentrations in the exposure chamber were monitored using continuous emission monitors for CO, CO₂, O₂, NO, NO₂, and SO₂. Particle concentrations were monitored continuously using a Tapered Element

Oscillating Microbalance (TEOM Model 1400A, Thermo Electron Corp.), and verified gravimetrically. Chamber flow rates, gas and particle concentrations, pressure, temperature, and humidity were controlled within specified ranges, and a second air only chamber was used as an exposure control.

Size classified samples of fly-ash from the two experimental combustion systems were analyzed by wavelength dispersive X-ray fluorescence (WD-XRF) spectroscopy, transmission electron microscopy (TEM), and by the element-specific techniques, ^{57}Fe Mossbauer and X-ray absorption fine structure (XAFS) spectroscopies. Ultrafine particles from the drop tube experiments were extracted from the exposure chamber (post cascade cyclone) onto polycarbonate substrates, conditioned and weighed before and after collection, covered with 4 μm Prolene film (Chemplex Industries), mounted in polyethylene holders, and analyzed in-house by WD-XRF spectroscopy (Philips, Model 2404 Panalytical). Ultrafine particles from the laboratory-scale combustor were collected in bulk from appropriate stages of the LPI and deposited onto polycarbonate substrates via 3M double-sided tape. The prepared substrates were weighed using a six-place balance in a conditioned weigh room before and after deposition of the particles, then covered with film and analyzed as above. Intensities were collected by Panalytical's SuperQ software and, inputting the mass and diameter of the loaded filter, were analyzed by UniQuant (Omega Data Systems) using the Fly-Ash calibration. Fine and coarse particles from both the drop tube and laboratory-scale experiments were recovered from appropriate cascade cyclone catches, mixed with liquid binder, and pressed into pellets either alone or layered onto X-ray mix prior to WD-XRF analysis. Bulk samples for TEM, Mossbauer, and XAFS spectroscopy as well as animal instillation experiments were collected from appropriate catches of the cascade cyclone/LPI operated in series. TEM was conducted on a JEOL (Model JEM-2010F) using procedures similar to those described elsewhere[16,17,18]. Mossbauer spectroscopy was conducted using a Halder Mossbauer (Model 351) driving system operating in the symmetric (triangular wave) constant

acceleration mode and a control unit linked to a personal computer by means of Canberra MCS/PHA acquisition boards. Iron Mossbauer spectra were accumulated for up to 10 days and analyzed using combinations of quadrupole (two peak) and magnetic (six peak) absorption units based on a lorentzian peak shape. XAFS spectra were collected either at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, NY, or at the Stanford Synchrotron Radiation Laboratory, Stanford University, CA. Elements anticipated to be volatile in coal combustion and potentially hazardous to health were selected for analysis by XAFS spectroscopy; including S, Cr, Zn, As, and Se. Additional details of XAFS experimentation are described elsewhere[10]. Analysis of XAFS spectra followed conventional data reduction practice; however, more advanced procedures (e.g., least-squares fitting, feff methods, etc.) available in WinXAS and SixPack software packages were also attempted, where appropriate.

2.3. Toxicological characterization of ultrafine ash

Pulmonary instillation studies were carried out in two strains of mice to compare the relative toxicity of the various sizes of coal fly-ash from the three different coals (Montana, Utah, and Illinois). The two strains of mice differ in a single point mutation in the Toll-like receptor 4 (Tlr-4) which has been implicated in controlling inflammatory responses to bacterial lipopolysaccharide (LPS) and particles such as residual oil fly-ash[19]. Briefly, mice were anesthetized with isofluorane and instilled via involuntary aspiration with 100µg of coal fly-ash suspended in 50µL of sterile saline. Eighteen hours later, mice were euthanized and the lungs were cannulated via the trachea and lavaged with three volumes of sterile saline. The lung washes were analyzed for microalbumin as a marker of pulmonary edema (Diasorin Inc.). Additional animals were instilled with saline to produce baseline control data or LPS which causes significant lung injury in the C3H/OUJ mice but less effect in the Tlr-4 mutant (C3H/HeJ) mice. To determine whether inhalation of the ultrafine coal fly-ash generated from the drop tube furnace could cause similar types of lung injury, additional groups of mice were exposed to

atmospheres of 200-400 $\mu\text{g}/\text{m}^3$ of PM for 4h per day for 3 days and similar endpoints were assessed after 18h. This exposure concentration compares to the current EPA 24h PM_{2.5} ambient standard of 65 $\mu\text{g}/\text{m}^3$.

