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Nickel Speciation of Residual Oil Fly Ash and Ambient Particulate Matter Using X-ray Absorption Spectroscopy

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ABSTRACT

The chemical speciation of Ni in fly ash produced from ~0.85 wt % S residual (no. 6 fuel) oils in laboratory (7 kW)- and utility (400 MW)-scale combustion systems was investigated using X-ray absorption fine structure (XAFS) spectroscopy, X-ray diffraction (XRD), and acetate extraction [1 M NaOAc–0.5 M HOAc (pH 5) at 25 °C]–anodic stripping voltammetry (ASV). XAFS was also used to determine the Ni speciation of ambient particulate matter (PM) sampled near the 400-MW system. Based on XAFS analyses of bulk fly ash and their corresponding acetate extraction residue, it is estimated that >99% of the total Ni (0.38 wt %) in the experimentally produced fly ash occurs as $NiSO_4 \cdot xH_2O$, whereas >95% of the total Ni (1.70 and 2.25 wt %) in two fly ash samples from the 400-MW system occurs as $NiSO_4 \cdot xH_2O$ and Ni-bearing spinel, possibly $NiFe_2O_4$. Spinel was also detected using XRD. Acetate extracts most of the $NiSO_4 \cdot xH_2O$ and concentrates insoluble $NiFe_2O_4$ in extraction residue. Similar to fly ash, ambient PM contains $NiSO_4 \cdot xH_2O$ and $NiFe_2O_4$; however, the proportion of $NiSO_4 \cdot xH_2O$ relative to $NiFe_2O_4$ is much greater in the PM. Results from this and previous investigations indicate that residual oil ash produced in the 7-kW combustion system lack insoluble Ni (e.g., $NiFe_2O_4$) but are enriched in soluble $NiSO_4 \cdot xH_2O$ relative to fly ash from utility-scale systems. This difference in Ni speciation is most likely related to the lack of additive [e.g., $Mg(OH)_2$] injection and residence time in the 7-kW combustion system.

IMPLICATIONS

The presence of a $NiSO_4 \cdot H_2O$ and Ni-rich spinel ($NiFe_2O_4$) mixture and lack of carcinogenic Ni subsulfide (Ni_3S_2) in fly ash and ambient PM associated with a 400-MW residual oil-fired boiler are contrary to the U.S. Environmental Protection Agency's (EPA) Ni inhalation cancer risk assessment (*Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units—Final Report to Congress*, February 1998), where it is assumed that the Ni compound mixture emitted from oil-fired utilities possesses 50% of the cancer potency of Ni_3S_2. This assumption appears to greatly overestimate the Ni inhalation cancer risk from residual oil-fired utilities.

INTRODUCTION

Although coal is the most commonly burned fossil fuel for commercial power generation in the United States, oil combustion accounts for ~9% of the total generating capacity (711,889 MW as of January 1, 1998).[1] Residual (no. 6 fuel) oil, a byproduct from the petroleum-refining industry, is the most widely used for steam generation because of its relative low cost compared with that of lighter oils. Residual oil production in the United States has declined since the late 1980s, but remains substantial at ~0.8 million barrels/day.[2] In addition to the electric utility industry, residual oil is an important fuel for marine and industrial boilers.

Fly ash from residual oil combustion contributes to ambient particulate matter (PM) pollution.[3-6] Controlling fly ash emissions, however, is difficult because a substantial fraction of residual oil ash particles is generally submicron, corresponding to the size range of 0.1–1 μm, where existing industrial gas-cleaning devices are least effective.[7-10] Submicrometer particles are susceptible to human inhalation and, therefore, pose significant health concerns. As part of the U.S. Environmental Protection Agency's (EPA) *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units—Final Report to*

Congress,[11] the inhalation risks associated with elemental (e.g., As, Cd, Cr, Pb, Hg, and Ni) emissions from oil-fired utility boilers were estimated. Nickel is the primary contributor to the inhalation cancer risk estimate for oil-fired utilities because of its relatively high concentration in fly ash emissions and known carcinogenic potency when in a subsulfide form (e.g., Ni_3S_2).[11-13] Many oil-fired utilities have recently had to report Ni emissions because of the EPA's new Toxics Release Inventory requirements for fossil fuel-fired power plants.[14,15]

Uncertainties in Ni speciation measurements greatly affect the inhalation risk estimates because health effects vary significantly for the different chemical species of Ni. For example, Ni_3S_2 is the most carcinogenic Ni species, based on available data from human epidemiology and animal studies.[11-13] The carcinogenicity of water-soluble Ni salts and insoluble Ni oxide compounds, such as $NiSO_4 \cdot xH_2O$ and Ni spinels (e.g., $NiFe_2O_4$), however, is controversial.[11-13,16] In addition to the health effects, as highlighted in the EPA study,[11] the speciation of Ni emissions from oil-fired utility boilers is uncertain and requires additional investigation. Total Ni emissions were measured at most of the 137 power plants that burned oil in 1990, but speciation measurements were conducted at only seven of them. Limited Ni speciation analyses indicate that 3–26% of the total Ni emissions are composed of Ni sulfides, although it is unknown whether Ni_3S_2 was present because of the limitations of the indirect (i.e., operationally defined) speciation method employed, sequential extraction–anodic stripping voltammetry (ASV).[17-19] This method, however, was recently modified to enable the direct measurement of Ni_3S_2, NiS_2, and NiS concentrations.[20,21]

In this investigation, three complementary methods [X-ray absorption fine structure spectroscopy (XAFS), X-ray diffraction (XRD), and acetate extraction–ASV] were used for determining the Ni speciation of residual oil fly ash produced from laboratory (7 kW)- and utility (400 MW)-scale combustion systems. The XAFS technique is especially well suited for determining the Ni speciation of residual oil fly ash because it can directly and nondestructively analyze bulk samples or PM filter samples with ppm sensitivity. XAFS was specifically used to determine whether the relatively insoluble Ni compounds measured by the acetate extraction (1 M NaOAc–0.5 M HOAc solution buffered at pH 5) procedure of the sequential extraction–ASV method[17-19] are composed of Ni_3S_2. In a previous investigation, the proportions of acetate-insoluble Ni measured in ash samples produced in the 7-kW combustion system were much lower, while the relative proportions of acetate-extractable NiX (e.g., X = SO_4, CO_3, or Cl_2) were much greater than previous sequential extraction–ASV measurements of oil ash collected from utility-scale systems.[22] These differences in Ni speciation suggest that the physicochemical properties of ash produced in the 7-kW combustion system are misrepresentative of those produced in utility-scale systems. A primary goal of this investigation was to identify the source(s) of disagreement in Ni speciation results.

In addition to analyzing the primary PM emissions from residual oil combustion, XAFS was used to determine the Ni speciation of ambient PM sampled near the 400-MW combustion system. Although XAFS has been used for determining the chemical speciation of primary combustion PM,[7,22,23] it has only recently been employed to determine the chemical speciation of ambient PM.[24,25] The relative proportions of Ni species identified in the ambient PM and fly ash samples are compared to evaluate the contribution of residual oil combustion to air pollution in the vicinity of the power plant.

