



17 March 1998

Dr. C. W. Jameson
National Toxicology Program
Report on Carcinogens, MD EC-14
P.O. Box 12233
Research Triangle Park, NC 27709

Re: Comments on Proposed Listing of Nickel and Nickel Compounds

Dear Dr. Jameson:

On 3 February 1998, the National Toxicology Program (NTP, Federal Register, 63: 5565-5566) proposed a change for the Ninth Report on Carcinogens to place "Nickel and Nickel Compounds" in the "Known to be a Human Carcinogen" category. (The previous edition of the Report on Carcinogens listed "Nickel and Certain Nickel Compounds" in the "Reasonably Anticipated to be a Human Carcinogen" category.) Florida Power & Light Company (FPL) believes that this action is not justified by the current scientific evidence on nickel and nickel compounds. In addition, FPL believes that such a change in designation would be a mistake for at least the following reasons:

- 1) the scientific data do not provide clear evidence of carcinogenicity for all nickel compounds;
- 2) there is a very large difference in cancer potency between those forms of nickel that have been associated with indicators of carcinogenic activity in animal studies;
- 3) lumping all forms of nickel into the single category of "Known Human Carcinogen" is misleading to regulatory agencies and may be counterproductive to rational risk management decisions to protect the human health;
- 4) a new single category could undermine use of the risk assessment approach in evaluating exposures just at a time when technical advances in the speciation of nickel compounds have provided a strong scientific basis to support risk-based regulation;
- 5) if all nickel compounds were to be regulated as potent carcinogens, costs associated with electric power generation, and options for energy diversification in the United States could be severely and unnecessarily adversely affected.

FPL's specific comments are provided below under two headings: Toxicological, and Speciation / Risk Assessment Considerations.

Toxicological Considerations

A number of authors have reported that certain forms of nickel lack carcinogenic activity or vary greatly with respect to potency. Oller et al. (Toxicology & Applied Pharmacology, 143:152-166, 1997) integrate data from the most relevant human, animal and *in vitro* studies to develop a mechanistic model for the carcinogenicity of nickel compounds.

These authors conclude that nickel subsulfide, by acting through two components of the carcinogenic process, presents the highest potency relative to other nickel compounds. They also conclude that, compared to nickel subsulfide, high temperature green nickel oxide "may pose an insignificant risk for carcinogenicity at exposures below the levels needed to impair macrophage clearance and cause chronic inflammation." (Any conclusions based on studies with green nickel oxide may not apply to other oxidic forms of nickel generated at lower temperatures than green nickel oxide and thus being more water soluble.) In the case of soluble nickel compounds, the authors conclude that "as a single agent acting alone, they should present no risk of carcinogenicity, at least at nonovertly toxic concentrations."

The work of Dr. Max Costa, now Chairman of the Department of Environmental Medicine at NYU Medical Center, has been instrumental in delineating mechanisms affecting nickel carcinogenic activity, including the role of phagocytosis and cellular distribution (e.g., Costa et al., *Cancer Research* 41:2868-2876, 1981). Dr. Costa has written a letter responding to the proposed change of category listing all forms of nickel as known human carcinogens, in which he provides evidence for, and suggests that nickel compounds be specifically classified as carcinogens based on the speciation of the compound. Dr. Costa's argument is attached to this letter.

The definitive animal inhalation studies of nickel subsulfide, green (high temperature) nickel oxide and nickel sulfate by the National Toxicology Program (NTP Technical Report Series nos. 451, 453, 454, U.S. Dept. of Health & Human Services, July 1996) provide perhaps the strongest empirical data that argue against the NTP's current proposal. Before this work, no appropriate animal chronic inhalation studies had been performed for either nickel oxides or soluble nickel compounds. Given NTP's own conclusions indicating clear evidence for carcinogenicity for nickel subsulfide in rats, but only a weakly positive carcinogenic response for nickel oxide and "no evidence of carcinogenic activity" in either rats or mice for nickel sulfate, it is puzzling why the NTP now seeks to label all nickel compounds as known human carcinogens. The NTP study conclusions were accepted unanimously by the NTP Board of Scientific Counselors' Technical Reports Review Subcommittee.

It appears that the NTP is proposing to follow the lead of the International Agency of Research in Cancer (IARC) in their decision to classify nickel and nickel compounds (with the exception of metallic nickel) as carcinogenic (IARC Monograph #49, 1990). The NTP has now gone one step further than IARC by even including metallic nickel for which no new data have been developed since IARC's pronouncement. The IARC decision was formulated at a final meeting of the IARC Working Party in Lyon, France, 5-13 June 1989. The Working Party had considered the same data that were available to the Doll Committee (A.K.A. International Committee on Nickel Carcinogenesis in Man, or ICNCM), whose report was available in draft at the time of the Lyon meeting. Several IARC Working Party members also served on the Doll Committee. The evidence for carcinogenicity of soluble forms of nickel came primarily from studies of workers at nickel refineries. Members of the two groups were not unanimous in their interpretation of these

