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Formation of Fine Particles from Residual Oil Combustion: Reducing Nuclei through the Addition of Inorganic Sorbent

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Abstract−The potential use of sorbents to manage emissions of ultrafine metal nuclei from residual oil combustion was investigated by using an 82-kW-rated laboratory-scale refractory-lined combustor. Without sorbent addition, baseline measurements of the fly ash particle size distribution (PSD) and chemical composition indicate that most of the metals contained in the residual oil form ultrafine particles (~0.1 μm diameter). These results are consistent with particle formation via mechanisms of ash vaporization and subsequent particle nucleation and growth. Equilibrium calculations predict metal vaporization at flame temperatures and were used to define regions above the dew point for the major metal constituents (iron [Fe], nickel [Ni], vanadium [V], and zinc [Zn]) where vapor-phase metal and solid-phase sorbents could interact. The addition of dispersed kaolinite powder resulted in an approximate 35% reduction in the ultrafine nuclei as determined by changes to the PSDs as well as the size-dependent chemical composition.

Key words: Ultrafine Particles, Heavy Metals, Fuel Oil Combustion, Particle Size Distribution, Sorbent

INTRODUCTION

Airborne fine particulate matter (PM) has recently become the subject of considerable environmental interest due to the results of a number of studies correlating short-term exposures to ambient levels of fine PM with acute adverse health effects [Wilson and Spengler, 1996; U.S. EPA, 1996; Bachmann et al., 1996; Wolff, 1996]. Consequently, ambient concentrations and source emissions of PM smaller than 2.5 μm in aerodynamic diameter ($PM_{2.5}$) face increased regulation [Federal Register, 1997]. Numerous theories exist to explain the mechanisms causing physiological damage. Health effects studies have identified theories related to ambient particle composition that appear to exacerbate adverse health effects, including the presence of transition metals (e.g., copper [Cu], iron [Fe], nickel [Ni], vanadium [V], and zinc [Zn]) [Dreher et al., 1997] and aerosol acidity. In addition to particle composition, another apparent factor influencing health impacts is the presence of ultrafine particles (<0.1 μm diameter) [U.S. EPA, 1996]. All these characteristics, transition metals, acidity, and ultrafine size, are exhibited by the PM generated from the combustion of residual fuel oils.

Whereas previous work examined the physical and chemical characteristics of fine PM from fuel oil combustion [Miller et al., 1998] and determined effects of combustor design on differences in emissions [Linak et al., 2000], the research presented here focuses on the potential of sorbent addition to reduce the emission of ultrafine ash nuclei from a residual oil fired refractory lined combustor. Particle size distributions (PSDs) and size-dependent chemical compositions were compared without and with sorbent injection. Experimental results were compared to predictions of an equilibrium chemistry model and also to an aerosol growth model. While not applied previously to fuel oil combustion, sorbent addition has been examined by a number of research groups as a means to control toxic metal emissions from incineration systems [Scotto et al., 1992; Linak et al., 1995; Shin et al., 1995; Yang et al., 1999, 2001; Davis et al., 2000; Linak, 2000].

EXPERIMENTAL

1. Experimental Protocol

Experiments were conducted using EPA's horizontal refractory-lined "Rainbow" combustor, which is designed to simulate the time/temperature environments of larger utility boilers and incinerators. This combustor is equipped with an 82-kW-rated (59-kW operated), International Flame Research Foundation (IFRF), moveable-block, variable-air swirl burner which incorporates an air-atomizing oil nozzle positioned along its center axis and annular swirling air to promote flame stability (IFRF Type 2 flame, swirl No.=1.48). Gas and particle samples were taken from available stack locations where temperatures were ~760 K. This combustor operates at high temperatures with low quenching rates (~200 K/s), resulting in particle emissions containing very little unburned carbon and approximating emission concentrations from large oil-fired utility boilers. Fig. 1 shows a diagram of the laboratory-scale refractory-lined combustor. The experiments presented here utilized a high-sulfur No. 6 fuel oil, the composition of which is presented in Table 1.

