

15 North 23rd Street — Stop 9018 / Grand Forks, ND 58202-9018 / Phone: (701) 777-5000 Fax: 777-5181 Web Site: www.undeerc.org

December 14, 2010

Mr. Paul Chu Project Manager Electric Power Research Institute 3412 Hillview Avenue PO Box 10412 Palo Alto, CA 94303

Dear Mr. Chu:

Subject: Final Report Entitled "Nickel Speciation Analyses of Residual Oil Fly Ashes Using X-Ray Techniques"; Agreement No. EP-P35394/C16047 EERC Fund 15901

Enclosed is the subject Energy & Environmental Research Center (EERC) final report. If you have any questions or comments, please contact me by phone at (701) 777-5127, by fax at (701) 777-5181, or by e-mail at kgalbreath@undeerc.org.

Sincerely,

Kevi C. Andreatt

Kevin C. Galbreath Research Manager, Fuel Properties

KCG/kmd

Enclosure

c/enc: Connie Monahan, Electric Power Research Institute Rodney Chong, Hawaiian Electric Company Stephen Ward, Hawaiian Electric Company Frank Huggins, University of Kentucky

NICKEL SPECIATION ANALYSES OF RESIDUAL OIL FLY ASHES USING X-RAY TECHNIQUES

Product ID #070441

Final Report, December 2010

EPRI Project Manager: Paul Chu

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University of North Dakota, Energy & Environmental Research Center 15 North 23rd Street, Stop 9018 Grand Forks, ND 58202-9018

Principal Investigator K. Galbreath

University of Kentucky 103 S. J. "Sam" Whalen Bldg 533 S. Limestone Street Lexington, KY 40506-0043

Principal Investigator F. Huggins

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ABSTRACT

Representative duplicate fly ash samples were obtained from the stacks of two 50-MW (Units 9 and 6 of the Honolulu and Waiau power plants, respectively) and one 80-MW (Unit 1 of the Kahe power plant) utility boilers using a modified U.S. Environmental Protection Agency Method 17 sampling train assembly as 0.3 to 0.4 wt% sulfur residual (No. 6 fuel) oils were burned during full-load power plant operations. Residual oil fly ash (ROFA) samples were analyzed for Ni speciation using x-ray absorption fine structure (XAFS) spectroscopy and x-ray diffraction (XRD). ROFA deionized H₂O extraction residues were also analyzed for Ni speciation analysis results indicated that 80% to 95% of the total Ni present in the ROFAs was NiSO₄.6H₂O with subordinate proportions, $\leq 20\%$ of the total Ni, present as a Ni-containing spinel compound, similar in composition to NiFe₂O₄ and/or NiO. XAFS and XRD analyses did not detect any sulfidic Ni compounds; the XAFS detection limit was 3% of the total Ni concentration.

Keywords

Nickel, nickel emissions, nickel speciation, residual (No. 6 fuel) oil, x-ray absorption fine structure spectroscopy, x-ray diffraction, residual oil fly ash

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1 INTRODUCTION

Nickel is a transition metal that occurs throughout the environment and is discharged into air, water, and soil from various natural and industrial sources. A significant natural source of atmospheric Ni is windborne dust particles derived from the weathering of rocks and soils and from volcanic eruptions [1]. The average Ni concentration of crustal rocks is 75 ppm [2]. Although Ni is a ubiquitous metal, industrialization has increased its flux into the environment [3]. Anthropogenic stationary sources that release Ni into ambient air include 1) combustion and incineration sources (oil- and coal-burning units in utility, industrial, and residential use sectors and medical, municipal, and sewage sludge incinerators), 2) high-temperature metallurgical operations (steel and Ni alloy manufacturing, secondary metals smelting, and coproduct Ni recovery), 3) primary production operations (mining, milling, smelting, and refining), and 4) chemical and catalyst production, use, and reclamation) [4, 5]. The mobile source contribution to Ni emission inventories is small and derived primarily from engine wear and impurities in engine oil and fuel additives [6]. However, commercial marine vessels are significant mobile sources of Ni in areas near harbors [7, 8].

In the United States, the impetus for focusing on individual elements, such as Ni, in air pollution derives from the 1990 Clean Air Act Amendments (CAAA) [9] and the attainment of National Ambient Air Quality Standards [10]. Title III of the CAAA identifies 188 chemicals, including Ni and 15 other inorganic trace elements (As, Be, Cd, Cl, Co, Cr, F, Hg, Mn, P, Pb, Sb, Se, Th, and U) as potential hazardous air pollutants (HAPs) or air toxics. The U.S. Environmental Protection Agency's (EPA's) Integrated Urban Air Toxics Strategy also classifies Ni as an urban HAP [11]. Many stationary sources have had to report Ni emissions as part of the EPA Toxics Release Inventory (TRI) [12]. Although TRI and similar reporting provide estimates of the amounts of Ni released into the environment, they are not an indicator of toxicity because the acute, chronic, and cancer-causing effects vary significantly for the different chemical species of Ni. For example, nickel subsulfide (Ni_3S_2) is considered the most carcinogenic Ni species on the basis of available human epidemiology and animal studies [5, 13, 14]. In contrast, inhalation exposure to water-soluble Ni salts alone, such as nickel hexahydrite (NiSO₄ \cdot 6H₂O), have not been shown to cause cancer in animal studies [15–17]. Soluble Ni compounds, however, are more toxic to the respiratory tract than less soluble compounds. Insoluble nickel oxide compounds such as Ni-containing spinels (e.g., NiFe₂O₄), although still under investigation, are expected to have relatively low cancer potencies compared to Ni₃S₂ and may not be bioaccessible [5, 13, 14, 18]. Therefore, determining the Ni speciation of emission sources is of the utmost importance for assessing the inhalation health risks associated with airborne Nicontaining particles.