EXPERIMENTAL

Residual oils were sampled and analyzed for H_2O, ash, and sulfur using American Society for Testing and Materials (ASTM) Standard Practice D 4057–88 and Methods D 95, D 482, and D 129, respectively. An elemental analyzer (Leeman Labs model CE440) was used for measuring carbon, hydrogen, and nitrogen concentrations of the oils. Inorganic trace element sample preparation was performed using microwave-assisted acid digestion (EPA Method 3050 and ASTM Standard Practice D 5513) followed by analysis using atomic absorption spectroscopy, graphite furnace atomic absorption spectroscopy, or inductively coupled plasma–atomic emission spectroscopy (EPA Method 6010A and 7000 series). Fly ash and ambient PM samples were also analyzed using this approach. Analysis quality was evaluated by analyzing National Institute for Standards and Technology (NIST) Standard Reference Materials (SRM) 1634C (no. 6 fuel oil), 1633B (coal fly ash), and 1648 (urban PM). Analysis results compared favorably to the NIST-certified values, with relative differences of <15%.[8]

Residual oil was burned in a 7-kW downfired cylindrical furnace, described in detail by Benson et al.,[26] at an excess O_2 concentration of ~3 mol %. Internal components of the system are constructed from ceramic or refractory components to eliminate contamination from metal surfaces. Fuel feed and operating parameters (e.g., mean droplet size, temperature, and excess O_2) were adjusted to simulate the actual combustion conditions in a utility boiler. A maximum flue gas temperature of ~1500 °C was attained for ~0.5 sec before the gas stream was cooled at a rate of ~600 °C/sec to the 300 °C sampling location at the convection pass outlet. Although the system was operated to simulate as closely as possible the combustion of residual oil in a utility-scale boiler, certain

common operating practices were not simulated, including a low-NO_x emission control strategy and the addition of alkaline earth metals to suppress sulfuric acid mist [H_2SO_4 (l, g)] and coke formation.

Fly ash and Ni concentrations in the flue gas produced from the 7-kW combustion system were determined in duplicate using EPA Method 29. Samples of oil ash (1.5–2.0 g) were also collected from the entire flue gas stream on heated (≥300 °C) Whatman-type QM-A pure silica microfiber filters.

Residual oil fly ash was sampled isokinetically from the stack of a 400-MW boiler using a modified EPA Method 17 sampling train assembly with the nozzle, probe, and quartz thimble filter maintained at >290 °C, well above the H_2SO_4 dew-point temperature. The sampling train and procedures used in obtaining representative fly ash samples are described in detail by the EPA.[27] The nozzle and filter holder were constructed of quartz and glass, respectively, to prevent contamination of the fly ash by metal surfaces. Representative fly ash samples (~0.6 g) were collected isokinetically from multiple traverse points in the stack. The traverses were conducted through four sampling ports located around the stack at 90° to each other. The sampling approach used is consistent with previous investigations of the Ni speciation of stack emissions from oil-fired utility boilers and sewage sludge incinerators.[17,18,28]

In addition to fly ash stack sampling, PM near the primary air duct of the 400-MW boiler was sampled using a high-volume aerosol-sampling system according to EPA specifications.[29] PM was collected onto a Whatman air-sampling filter. The PM sampling was conducted on November 13, 1998, concurrently with the stack fly ash sampling over a period of 546 min. A variety of quality assurance (QA) and quality control (QC) activities were performed, including trip and field impinger and filter blanks; collection and analyses of duplicate samples; analyses of Ni-, Cr-, and As-spiked impinger solutions; duplicate analyses of NIST SRM 1633B and 1649; and an interlaboratory comparison of Ni fly ash analyses to assess and ensure the quality of emission measurement and ambient PM analysis results. Results of these QA/QC activities are presented by Galbreath et al.[8]

XRD analyses were performed on the oil ash samples to identify crystalline phases. Samples were hand-ground in an agate mortar and pestle and mounted on a "zero"-background quartz plate for analysis. XRD patterns were collected over 5–70° 2θ with a Phillips X'Pert diffractometer system (graphite monochromatized CuK ∝ radiation, 0.02° 2θ steps, 1 sec/step).

The Ni K-edge XAFS spectra were obtained from beam line IV–3 at the Stanford Synchrotron Radiation Laboratory, Stanford University, CA, or from beam line X-19A or X-18B of the National Synchrotron Light Source at Brookhaven National Laboratory, NY. An Ni^0 foil was used as the primary standard.

Ash samples were suspended in the monochromatic X-ray beam in 6-μm-thick polypropylene bags. XAFS spectra were collected using a 13-Ge fluorescent X-ray detector. Spectra were collected at X-ray energies ranging from »100 eV below to ~600 eV above the Ni K-absorption edge (8333 eV). K-edge XAFS spectra were divided into two distinct regions for analysis: the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS) regions. The EXAFS spectral regions were processed using relatively standardized procedures, as described in Brown et al.[30] and Huggins and Huffman[31] to create radial structure function (RSF) spectra that provide structural information, including average interatomic distances and the number and chemical identity of atoms within about a 5-Å radius of the absorbing Ni atom. The position of each peak in an RSF spectrum represents the radial distance from each shell of neighboring atoms to the central Ni atom. However, the RSF spectra are not phase-shift corrected; thus, RSF peak positions are ~0.3–0.5 Å less than the true distances.

XANES and RSF spectra of reagent-grade Ni compounds, acquired in previous investigations,[7,22] were used essentially as "fingerprints" for identifying Ni species. In addition to Ni^0, the following Ni compounds are included in this spectral database: NiS_2, NiS, Ni_3S_2–Ni_7S_6 mixture, NiO, $Ni(OH)_2$, NiSO4·xH2O, $C_4H_6NiO_4{\cdot}4H_2O$, and $NiCO_3$. The Ni-rich spinel end member—$NiFe_2O_4$—was added to the database as part of this investigation. The $NiFe_2O_4$ was synthesized for XAFS analysis by reacting equimolar amounts of stoichiometric green NiO (Aldrich Chemical Co., 99.99%) and Fe_2O_3 (Aldrich Chemical Co., 99.8%) at 1600 and 1400 °C for 2 and 3 hr, respectively, in air. Purity of the $NiFe_2O_4$ was confirmed using XRD. A calculated *a* cell edge of 8.331 ± 0.006 Å compares favorably with the 8.339-Å value reported in Powder Diffraction File No. 10-325 for $NiFe_2O_4$. The $NiFe_2O_4$ was diluted with plastic and pressed into a pellet for XAFS measurements. The XAFS spectrum for $NiFe_2O_4$ was acquired in absorption geometry using a Lytle detector.