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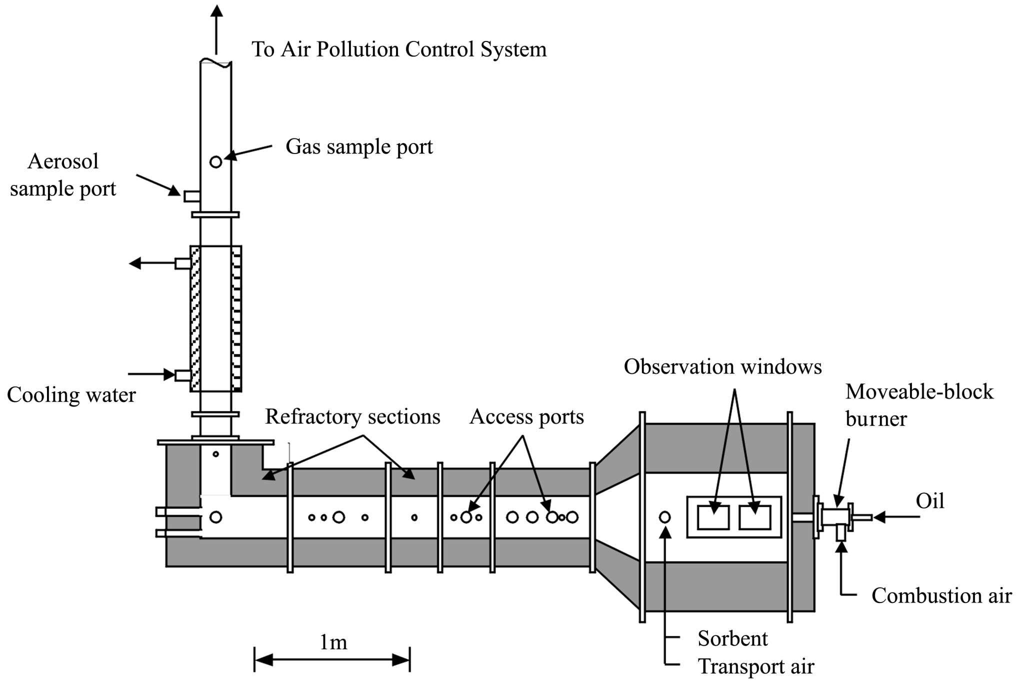

Fig. 1. EPA refractory-lined combustor.

Table 1. Ultimate analysis, concentration of major metals and calorific value of oil

Water (%)	0.3
Carbon (%)	83.3
Hydrogen (%)	8.98
Nitrogen (%)	0.31
Sulfur (%)	2.35
Ash (%)	0.1
Oxygen (%)	4.71
Vanadium (μg/g)	146
Nickel (μg/g)	132
Iron (μg/g)	48.6
Zinc (μg/g)	68.6
Gross calorific value (kcal/kg)	10,077

Powdered kaolinite sorbent (Burgess Pigment Co., Sandersville, GA, No. 40, nominally 1.4 μm diameter) was introduced into the combustor by using a twin-screw loss-in-weight feeder and air eductor (K-Tron model KCL KT20). Transport air introduced at the screw exit entrained the kaolinite and carried it into the combustor at a postflame location between 1,550 and 1,650 K (see Fig. 1). Physical properties and chemical composition of the kaolinite used are shown in Table 2. Sorbent feed rates were determined so that the molar ratio of kaolinite (Al_2O_3-$2SiO_2$) to the concentration of vanadium in the flue gas was 15 : 1. One experiment also examined a kaolinite:vanadium ratio of 60 : 1 (these data are not presented here).

Table 2. Properties of kaolinite used as a sorbent

Specific gravity	2.63	Silica	44.8-45.3 wt%
Average particle size	1.4 μm	Alumina	37.5-39.7 wt%

2. Particulate Sampling and Analysis

Standard EPA Test Method 5 [U.S. EPA, 1994] sampling was used to determine total particulate concentrations. PSDs were determined by electrical mobility, time-of-flight, and inertial impaction techniques for sampled aerosols. Extractive samples were taken by using an isokinetic aerosol sampling system described elsewhere [Linak et al., 1994]. Diluted samples were directed to a TSI Inc. scanning mobility particle sizer (SMPS) configured to yield 54 channels evenly spaced (logarithmically) over a 0.015 to 0.7 μm diameter range and to a TSI Inc. aerodynamic particle sizer (APS) which uses time-of-flight principles to measure particles with diameters 0.5 to 20 μm. Together, these two analyzers can measure PSDs over a range from approximately 0.01 to 20 μm diameter. An MSP Inc. ten-stage, 30 L/min Micro-Orifice Uniform Deposit Impactor (MOUDI) was used to collect physical samples for chemical analysis. As configured, the MOUDI had a working range of between 0.05 and 18 μm diameter. MOUDI samples were examined by x-ray fluorescence (XRF) spectroscopy to examine changes in metal PSDs as a result of sorbent injection.