INTRODUCTION

The combustion of petroleum fuels (distillate fuel oils, residual fuel oil, jet fuel, kerosene, petroleum coke [converted to liquid petroleum], and waste oil) for generating steam and electricity is a significant anthropogenic source of Ni release to the atmosphere. Petroleum-fired capacity represented 1.1% (46,000,000 MWh) of the total U.S. electric utility capacity in 2008 [19]. Residual (No. 6 fuel) oil, a by-product from the petroleum-refining industry, is the most widely used for generating steam and electricity because of its relatively 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 \approx 42,000 barrels per month [20]. In addition to the electric utility industry, residual oil is an important fuel for marine and industrial boilers.

The fly ash produced from residual oil combustion (i.e., residual oil fly ash [ROFA]) contributes to ambient particulate matter pollution. Controlling fly ash emissions, however, is difficult because a substantial fraction of residual oil ash particles is generally submicrometer, corresponding to the size range of $0.1-1 \mu m$, where existing industrial gas-cleaning devices are least effective [21–23]. As part of the EPA *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units—Final Report to Congress* [14], the inhalation health risks associated with HAP emissions from oil-fired utility boilers were estimated. EPA estimated that the contribution of Ni to the maximum individual risk exceeded that from all other HAPs by about an order of magnitude primarily because of its relatively high concentration, generally 1–4 wt% Ni, in ROFA and known carcinogenic potency when in a Ni₃S₂ form. In 2004, EPA proposed Ni emission limits of 210 lb/10¹² Btu on an input basis or 0.002 lb/MWh on an output basis for residual oil-fired electric utility units [24].

As highlighted in EPA's study [14] and proposed emission limit ruling [24], the speciation of Ni emissions from oil-fired utility boilers is uncertain and requires additional investigation. Total Ni emissions were measured at 13 of the 149 power plants that burned oil in 1994, and speciation measurements were conducted at seven of them. The limited Ni speciation analyses performed indicate that 3%–26% of the total Ni emissions were composed of sulfidic Ni, 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 Ni extraction [25–28]. Sequential Ni extraction methods are based on treating a small but representative sample of fly ash or particulate matter to successive leaching steps to separate analyte Ni species from the sample matrix. Ni species concentrations in the extracted fractions are then determined using sensitive analytical techniques, such as anodic stripping voltammetry, graphite furnace atomic absorption spectroscopy (GFAAS), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Sequential extractions provide an operationally defined (e.g., based on particle size, solubility, bonding, and reactivity differences) determination of Ni forms (soluble, sulfidic, metallic, and oxidic) that is susceptible to errors because of inefficient and nonselective extractions and subsequent Ni redistribution effects [29]. In contrast, Galbreath et al. [30, 31] used definitive speciation techniques, x-ray diffraction (XRD) and x-ray absorption fine structure (XAFS) spectroscopy, to identify the Ni species occurring in ROFAs sampled from 385- and 400-MW utility boiler stacks. Direct speciation measurements indicated that >95% of the total Ni in ROFAs was present as a mixture of NiSO₄ \cdot xH₂O and nickel oxide spinel compound, similar in composition to NiFe₂O₄. The lack of sulfidic Ni emissions from these particular boilers was contrary to EPA's risk assessment assumption that the Ni compound mixture emitted from oilfired utilities is 50% as carcinogenic as Ni_3S_2 [14]. The Ni cancer risk from residual oil-fired boilers may be greatly overestimated [30, 31].

In this investigation, three complementary methods—XAFS, XRD, and water-soluble Ni extraction—were used to identify and quantify the Ni species occurring in fly ashes stacksampled in duplicate from three residual oil-fired units, owned and operated by Hawaiian Electric Company, Inc. (HECO).The XAFS technique is especially well suited for determining Ni speciation because it can directly and nondestructively analyze fly ash filter samples with ppm sensitivity [29–34]. XAFS spectroscopy involves recording the variation of the x-ray absorption coefficient as a function of energy in the vicinity of a characteristic absorption edge for an element of interest. The x-ray flux is supplied from a very intense synchrotron x-ray source such as those used in this investigation at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, New York, and the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford University, California. Analysis of x-ray absorption coefficient variations in the x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectral regions of the XAFS spectrum provides structural information concerning the local environment of the analyte element in terms of oxidation state, interatomic distances, and the type and number of coordinating ligands.

2 BACKGROUND

XAFS Spectroscopy

XAFS spectroscopy is a powerful method for determining the speciation of an element in any material (gas, liquid, crystalline solid, amorphous solid). As its name implies, XAFS spectroscopy measures the fine structure associated with one of the characteristic x-ray absorption edges of an element of interest. The fine structure is usually of two types (Figure 2-1): a fine structure associated with the absorption edge itself and a second fine structure consisting of a weak, periodic oscillatory structure that occurs above the absorption edge and normally diminishes in intensity the further it is from the edge. Either or both of these regions of the XAFS spectrum can be used to determine how the element occurs in a material.



Figure 2-1

XAFS Spectrum of Elemental Selenium Showing the Division of the Spectrum into Separate XANES and EXAFS Regions and the Subsequent Generation of a Radial Structure Function (RSF) by Fourier Transform of the EXAFS Region of the Spectrum. The Peak in the RSF Spectrum Represents X-Ray Scattering Interactions Between the Selenium Atom and Its Immediate Neighbors and Can Be Considered a One-Dimensional Representation of the Structure Local to the Selenium Atom

BACKGROUND

The structure associated with the edge itself is known as the XANES region, whereas the periodic structure above the edge is known as the EXAFS region. Analysis of each region is performed independently. Typically, the XAFS spectrum is first normalized to the edge step and then divided into separate XANES and EXAFS regions. The latter region can be further manipulated mathematically to obtain a RSF. Where the EXAFS region provides structural information, the XANES region provides bonding and valence state information.