After the nondestructive XAFS analyses were performed, all the ash samples were submitted for sequential extraction–ASV analysis. This method involves a five-step extraction procedure to infer Ni speciation.[17-19] However, only the first acetate extraction step was performed to provide enough residue for XAFS analyses. A known weight of ash sample was suspended in a 1 M NaOAc–0.5 M HOAc solution buffered at pH 5 in an 8-mL centrifuge tube and bubbled with N_2 for 10 min. The capped tube was then sonicated in a Bransonic bath for 2 hr at 25 °C and centrifuged at 10,000 rpm for 20 min. In the supernatant, Ni was quantified by ASV of Ni dimethylglyoxime collected

on a hanging Hg drop electrode with a CH-620 electroanalytical system in square-wave voltammetry mode. Concentrations of Ni were obtained using the standard additions method. The residue remaining in the centrifuge tube was repeatedly extracted until Ni was not detected in the supernatant. This extraction procedure is designed to separate soluble Ni compounds from residual oil fly ash. As used in this paper, however, "insoluble Ni" refers to solubility in a 1 M NaOAc–0.5 M HOAc solution buffered at pH 5 and includes Ni^0, NiO, and Ni sulfide and subsulfide compounds. Development of the sequential extraction–ASV Ni speciation method is described by Wong et al.[19]

RESULTS AND DISCUSSION

Residual Oil Compositions

Ultimate and trace element analysis results for the residual oils burned in the 7-kW and 400-MW boilers are presented in Table 1. Two oils, supplied from different primary tanks, were sampled on November 11 and 12, 1998, from the daily holding tank of the 400-MW system. The Mg concentrations in Table 1 are not strictly representative of the oil burned in the 400-MW system, because $Mg(OH)_2$ was injected into the oil downstream from the sampling location primarily to minimize H_2SO_4 (l, g) formation in the boiler. The three oils are intermediate in sulfur concentration relative to the low- and high-sulfur (0.33 and 1.80 wt % S, respectively) oils previously tested in the 7-kW combustion system.[7,22]

Table 1. Residual oil chemical compositions.

System:	7 kW	400 MW	
Date:	Aug 29, 1998	Nov 12, 1998	Nov 13, 1998
H_2O, wt %	0.64	0.41	0.25
S, wt %	0.86	0.80	0.88
Ash, wt %	0.12	0.09	0.04
C, wt %	88.7	87.2	87.3
N, wt %	0.25	0.22	0.32
H, wt %	10.1	10.4	10.6
Al, mg/kg	22	41	17
As, mg/kg	0.052	<0.04	<0.04
Ca, mg/kg	NA[a]	64	31
Cr, mg/kg	NA	0.40	0.50
Fe, mg/kg	30	34	16
Mg, mg/kg	28	18	10
Ni, mg/kg	22	14	11
Si, mg/kg	140	120	50
Na, mg/kg	48	24	13
V, mg/kg	70	32	18

[a]Not analyzed.

Flue Gas Compositions

The concentrations of fly ash, Ni, and several other elements were measured in the residual oil combustion flue gases from the 7-kW and 400-MW systems using EPA Methods 29 and 17, respectively. Sampling was conducted at a flue gas temperature of ~150 °C on both systems. Measurement results from the two methods, however, may not be strictly comparable because of the much higher filter temperature (>290 °C) used during EPA Method 17 sampling.

Ni, Cr, and As were concentrated in the ash collected on the sample filter and probe but not in the absorbing solution of the EPA Method 29 sampling train. This partitioning indicates that at ~150 °C, Ni, Cr, and As are associated with fly ash. Presented in Table 2 are the fly ash and elemental concentrations for the stack gases sampled from the 7-kW and 400-MW systems.

Even though the residual oil burned in the 7-kW system contains higher Ni concentrations relative to the other two oils (see Table 1), the fly ash produced from the 7-kW system is depleted in Ni relative to the fly ash sampled from the 400-MW system. This discrepancy most likely reflects the much lower filter temperature used during the sampling of the 7-kW system. The lower temperature probably promoted fly ash sulfation, thus diluting the Ni concentration. Consistent with the residual oil trace element analysis results in Table 1 for the 400-MW system, the elemental concentration relationships in the fly ash were Fe > V > Ni > Cr > As on November 12, 1998, and V > Fe > Ni > Cr > As on November 13, 1998. Element concentrations were generally greater on November 13, 1998, primarily because of an increase in fly ash concentration.

Fly Ash Compositions

XRD Analyses. XRD analysis results in Table 3 indicate that amorphous components (glass and unburned carbon) and $CaSO_4$ are ubiquitous in the fly ash samples. Fly ash from the 7-kW system is also characterized by the presence of $CaSO_4 \cdot 2H_2O$ and $Na_2Ca[SO_4]_2$. The fly ash sampled

Table 2. Fly ash and elemental flue gas concentrations.

System:	7 kW	400 MW	
Date:	Aug 29, 1998 (n = 2)	Nov 12, 1998	Nov 13, 1998
Fly ash, mg/m^3	58	56	79
Ni, μg/m^3	200	840	1880
Fe, μg/m^3	NA[a]	1650	2100
V, μg/m^3	NA	1360	2210
Cr, μg/m^3	39	32	18
As, μg/m^3	5.6	2.6	4.4

[a]Not analyzed.

Table 3. Fly ash amorphous and crystalline phase assemblages.

System:	7 kW	400 MW	
Date:	Aug 29, 1998	Nov 12, 1998	Nov 13, 1998
Glass and unburned carbon	X[a]	X	X
$CaSO_4$	X	X	X
$CaSO_4 \cdot 2H_2O$	X		
$Na_2Ca(SO_4)_2$	X		
$MgSO_4 \cdot 6H_2O$		X	
$(Na,Ca)_{4-8}Al_6Si_6O_{24}(SO_4,Cl)_{1-2}$			X
MgO		X	
Fe_2O_3			X
AB_2O_4		X[b]	

[a]X denotes that the corresponding amorphous or crystalline phase was identified using XRD; [b]Tentative identification because of peak overlaps in the XRD pattern (see Figure 1).

on November 12, 1998, from the 400-MW system is distinguished from the fly ash sampled on November 13, 1998, by the presence of $MgSO_4 \cdot 6H_2O$ and MgO, and the absence of $[Na, Ca]_{4-8}Al_6Si_6O_{24}[SO_4, Cl]_{1-2}$ and Fe_2O_3. Most likely, $MgSO_4 \cdot 6H_2O$ and MgO are sulfation and decomposition products of the $Mg(OH)_2$ additive that is injected into the oil primarily to mitigate H_2SO_4 (l, g) formation in the boiler. The presence of $MgSO_4 \cdot 6H_2O$ and MgO in the fly ash collected on November 12 suggests that the $Mg(OH)_2$ injection rate was higher on November 12 relative to November 13. Spinel (AB_2O_4; e.g., where A^{2+} = Ni, Fe, or Mg, and B^{3+} = Al, Fe, or V) was also tentatively identified in the November 12, 1998, fly ash sample because, as shown in Figure 1, peak overlaps and weak intensity peaks in the XRD pattern inhibited the positive identification of spinel.