RESULTS AND DISCUSSION

1. Equilibrium Predictions

Thermochemical predictions were determined with the Chemical Equilibrium Analysis (CEA) code with species listed elsewhere [Linak et al., 1999] and thermochemical data taken from the literature [Chase, 1986; Barin et al., 1973, 1977; Barin, 1989, 1993; TAPP, 1995; Ebbinghaus, 1993, 1995]. The chemical composition for the No. 6 oil (see Table 1) and combustion at a stoichiometric ratio (SR) of 1.2 were used in the CEA calculation since these correspond to the experimental conditions. Fig. 2 presents the predicted element speciation, and more importantly, shows the fractions of condensed-phase species for the four principal metals of interest

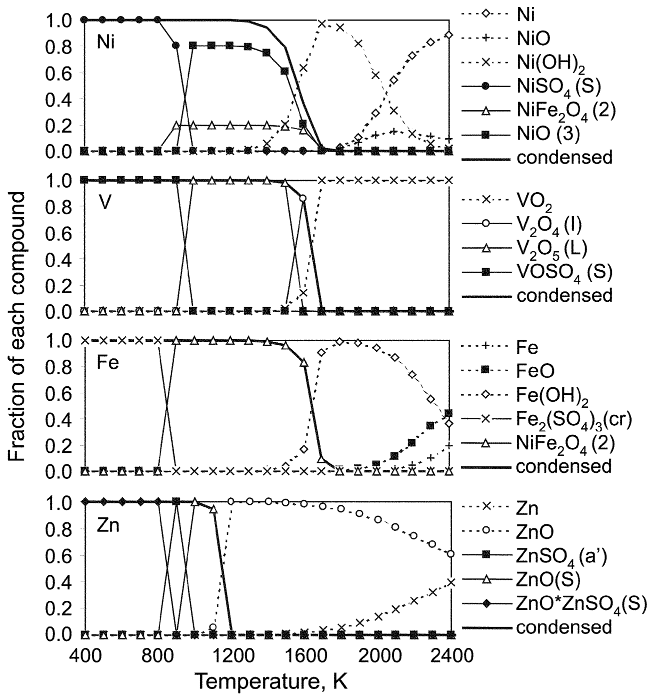

Fig. 2. Equilibrium predictions for major metals from residual oil combustion at SR=1.2.

(Fe, Ni, V, and Zn) as a function of temperature. These equilibrium predictions suggest some Fe, Ni, and V species to be present in vapor phase above 1,400 to 1,500 K, and Zn species to be present in vapor phase above 1,000 K. These temperatures are below those at which the kaolinite sorbent was introduced (1,550-1,650 K). Fe, Ni, and V species were expected to vaporize in the flame zone and nucleate at or closely downstream of the sorbent injection location. Hence, the time available for interaction between the sorbent and vapor-phase species was limited by the combustor access ports, and by mixing, and might explain the partial sorbent utilization observed. Equilibrium also predicts that metal-sulfates are most stable at low temperatures.

2. Particle Size Distributions

Fig. 3 presents representative volume PSDs for the combustion of the No. 6 oil without and with sorbent, and depicts one of at least six data sets that were taken. Representative, rather than average, PSDs are presented in order to preserve detail. These PSDs are composed of the data from two instruments (SMPS and APS). The distinctive submicron mode (between 0.07 and 0.08 μm diameter) for the baseline run (without sorbent) is clearly indicative of particles formed by nucleation and coagulation of vaporized materials. In contrast to the baseline PSD, the PSD with sorbent addition consists of two modes, a smaller submicron mode between 0.05 and 0.06 μm diameters, and a supermicron mode (~1.5 μm diameter), that is consistent with the reported kaolinite particle size of 1.4 μm diameter. Fig. 3 indicates that kaolinite addition reduced the submicron volume (directly related to mass) by approximately 34%. However, it is interesting to note that this reduction did not increase when the kaolinite:vanadium ratio was increased from 15 : 1 to 60 : 1 (data not shown). This may indicate that capture by sorbent was not limited by amount of sorbent present but rather by short residence times between sorbent injection and metal condensation. These experiments have not excluded the possibility of simple condensation of metal species on the kaolinite particle surfaces. This may happen within the combustor, but not within the sampling probe, because of the rapid dilution at the probe tip [Davis et al., 1998]. Ongoing activities are examining the manner in which the metals are bound to the kaolinite through the use of x-ray diffraction (XRD) analysis and the use of progressive leaching with various acidic solvents to determine the relative metal solubility.