Power Plant Sites

The oil-fired power plants that were sampled for Ni speciation are described in Table 2-1. AirKinetics, Inc., was at the Honolulu, Kahe, and Waiau power plants April 12–15; June 7–11, 13, and 14; and May 9–13, 2010, respectively, to perform EPA Section 114 HAP emissions and Ni speciation testing. The average electric generation attained for each unit during metals testing is presented in Table 2-1.

Facility	Unit	Abbreviation	Unit Gross Electric Generation, MWe
Honolulu Power Plant (HPP)	9	Н9	53
Kahe Power Plant (KPP)	1	K1	85
Waiau Power Plant (WPP)	6	W6	52

Table 2-1Power Plant Descriptions and Abbreviations

3 EXPERIMENTAL

Residual Oil Analyses

Proximate, ultimate, and metal analyses were performed on composite residual oil samples collected from HPP, KPP, and WPP as described in AirKinetics reports [35–37].

Fly Ash Stack Sampling and Analysis Methods

ROFA was sampled isokinetically and in duplicate by AirKinetics personnel for ≤ 5 hr/day from the stacks of the three units (Table 2-1) using a modified EPA Method 17 sampling train assembly, with the nozzle, probe, and quartz thimble filter maintained at >290°C, well above the sulfuric acid dew point temperature. The nozzle and filter holder were constructed of quartz and glass, respectively, to prevent contamination of ROFA by metal surfaces. The sampling train and procedures used in obtaining representative fly ash samples are described in detail by EPA [38]. The sampling approach employed is consistent with previous investigations of the Ni speciation of stack emissions from oil-fired utility boilers and sewage sludge incinerators [26–28, 30, 31, 39]. Plant operating and monitoring data and continuous emission monitoring results indicated that the modified EPA Method 17 stack sampling occurred during steady, representative power plant operations. In addition to modified EPA Method 17, ROFA samples were sampled according to EPA Method 29 and analyzed for Ni as described in Air Kinetics reports [35–37].

All of the quartz thimble samples received by the Energy & Environmental Research Center (EERC) and University of Kentucky for analysis are described in Tables 3-1 and 3-2. Several of the field and trip blanks were not analyzed using XAFS, but were prepared using microwave-assisted acid digestion (EPA Method 3050 and ASTM International Standard Practice D5513) and analyzed using ICP–AES (EPA Method 6010A and 7000 series).

Soluble Ni Extraction

The ROFA filters were exposed to deionized H_2O for about 30 minutes. ROFA H_2O extraction residues were dried in an oven at 50°C before analyzing them using XAFS spectroscopy and XRD. The leaching procedure was intended to dissolve readily soluble species such as NiSO₄·6H₂O from the filters and preconcentrate insoluble Ni species such as Ni oxides and sulfides. Analyses of ROFA H_2O extraction residues minimize potential x-ray absorption and diffraction spectral overlaps caused by the presence of multiple Ni species. The extraction residue samples are listed in Table 3-2.

EXPERIMENTAL

Table 3-1
List of Samples Cross-Referenced to XAFS File Names

Power Plant and Unit	XAFS Analysis Facility	Thimble Filter	Identification	XAFS File
HPP 9	SSRL, May 2010	1	H9-Ni-1	NiASH_011.003
		2	H9-Ni-2	NiASH_010.003
		Field blank	H9-Ni-FB	NiASH_017.001
		Trip blank	H9-Ni-TB	NiASH_018.001
WPP 6 NSLS, August		1	W6-Ni-1	NiROFA_025 – 027
	2010	2	W6-Ni-2	NiROFA_028 – 030
		Field blank	W6-Ni-FB	NA ¹
		Trip blank	W6-Ni-TB	NA
KPP 1 NSLS, August		1	K1-Ni-1	NiROFA_031 – 033
	2010	2	K1-Ni-2	NiROFA_034 – 036
		Field blank	K1-Ni-FB	NA
		Trip blank	K1-Ni-TB	NA

¹ Not analyzed by XAFS.

Table 3-2 List of ROFA H_2O Extraction Residue Samples Cross-Referenced to XAFS File Names

Power Plant and Unit	XAFS Analysis Facility	Thimble Filter	Identification	XAFS File
HPP 9	SSRL, May 2010	2	H9-Ni-2R	NiLEACH_026.016
WPP 6	NSLS, August 2010	1	W6-Ni-1R	NiROFAL_045 – 048
		2	W6-Ni-2R	NiROFAL_049 – 053
KPP 1	NSLS, August 2010	1	K1-Ni-1R	NiROFAL_037 – 040
		2	K1-Ni-2R	NiROFAL_041 – 044

Ni XAFS Spectroscopy

Nickel XAFS measurements were made in both absorption and fluorescence geometry at Beamline 4-1 at SSRL or at Beamline X-18B at NSLS using a fluorescence detector to detect the x-rays emitted by Ni in the investigated materials in response to the x-ray absorption process. Soller slits and a 6-µm cobalt filter were also used at SSRL to enhance the fluorescent signal/noise ratio. Harmonic rejection was accomplished by detuning the intensity of the incident beam by about 30%. The spectra were collected as a function of energy from about 200 eV below the K absorption edge of Ni at 8333 eV to as much as 1000 eV (16 k) above by measuring the absorption and fluorescence signals as a function of the angular rotation of the silicon (220) monochromator at SSRL or the Si (111) monochromator at NSLS. The absorption spectrum of a Ni⁰ foil, obtained simultaneously in absorption geometry, was used as the primary energy calibration standard in both sets of experiments.