data. The Doll Committee, publishing their report in February 1990 (ICNCM, Scand. J. Work Environ. Health, 16: 1-82), did not reach firm conclusions with respect to soluble nickel compounds. The exposure link to soluble nickel was not conclusive since the workers were exposed to a variety of soluble and insoluble nickel compounds (see attached letter from Dr. Costa). The evidence for soluble nickel being carcinogenic was also inconsistent across cohorts. For example, Oller et al. (1997) point out that comparisons of electrolysis workers at Port Colborne and Kristiansand reveal that only Kristiansand workers had excess lung cancers. While the Kristiansand workers were believed to have been exposed to slightly higher levels of soluble nickel than those at Port Colborne, the main difference was that the Kristiansand workers were handling approximately seven times more insoluble nickel per unit of soluble nickel than those at Port Colborne. The Doll Committee suggested that soluble nickel in the Kristiansand exposure data "in some way" seemed to accentuate cancer, whereas in the Port Colborne cohort they found no evidence of cancer risk. The Doll Committee also suggested that only animal studies with exposures to individual nickel compounds would provide the answer to the role of soluble nickel. The NTP has now provided that additional evidence and it has been negative.

Speciation / Risk Management Considerations

Available evidence on nickel carcinogenicity has provided the impetus for several major studies on nickel speciation by the oil-burning electric utility industry. The results of these studies were intended to provide the basis, in concert with definitive studies on the carcinogenic potency of nickel species, for a risk-based approach to cost-effective management of environmental releases. While the animal data support a prudent management approach to speciate nickel and, may, in some cases, support additional animal studies on specific constituents of major source releases where definitive data do not exist, such investigative options could be preempted by a broad cancer classification that is, at best, based on inconclusive evidence.

The results of nickel speciation work sponsored by Florida Power & Light Company provide an example of the major effort that the industry, including the Electric Power Research Institute, has undertaken to develop exposure data. A detailed summary of the ongoing FPL work is provided with these comments in an attached letter and data sheets from Dr. John Wong of the University of Louisville. Dr. Wong holds joint professorial appointments in the Departments of Pharmacology & Toxicology and Chemistry and has published extensively in both disciplines. This includes numerous peer-reviewed publications as well as invited lectures on the toxicology and chemistry of nickel and other metals. His work, in conjunction with collaborators from the Energy & Environmental Research Center, shows for both the ash component of emissions and fly ash from mechanical collectors, that sulfidic nickel is not a major combustion product. Soluble nickel compounds, primarily nickel sulfate, are the largest contributors at about 34% to 92% of total nickel, depending on conditions of combustion. Oxidic nickel is intermediate in abundance, ranging from 5% to 48% of total nickel.

Other work with Dr. Peter Walsh on the physical processes of aerosol formation during oil combustion (begun at Penn State and now continuing at Sandia National Laboratories), provides additional insight into the exposure parameters of various nickel emissions. For example, for a nickel sulfide (or subsulfide) particle to survive both the combustion process and the high temperature regions of the boiler, highly reducing conditions must prevail. Such conditions only exist within the char cenospheres (cenospheres are relatively large carbonaceous particles resulting from the fractional distillation of oil droplets during combustion). It is reasonable to assume, therefore, that any nickel sulfide particles present in the particulate may be locked in the structure of the char cenospheres. This would be relevant to the bioavailability of sulfidic nickel from oil combustion since the cenospheres typically have diameters greater than about 30 microns and, thus, would not be respirable. Dr. Wong's 5-step extraction is currently being applied to specific size fractions of oil ash, in collaboration with SEM work by Dr. Walsh, to test this conclusion.

On the basis of current scientific knowledge as outlined in this limited review, FPL strongly objects to a categorical change for nickel and nickel compounds unless specific categories are assigned based on the chemical form of nickel compounds being considered, with evidence for differences in cancer potency being addressed. Furthermore, FPL specifically objects to any classification of metallic nickel or soluble nickel compounds as either known or presumed carcinogens.

Sincerely,

A handwritten signature in black ink, appearing to read "Edward J. Zillioux", with a long horizontal flourish extending to the right.

Edward J. Zillioux, Ph.D.
Manager, Toxicology & Risk Assessment Services

cc: Dr. Max Costa
Dr. John L. Wong
Class of '85 Regulatory Response Group



Max Costa, Ph.D.

Professor and Chairman

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February 27, 1998

Edward J. Zillioux, Ph.D.
Manager, Risk Assessment Services
Florida Power & Light Company
700 Universe Boulevard
Juno Beach, FL 33408

Dear Dr. Zillioux:

This letter is in response to the proposed change of category listing all forms of nickel as known human carcinogens.