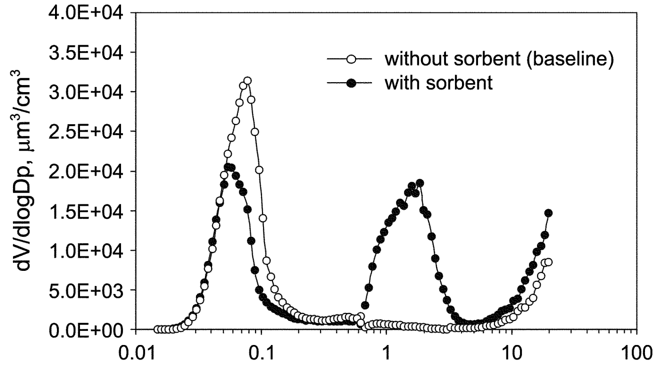

Fig. 3. Measured volume PSDs using SMPS (0.015-0.7 μm) and APS (0.5-20 μm).

3. Metal Composition and Reduction of Nuclei

Particles collected on the MOUDI stages were analyzed for the four principal elements. Fig. 4 presents elemental mass fractions as

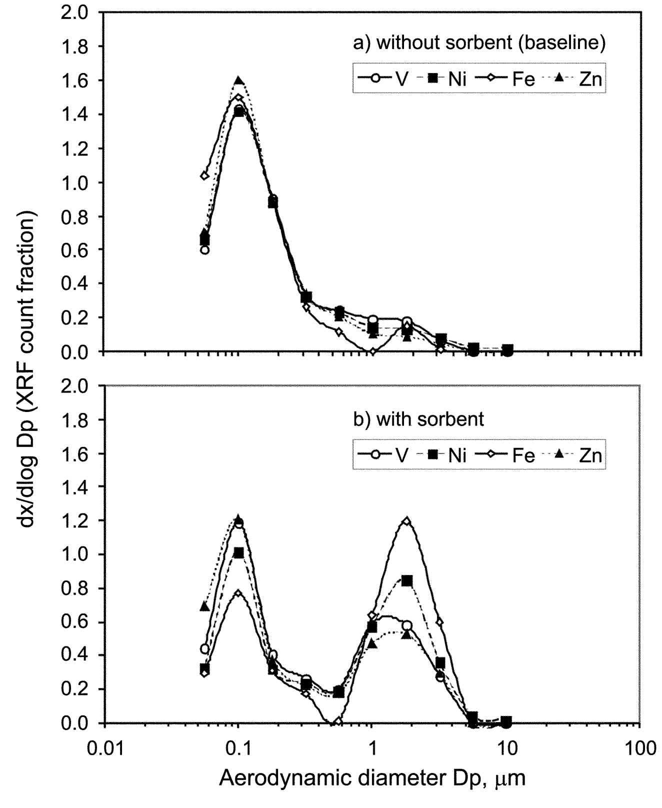

Fig. 4. Measured elemental PSDs for four major metals: a) baseline, without sorbent; b) with sorbent.

Table 3. Reduction of metals in the ultrafine particle size mode, as determined by XRF analysis

	Total intensities (particles <0.56 μm)		Reduction (%)
	without sorbent	with sorbent	
V	7771	5045	35.1
Ni	1507	662.1	56.1
Fe	1409	613.9	56.4
Zn	1686	1019	39.6