If necessary, the thimble filters were cut in half lengthwise to expose the deposited material, and then a 5-cm-long section containing the thickest and most coherent deposit was cut from one-half of the filter (Figure 3-1). This section, approximately 3×5 cm in size, was taped to the sample holder so as to expose the ROFA to an x-ray beam. Photographs of the other filters from KPP and WPP Units 1 and 6, respectively, are presented in Appendix A. Excellent-quality fluorescence spectra were obtained at SSRL from the samples prepared in this manner using a standard Lytle fluorescence detector. Data of almost as good quality were obtained at NSLS using a passivated, implanted, planar silicon (PIPS) detector to measure fluorescence radiation. The XAFS spectra of eight standard Ni compounds, Ni₃S₂, NiS, NiS₂, NiSO₄, NiSO₄·H₂O, NiSO₄·6H₂O, NiSO₄·7H₂O, and NiO, obtained during the course of a similar testing program for an additional utility provider, were also used as reference spectra for this investigation.



Figure 3-1

Photograph of Deposits on Quartz Thimble Filters from HPP 9. Thimbles Have Been Cut to Expose ROFA to the X-Ray Beam

EXPERIMENTAL

XRD

Representative sections of the ROFA-containing thimble filters were mounted in the XRD for analysis. XRD patterns were collected over $5-60^{\circ}$ 2-theta with a Bruker D8 Advance theta–thetax-ray diffractometer system operating at 40 kV and 40 mA (parallel-beam geometry using an incident beam Goebel mirror to monochromatize and collimate Cu K-á radiation, 0.02° 2-theta steps, 7 to 15 sec/step). Diffraction peaks were identified using the Bruker EVA evaluation software utilizing the International Centre for Diffraction Data (ICDD) PDF-2 inorganic and organic powder diffraction database.

Residual Oil Analyses

Presented in Table 4-1 are proximate and ultimate analysis results for the composite residual oil samples. Sulfur only ranged from 0.3 to 0.4 wt%. The calorific (i.e., heating) value of the residual oil sampled from WPP Unit 6 is significantly greater relative to the two other oils. AirKinetics also had the composite oil samples analyzed for Ni and many other elements, but the Ni concentrations were all reported as <5.0 mg/kg [35–37].

Analysis Parameters	HPP Unit 9		KPP Unit 1		WPP Unit 6	
	Avg. ±95% C.I. ¹	n²	Avg. ±95% C.I.	n	Avg. ±95% C.I.	n
Proximate Analysis						
Water, vol%	<0.05	4	<0.05	7	<0.05	5
Ash, wt%	<0.01	4	0.02 ±0.01	7	0.05 ±0.02	5
Ultimate Analysis, wt%						
Hydrogen	10.9 ±0.1	4	11.6 ±0.2	7	11.1 ±0.6	5
Carbon	87.3 ±0.1	4	87.5 ±0.2	7	84.9 ±4.6	5
Nitrogen	0.25 ±0.07	4	0.21 ±0.08	7	0.31 ±0.07	5
Sulfur	0.37 ±0.01	4	0.39 ±0.02	7	0.32 ±0.00	5
Oxygen	1.23 ±0.22	4	0.38 ±0.19	7	0.74 ±0.14	4
Calorific Value, Btu/lb	17958 ±22	4	17963 ±183	7	18346 ±583	5

 Table 4-1

 Residual Oil Proximate and Ultimate Analysis Results, as-received basis

¹Average $\pm 95\%$ confidence interval.

²Number of samples analyzed.

ROFA Ni Analyses

EPA Method 29

Compared in Table 4-2 are the average Ni contents of the ROFAs based on triplicate EPA Method 29 results. ROFA from the KPP contains significantly less Ni relative to the other two

Facility	Average Ni ±95% Confidence Interval, wt%	Average Ni Emission, lb/10 ⁶ Btu
HPP, Unit 9	4.26 ±0.97	6.33E-04 ±1.6E-05
KPP, Unit 1	2.40 ±0.37	1.19E-03 ±2.3E-04
WPP, Unit 6	4.78 ±0.14	4.28E-04 ±1.7E-05

 Table 4-2

 Average ROFA Ni Concentrations and Emission Rates

power plants, but the Ni emissions from KPP were the highest, probably because it was consuming the most oil to produce the most power, as indicated in Table 2-1. Even though ROFA from WPP had the highest Ni concentration, its Ni emission rate was intermediate to HPP and KPP, probably because it was producing a similar amount of power (Table 2-1) to HPP but with a residual oil whose calorific value was significantly higher.

Ni XAFS Spectroscopy

Spectra collected for the HPP Unit 9 samples are shown in Figure 4-1. Spectra of the duplicate ROFA samples are very similar, both in overall intensity and appearance. Also compared in Figure 4-1 are the corresponding spectra of the trip and field filter blanks and the ROFA H₂O



Figure 4-1

Ni XAFS Spectra Collected at SSRL for Thimble Filter Samples from HPP Unit 9. The Spectra for the Field and Trip Blanks Do Not Differ Significantly and, Thus, Superimpose as a Single Trace at the Plotted Scale. Inset Shows a Vertical Expansion of the Scale for the H9-Ni-2R and Blank Samples

extraction residue. The spectrum for the residue sample is much weaker relative to bulk ROFA samples, indicating that the leaching extracted a large amount of soluble Ni species. No significant feature appears at the Ni absorption edge in the blank sample spectra, indicating that Ni was below the XAFS detection limit.

Presented in Figure 4-2 are the XAFS spectra for the ROFA samples obtained from KPP and WPP Units 1 and 6, respectively. Spectra for the duplicate ROFA samples are essentially identical for a given power plant. The field and trip blank thimble filters for the KPP and WPP Units 1 and 6, respectively, were not analyzed because ICP–AES measurements, presented in Table 4-3, indicated that Ni was not present in high enough concentrations to produce Ni XAFS spectra from them. Comparative data for the ROFA H₂O extraction residue, H9-Ni-2R, are also shown in Figure 4-2.