Acetate Extraction–ASV Analyses. Acetate extraction results for the fly ash sampled from the 7-kW and 400-MW systems are presented in Figure 2. The chemical extraction results indicate that soluble Ni species are dominant in the ash produced from the 7-kW system. These extraction results are very similar to those from a previous investigation of low- and high-sulfur oil ash produced in the 7-kW combustion system.[22] Both fly ash samples from the 400-MW system possess much greater Ni concentrations and lower soluble–insoluble Ni ratios relative to the ash sample from the 7-kW combustion system. These Ni concentration and solubility differences reflect variations in Ni speciation or mode of occurrence. The fly ash sampled on November 12 contains more soluble Ni but less insoluble Ni relative to the ash sampled on November 13.

XAFS Analyses. The Ni XANES and RSF spectra for the bulk fly ash sample produced in the 7-kW system, its corresponding acetate extraction residue, $NiSO_4 \cdot 7H_2O$, and Ni_3S_2 are compared in Figures 3 and 4. The Ni XANES and RSF spectra of $NiSO_4 \cdot xH_2O$ indicate that the shape, energy position, and relative intensity of the Ni K-edge crest in the XANES spectra and the prominent RSF peak at an apparent distance of 1.6 Å (uncorrected for phase shift) are characteristic of the $Ni(H_2O)_6$ polyhedra that compose the $NiSO_4 \cdot xH_2O$ (where x = 4, 6, or 7) crystal structure.[32-34] Spectral features for the fly ash sample are consistent with the presence of $NiSO_4 \cdot xH_2O$. Similar spectral features for the corresponding ash residue sample indicate that the acetate extraction did not completely remove $NiSO_4 \cdot xH_2O$ from the ash. Most importantly, no evidence exists in the ash residue spectra for the presence of Ni sulfide or subsulfide compounds.

If present, insoluble Ni sulfide or subsulfide compounds would concentrate by a factor of ~5 in the acetate extraction residue relative to the bulk ash (see Figure 2). A small proportion, >5%, of NiS_2, NiS, or Ni_3S_2 would produce a detectable XANES pre-edge (0–5 eV) feature, as exemplified for Ni_3S_2 in Figure 3, based on signal-to-noise ratio criteria.[7,22] The lack of a pre-edge feature and the presence of prominent peaks at about 20 eV above the Ni K-edge energy in the XANES spectra, and at 1.6 Å in the RSF spectra for the residue ash sample in Figures 3 and 4, suggest that >99% of the Ni occurs as $NiSO_4 \cdot xH_2O$. The oil ash spectra are identical, within analytical uncertainty, to those from a previous XAFS investigation of the Ni

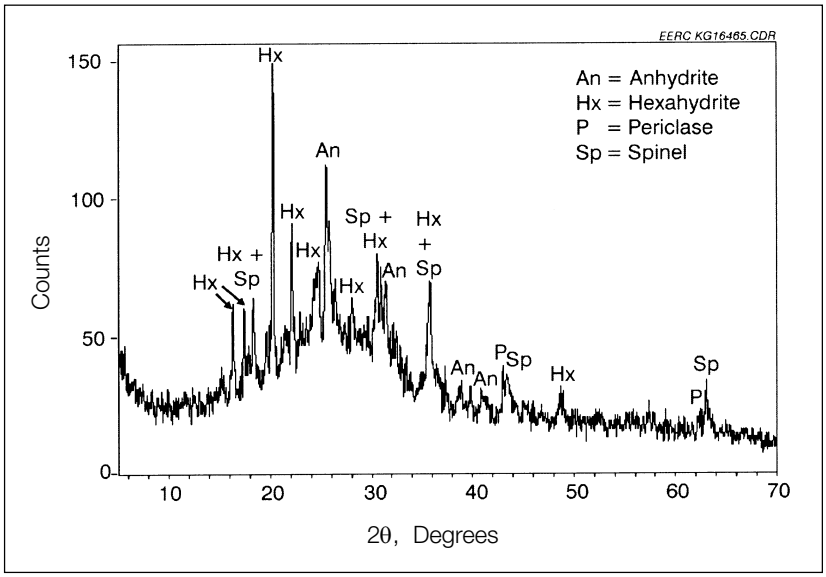

Figure 1. XRD pattern of residual oil fly ash sampled on November 12, 1998, from a 400-MW boiler.

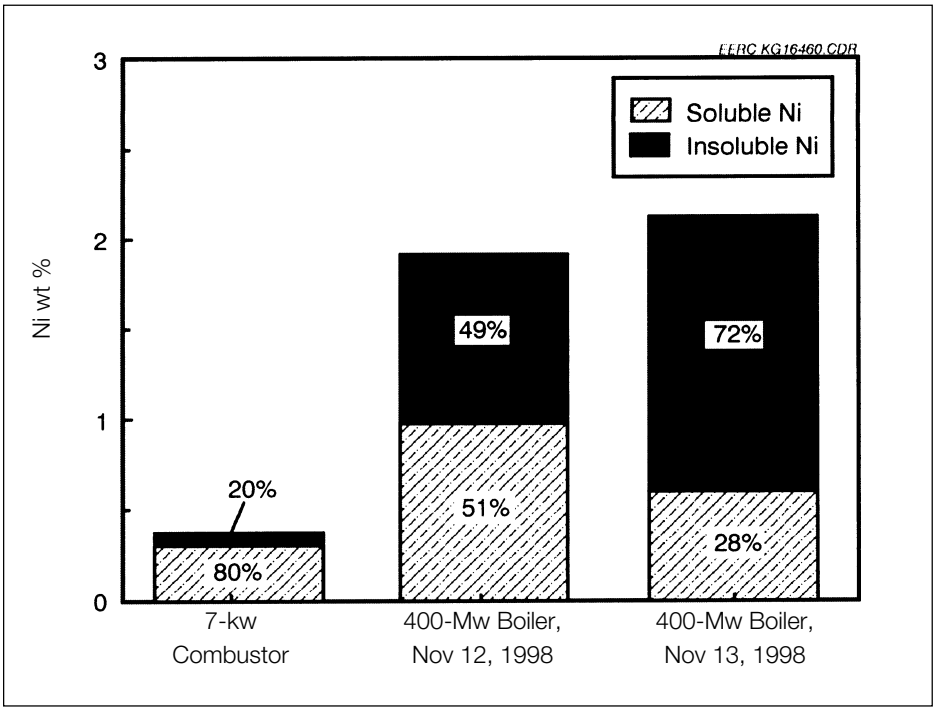

Figure 2. Ni species acetate extraction results for fly ash sampled from the 7-kW and 400-MW combustion systems.

species present in fly ash produced from burning low- and high-sulfur (0.33 and 1.80 wt %, respectively) residual oils in the 7-kW combustion system.[7,22] The dominant species in the three residual oil (low-, medium-, and high-sulfur) ash produced in the 7-kW system is $NiSO_4 \cdot xH_2O$.