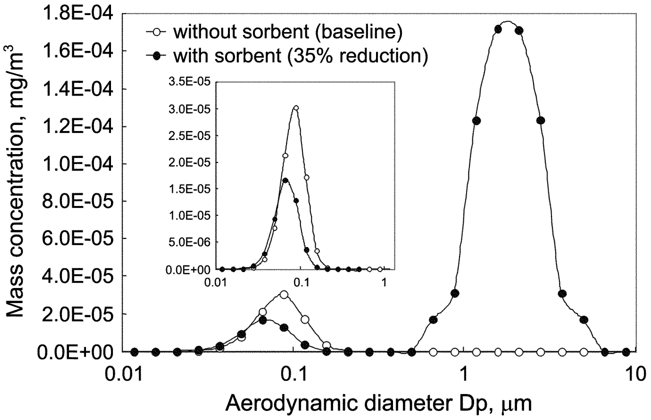

Fig. 5. Theoretical PSD predictions using MAEROS2. PSDs without and with sorbent addition (assuming that sorbent removed 35% of the metal vapor).

determined by XRF vs. particle diameter for Fe, Ni, V, and Zn without and with the addition of kaolinite sorbent. A description of the XRF method employed can be found elsewhere [Linak et al., 2000]. The top and bottom panel show the elemental PSDs without and with sorbent for the No. 6 fuel oil, respectively. The elemental PSDs are similar to the volume PSDs shown in Fig. 3, and the interactions of the metals and sorbent can be calculated in the same manner as above. As shown in Table 3, relative reductions (as measured by XRF counts) of the submicron mode due to sorbent addition range from 35 and 39% for V and Zn to 56% for Ni and Fe. These values are comparable to the reduction (34%) calculated from volume PSD measurements (Fig. 2). These data show that the ultrafine particles consisted of metals, not just sulfuric acid mist, although the latter cannot be excluded. The data also show that the reduction of ultrafines was due to a scavenging of metals (and not necessarily of sulfuric acid) by the sorbent.

4. Model Predictions of Ultrafine Particle Growth

Experimental results were compared to model predictions by using a multicomponent aerosol simulation (MAEROS) code [Gelbard and Seinfeld, 1980]. The purpose of these calculations was to provide insight into mechanisms controlling the observed ash aerosol PSDs both without and with sorbent present. Details regarding the application of MAEROS to combustion environments can be found elsewhere [Linak and Wendt, 1993]. Coagulation was the only mechanism considered.

In the absence of sorbent, the calculated mass concentration of PM (estimated from the ash content in oil and flue gas volume) was 83 mg/m^3. This value compares favorably to the PM concentration measured at 85 mg/m^3 (using EPA Method 5) without sorbent addition (based on an average of three replicate samples). From the measurements noted above, the effect of sorbent addition was taken to be that of decreasing the amount of metal vapor subject to nucleation from 83 mg/m^3 to 54 mg/m^3, and of introducing an additional 680 mg/m^3 of particle mass (kaolinite : vanadium ratio of 15 : 1) with an average diameter of 1.4 μm. MAEROS predictions were used to address the following issues: 1) to what extent are the measured ash aerosol PSDs consistent with ash vaporization, nucleation, and coagulation alone; 2) to what extent does the shift in the mean ultrafine particle diameter reflect the decrease in ash nucleating from the vapor phase; and 3) to what extent is there any interaction through coagulation between the ultrafine metal ash aerosol and the larger sorbent articles?

Results of calculations for the cases without and with sorbent simulations are presented on Fig. 5. In each case, either 83 or 54 mg/m^3 (without and with sorbent, respectively) of metal vapor was assumed to nucleate to form 0.002 to 0.004 μm particles (the difference in vapor mass being adsorbed by the sorbent). With sorbent addition, these nuclei were allowed to coagulate in the presence of the 1.4 μm diameter sorbent particles and this served to examine possible interactions between solid-phase metal nuclei and sorbent particles. In both cases, the aerosol systems were allowed to evolve for 4.1 s, simulating the approximate residence time between the post-flame region and the particle sampling location. The two PSDs presented in Fig. 5 can be compared directly with those in Fig. 3. It is interesting to note that the experimental and predicted baseline (without sorbent) ultrafine modes have similar mean diameters of 0.075 and 0.08 μm, respectively. This supports the hypothesis that all the oil ash vaporized, subsequently to form nanometer scale nuclei and these coagulated in the time available to the observed ultrafine particle size. Likewise, the ultrafine modes with sorbent added resulted in slightly smaller mean diameters of 0.065 and 0.07 μm for the experiments and predictions, respectively. This agreement is consistent with the assumption that particle coagulation is likely the dominant mechanism controlling ultrafine particle growth since coagulation was the only mechanism modeled by MAEROS. Additionally, the MAEROS predictions suggest very little interaction between solid-phase nuclei and the sorbent.