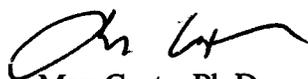
There is no question that certain nickel compounds represent potent human carcinogens and are positive in inhalation NTP bioassays. These compounds include insoluble crystalline nickel subsulfide and less potent insoluble green and black nickel oxide. However, water-soluble nickel salts were negative in the recent NTP bioassay. Other work concerning the mechanisms of nickel carcinogenesis have pointed out why these water-insoluble Ni compounds are potentially carcinogenic. In 1980 I discovered that the potent carcinogenic forms of nickel (nickel subsulfide) were actively phagocytized by target cells that would become cancerous (Costa and Mollenhauer, *Science* 209:515-517, 1980). Further work showed that following phagocytosis of these particles, they were dissolved inside the cell by the acid pH of the vacuole containing them. This yielded very high concentrations of soluble nickel inside the cell cytoplasm and high concentrations of soluble nickel entered the nucleus and interacted with chromatin. The current mechanism of nickel carcinogenesis, as has been worked out in my lab, appears to involve the ability of nickel to substitute for magnesium in the binding to the phosphate backbone of DNA which increases chromatin condensation (Klein et al., *Science* 251:796-799, 1991; Lee et al., *Mol. Cell. Biol.* 15:2547-2557, 1995). This increased chromatin condensation triggers *de novo* methylation of the DNA and because this DNA methylation is induced *de novo* and inherited in subsequent cell generation, it results in the loss of expression of genes. When tumor suppressor genes and senescence genes are lost in their expression, nickel drives the cell towards the cancer state. In order for this occur, however, the nickel concentration inside the cell must reach very high levels; high enough to compete with the magnesium levels that are close to mM in the cell. This can be achieved with a water-insoluble nickel compound that is phagocytized where hundreds of mM concentrations of nickel could potentially buildup inside the cell following particle dissolution.

With respect to the water-soluble nickel compounds, they have consistently been shown not to enter cells readily and there is little Ni^{2+} that appears in the nucleus of cells treated with water-soluble nickel compounds. The reason for this is that the water-soluble nickel compounds must compete with magnesium for entry inside the cell. Magnesium levels are mM outside the cell and, therefore, water-soluble nickel compounds must approach the high mM range in order to even enter the cell. These levels are never obtained in humans. If they were, humans would experience toxic reactions from the Ni^{2+} at this high level where they would have heart attacks, brain seizures, etc. from the ability of the nickel to affect cellular calcium metabolism. Therefore, the water-soluble nickel salts offer little threat to human cancer and it is a mistake to classify these compounds in the same category as crystalline nickel subsulfide and nickel oxide. Although nickel metal has not been extensively studied, it is relatively inert and would not be phagocytized, at least in studies that I have conducted and, therefore, it should not be classified as a carcinogen. I would propose, therefore, that the regulation be limited to stating that there is evidence for carcinogenicity of nickel sulfides, nickel oxides, and other such insoluble nickel compounds causing human cancer by inhalation but at the present time, there is no need to classify water-soluble nickel salts, such as nickel sulfate, chloride, acetate, etc. as human carcinogens.

Epidemiological studies that have attempted to classify water-soluble nickel salts as carcinogens have had significant problems in establishing a unique exposure of the workers to water-soluble nickel compounds. The claim has been that workers in the electrolysis area of nickel refineries are exposed to mostly water-soluble nickel salts and those workers have a higher incidence of nasal cancers but many of these workers are also very heavy smokers (IARC, Vol. 49, 1990). They are also exposed to water-insoluble nickel compounds in this same area. In view of the lack of the ability of epidemiological studies to assess speciation of exposure, it is difficult to rely upon these studies as evidence that water-soluble nickel salts are carcinogenic. Clearly the animal studies, not only conducted by NTP but conducted by other workers, where one investigator injected water-soluble nickel salts multiple times to an animal, did not induce tumors (Costa, *Annu. Rev. Pharmacol. Toxicol.* 31:321-337, 1991; Kasprzak et al., *Carcinogenesis* 4(3):275-279, 1983) points to the fact that there is little hazard in terms of cancer from human exposure to water-soluble nickel compounds.

I, therefore, suggest that nickel compounds be specifically classified as carcinogens based on the speciation of the compound. I would be happy to provide any further information regarding this point.

Sincerely,



Max Costa, Ph.D.
Professor and Chairman

UNIVERSITY of LOUISVILLE

March 2, 1998

Dr. Ed J. Zillioux
Manager, Risk Assessment Services
Florida Power and Light Co.
700 Universe Blvd.
Juno Beach, FL 33408

Dear Dr. Zillioux:

This letter is written to summarize our findings on nickel speciation of oil-fired ash samples supported by Florida Power and Light Co. Our laboratory has been engaged in metal speciation of particulate matter, and the approach applied to nickel is based on sequential extraction of unique nickel phases from the ash.

Methods. The current sequential phase extraction procedure produces 5 phases of nickel. In step (1), sodium acetate solution at pH 5 removes soluble nickel compounds like NiSO_4 . In step (2), Na-citrate and Na-dithionite solution at pH 5 is used to extract nickel in the iron oxide matrix. Step (3) removes metallic nickel by an electromagnet. In step (4), sulfidic nickel including nickel subsulfide is released by hydrogen peroxide at pH 2. The last step (5) makes use of HF-HClO_4 to extract any remaining nickel primarily in the silica matrix. The aqueous extracts containing Ni^{2+} was determined by adsorptive stripping voltammetry (ASV) as Ni-dimethylglyoximate on a hanging mercury drop electrode.