The Ni XAFS data obtained from the ROFA samples were divided into separate XANES and EXAFS regions according to the procedures described in Figure 2-1. Plots of the XANES and EXAFS data were prepared for each set of samples from the three units. These spectra are shown in Figures 4-3 and 4-4 for the samples measured at SSRL and NSLS, respectively. Spectra obtained from the ROFA H_2O extraction residue sample, H9-Ni-2R, are also included in Figure 4-3.

The Ni XANES and EXAFS spectra of the four ROFA H₂O extraction residues from KPP and WPP are presented in Figure 4-5. Except for the W6-Ni-2R sample, there was sufficient Ni





Ni XAFS Spectra Collected at NSLS for Thimble Filter Samples from KPP and WPP Units 1 and 6, Respectively. The Spectrum of a ROFA H_2O Extraction Residue, W6-Ni-2R, is Shown for Comparison

Sample	Ni, ppm
KPP Unit 1 Trip Blank	1.16
KPP Unit 1 Field Blank	0.81
WPP Unit 6 Trip Blank	0.88
WPP Unit 6 Field Blank	1.10

Table 4-3Ni Contents of the Filter Blank Samples from KPP and WPP Units 1 and 6, respectively

remaining on the filters after the aqueous leaching procedure to produce acceptable-quality spectra at all stages of the spectral data reduction process. For the W6-Ni-2R sample, however, the EXAFS region was too noisy to permit a meaningful RSF spectrum to be generated from the EXAFS (k^3 chi) spectrum.

Nickel XAFS spectra of various reference Ni compounds are presented in Figures 4-6–4-8. Figure 4-6 compares the Ni XAFS data obtained for three different nickel sulfates, NiSO₄ (anhydrous), NiSO₄·H₂O, and NiSO₄·6H₂O. Figure 4-7 shows the processed XAFS spectra for the three Ni sulfides, Ni₃S₂, NiS, and NiS₂. These spectra differ significantly from those shown in Figure 4-6 for the Ni sulfates in three major ways: (i) there is no sharp large peak at the absorption edge for the Ni sulfides compared to the Ni sulfates; (ii) the major peak in the RSF occurs at about 2.0 Å for the Ni sulfides and at about 1.5 Å for the Ni sulfates; and (iii) the peak maximum in the derivative XANES spectra occurs at a significantly lower energy for the Ni sulfides than for the Ni sulfates (compare Figures 4-6 [b] and 4-7[b]). These differences make it easy to distinguish Ni sulfides from Ni sulfates. Furthermore, the Ni sulfides all show significant absorption in a small region of the spectrum (8335 to 8340 eV) that is devoid of significant absorption for Ni oxide and sulfate compounds.

Figure 4-8 shows Ni XAFS data for three Ni oxide species, NiO, NiFe₂O₄, and NiAl₂O₄. These spectra are the best that we have in our database for these compounds; however, it seems possible to improve on the quality of these data. In particular, the spectral data for the nickel ferrite, NiFe₂O₄, are quite weak, as indicated by the noisy nature of the derivative XANES spectrum (Figure 4-8 [b]). The EXAFS regions and RSF spectra of all three compounds (Figures 4-8 [c], [d]) are complex, which is typical of the high-symmetry structures exhibited by compounds with cubic crystal structures, MO (halite [NaCl]-type) and AB₂O₄ (spinel-type). For NiO, peaks representing the 4th and 5th and even more distant coordination shells are discernable in the RSF (Figure 4-8 [d]). For both NiO and NiFe₂O₄, the second peak in the RSF spectrum at $\approx 2.5-2.6$ Å exceeds the height of the NiO peak at ≈ 1.5 Å. This peak derives from the second nearest coordination shell in the oxide structure and consists of metal (Ni or Fe) atoms. The enhanced back-scattering power of the higher-atomic-number elements, Ni and Fe, compared to oxygen, as well as the larger coordination number for the second coordination shell in these structures, account for the enhanced nature of this peak relative to the first coordination shell peak.





Ni XAFS Spectra of Duplicate ROFA Samples and a ROFA Residue Sample from the Stack of HPP Unit 9; (a) XANES Spectra, (b) Derivative XANES Spectra, (c) EXAFS (K³chi) Spectra, and (d) RSF Spectra. Data Collected at SSRL



Figure 4-4

Ni XAFS Spectra of Duplicate ROFA Samples from the Stacks of KPP and WPP Units 1 and 6, Respectively; (a) XANES Spectra, (b) Derivative XANES Spectra, (c) EXAFS (K³chi) Spectra, and (d) RSF Spectra. Data Collected at NSLS



Figure 4-5

Ni XAFS Spectra of ROFA Residues Corresponding to KPP and WPP Units 1 and 6, Respectively; (a) XANES Spectra, (b) Derivative XANES Spectra, (c) EXAFS (K3chi) Spectra, and (d) RSF Spectra. Data Collected at NSLS



Figure 4-6

Ni XAFS Spectra of NiSO₄, NiSO₄·H₂O, and NiSO₄·6H₂O; (a) XANES Spectra, (b) Derivative XANES Spectra, (c) EXAFS (K^3 chi) Spectra, and (d) RSF Spectra



Figure 4-7

Ni XAFS Spectra of Ni₃S₂, NiS, and NiS₂; (a) XANES Spectra, (b) Derivative XANES Spectra, (c) EXAFS (K^3 chi) Spectra, and (d) RSF Spectra



Figure 4-8 Ni XAFS Spectra of NiO, NiFe₂O₄, and NiAl₂O₄; (a) XANES Spectra, (b) Derivative XANES Spectra, (c) EXAFS (K^{3} chi) Spectra, and (d) RSF Spectra

All of the RSFs for the ROFA samples (Figures 4-3 [d] and 4-4 [d]) have a small but significant peak at 2.5 Å, which is always more prominent for the corresponding ROFA H₂O extraction residue samples (Figure 4-5 [d]). Of the sulfates, only NiSO₄ shows a significant second coordination shell peak (Figure 4-6 [d]); however, the peak is located at \approx 2.8 Å, rather than 2.5 Å. Conversely, NiSO₄·6H₂O, which is most likely the Ni sulfate contributing to the spectra of the residual oil samples, lacks a significant second coordination shell peak. Also, none of the Ni sulfide species exhibit a peak at 2.5 Å in their RSFs (Figure 4-7 [d]). These observations suggest that the source of the 2.5-Å peak in the ROFA sample spectra is a minor amount of NiFe₂O₄ or NiO rather than a Ni sulfate or sulfide compound. For the ROFA H₂O extraction residues, the enhanced nature of the 2.5-Å peak, especially for the H9-Ni-2R sample (Figure 4-3[d]) and K1-Ni-1R and-2R samples (Figure 4-5[d]), indicates the prevalence of NiFe₂O₄ or NiO.