Measurements of the large sorbent particle size mode suggest that a substantial amount of the injected sorbent was lost, presumably due to settling in the horizontal chamber of the combustor. Losses of 70-80% can be calculated based on known sorbent injection rates and integration of the volume PSDs (Fig. 3). The MAEROS runs did not account for this settling behavior, but assumed that 100% of the sorbent was available for interaction with the ultrafine nuclei. Even with this significant difference between model and experiment, the model still accurately predicts the measured growth of the ultrafine mode. Additional runs of MAEROS using different sorbent particle concentrations also failed to significantly change the growth rate of the ultrafine mode (the additional data are not presented here). These results suggest that the extent of metal vaporization and contact between metal vapor and sorbent may be limiting metal capture, and that there is little interaction between solid-phase metal nuclei and sorbent particles. This indicates that, for sorbent injection to effectively reduce the number of ultrafine particles generated by fuel oil combustion, the sorbent must be injected at temperatures where vapor-phase metal species are stable.

CONCLUSIONS

The formation and growth of ultrafine ash nuclei and their reduction by the addition of inorganic sorbent in residual fuel oil combustion were examined. A refractory-lined combustor, which simulates combustion conditions of a utility-scale residual oil-fired boiler, produced an essentially unimodal PSD with a mean diameter of ~0.075 μm when burning No. 6 fuel oil. For oil combusted to maximize the carbon conversion, all the mineral matter is vaporized, which is not the case for coal. Injection of an inorganic sorbent (kaolinite) at high temperatures (>1,500 K), reduced the ultrafine particle volume by approximately 35%, presumably by the interaction of major metal vapors such as Fe, Ni, V, and Zn, with the alumina-silicate sorbent. The size and volume of ultrafine particles from the combustion of oil without and with sorbent are consistent with an evolving aerosol formed by the nucleation of vapor-phase metal ash constituents. Both experimental measurements and modeling predictions were able to discern differences in the mean diameters of the evolving nuclei, and it was noted that lower nuclei number concentrations caused by sorbent addition lead to slower submicron particle growth and a slight shift of the PSD toward smaller diameters.

ACKNOWLEDGMENTS/DISCLAIMER

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REFERENCES

Bachmann, J. D., Damberg, R. J., Caldwell, J. C., Edwards, C. and Koman, P. D., "Review of the National Ambient Air Quality Standards for Particulate Matter: Policy Assessment of Scientific and Technical Information," EPA-452/R-96-013 (NTIS PB97-115406), Office of Air Quality Planning and Standards, Research Triangle Park, NC (1996).

Barin, I., Knacke, O. and Kubaschewski, O., "Thermochemical Properties of Inorganic Substances," Springer-Verlag, New York, NY (1973).

Barin, I., Knacke, O. and Kubaschewski, O., "Thermochemical Properties of Inorganic Substances," supplement, Springer-Verlag, New York, NY (1977).

Barin, I., "Thermochemical Data of Pure Substances," VCH Verlagsgesellschaft, New York, NY (1989).

Barin, I., "Thermochemical Data of Pure Substances," VCH Verlagsgesellschaft, New York, NY (1993).

Chase, M. W. Jr., "JANAF Thermochemical Tables," 3rd ed., parts 1&2, American Institute of Physics, New York, NY (1986).

Davis, S. B., Gale, T. K., Wendt, J. O. L. and Linak, W. P., "Multicomponent Coagulation and Condensation of Toxic Metals in Combustion," Proceedings of the Combustion Institute, Pittsburgh, PA, **27**, 1785 (1998).

Davis, S. B. and Wendt, J. O. L., "Quantitative Analysis of High Temperature Toxic Metal Sorption Rates Using Aerosol Fractionation," *Aerosol Sci. & Technol.*, **33**, 536 (2000).

Dreher, K., Jaskot, R., Lehmann, J. R., Richards, J. H., McGee, J. K., Ghio, A. J. and Costa, D. L., "Soluble Transition Metals Mediate Residual Oil Fly Ash induced Acute Lung Injury," *J. Toxicol. Environ. Health*, **50**, 285 (1997).