Method variation and relevance. The significance of this nickel fractionation scheme is that the ash nickel components can be determined as unique phases each with its own biological relevance. For example, nickel sulfate and nickel carbonate are found in the water-soluble phase obtained from step 1. Nickel oxide present in the iron oxide matrix is released in step 2. This particular nickel oxide may be considered to be bioavailable whereas that found in the silica matrix by step 5 is not. The sulfidic nickel which could include Ni_3S_2 , the nickel form of primary concern, is determined by step 4. In case where the oxidative treatment may interfere with other speciation study, 2N HCl may be used to replace the peroxide. Further differentiation of these nickel species can be extended to yield nine phases. Thus, step 1 extraction is subdivided into 3 steps using deionized water, magnesium chloride solution, and sodium acetate sequentially to extract nickel sulfate, specifically adsorbed Ni^{2+} which is displaceable by Mg^{2+} , and nickel carbonate associated with dolomite, respectively. Step 2 is subdivided into two steps: sodium citrate is followed by a sodium citrate-dithionite combination to release first the nickel

oxide bound to the amorphous iron (II) oxide coating and then the nickel oxide bound to the iron (III) oxide lattice. After step 5, if any black carbon residue remains, a final step of burning it in oxygen is added to release the last trace of nickel. For the propose of evaluating the environmental risk of nickel in fly ash, the 5 step extraction scheme should be adequate. Thus, the water soluble nickel compounds like nickel sulfate found in step 1 are relatively innocuous with respect to carcinogenicity. The nickel oxide from step 2 is bioavailable and hence its carcinogenicity potential is a matter of interest. The sulfidic nickel determined by step 4 where nickel subsulfide could be found is the focal point of attention, whereas the nickel metal and nickel oxide in silica from steps 3 and 5, respectively, are not bioavailable. Ongoing work will determine the percentages of the subsulfide and other sulfides in this phase via solid state electrochemical analysis.

Ash Samples. The ashes analyzed in this project include a variety of sample origins, and their data are presented in five sections. Section 1 describes two slurry pond samples of composite ash: sample-101 came from an oil-fired plant burning residual oil with 1.4 % sulphur, and sample-17 from a plant using 0.7 % sulphur residual oil. Section 2 describes two hopper ash samples: sample-973 from co-firing 1 % sulfur fuel oil and natural gas in a 7 : 3 ratio and sample-3B-side from a plant burning 2.0 to 2.5 % sulfur residual oil. Section 3 presents data on six stack samples collected at an oil-fired plant using filter membranes. Section 4 deals with stack ash produced by a laboratory scale combustion system at the Energy & Environmental Research Center (EERC) burning a high-sulphur (1.48 wt %) residual oil and a low-sulphur (0.33 wt %) residual oil. Section 5 describes nickel speciation of a coke ash produced by Dr. Peter Walsh at the University of Pennsylvania from a petroleum coke containing 1.74 % sulfur and spiked with 1.14 wt % nickel. The latter is a reference ash for high sulfidic nickel content.

Results. Table 1 of Section 1 gives a summary of nickel speciation of two ash samples. An article on this subject entitled "Nickel speciation of fly ash by phase separation" is published in *Analytica Chimica Acta* 1997, and a reprint is attached as an appendix. Section 2 contains four tables on two ash samples showing size distributions, comparison of nickel total of two particle sizes, nickel speciation by 5-step phase separation and a repeat of this procedure with one modification: 2N HCl replaces hydrogen peroxide in step 4. Section 3 contains four tables on six stack ash samples showing sampling data and total nickel, a full data sheet of nickel species obtained from 5-step fractionation and 1-step total digestion, as well as a comparison of nickel speciation across the samples and statistical means. Section 4 contains four tables on four EERC ash samples showing sample description, nickel total analysis by acid digestion and X-ray, nickel speciation by 5-step phase separation and reproducibility. Section 5 has two tables dealing with properties of the reference coke ash and nickel speciation with mass balance.

Discussion. Based on nickel speciation performed on a variety of oil ash samples, some generalizations about the chemical nature of nickel distribution in ash particulate can be made. It should be noted that the unique nickel phases determined by sequential extraction are highly reproducible with coefficients of variation of about 5 % or less. As quality assurance, mass balance of nickel phase fractionation with nickel from total digestion is also obtained. In terms of the sulfidic nickel fraction, none of the field

samples analyzed amounted to a third of the ash nickel content. The outer limit of sulfidic nickel as given by the reference coke ash prepared by burning a high sulfur coke spiked with nickel was about 32 %. For the composite ash from slurry pond, the sulfidic nickel fraction ranged between 12 to 15 %. The two hopper ash samples were between 4 to 7 %. The six stack ash samples collected on filter membrane showed a higher range of sulfidic nickel of 15 to 25 %. However, under laboratory-controlled combustion conditions, the EERC samples #1 and #3, derived from the high sulphur oil, gave about 1 % of sulfidic nickel and the stack ash from the low sulfur oil was about the same. It is therefore reasonable to suggest that sulfidic nickel is not a major combustion product of nickel in fuel oil.