3. Results and discussion

Figure 1 presents the bulk compositions determined by WD-XRF for the various fractions of the three coals examined. As mentioned above, samples from the Montana subbituminous coal were collected during operation of the laboratory-scale 20kW down-fired furnace. Samples from the Illinois and Utah bituminous coals were collected from the bench-scale externally heated drop tube furnace. Proximate and ultimate analyses for the three coals are presented elsewhere[1]. Evident from Fig. 1 is that the coarse and fine fractions for all three coals exhibit similar bulk compositions. However, the ultrafine fractions of each coal exhibit notably different bulk compositions compared to their coarse and fine fractions. Consistent with numerous published studies, these data also suggest ultrafine particle enrichment in a number of elements including S, Cl, Na, K, V, and P, and depletion in a number of relatively non-volatile elements including Si, Al, Ca, Ti, and Mg. Other elements, including Fe, indicate inconsistent or no enrichment trend. Trace indicates the sum of all other elements not specifically listed. All elements were assumed as their stable oxides and, based on known sample mass, the WD-XRF reported the fraction of each sample that was undetermined and presumed to be carbon. While carbon contents for the coarse and fine fractions could be verified, sample size limitations prevented carbon analysis for the ultrafine samples. As a result, the undetermined mass fractions for the three ultrafine samples presented in Fig. 1 can only be presumed to be carbon based on the WD-XRF analysis as well as visual evidence that these samples were black and always notably darker than their coarse and fine counterparts. However, carbon analysis (Sunset Labs Inc. Model 107A) of additional ultrafine samples collected on quartz filters after the TEM, Mossbauer, XANES, and toxicity

analyses were completed indicate that the undetermined fraction (determined by WD-XRF) was a mixture of organic and elemental carbon.

It is possible based on both Mossbauer and XAFS data to augment the WD-XRF data and estimate and compare the approximate relative enrichment of Fe or other selected elements in the coarse, fine, and ultrafine fly-ash fractions. Such estimates are based on the effective Mossbauer absorption per unit mass for Fe and on the XAFS step-height for various elements measured by XAFS spectroscopy, including As (Fig. 2). It should be emphasized that these methods, particularly for XAFS spectroscopy, are only semi-quantitative. However, the trends are informative because of the large differences measured for most elements, as summarized in Table S1.

It is apparent from Table S1 that certain elements, particularly the more volatile elements including S, As, Se, and Pb, fractionate significantly among the three size fractions. However, surprisingly perhaps, Cr for the Utah coal also shows enrichment behavior like that anticipated for a volatile element. Such behavior is also indicated by TEM observations (Fig. 3) where an ultrafine Fe-Cr rich particle is shown attached to the surface of an aluminosilicate cenosphere. This behavior can likely be attributed to the small particle (nano-sized), isolated occurrence of Cr^{3+} oxyhydroxides located within pore space in coal macerals, which has been recently proposed for this element[20]. During coal combustion, such small, isolated occurrences will lead to volatile-like behavior of an element that would otherwise be expected to be refractory.