Ebbinghaus, B. B., "Thermodynamics of Gas Phase Chromium Species: the Chromium Oxides, the Chromium Oxyhydroxides, and Volatility Calculations in Waste Incineration Processes," *Combust. & Flame*, **93**, 119 (1993).

Ebbinghaus, B. B., "Thermodynamics of Gas Phase Chromium Species: The Chromium chlorides, Oxychlorides, Fluorides, Oxyfluorides, Hydroxides, Oxyhydroxides, Mixed Oxyfluorochlorohydroxides, and Volatility Calculation in Waste Incineration Processes," *Combust. & Flame*, **93**, 311 (1995).

Federal Register, 62 FR 38652, July 18 (1997).

Gelbard, F. and Seinfeld, J. H., "Simulation of Multicomponent Aerosol Dynamics," *J. Colloid Interface Sci.*, **78**, 485 (1980).

Linak, W. P., "Metal Partitioning in Combustion Processes," *Environ. Comb. Technol.*, **1**, 95 (2000).

Linak, W. P., Srivastava, R. K. and Wendt, J. O. L., "Sorbent Capture of Nickel, Lead, and Cadmium in a Laboratory Swirl Flame Incinerator," *Combust. & Flame*, **100**, 214 (1995).

Linak, W. P., Miller, C. W. and Wendt, J. O. L., "Fine Particle Emissions from Residual Fuel Oil Combustion - Characterization and Mechanisms of Formation," 5th International Congress on Combustion Technologies for a Clean Environment, Lisbon, Portugal, July 12-15 (1999).

Linak, W. P., Miller, C. W. and Wendt, J. O. L., "Fine Particle Emissions from Residual Fuel Oil Combustion: Characterization and Mechanisms of Formation," Proceedings of the Combustion Institute, Pittsburgh, PA, **28**, 2651 (2000).

Linak, W. P., Srivastava, R. K. and Wendt, J. O. L., "Metal Aerosol Formation in a Laboratory Swirl Flame Incinerator," *Combust. Sci. & Technol.*, **101**, 7 (1994).

Linak, W. P. and Wendt, J. O. L., "Toxic Metal Emissions from Incineration: Mechanisms and Control," *Prog. Energy Combust. Sci.*, **19**, 185 (1993).

Miller, C. A., Linak, W. P., King, C. and Wendt, J. O. L., "Fine Particle Emissions from Heavy Fuel Oil Combustion in a Firetube Package Boiler," *Combust. Sci. & Technol.*, **134**, 477 (1998).

Scotto, M. V., Peterson, T. W. and Wendt, J. O. L., "Hazardous Waste Incineration: The In-Situ Capture of Lead by Sorbents in a Laboratory Down-Flow Combustor," Proceedings of the Combustion Institute, Pittsburgh, PA, **24**, 1109 (1992).

Shin, B. S., Lee, S. O. and Kook, N. P., "Preparation of Zeolitic Adsorbents from Waste Coal Fly Ash," *Korean J. Chem. Eng.*, **12**, 352 (1995).

TAPP - Thermodynamic Properties Software, V2.2, ES Microware Inc., Hamilton, OH (1995).

U.S. EPA, National Ambient Air Quality Standards for Particulate Matter: proposed decision, 40 CFR, Part 50 (1996).

US EPA, Test Method 5 - Determination of Particulate Emissions from Stationary Sources, in 40 CFR, Part 60, Appendix A, Government Institutes, Inc., Rockville, MD (1994).

Wilson, R. and Spengler, J. D., eds., "Particles in Our Air: Concentrations and Health Effects," Harvard Univ. Press, Cambridge, MA (1996).

Wolff, G. T., "Closure by the Clean Air Scientific Advisory Committee (CASAC) on the Staff Paper for Particulate Matter," EPA-SAB-CASAC-LTR-96-008, U.S. EPA, Science Advisory Board, Washington, DC, June 13 (1996).

Yang, H., Yun, J. S., Kang, M. J., Kim, J. H. and Kang Y., "Capture of Volatile Hazardous Metals Using a Bed of Kaolinite," *Korean J. Chem. Eng.*, **16**, 646 (1999).

Yang, H., Yun, J. S., Kang, M. J., Kim, J. H. and Kang Y., "Mechanisms and Kinetics of Cd and Pb Capture by Calcined Kaolinite at High Temperatures," *Korean J. Chem. Eng.*, **18**, 499 (2001).