Another observation worthy of note is that the bioavailable nickel oxide species present in the iron oxide matrix, among other nickel species, showed considerable variability with combustion parameters. Thus, step 2 extraction of the hopper ash sample-973, from co-firing low sulfur fuel oil and natural gas, and sample-3B-side, from burning high sulfur residual oil, showed 27 % and 43 % of the nickel oxide, respectively. Likewise, that from EERC #1 was 23 % vs. 6 % from EERC #3. These laboratory ashes were from the same fuel oil which was burned at an excess oxygen of 1.1 % and 2 - 3 %, respectively. Even the six stack ash samples collected on three consecutive days at the same oil-fired unit gave a range of nickel oxide percentages by step 2, with a coefficient of variation of 62 %. When more sampling of ash particulate is performed with conditions documented, particularly current work on the differentiation of Ni_3S_2 , if any, from other forms of sulfidic nickel, a more comprehensive nickel speciation database may be constructed to serve two functions: correlation of the chemical nature of nickel species in ash emissions with oil combustion characteristics, and a strong scientific basis for risk assessment and risk management of potential health effects due to distinct forms of nickel present in emissions and ash from oil-fired power plants.

For further information and discussion of our nickel speciation program, please contact me at the above letterhead addresses or email me at: jlwong01@homer.louisville.edu.

Sincerely,



John L. Wong, Ph.D.
Professor of Chemistry
Professor of Pharmacology & Toxicology

Section 1

Table 1. Nickel speciation of two oil ash samples

Extraction steps	Sample-101 (Total Ni 5222.5 ± 207.7 ug/g)			Sample-17 (Total Ni 7513.0 ± 282.7 ug/g)		
	Ni Found (ug/g)	CV (%)	Ni (%)	Ni Found (ug/g)	CV (%)	Ni (%)
1. Deionized H ₂ O	8.8 ± 0.3	3.1	0.2	417.2 ± 5.9	1.1	5.7
2. Mg ²⁺ , pH5	52.6 ± 0.9	1.3	1.0	48.8 ± 2.2	3.6	0.7
3. Acetate, pH5	1243.0 ± 54.9	3.6	24.6	3.6 ± 0.2	5.3	0.0
4. Citrate, pH5	287.5 ± 7.6	2.1	5.7	551.0 ± 9.3	1.4	7.5
5. Citrate-dithionite, pH5	743.4 ± 12.1	1.3	14.7	1872.5 ± 35.6	1.5	25.4
6. Electromagnet	460.2 ± 14.6	2.5	9.1	1642.6 ± 50.4	2.5	22.3
7. H ₂ O ₂ , pH2	581.3 ± 11.0	1.5	11.5	1113.1 ± 25.4	1.8	15.1
8. HF-HClO ₄	1674.8 ± 84.6	4.1	33.1	1714.8 ± 97.1	4.6	23.3
9. Burn; H ⁺	<u>1.6 ± 0.1</u> 5053.2 ± 103.5	<u>4.5</u> 1.6	<u>0.0</u> 100.0	<u>6.8 ± 0.3</u> 7370.4 ± 118.4	<u>4.0</u> 1.3	<u>0.1</u> 100.0
Mass Balance	96.8%			98.1%		

Section 2

Table 1. Size distribution of two oil ash samples

A. by sieving

Particle Size Micron(um)	Sample-973		Sample-3B-side	
	Weight(g)	%	Weight(g)	%
590	1.353	16.36	0.088	0.8
500	0.4	4.84	0.047	0.4
163	2.465	29.82	3.753	35
83	1.755	21.22	4.988	46.5
74	0.284	3.43	0.305	2.85
<74*	2.011	24.32	1.537	14.34
	8.267	99.99	10.72	99.89

B. by sonic autostieving

63	0.942	93.6	0.724	94.2
53	0.0388	3.8	0.0315	4.1
45	0.0251	2.5	0.0131	1.7
25	none		none	
10	none		none	
5	none		none	
	1.006	99.90	0.768	100

* Particle size used for metal speciation studies.

Table 2. Ni total of two oil ash samples in two size distributions

Sample	Independent expt.	Ni found(ug/g)	
		163 um	63 um
Sample-973	1	27,023.5	27,735.3
	2	27,070.2	27,728.8
	3	27,319.9	27,656.0
	4	27,446.2	27,816.7
		Mean	Mean
		CV%	CV%
		27,215.0	27,734.2
		0.7	0.2
Sample-3B-side	1	42,678.6	43,018.3
	2	43,154.9	43,675.8
	3	42,294.5	42,564.9
	4	43,339.8	43,098.0
		Mean	Mean
		CV%	CV%
		42,882.0	43,089.3
		1.1	1.1

Table 3. Nickel speciation of two oil ash samples and SRM 1633b by five-step phase separation*

<u>Extraction</u>	<u>1633b</u> ug/g	<u>%</u>	<u>Sample-973</u> ug/g	<u>%</u>	<u>Sample-3B-side</u> ug/g	<u>%</u>
1	33.6	27.77	13,565.0	50.87	26,487.2	60.03
2	47.3	39.09	11,352.6	42.58	11,949.8	27.08
3	7.1	5.87	78.9	0.29	2,231.7	5.06
4	23.5	19.42	980.4	3.67	3,267.6	7.41
5	9.5	7.85	683.6	2.56	189.0	0.43
Total	121.0	100	26,663.9	100	44,125.3	100
Mass Balance	99.9%		96.1%		102.0%	