The Ni K-edge XANES and RSF spectra for the stack fly ash samples collected on November 12 and 13, 1998, and their corresponding acetate extraction residue are presented in Figures 5 and 6, respectively. The Ni K-edge XANES and RSF spectra for the fly ash and residue are analogous in terms of the number and positions of spectral peaks, but relative peak intensities are much different. These spectral characteristics are consistent with the presence of similar Ni compound assemblages, but with varying concentrations. Comparable to the spectra for the residual oil ash produced in the 7-kW combustion system (Figures 3 and 4), the spectral features in Figures 5 and 6 (e.g., presence of prominent XANES and RSF peaks at about 20 eV and 1.6 Å, respectively) are consistent with the presence of $NiSO_4 \cdot xH_2O$. Spectral features unaccounted for by $NiSO_4 \cdot xH_2O$, most prominent in the extraction residue spectra, include a XANES peak at 35 eV and RSF peaks at apparent distances of 2.7 and 4.8 Å. Spectral comparisons with $NiFe_2O_4$ spectra in Figure 7 indicate that a mixture of $NiSO_4 \cdot xH_2O$ and $NiFe_2O_4$ accounts for all the spectral features in Figures 5 and 6, thus corroborating the XRD evidence in Figure 1 for the presence of spinel. It is unlikely, however, that the spinel in these fly ash is as pure as the $NiFe_2O_4$ reference standard. Cations such as Fe^{2+} and Mg^{2+}, as well as V^{3+} and Al^{3+}, probably substitute for Ni^{2+} and Fe^{3+} in the spinel structure.

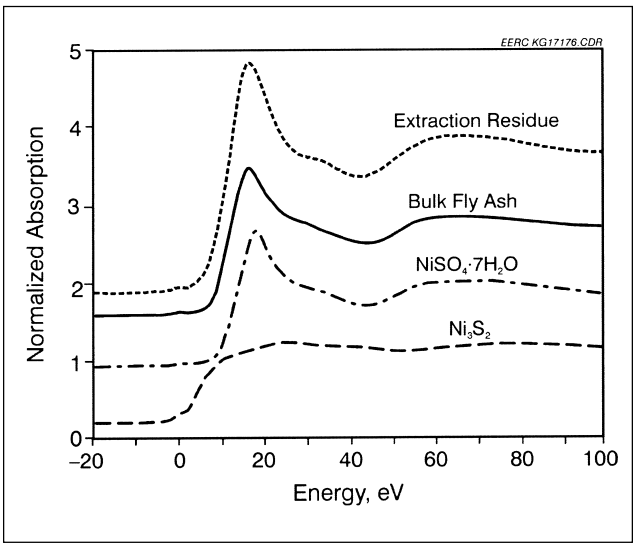

Figure 3. Ni K-edge XANES spectra for oil combustion fly ash produced in a 7-kW combustion system, its corresponding extraction residue, $NiSO_4 \cdot 7H_2O$, and Ni_3S_2. Value of 0 on the abscissa corresponds to the actual Ni K-edge absorption energy of 8333 eV.

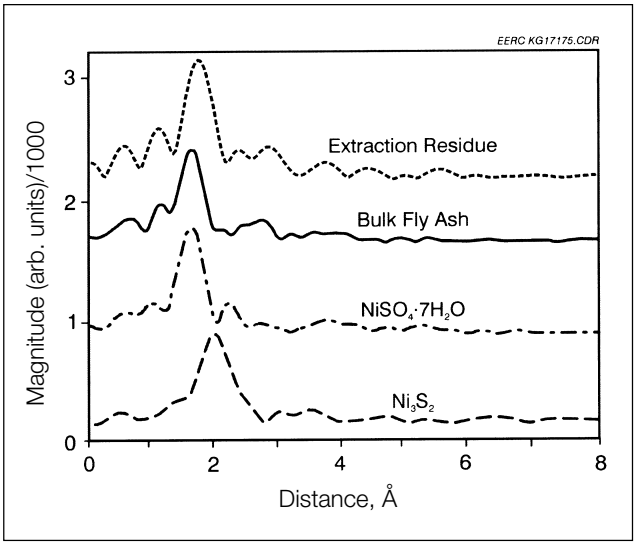

Figure 4. Ni RSF spectra for oil combustion fly ash produced in a 7-kW combustion system, its corresponding extraction residue, $NiSO_4 \cdot 7H_2O$, and Ni_3S_2.

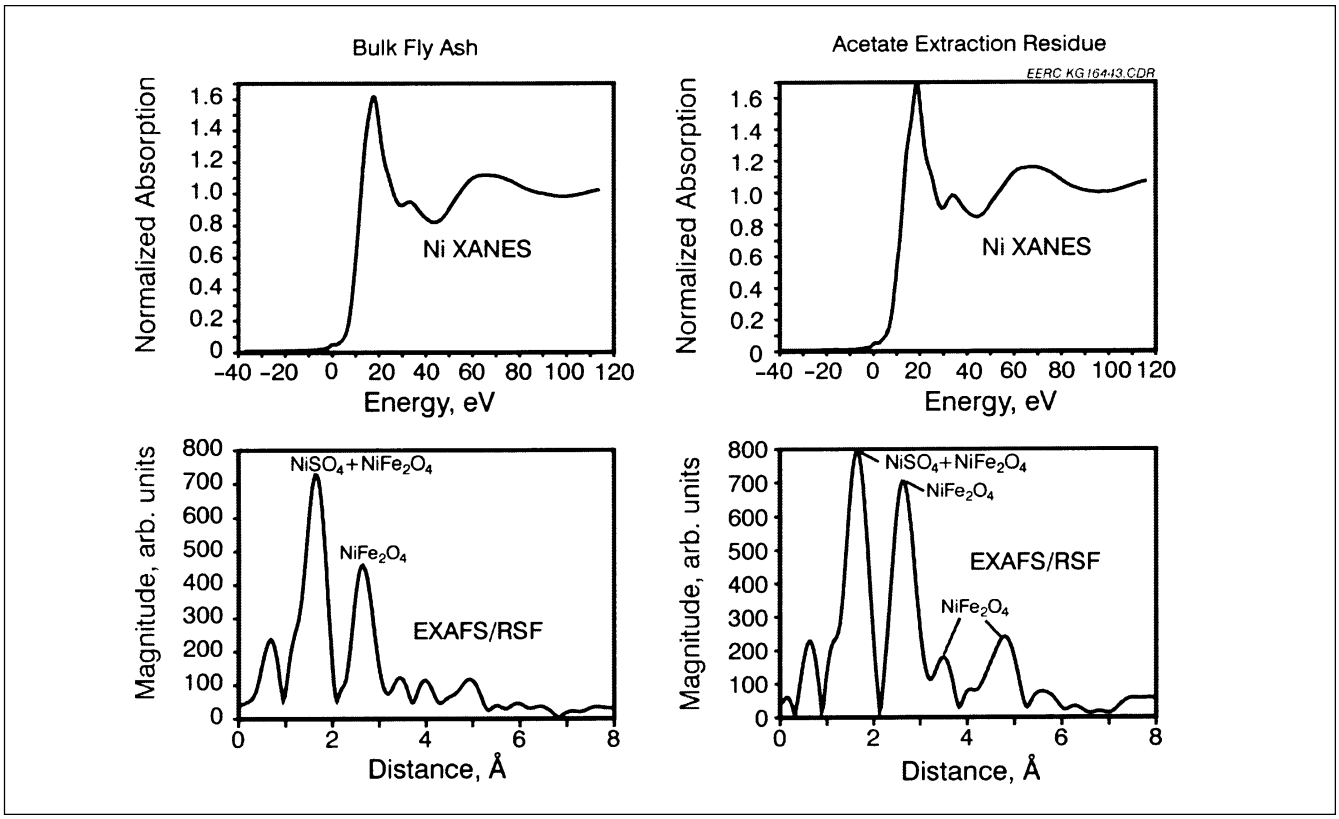

Figure 5. Ni K-edge XANES and RSF spectra for the fly ash sampled from the 400-MW unit stack on November 12, 1998, and its corresponding acetate extraction residue.