Iron is of significant concern to human health from inhalation of fine PM from coal combustion because it is typically the most abundant element of variable valency in coal ash. Further, recent studies have shown that it can catalyze the formation of free radicals that might lead to oxidative stress within the cardiovascular system[21]. Mossbauer spectroscopy (Table S1) shows that Fe

occurs fairly uniformly in all fly-ash fractions and indicates that much of it in the ultrafine fly-ash fractions occurs as nano-sized iron oxides (in the form of $\gamma\text{-Fe}_2\text{O}_3$). TEM studies show that such nanoparticles of iron oxides are often associated with carbonaceous materials (Fig. 4). We suspect that such iron oxides form during the oxidative decomposition of pyrite (FeS_2), which is anticipated to be very effective at creating small iron-rich particles. The presence of such small particles of iron oxides in the ultrafine fractions may, in combination with carbon, cycle between oxidation states and contribute significantly to reactive oxygen species formation in the body.

The persistence of soot, originating from coal tars, in fly-ash fractions is indicated by the presence of significant *thiophenic* sulfur in sulfur XANES spectra (Fig. 5). Typically, we observed such components to be largest for the ultrafine fraction, suggesting that there is a higher concentration of soot or carbonaceous materials in these fractions than in the corresponding coarser fractions. Such particles, occurring in conjunction with iron oxides, may contain more oxygen functional groups at their surfaces, which may further enhance the reactivity of the carbonaceous particles.

The inhalation experiments with the Illinois and Utah coals combusted with the drop tube furnace did not result in any significant lung injury compared to air exposed controls. This result was unexpected, given that exposure levels of $200\text{--}400\mu\text{g}/\text{m}^3$ of only ultrafine particles consist of extremely high number concentrations ($\sim 10^6/\text{cm}^3$).

The instillation studies (Fig. 6), however, did show some striking differences in the ability to cause lung injury, according to the type of coal burned and the size fraction of fly-ash examined. The Montana coal seemed to have the largest effect, and this was most evident with the ultrafine fraction although the coarse and fine fractions had higher levels of lung edema than the saline controls. The Utah samples had little to no increase in lung edema suggesting that these samples

were not particularly inflammatory. Similarly, the Illinois coarse and fine samples had quite low effects, whereas the ultrafine fraction caused a robust increase in lung injury. It is now generally accepted that ultrafine particles are more toxic than larger particles of the same chemical makeup (reviewed by Donaldson and Stone[22]), although the exact mechanisms are not clear. Possible reasons include enhanced free radical activity and greater surface area. The observation that the Utah ultrafine particles had no toxicity under these experimental conditions however would argue that chemical composition also likely plays a role in these effects. To that effect we have recently reported that diesel exhaust particles have greater biological effects than ultrafine carbon particles, and that ultrafine carbon particles have more potency in a rat asthma model than fine carbon particles[23]. An important inference can be drawn from Fig. 7, which suggests a correlation between potential lung injury (here marked by an increase in microalbumin) and the carbon (presumed soot) content of the ultrafines. Since this carbon most probably originates as soot formed from coal tars it may well contain aromatic compounds known to be injurious to human health, and as such may behave in a similar way to diesel exhaust where the toxicity is enhanced by additional organic components condensed on the elemental carbon core.

In terms of the strain comparison, the C3H/OUJ animals produced more lung injury in response to LPS instillation as would be expected. In general, however, the Tlr-4 mutant strain (C3H/HeJ) which is LPS-resistant had stronger responses to the coal fly-ash suggesting that this effect is not mediated through Tlr-4 and in fact that Tlr-4 might be protective for this effect. This approach is very useful since it provides information on the biological mechanisms responsible for the health effects and identifies candidate genes which may be involved in development or protection of lung injury.

4. Conclusions

WD-XRF analysis of size classified samples of fly-ash collected from three coals derived from two experimental combustion units indicate that the composition of the ultrafine fraction is significantly different than the coarse and fine fractions and that this is consistent with the different mechanisms that control the formation of primary coal fly-ash particles. Characterization of these fly-ash fractions by TEM and by Mossbauer and XAFS spectroscopies suggest a number of reasons why the ultrafine fraction may be *chemically* more toxic and reactive to the human body. Such reasons include:

- (1) Higher concentrations of hazardous and volatile elements occur in the ultrafine fractions than in either the coarse or fine fractions, with enrichments of up to 50 times observed for some elements.
- (2) Iron oxides are present in nanoparticle forms in the ultrafine fraction, and such forms are likely to be highly reactive leading to oxidative stress when put in contact with tissue. Iron may also be associated with chromium in the ultrafine ash fraction.
- (3) Soot (originating from tars or other carbonaceous entities) comprised a larger fraction of the ultrafine PM compared to the coarser fractions. This correlated with particle toxicity which was most apparent with the ultrafine fractions of the Montana and Illinois coals where it was associated with increased metals and carbonaceous materials.