Step 1, HOAc-NaOAc, pH 5
 Step 2, Na₂S₂O₄-Citrate, pH 5
 Step 3, Electromagnet
 *Step 4, H₂O₂-HNO₃
 Step 5, 50% HF

*Particle size: 163 um
 Run 1

Table 4. Nickel speciation of two oil ash samples and SRM 1633b by five-step phase separation*

Extraction	1633b		Sample-973		Sample-3B-side	
	ug/g	%	ug/g	%	ug/g	%
1	32.5	27.01	13,696.7	49.77	25,826.0	60.03
2	48.9	40.69	11,590.5	42.18	11,508.3	26.75
3	6.9	5.69	47.8	0.17	2,308.3	5.37
4	23.1	19.19	1,298.4	4.72	3,193.6	7.42
5	8.8	7.32	885.8	3.20	182.1	0.42
Total	120.2	99.9	27,519.2	100	43,018.3	99.9
Mass Balance	99.7%		99.2%		99.2%	

Step 1, HOAc-NaOAc, pH 5

Step 2, Na2S2O4-Citrate, pH 5

Step 3, Electromagnet

*Step 4, 2NHCl

Step 5, 50% HF

*Particle size: 163 um

Run II

Section 3

Table 1. Stack ash sampling description and total Ni

Sample #	37-P-1	37-P-2	37-P-3	37-P-4	37-P-5	37-P-6	37-P-7	37-P-8	1633b	1633b certified
Test #	8-Mtis/Spec	9-Mtis/Spec	10-Mtis/Spec	11-Mtis/Spec	12-Mtis/Spec	13-Mtis/Spec	Filter Blank	Filter Blank		
Blank Weight (mg)	65.55	65.55	65.55	65.55	65.55	65.55	---	---		
Total Weight (mg)	89.55	76.25	81.85	74.65	91.55	80.25	65.50	65.60		
Net Weight (mg)	24.00	10.70	16.30	9.10	26.00	14.70	---	---		
Weight gain (mg)	19.7	9.9	24.5	7.4	24.1	11.8	---	---		
Weighing Difference	4.3	0.8	-8.2	1.7	1.9	2.9				
% Difference	21.8%	8.1%	-33.5%	23.0%	7.9%	24.6%				
Sample volume (dscf)	23.54	26.42	24.95	24.62	25.10	23.80	---	---		
Sample volume (Cubic M)	0.667	0.748	0.706	0.697	0.711	0.674				
Flow Rate F (dscfm)	665,000	665,000	662,000	662,000	647,000	647,000	---	---		
Sampling Date	10/8/92	10/8/92	10/9/92	10/9/92	10/10/92	10/10/92	---	---		
Sampling Time	10:50-13:13	14:25-16:25	09:25-11:30	12:35-14:50	09:15-11:15	12:00-14:10	---	---		
Sampling Period (min)	143	120	125	135	120	130	---	---		
Total Ni (ug/g)	21,669.4	25,804.3	55,460.2	12,986.5	22,013.6	11,729.1	0.0	---	125.2	120.6
Total Ni (ug/cubic M)	780.25	369.08	1279.61	169.52	805.32	255.85				
CV, %	3.2	4.7	2.9	4.3	3.6	4.5	---	---	1.4	
Recovery										103.8%

1 cf = 0.0283152 cubic m

Table 2. Full data sheet of Ni species of stack ash using half-filter samples

Sequential Extractions Steps	P-1		P-2		P-3		P-4		P-5		P-6		Mean P-(1-6)													
	Ni ug/g	Ni %	Ni ug/g	Ni %	Ni ug/g	Ni %	Ni ug/g	Ni %	Ni ug/g	Ni %	Ni ug/g	Ni %	SD	CV(%)	SD	CV(%)	Ni %									
1	9431.9	339.6	45.9	9481.0	135.6	38.4	27667.0	522.9	42.6	5030.2	65.7	40.5	4696.8	171.8	22.4	3913.2	85.3	34.4	9203.4	7030.1	76.4	220.1	177.5	80.6	38.6	
2	6971.2	251.0	33.9	9470.5	135.4	38.4	20032.5	462.1	37.7	4443.9	58.0	35.8	10119.2	370.1	48.2	4645.6	101.3	40.8	9280.5	5771.5	62.2	229.7	160.7	70.0	38.9	
3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	3171.7	114.2	15.4	4619.1	66.1	18.7	8330.3	192.2	15.7	2424.1	31.6	19.5	5326.5	194.8	25.4	2286.8	49.9	20.1	4359.8	2290.1	52.5	108.1	71.6	66.2	18.3	
5	990.7	35.7	4.8	1098.8	15.7	4.5	2153.2	49.7	4.0	530.3	6.9	4.3	844.6	30.9	4.0	527.8	11.5	4.6	1024.2	600.7	58.6	25.1	16.4	65.6	4.3	
	20565.5	740.4	100.0	24669.4	352.8	100.0	53183.0	1226.9	100.0	12428.5	162.2	100.0	20987.1	767.6	100.0	11373.4	248.0	100.0	23867.8			583.0			100.0	
Net weight (g)	0.0240			0.0107			0.0163			0.0091			0.0260			0.0147										
Sample vol (dec)	23.54			26.42			24.95			24.62			25.1			23.8										
Sample vol (m ³)	0.667			0.748			0.707			0.697			0.711			0.674										
1-Step Digestion of the Other Half-Filter	21669.4			25804.3			55460.2			12986.5			22013.6			11729.1										
Ratio of 5-step to 1-step Digestion	0.95			0.96			0.96			0.96			0.95			0.97										