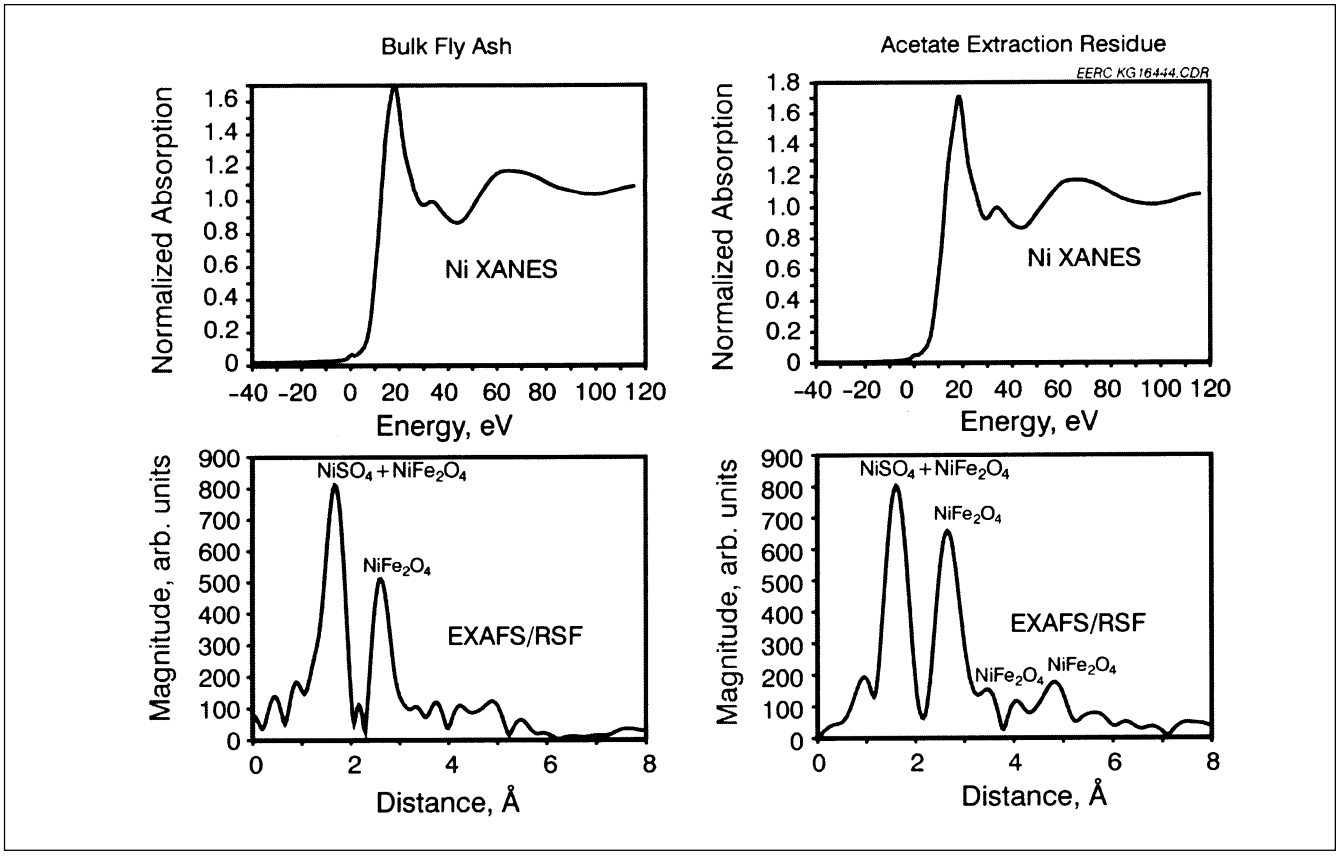

Figure 6. Ni K-edge XANES and RSF spectra for the fly ash sampled from the 400-MW unit stack on November 13, 1998, and its corresponding acetate extraction residue.

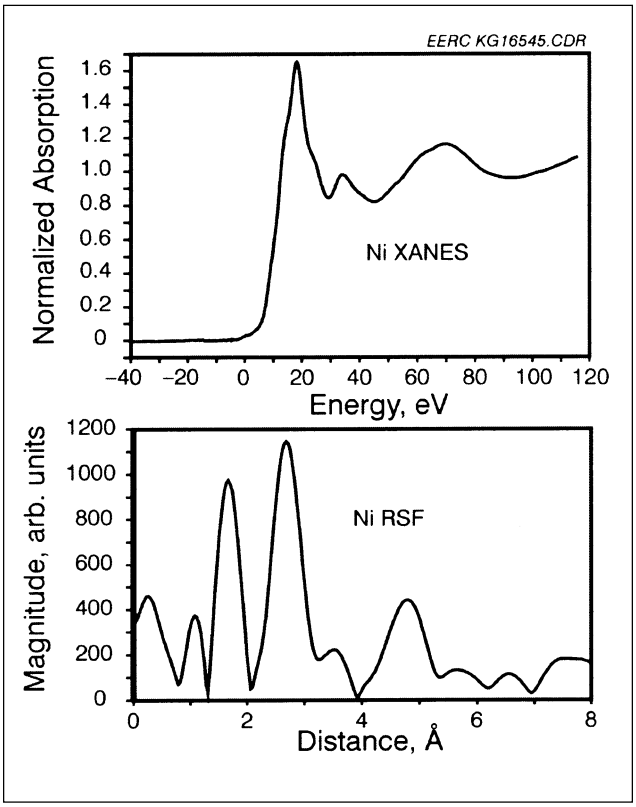

Figure 7. Ni K-edge XANES and RSF spectra for $NiFe_2O_4$.

Comparisons of 1.6- to 2.7-Å peak intensities in the RSF spectra of Figures 5 and 6 provide estimates of $NiSO_4 \cdot xH_2O$ and $NiFe_2O_4$ relative proportions. $NiSO_4 \cdot xH_2O$ is more abundant in the bulk fly ash samples, whereas $NiFe_2O_4$ is significantly more concentrated in the Ni extraction residue. Acetate extracted most of the $NiSO_4 \cdot xH_2O$ from the fly ash samples and concentrated $NiFe_2O_4$ in the residue.