These conclusions suggest that soot may either be the causal component of the observed health effects associated with ultrafine coal ash particles or that it serves as a surrogate marker for other active agents such as metals which complex to the soot particles. This finding may have implications on a potential health related side effect of combustion modifications in that carbon in the ash from low NO_x burners has been found to consist appreciably of soot[24]. Preliminary data from direct inhalation tests of externally heated drop tube generated ultrafine particles (Utah and Illinois) failed to indicate increased toxicity even though particles number concentrations in the exposure chamber were high ($\sim 10^6/\text{cm}^3$).

Acknowledgements/disclaimer

Portions of this work were sponsored under P.O. 4C-R278NASA with J.O.L. Wendt and Contract EP-C-04-023 with ARCADIS G&M Inc. The analytical work carried out at the University of Kentucky was supported by a NSF CRAEMS grant CHE 0089133. The authors also acknowledge the U.S. Department of Energy for its support of synchrotron facilities in the U.S. The authors are grateful to Mrs. Mary Daniels and Liz Boykin for excellent technical assistance in the health effects studies. The research described in this article has been reviewed by the Air Pollution Prevention and Control Division, U.S. EPA, and approved for publication. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

References

1. W.P. Linak, C.A. Miller, W.S. Seames, J.O.L. Wendt, T. Ishinomori, Y. Endo, S. Miyamae, *Proc. Combust. Inst.* 29 (2002) 441-447.
2. M.I. Gilmour, S. O'Connor, C.A.J. Dick, C.A. Miller, W.P. Linak, *J. Air & Waste Manage. Assoc.* 54 (2004), 286-295.
3. G. Oberdorster, E. Oberdorster, J. Oberdorster, *Environ. Health Perspectives* 113 (7) (2005) 823-839.
4. L. Calderon-Garciduenas, *Central Nervous System Effects: Are Particles a Risk Factor for Alzheimer's Disease?* International Congress on Combustion By-Products and Their Health Effects, University of Arizona, Tucson AZ, 2005.
5. W.P. Linak, J.O.L. Wendt, *Fuel Processing Technol.* 39 (1994) 173-198.
6. W.S. Seames, J.O.L. Wendt, *Fuel Processing Technol.* 63 (2000) 179-196.
7. A.F. Sarofim, J.B. Howard, A.S. Padia, *Combust. Sci. Technol.* 16 (1977) 187-204.
8. R.J. Quann, A.F. Sarofim, *Proc. Combust. Inst.* 19 (1982) 1429-1440.
9. R.C. Flagan, D.D. Taylor, *Proc. Combust. Inst.* 18 (1981) 1227-1237.
10. T. Shoji, F.E. Huggins, G.P. Huffman, W.P. Linak, C.A. Miller, *Energy & Fuels* 16 (2) (2002) 325-329.