XANES Pre-Edge Systematics

Based on the spectral features for the Ni sulfate and sulfide standards (Figures 4-6 and 4-7), there are several systematic differences that enable a distinction between Ni sulfate and sulfide species. Oxidic Ni species, such as NiO and various Ni spinels (NiFe₂O₄, NiAl₂O₄, NiV₂O₄, etc.), are similar to Ni sulfates because the Ni²⁺ ion is bonded to oxygen anions, thus their XAFS spectra have more in common with those of Ni sulfates than Ni sulfides. Indeed, the spectra for NiFe₂O₄ and NiAl₂O₄ show much the same pre-edge characteristics as the Ni sulfate standards. These systematic differences were used to evaluate whether a sulfidic Ni species was present in ROFA.

Detailed examinations of the pre-edge region (8330–8340 eV) of the XANES and derivative XANES spectra for all Ni²⁺ compounds revealed that there is a ubiquitous peak or inflection feature at about 8332–8333 eV that occurs because of the electron transition from Ni 1s orbitals to 3d orbitals induced by the x-ray absorption process. Furthermore, the intensity of this feature can be used to discriminate Ni²⁺ ions coordinated with sulfur anions versus oxygen anions. Plotted in Figure 4-9 are the relative intensities of the inflection feature for various Ni compounds.

As indicated in Figure 4-9, the relative height of the inflection feature is always more than 0.05 for metallic Ni and Ni sulfides and less than 0.025 for Ni sulfate and oxide phases, except for NiO, which exhibits an intermediate value of about 0.032. Figure 4-10 presents the normalized pre-edge inflection feature heights determined from the derivative XANES spectra of the bulk ROFA samples and their corresponding ROFA H₂O extraction residues. The relative heights for the bulk ROFAs and corresponding residues range similarly between 0.009 and 0.017, whereas in comparison, the range for a suite of ROFA samples from Florida power plants was much smaller at 0.015 to 0.018. Clearly, data for the ROFA samples measured at NSLS (KPP and WPP Units 1 and 6, respectively) have values consistently lower than those measured at SSRL for ROFA samples from HPP Unit 9. This difference is attributable to resolution differences between the two synchrotrons, principally as a result of different monochromator crystal orientations. The use of the Si (111) crystals at NSLS results in a somewhat broadened and less intense pre-edge peak at NSLS compared to that measured at SSRL.



Figure 4-9

Comparison of the Normalized Height of the Pre-Edge Inflection Feature at 8333 eV in Ni Derivative XANES Spectra for Ni Compounds





Comparison of the Normalized Height of the Pre-Edge Inflection Feature at 8333 eV in Derivative Xanes Spectra of Rofa Sampled from the Three Hawaiian Units. Light Bars Represent Data for the ROFA H₂O Extraction Residue Samples

Since the inflection feature height values for the ROFA samples from Hawaii are less than or comparable to those for the Ni sulfates and oxides, such small values indicate that there may be a minimal contribution from Ni sulfides. However, the difference between the two synchrotrons in the intensity of this feature implies that we cannot develop the height of the pre-edge peak as a general quantitative measure for estimating sulfide contents; such correlations would have to be restricted to a given monochromator orientation or beamline.

In a companion study of ROFA emissions from Florida power plants, various correlations were established between composition and absorption intensity at the positions of the major peaks in the Ni derivative XANES spectra for mixtures of Ni_3S_2 and $NiSO_4 \cdot 6H_2O$, Ni_3S_2 and $NiFe_2O_4$, and NiS and $NiSO_4 \cdot 6H_2O$. From these correlations, the following equations were derived for estimating the proportions of Ni_3S_2 or NiS in ROFA:

For
$$Ni_3S_2$$
- $NiSO_4 \cdot 6H_2O$ mixtures: Ni_3S_2 , % = 813 h(8336) - 4.3 [Eq. 1]

For Ni₃S₂-NiFe₂O₄ mixtures: Ni₃S₂,
$$\% = 892 h(8336) - 13.8$$
 [Eq. 2]

For NiS–NiSO₄·
$$6H_2O$$
 mixtures: NiS, % = 952 h(8337) – 8.0 [Eq. 3]

Equations 1 and 3 are applicable to the bulk ROFA samples in which $NiSO_4 \cdot 6H_2O$ is the major phase, while Equation 2 is more appropriate for the Ni extraction residues after Ni sulfates have been removed.

Using Equations 1–3, Ni₃S₂ and NiS contents were estimated from the derivative Ni XANES spectra; estimates are presented in Table 4-4. The proportions in Table 4-4 are ≤ 3 % of the total Ni present in the bulk ROFA, but the analytical uncertainty is ±2% so the values are essentially equal to zero. These proportions are maximum estimates for Ni₃S₂ and NiS in the bulk ROFA samples because NiSO₄·6H₂O has the lowest h (8336) value of all the standards. Substitution of any other Ni sulfate or a Ni oxide species for NiSO₄·6H₂O in the calibration procedure results in smaller estimates of the Ni sulfide proportions, as would the presence of a third component such as NiFe₂O₄ or NiO in the calibration procedure. Applying similar calculations to the ROFA H₂O extraction residues, it is likely that NiFe₂O₄ or NiO are present and should be used in the calibration procedures rather than a Ni sulfate. Using NiFe₂O₄ in the calibration procedures results in residues, based on the use of h (8336) values in Table 4-4 and Equation 3. Such negative values probably indicate that some Ni sulfate remained on the ROFA H₂O extraction residues.