^a Half-filter fly ash weights of P-1, 2, 3, 4, 5 and 6 are 12.00, 5.35, 8.15, 4.55, 13.00 and 7.35 mg, respectively.

Table 3. Comparison of nickel speciation of stack ash using half-filter samples

Sequential Extractions Steps	P-1		P-2		P-3		P-4		P-5		P-6		Std Coal Fly Ash 1633b	
	Ni ug/g	Ni %	Ni ug/g	Ni %										
1	9431.9	45.9	9481.0	38.4	22667.0	42.6	5030.2	40.5	4696.8	22.4	3913.2	34.4	33.4	27.0
2	6971.2	33.9	9470.5	38.4	20032.5	37.7	4443.9	35.8	10119.2	48.2	4645.6	40.8	50.5	40.7
3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.1	5.7
4	3171.7	15.4	4619.1	18.7	8330.3	15.7	2424.1	19.5	5326.5	25.4	2286.8	20.1	23.8	19.2
5	990.7	4.8	1098.8	4.5	2153.2	4.0	530.3	4.3	844.6	4.0	527.8	4.6	9.1	7.3
	20565.5	100.0	24669.4	100.0	53183.0	100.0	12428.5	100.0	20987.1	100.0	11373.4	100.0	123.9	100.0
<hr/>														
1-Step Digestion of the Other Half-Filter	21669.4		25804.3		55460.2		12986.5		22013.6		11729.1			(120.6 Certified)
Ratio of 5-step to 1-step Digestion	0.95		0.96		0.96		0.96		0.95		0.97			1.03

^a Half-filter fly ash weights of P-1, 2, 3, 4, 5 and 6 are 12.00, 5.35, 8.15, 4.55, 13.00 and 7.35 mg, respectively.

Table 4. Statistical means of nickel speciation of stack ash

Based on ug/g of particulates		(1) Soluble Ni salt		(2) NiO in Fe-oxide matrix		(3) Metallic Ni		NixSy		(5) NiO in silica matrix & resistant sulfide		Ratio of step (1-5)
Stack ash	Ni Total ug / g	ug / g	%Total	ug / g	%Total	ug / g	%Total	ug / g	%Total	ug / g	%Total	Ni Total
P-(1-6)	24,944	9,203	38.6	9,280	38.9	0	0.0	4,360	18.3	1,024	4.3	0.96
	(64)	(76)		(62)		(0)		(53)		(59)		
SRM 1633b (certified 120.6 ug/g)	124	33	27.0	51	40.8	7	5.7	24	19.2	9	7.3	1.00

CV% in parenthesis.

Section 4

Table1. EERC sample description

Name	Description
EERC1	ash, CEPs Runs 26-32 5.13 wt% C, 5.51 wt% Ni, 760 ppm Cr, 14.6 wt% V, <1.1% excess O2
EERC2	ash, Runs 13-14 28.9 wt% C, 1.49 wt% Ni, 840 ppm Cr, 1.69 wt% V, ~2% excess O2
EERC3	ash, CEPs Runs 23-25, 1.19 wt% C, 4.21 wt% Ni, 790 ppm Cr, 13.4 wt% V, 2-3% excess O2
EERC4	ash, Runs 15-16 4.19 wt% C, 1.93 wt% Ni, 1080 ppm Cr, 2.35 wt% V, ~3% excess O2

Table 2. Ni total analysis of EERC samples by acid digestion and X-ray

EERC Samples	Ni Total by ASV(ug/g)		Ni Total (Avg)(ug/g)	Ni found by X-ray (ug/g) (Data on vial)	Ni Total by ASV Ni by X-ray
	1#	2#			
EERC1	92,939.7	91,760.5	92,350.1	55,100	1.7
EERC2	34,311.2	33,433.2	33,872.2	14,900	2.3
EERC3	76,272.5	77,479.3	76,875.9	42,100	1.8
EERC4	39,981.6	38,306.5	39,144.1	19,300	2.0

Table 3. Nickel speciation of Four EERC samples and SRM 1633b by five-step phase separation*(Run 1)