11. F.E. Huggins, G.P. Huffman, W.P. Linak, C.A. Miller, *Environ. Sci. Technol.* 38 (6) (2004) 1836-1842.
12. Y. Chen, N. Shah, F.E. Huggins, G.P. Huffman, W.P. Linak, C.A. Miller, *Fuel Processing Technol.* 85 (6-7) (2004) 743-761.
13. W.P. Linak, C.A. Miller, J.O.L. Wendt, *J. Air & Waste Manage. Assoc.* 50 (2000) 1532-1544.
14. SRI Procedure Manual for the Recommended ARB Sized Chemical Sample Method (Cascade Cyclones), Report No. SoRI-EAS-86-467, Southern Research Institute, 1986.
15. R.J. Quann, M. Neville, M. Janghorbani, C.A. Mims, A.F. Sarofim, *Environ. Sci. Technol.* 16 (11) (1982) 776-781.
16. S.J. Wasson, W.P. Linak, B.K. Gullett, C.J. King, A. Touati, F.E. Huggins, Y. Chen, N. Shah, G.P. Huffman, *Environ. Sci. Technol* 39 (22) (2005) 8865-8876.
17. Y. Chen, N. Shah, F.E. Huggins, G.P. Huffman, *Environ. Sci. Technol.* 39 (2005a) 1144-1151.
18. Y. Chen, N. Shah, F.E. Huggins, G.P. Huffman, A. Dozier, *J. Microscopy* 217 (2005b) 225-234.

19. H.Y. Cho, A.E. Jedlicka, R. Clarke, S.R., Kleeberger, *Physiol. Genomics* 22 (1) (2005) 108-117.
20. F.E. Huggins, G.P. Huffman, *Int. J. Coal Geol.* 58 (3) (2004) 193-204.
21. K.R. Smith, A.E. Aust, *Chem. Res. Toxicol.* 10 (1997) 828-834.
22. K Donaldson, V. Stone, *Ann. Inst.Super Sanita* 39 (3) (2003) 405-410.
23. P. Singh, M. Madden, M.I. Gilmour, *J Immunotoxicology* (2) (2005) 41-49.
24. J.M. Veranth, D.W. Pershing, A.F. Sarofim, J.E. Shield, *Proc. Combust. Inst.* 27 (1998) 1737-1744.

List of figures

Fig. 1. Bulk composition of size classified coal fly-ash particles determined by WD-XRF analysis. C/Und indicates undetermined fraction presumed carbon.

Fig. 2. Arsenic XAFS data (before normalization) for the coarse, fine and ultrafine fly-ash fractions derived from the Utah coal. Note the large difference in the absorption effect for the three ash fractions. The step-height, defined as the difference in absorption between the pre-edge and the post-edge regions of the XAFS spectrum, is approximately proportional to the arsenic content of the fly-ash fraction.

Fig. 3. Image of a micron-sized aluminosilicate cenosphere for the fine fly-ash fraction derived from the Utah coal to which is attached (indicated by the arrow) an ultrafine Fe-Cr particle at the surface. EDX spectra of the cenosphere (top) and arrowed particle (bottom) are also shown.

Fig. 4. Transmission electron micrograph and selected area electron diffraction (SAED) pattern from circled area (inset) of an ultrafine particle agglomerate derived from the Utah coal consisting of carbonaceous and iron-rich particles. SAED pattern is indexed to the spinel form of iron oxide ($\gamma\text{-Fe}_2\text{O}_3$).

Fig. 5. Sulfur XANES data for the coarse, fine, and, ultrafine fly-ash fractions derived from the Montana coal. The small peak at about 2473.3eV in the lowest spectrum represents ~5% of the total sulfur in the ultrafine fraction that is present in thiophenic or similar aromatic structures in the unburnt carbon.

Fig. 6. Concentration of microalbumin in lavage fluid of C3H/HeJ and C3H/OUJ mice 18h after instillation with 100 μg of different size and source of coal fly-ash particles or bacterial

lipopolysaccharide (LPS). Data are presented as fold increase over saline controls. N=6-8 per treatment group.

Fig. 7. Microalbumin in lavage fluid (relative to saline) of C3H/HeJ mice vs. carbon/undetermined mass fraction in each size classified coal fly-ash sample.