In conclusion, a detailed examination of Ni pre-edge XANES systematics indicates that the Ni_3S_2 or NiS contents of ROFA from the three HECO units are negligible and comprise $\leq 3\%$ of the total Ni, if any. This simple two-component calibration procedure is sufficient because both Ni sulfides are negligible in all the ROFA samples. A more sophisticated three-component approach would be applicable if significant amounts of either or both of the sulfides were present.

	Bulk ROFA			ROFA H₂O Extraction Residues				
Sample	h(8336)	Ni₃S₂, %	h(8337)	NiS, %	h(8336)	Ni₃S₂, %	h(8337)	NiS, %
H9-Ni-1	0.0043	-1	0.0067	-2	NA ¹	NA	NA	NA
H9-Ni-2	0.0042	-1	0.0065	-2	0.0079	2 (-7) ²	0.0145	6
W6-Ni-1	0.0054	0	0.0103	2	0.0114	5 (-4)	0.0175	9
W6-Ni-2	0.0058	0	0.0091	1	0.0172	10 (2)	0.0072	-1
K1-Ni-1	0.0072	2	0.0113	3	0.0126	6 (-3)	0.0171	8
K1-Ni-2	0.0079	2	0.0108	2	0.0139	7 (-1)	0.0154	7

Table 4-4 Estimates of NiS and Ni_3S_2 in ROFA from Three HECO Units

Least-Squares Fitting of Ni XANES and EXAFS Spectra

In addition to the Ni derivative XANES spectral correlations (Equations 1–3), a least-squares fitting of Ni XANES and EXAFS spectra was performed to evaluate the Ni species contents of the ROFAs. The most reliable simulation approach consisted of combining the spectra for the bulk ROFA (consisting predominantly of NiSO₄·6H₂O) and corresponding ROFA H₂O extraction residue (consisting mainly of NiFe₂O₄ and/or NiO) with that of NiSO₄·6H₂O and NiO. These simulations were performed for the EXAFS (k³chi) spectra of all six samples. As indicated in Table 4-5, these simulations confirm that NiSO₄·6H₂O is the predominant sulfate phase. Some of the fits were marginally improved with the addition of NiO in the least-squares fitting, especially for the W6-Ni-1 and -2 samples. However, we suspect that NiO is a major component of the Ni remaining in the ROFA H₂O extraction residues and that the difference in least-squares fitting between fits with and without NiO is largely an experimental artifice. This is most likely the case for the K1-Ni-1 and -2 samples, where the Ni proportion as NiO is relatively minor and clearly complements the Ni % for the ROFA H₂O extraction residue sample in the fitting.

Least-squares fitting of bulk ROFA and corresponding ROFA H_2O extraction residue Ni EXAFS spectra to linear combinations of spectra for two or more standard compounds (NiSO₄·6H₂O, NiFe₂O₄, and/or NiO) was performed as shown in Figure 4-11 and reported in Table 4-6. The fits did not require the presence of Ni sulfide(s). For the H9-Ni-1 and -2 samples, several different fits were statistically similar, and these results are also included in Table 4-6, in addition to the best linear combination fit.

The least-squares fitting results indicate that the Ni in H9-Ni-1 and -2 samples are predominantly (>95%) present as NiSO₄·6H₂O, with only very minor amounts of NiFe₂O₄ and/or NiO. In a corresponding ROFA H₂O extraction residue, H9-Ni-2R, NiSO₄·6H₂O remains dominant despite the large reduction in soluble Ni as indicated by the reduction in the overall absorption intensity

Table 4	4-5
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Results of Least-Squares Fitting of Combined Bulk ROFA and Corresponding ROFA H ₂ O
Extraction Residue Spectra to Spectra for NiSO ₄ -6H ₂ O and NiO

Sample	EXAFS Region (3–10 Å ⁻¹) Fitting					
	Residue, %	NiSO₄, %	NiO, %	Red χ^2		
H9-Ni-1	11	89	_	0.124		
H9-Ni-2	5	95	-	0.159		
W6-Ni-1	9	77	14	0.407		
W6-Ni-2	3	84	14	0.452		
K1-Ni-1	28	72	-	0.320		
	18	76	6	0.269		
K1-Ni-2	26	74	_	0.372		
	15	78	7	0.302		





(Figure 3-1). Each of the two Ni oxides comprise about 20% of the total Ni in H9-Ni-2R. The proportions of oxidic Ni in the bulk ROFA samples from the other two units were significantly larger than those in the H9-Ni-1 and -2 samples. Least-squares fitting indicated that between 10% and 20% of the Ni in these unleached samples was present as NiFe₂O₄ and/or NiO. In the K1-Ni-R1 and -R2 samples, NiSO₄·6H₂O is reduced to about 30%, while NiFe₂O₄ and NiO account for the remaining Ni. Spectra of the ROFA H₂O extraction residue W6-Ni-1R and -2R samples were too weak to perform similar analyses.