Similar to the oil ash produced in the 7-kW combustion system, no evidence (i.e., Ni K-edge XANES or RSF spectral features) for the presence of a Ni sulfide or subsulfide species exists in the bulk fly ash or acetate-extractable residue samples from the 400-MW system. A Ni K-edge XANES spectral simulation for a mixture of 90% fly ash and 10% NiS, as shown in Figure 8, demonstrates that the presence of a small proportion of NiS produces a detectable pre-edge feature, most pronounced at ~5 eV greater than the Ni K-edge absorption energy. This pre-edge feature is indicative of the covalent nature of Ni–S bonds.[35] The lack of this pre-edge feature in the Ni K-edge XANES spectra of the extraction residue (see Figures 5 and 6), where insoluble $NiFe_2O_4$ and potentially any Ni sulfide and subsulfide species have been concentrated, indicates that Ni sulfide and subsulfide species are either absent or are a very insignificant component of the residual oil fly ash. Based on the spectral simulation in Figure 8 and signal-to-noise ratio criteria, $NiSO_4 \cdot xH_2O$ and $NiFe_2O_4$ account for >95% of the total Ni in the residual oil fly ash.

Ambient PM Composition

Ambient PM and elemental concentrations for air entering the primary fan of the 400-MW system on November 13, 1998, are presented in Table 4. The Ni concentration at the air intake is greater than the average Ni concentrations of ambient air in U.S. and Canadian cities, which range from 0.005 to 0.050 mg/m^3 and 0.001 to 0.020 mg/m^3, respectively.[36, 37] The occurrence of relatively high Ni and other transition-metal concentrations close to residual oil-fired boilers and other point sources, including smelters, has been described previously.[3-6] The transition-metal concentration relationship of Fe > V ≈ Ni for the ambient PM sampled on November 13 is different from the corresponding stack fly ash in Table 2, where V ≈ Fe > Ni, suggesting that other sources are contributing to air pollution in the vicinity of the 400-MW system. Potential sources include additional boiler units at the power plant, marine boilers, and petroleum storage facilities. Alternatively, the differences in interelement concentration relationships may reflect different Fe, V, and Ni transport/deposition characteristics.

The Ni XANES and RSF spectra for the ambient PM sample are presented in Figure 9. These spectra are similar to the spectra of bulk fly ash (prior to chemical extraction) samples shown in Figures 5 and 6. Based on a comparison of the relative 1.6- and 2.7-Å peak intensities in the RSF spectra, however, $NiSO_4 \cdot xH_2O$ is more abundant relative to $NiFe_2O_4$ in the ambient PM sample. Similar to the interelement concentration relationships discussed previously, these differences in $NiSO_4 \cdot xH_2O$ and $NiFe_2O_4$ relative proportions suggest that other oil combustion sources are contributing to Ni air pollution at the site or that $NiSO_4 \cdot xH_2O$ and $NiFe_2O_4$ transport/deposition characteristics are different.

Evaluation of Experimental Combustion Testing

Table 5 shows a comparison of Ni properties of the fly ash produced from intermediate-sulfur (~0.85 wt % S) residual oils in the 7-kW and 400-MW combustion systems. Ash from the 7-kW system is distinguished from the 400-MW system fly ash by possessing a greater proportion of soluble Ni present as $NiSO_4 \cdot xH_2O$. The soluble $NiSO_4 \cdot xH_2O$ enrichment of residual oil fly ash produced in the 7-kW combustion system relative to fly ash from utility-scale systems was also documented by Galbreath et al.[22]

Potential sources for these differences in Ni solubility and speciation are summarized in Table 6. Sampling conditions were generally similar at the 7-kW and 400-MW systems, suggesting that differences in combustion conditions primarily affected fly ash Ni properties. The predominance

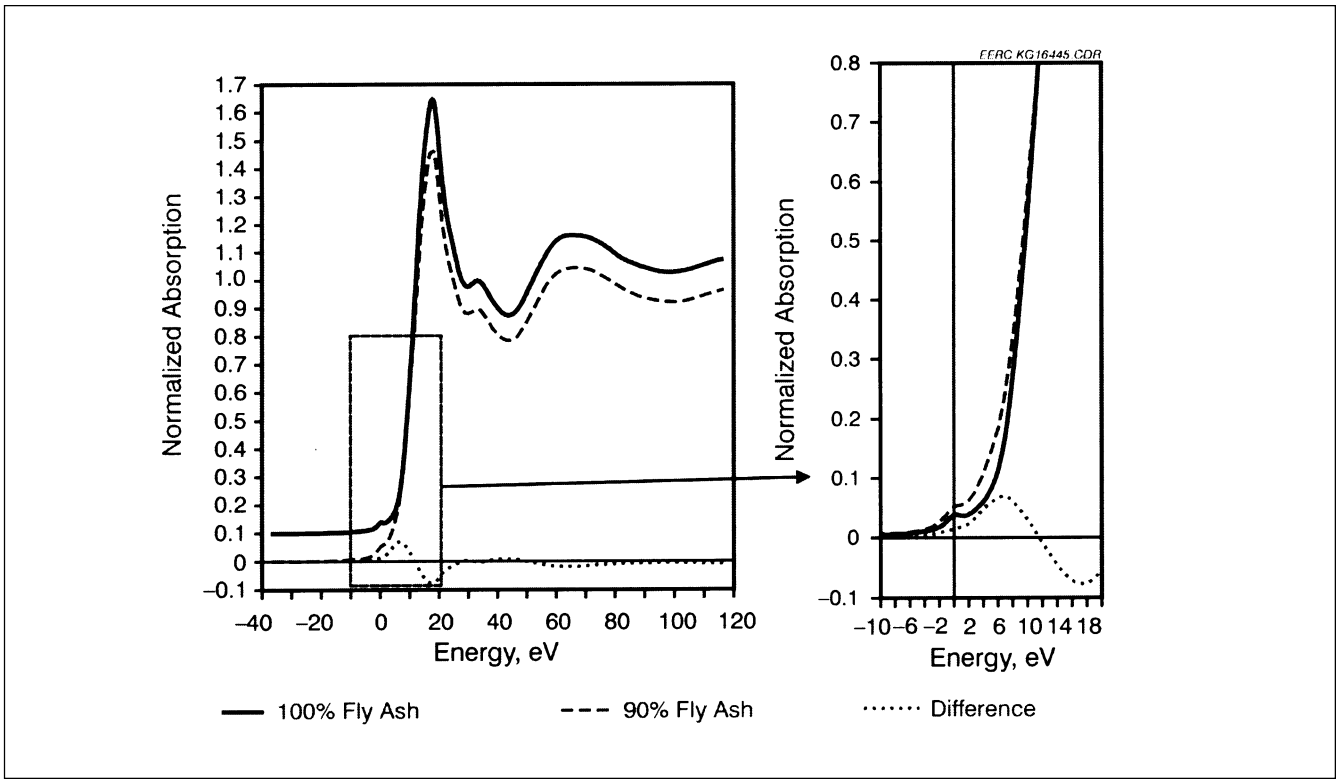

Figure 8. Ni K-edge XANES spectrum for the fly ash sampled from the 400-MW unit on November 13, 1998, and a simulated spectrum resulting from the theoretical addition of 10% NiS to the fly ash. Spectral differences are represented by the dotted line.