Extraction	1633b#1		EERC1#1		EERC2#1		EERC3#1		EERC4#1	
	ug/g	%	ug/g	%	ug/g	%	ug/g	%	ug/g	%
1	34.5	29.4%	65,819.1	74.8%	25,430.8	78.2%	69,398.8	92.2%	33,700.8	90.2%
2	42.5	36.2%	20,178.9	22.9%	5,563.9	17.1%	4,673.2	6.2%	1,964.6	5.3%
3	7.4	6.3%	265.1	0.3%	161.7	0.5%	111.5	0.1%	54.8	0.1%
4	22.4	19.1%	1,030.2	1.2%	543.5	1.7%	613.0	0.8%	631.7	1.7%
5	10.7	9.1%	718.4	0.8%	822.1	2.5%	486.0	0.6%	1021.5	2.7%
Total	117.5	100.0%	88011.7	100.0%	32522.0	100.0%	75282.5	100.0%	37373.4	100.0%

*Step1, HOAc-NaOAc, pH5

Step2, Na2S2O4-Citrate, pH5

Step3, Electromagnet

Step4, H2O2-HNO3

Step5, 50% HF

1633b#1, W=0.0294

EERC1#1, W=0.0217g

EERC2#1, W=0.0394g

EERC3#1, W=0.0265g

EERC4#1, W=0.0261g

Table 4. Nickel speciation of Four EERC samples and SRM 1633b by five-step phase separation*(Run 2)

Extraction	1633b#2		EERC1#2		EERC2#2		EERC3#2		EERC4#2	
	ug/g	%	ug/g	%	ug/g	%	ug/g	%	ug/g	%
1	31.8	25.8%	65,382.9	73.7%	26,963.9	79.2%	69,865.3	92.4%	33,559.6	89.4%
2	50.4	40.9%	21,442.8	24.2%	5,461.9	16.1%	4,556.8	6.0%	2,061.1	5.5%
3	6.8	5.5%	268.8	0.3%	163.6	0.5%	103.6	0.1%	96.6	0.3%
4	23.2	18.8%	1,025.2	1.2%	551.2	1.6%	693.1	0.9%	749.0	2.0%
5	10.9	8.9%	628.2	0.7%	886.4	2.6%	400.4	0.5%	1060.6	2.8%
Total	123.1	100.0%	88747.9	100.0%	34027.0	100.0%	75619.2	100.0%	37526.9	100.0%

*Step1, HOAc-NaOAc, pH5
 Step2, Na2S2O4-Citrate, pH5
 Step3, Electromagnet
 Step4, H2O2-HNO3
 Step5, 50% HF

1633b#2, W=0.0337
 EERC1#2, W=0.0250g
 EERC2#2, W=0.0109g
 EERC3#2, W=0.0261g
 EERC4#2, W=0.0230g

Section 5

Table 1. Properties of Pennstate #L-12 from Dr. Peter Walsh

<u>Chemical property</u>	<u>Petroleum coke no additive</u>	<u>Petroleum Coke 1.14 wt% Ni</u>
Ultimate Analysis, wt%(Air-Dried)		
Carbon	96.25	96.25
Hydrogen	0.75	0.75
Nitrogen	0.25	0.25
Sulfur	1.74	2.12
Chlorine	0.003	0.003
Proximate Analysis, wt%(Air-Dired)		
Volatile Matter	1.86	1.86
Ash	0.172	2.2
Mataals, wt%		
Vanadium	0.004	0.004
Nickel	<0.0012	1.14
Iron	0.016	0.016
Calcium	0.003	0.003
Magnesium	<0.0012	<0.0012
Sodium	0.078	0.078
Potassium	<0.0005	<0.0005
Aluminum	0.005	0.005
Silicon	0.001	0.001
Copper	0.004	0.004
Tin	0.002	0.002

Table 2. Sequential extraction of Ni from PENNSTATE #L-12

(#L-12 containing approximately 10000 ug Ni/g sample)

Step	Run a (52.0mg)		Run b (45.6 mg)		Run c (64.7mg)		Run d (49.0mg)		Run d (35.8 mg)	
	Ni ug/g	%	Ni ug/g	%	Ni ug/g	%	Ni ug/g	%	Ni ug/g	%
1. NaOAc	(1-4)	1100.4	9.9	1068.7	9.9					
2. Na2S2O4-citrate	(1-4)	791.7	7.1	841.4	7.8					
3. Magnetic		0.0		0.0	0.0					
4. H2O2-HNO3	(1)	1107.1	10.0	1051.5	9.8					
	(2)	873.5	7.9	990.7	9.2					
	(3)	722.9	6.5	664.9	6.2					
	(4)	567.7	5.1	532.6	4.9					
	(5)	158.8	1.4	286.1	2.7					
(1-5)	3430.0	31.0	3525.8	32.7						
5. HF-HClO4 digestion		4782.8	43.2	4871.5	45.2					
residue from above with HNO3-HClO4-HF digestion		972.0	8.8	472.8	4.4					
Total		11076.9	100.0	10780.2	100.0					
1. HF-HClO4 digestion				9470.4	94.7			9923.9	99.2	
2. residue from above with HF-HClO4-HNO3 digestion				935.1	9.4			639.9	6.4	
Total				10405.5	104.1			10563.8	105.6	