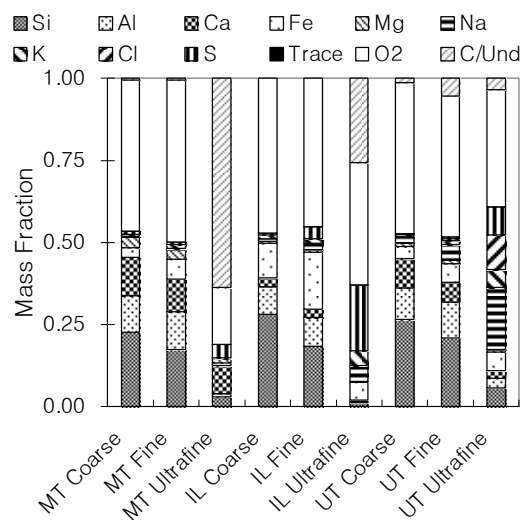


Fig. 1. Bulk composition of size classified coal fly-ash particles determined by WD-XRF analysis. C/Und indicates undetermined fraction presumed carbon.

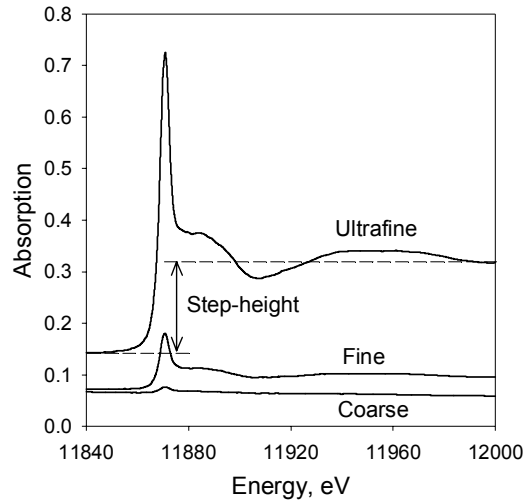


Fig. 2. Arsenic XAFS data (before normalization) for the coarse, fine and ultrafine fly-ash fractions derived from the Utah coal. Note the large difference in the absorption effect for the three ash fractions. The step-height, defined as the difference in absorption between the pre-edge and the post-edge regions of the XAFS spectrum, is approximately proportional to the arsenic content of the fly-ash fraction.

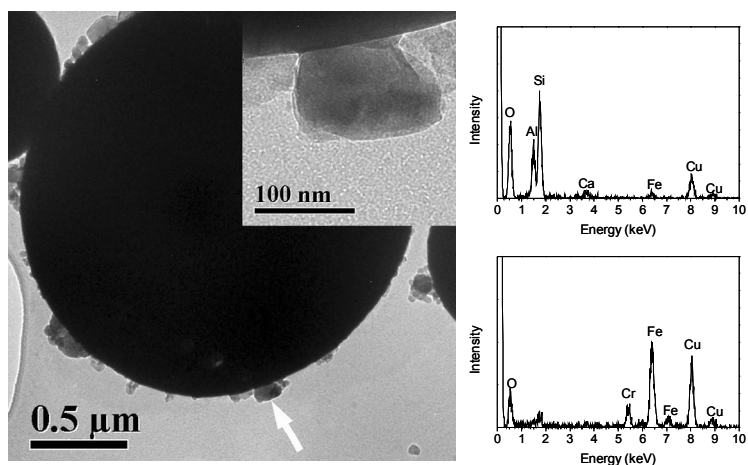


Fig. 3. Image of a micron-sized aluminosilicate cenosphere for the fine fly-ash fraction derived from the Utah coal to which is attached (indicated by the arrow) an ultrafine Fe-Cr particle at the surface. EDX spectra of the cenosphere (top) and arrowed particle (bottom) are also shown.

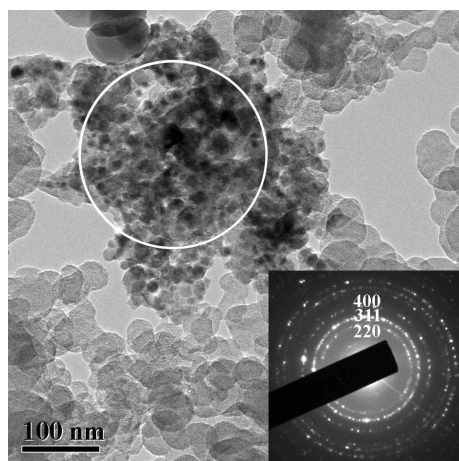


Fig. 4. Transmission electron micrograph and selected area electron diffraction (SAED) pattern from circled area (inset) of an ultrafine particle agglomerate derived from the Utah coal consisting of carbonaceous and iron-rich particles. SAED pattern is indexed to the spinel form of iron oxide ($\gamma\text{-Fe}_2\text{O}_3$).