Table 4-6

Results of Least-Squares Fitting of EXAFS Spectra (3–10 Å-1) for Bulk ROFA and ROFA H_2O Extraction Residues to Linear Combinations of the Corresponding Spectra for NiSO₄·6H₂O, NiFe₂O₄, and NiO

		2		
Sample	NiSO₄·6H₂O, %	NiFe₂O₄, %	NiO, %	Red. χ ²
	96	4	-	0.177
H9-Ni-1	97	_	3	0.169
	96	2	2	0.165
	100	_	-	0.180
	98	2	-	0.168
H9-INI-2	98	-	1	0.173
	98	2	0	0.169
H9-Ni-2R	63	16	21	0.600
W6-Ni-1	85	-	15	0.471
W6-Ni-2	91	-	9	0.485
K1-Ni-1	83	10	7	0.438
K1-Ni-2	81	9	9	0.314
K1-Ni-1R	34	45	21	0.821
K1-Ni-2R	34	39	27	1.720

Analyses of XAFS spectra obtained for ROFA samples from Hawaiian oil-burning power plants indicate that $NiSO_4 \cdot 6H_2O$ is the most abundant Ni-bearing phase in them. Minor amounts of oxide phases such as $NiFe_2O_4$ and NiO are also present, but in subordinate amounts. No evidence exists for the presence of Ni sulfide(s) or other Ni sulfates.

XRD Analyses

XRD analyses were performed on the bulk ROFA samples primarily to identify crystalline phases. X-ray diffractograms for the six ROFA samples are presented in Appendix B. The XRD results in Table 4-7 for the bulk ROFA samples indicate that amorphous components, glass and unburned carbon, are ubiquitous in the ROFAs. NiSO₄·6H₂O and CaSO₄ are also present in all the ROFAs. The KPP Unit 1 ROFA is distinguished by the presence of FeNi₂O₄ which is very similar to the NiFe₂O₄ compound identified by XAFS. XRD analysis results of the ROFA H₂O extraction residues indicated that the H₂O extraction removed most of the ROFA, and no crystalline phases were detected. The sensitivity (i.e., limit of detection) of XRD is much poorer relative to XAFS spectroscopy.

ROFA Sample	NiSO ₄ .6H ₂ O	FeNi ₂ O ₄	CaSO₄	Glass and Unburned Carbon
H9-Ni-1	х		Х	Х
H9-Ni-2	х		Х	Х
K1-Ni-1	х	Х	Х	Х
K1-Ni-2	х	Х	Х	Х
W6-Ni-1	х		Х	Х
W6-Ni-2	х		Х	х

Table 4-7 Bulk ROFA Phase Assemblages

¹An "X" denotes that the corresponding amorphous or crystalline phase was identified using XRD.

5 CONCLUSIONS

The Ni speciation of ROFA samples collected in duplicate on quartz thimble filters from three oil-burning utility boilers was evaluated using two x-ray techniques, XAFS spectroscopy and XRD. ROFA deionized H₂O extraction residues were also analyzed for Ni speciation using XAFS and XRD. Ni pre-edge XANES systematics and the least-squares fitting of XANES and EXAFS spectra of the six ROFA samples with those from standard Ni compounds indicated that the major Ni phase, comprising 80%–95% of the total Ni, was NiSO₄·6H₂O with subordinate proportions, $\leq 20\%$ of the total Ni, present as a spinel compound, similar in composition to NiFe₂O₄ and/or NiO. XRD confirmed the presence of NiSO₄·6H₂O and NiFe₂O₄ but not NiO. Spectral evidence for the presence of Ni sulfide compounds (Ni₃S₂, NiS, or NiS₂) was absent and, at most, does not exceed 3% of the Ni in any sample. Based on these species proportions and the total Ni emission rates in Table 4-2, the emission rates for the Ni species were calculated as indicated in Table 5-1.

Table 5-1		
Ni Species	Emission	Estimates

Facility	NiSO₄·6H₂O, Ib/10 ⁶ Btu	NiFe ₂ O ₄ ± NiO, lb/10 ⁶ Btu	Ni _x S _y , Ib/10 ⁶ Btu
HPP, Unit 9	5.06E-4-6.01E-4	≤ 1.27E-4	≤ 1.90E-5
KPP, Unit 1	9.52E-4—1.13E-3	≤ 2.38E-4	≤ 3.57E-5
WPP, Unit 6	3.42E-4-4.07E-4	≤ 8.56E-5	≤ 1.28E-5

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A APPENDIX

PHOTOGRAPHS OF QUARTZ THIMBLE FILTERS



Figure A-1 Photograph of a Thimble Filter with ROFA Sampled from KPP Unit 1

Appendix



Figure A-2 Photograph of a Duplicate Thimble Filter with ROFA Sampled from KPP Unit 1



Figure A-3 Photograph of a Thimble Filter with ROFA Sampled from WPP Unit 6

Appendix



Figure A-4 Photograph of a Duplicate Thimble Filter with ROFA Sampled from WPP Unit 6

B APPENDIX

X-RAY DIFFRACTOGRAMS OF BULK ROFA AND NI EXTRACTION RESIDUES



Figure B-1

X-ray Diffractogram of ROFA Sample from HPP Unit 9 Indicating Spectral Matches with $NiSO_4.6H_2O$ and $CaSO_4$



Figure B-2

X-ray Diffractogram of Duplicate ROFA Sample from HPP Unit 9 Indicating Spectral Matches with $NiSO_4 \cdot 6H_2O$ and $CaSO_4$



Figure B-3 X-ray Diffractogram of ROFA Sample from KPP Unit 1 Indicating Spectral Matches with $NiSO_4 \cdot 6H_2O$, $NiFe_2O_4$, and $CaSO_4$

Appendix



Figure B-4

X-ray Diffractogram of Duplicate ROFA Sample from KPP Unit 1 Indicating Spectral Matches with $NiSO_4 \cdot 6H_2O$, $NiFe_2O_4$, and $CaSO_4$



Figure B-5 X-ray Diffractogram of ROFA Sample from WPP Unit 6 Indicating Spectral Matches with $NiSO_4 \cdot 6H_2O$ and $CaSO_4$



Figure B-6

X-ray Diffractogram of Duplicate ROFA Sample from WPP Unit 6 Indicating Spectral Matches with $NiSO_4 \cdot 6H_2O$ and $CaSO_4$