of $NiSO_4 \cdot xH_2O$ and lack of $NiFe_2O_4$ in the ash produced experimentally is most likely attributable to differences in residence time–temperature profiles for the two systems and the absence of $Mg(OH)_2$ injection, a SO_x(g) and H_2SO_4 (l, g) sorbent. Trevorite is a refractory metal oxide phase that can be synthesized by reacting stoichiometric mixtures of NiO and Fe_2O_3 at 1600–1100 °C.[38,39] Fly ash precursors and particles in utility-scale combustion systems experience a much longer residence time at 1600–1100 °C relative to fly ash produced in the laboratory-scale system. The lack of residence time at the appropriate temperatures may kinetically inhibit the formation of $NiFe_2O_4$ in the 7-kW combustion system. The $Mg(OH)_2$ injected into the 400-MW system competes with Ni in reacting with SO_x (g) and H_2SO_4 (l, g). The lack of sorbent injection in the 7-kW combustion system most likely promotes Ni sulfation.

Table 4. Ambient PM and trace element concentrations, $\mu g/m^3$.

Analyte	Nov 13, 1998
PM	75.8
Ni	1.01
Fe	3.09
V	1.65
Cr	<0.02
As	<0.01

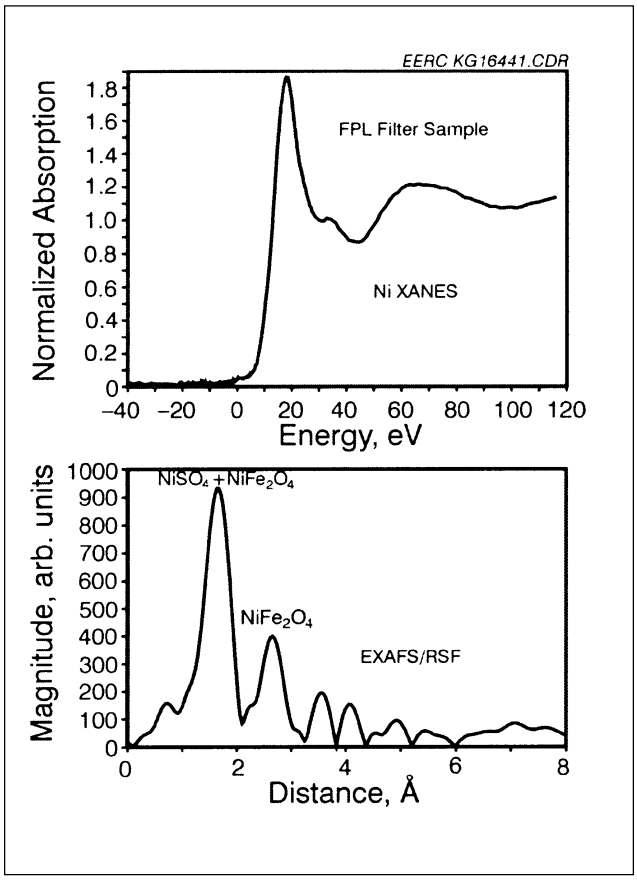

Figure 9. Ni K-edge XANES and RSF spectra for the PM sampled near the 400-MW unit on November 13, 1998.

Table 5. Comparison of fly ash Ni properties produced from intermediate-sulfur residual oils in laboratory- and utility-scale combustion systems.

System:	7 kW	400 MW	
Date:	Aug 29, 1998	Nov 12, 1998	Nov 13, 1998
Soluble/insoluble Ni[a]	4.4	1.0	0.4
Ni species	$NiSO_4 \cdot xH_2O$	$NiSO_4 \cdot xH_2O + NiFe_2O_4$	$NiSO_4 \cdot xH_2O + NiFe_2O_4$

[a]Determined using 1 M NaOAc–0.5 M HOAc (pH 5) at 25 °C.

CONCLUSIONS

The chemical speciation of Ni in fly ash produced from ~0.85 wt % S residual oils in 7-kW and 400-MW combustion systems was analyzed using XAFS, XRD, and acetate extraction–ASV. Fly ash acetate extraction residue were also analyzed using XAFS to investigate the Ni species selectivity of the extraction procedure and to minimize potential XAFS spectral overlaps caused by the presence of multiple Ni species. In addition, XAFS was used to determine the Ni speciation of ambient PM sampled near the 400-MW system. Results from the speciation measurements were used to evaluate the validity of sequential extraction–ASV and experimental combustion testing for characterizing Ni species emissions from oil-fired utility boilers. Conclusions from this investigation are:

- Based on XAFS analyses of bulk fly ash and their corresponding acetate extraction residue, it is estimated that >99% of the total Ni in the experimentally produced fly ash occurs as $NiSO_4 \cdot xH_2O$, whereas >95% of Ni in two fly ash samples from the 400-MW boiler occurs as a mixture of $NiSO_4 \cdot xH_2O$ and $NiFe_2O_4$. Ambient PM near the 400-MW boiler also contains $NiSO_4 \cdot xH_2O$ and $NiFe_2O_4$, but $NiSO_4 \cdot xH_2O$ is more abundant.
- The presence of a $NiSO_4 \cdot xH_2O$–$NiFe_2O_4$ mixture and lack of carcinogenic Ni_3S_2 in fly ash and ambient PM associated with a 400-MW residual oil-fired boiler are contrary to the EPA's Ni inhalation cancer risk assessment,[11] where it is assumed that the Ni compound mixture emitted from oil-fired utilities is 50% as carcinogenic as Ni_3S_2. Apparently, this assumption greatly overestimates the Ni inhalation cancer risk from residual oil-fired utilities.
- An acetate extraction procedure[17-19] that has been used for investigating Ni speciation removes most of the $NiSO_4 \cdot xH_2O$ from residual oil fly ash and concentrates insoluble $NiFe_2O_4$ in extraction residue. Consequently, this procedure underestimates soluble Ni/insoluble Ni.
- Results from this and a previous investigation[22] indicate that residual oil ash produced in the 7-kW combustion system are depleted in insoluble Ni (e.g., $NiFe_2O_4$) but enriched in soluble Ni (i.e., $NiSO_4 \cdot xH_2O$) relative to fly ash from utility boilers. These differences in Ni speciation are most likely related to the lack of additive (e.g., $Mg[OH]_2$) injection and residence time in the 7-kW combustion system.

Table 6. Comparison of combustion and sampling conditions in the laboratory- and utility-scale combustion systems.

System	7 kW	400 MW
Bottom ash/fly ash partitioning	Absent	Present
Residence time	~3.5 sec	~10 sec
NO_x control	Absent	Present
Additive injection	Absent	$Mg(OH)_2$
Furnace outlet temperature	1290 °C	1240 °C
Sampling location	Convection pass	Stack
Gas temperature at sampling location	~300 °C	145 °C
Sample filter temperature	~300 °C	~300 °C

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