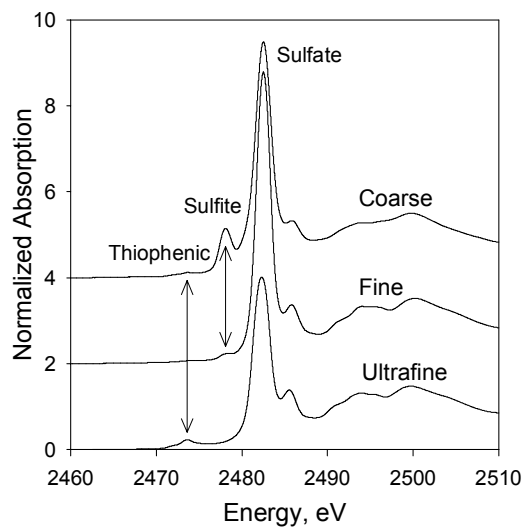


Fig. 5. Sulfur XANES data for the coarse, fine, and, ultrafine fly-ash fractions derived from the Montana coal. The small peak at about 2473.3eV in the lowest spectrum represents ~5% of the total sulfur in the ultrafine fraction that is present in thiophenic or similar aromatic structures in the unburnt carbon.

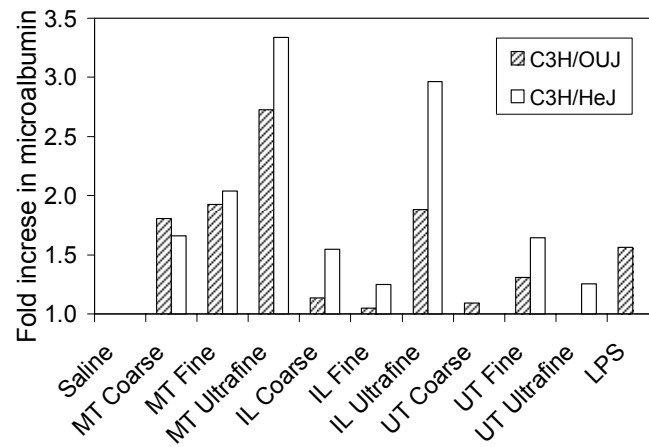


Fig. 6. Concentration of microalbumin in lavage fluid of C3H/HeJ and C3H/OUJ mice 18h after instillation with 100 μ g of different size and source of coal fly-ash particles or bacterial lipopolysaccharide (LPS). Data are presented as fold increase over saline controls. N=6-8 per treatment group.

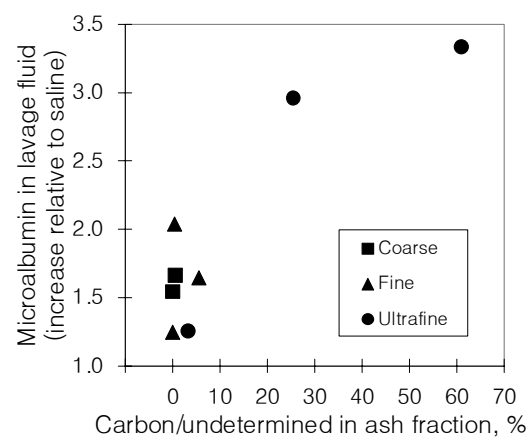


Fig. 7. Microalbumin in lavage fluid (relative to saline) of C3H/HeJ mice vs. carbon/undetermined mass fraction in each size classified coal fly-ash sample.