

# Speciation of Nickel in Aerosols: Comparison of Synchrotron XANES and Sequential Leaching

B. Ajiboye (1), J. Warner (1) and M. Dutton (2)

1 Canadian Light Source, Inc.

2 Sustainability, Vale Inco Ltd., Toronto, ON Canada

# 29

## PRINCIPAL CONTACT:

**J. Warner**

Industrial Liaison Scientist

jeff.warner@lightsource.ca

1.306.657.3568

## Introduction

The toxicity of nickel compounds in the environment varies significantly among the different chemical species of nickel. Nickel subsulphide ( $\text{Ni}_3\text{S}_2$ ) is considered the most carcinogenic nickel species, whereas the toxicity of water soluble nickel species (eg.  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) and insoluble nickel species (eg.  $\text{NiO}$ ) is more controversial [1]. In 2008, the European Union Risk Assessment Report on Nickel will be released, listing several soluble

nickel compounds as Category 1 Carcinogens (known or presumed human carcinogens) with a possible “Read-Across” recommendation, which would further classify 150 nickel compounds as Category 1 Carcinogens – solely on the basis of solubility. The impact on the perception, marketing and use of all nickel compounds will be substantial. The Read-Across recommendation categorizes nickel based upon a sequential chemical leaching method common to the nickel industry (the Zatka method) [2]. In this preliminary work, we compare nickel speciation results obtained from the Zatka sequential extraction technique and synchrotron Ni *K*-edge X-ray absorption near-edge structure (XANES) spectroscopy on a flue dust sample. The XANES work was carried out on the 06ID-1 (HXMA) beamline at the CLS. An aspect of the future work of this project is to establish, using other methods, the accuracy of both techniques.

## Science

The Zatka sequential leaching technique differentiates among similarly reacting nickel compounds rather than individual species. The Zatka method was originally designed for mineralogical analysis but was then adapted to the characterization of Ni-containing aerosols relevant to occupational exposure. Typically, these workplace dust samples contain a limited number of nickel species so that the four groups used to categorize analogous species in the Zatka method are sufficient. Application of the chemical leaches of the Zatka method results in the extraction of four subsamples categorized as shown in Figure 1.

With respect to workplace dusts and aerosols, each Zatka category allegedly corresponds to a group of particular Ni species. However, the specificity of the reagents to discrete mineral phases cannot be guaranteed unless additional techniques such as XANES are applied to the residues from each leaching stage to identify the species remaining [3].

The characteristics of XANES that make it a valuable method of quantitative analysis are the minimal sample preparation required, its element selectivity, its sensitivity to changes in oxidation states and the ease of its application to samples in various physical forms. XANES is also a convenient choice for workplace inhalation studies because it can measure all the nickel in a given aerosol sample *in situ* on the air filter.

## Results

The Zatka method was applied to a flue dust sample obtained from a smelter operation in Thompson, Manitoba. The extracts from each leaching stage were analyzed for total Ni. The proportions of Ni species expected in each residue were obtained from a back calculation to the starting dust material to allow for comparison with the XANES analysis. Ni *K*-edge XANES spectra were taken on the intact flue dust and for each Zatka residue in addition to a number of standards (Figure 2).

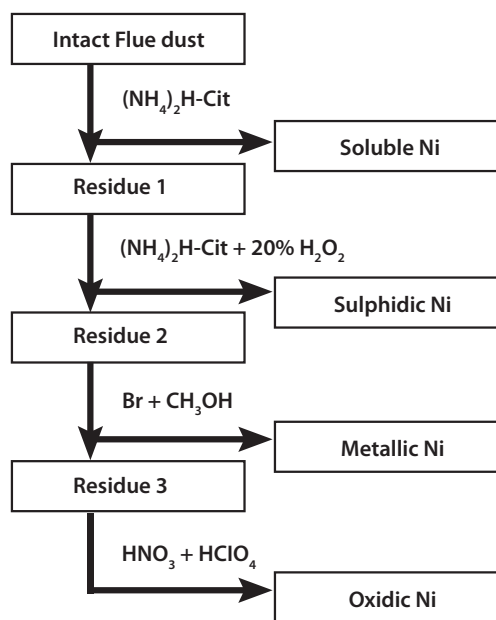


Figure 1. Overview of the sequential leaching scheme [1].

Fit values using the Ni standards were combined to match the operational categories defined by the Zatka method. Uncertainties on the XANES results were taken from fits to samples of known concentration and are estimated at  $\pm 5\%$ .

## Discussion

Comparison of the results in Table 1 shows that XANES is reporting a larger oxidic component in many of the residues than the proportions obtained from sequential leaching. There

are also significant differences in the amount of sulphidic component between the two methods.

With sequential chemical extraction procedures, a major concern is the operational conditions employed. During exposure to various chemical reagents used for extraction or leaching, new particle surfaces are continually exposed allowing oxidation reactions to occur. There is also a concern that some particle interiors may not be adequately extracted into the appropriate category depending on the extraction conditions.

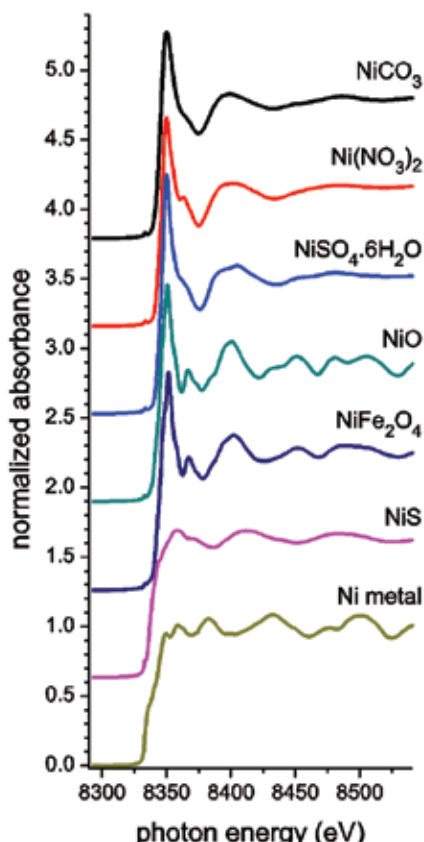


Figure 2. Ni K-XANES spectra of relevant reference compounds

Table 1. Proportion of Ni species expected in the flue dust residues based on the amount of Ni extracted from each stage of the sequential leaching scheme.

Proportions of Ni Species (%)				
	Soluble <sup>a</sup>	Sulphidic <sup>b</sup>	Metallic	Oxidic <sup>c</sup>
<b>Sequential Leaching</b>				
Intact	9	65	4	22
Residue 1	0	71	4	24
Residue 2	0	0	15	85
Residue 3	0	0	0	100

#### XANES

Intact	7	59	0	34
Residue 1	0	58	0	42
Residue 2	0	2	0	98
Residue 3	0	0	12	88

<sup>a</sup> Ni nickel acetate, sulphate, nitrate, chloride, etc.

<sup>b</sup> Ni sulphide, subsulphide,

<sup>c</sup> Ni oxides, hydroxides, silicates, carbonates, and complex nickel oxides

Our current investigation of workplace aerosols has revealed many instances of significant differences in nickel speciation between Zatka and XANES results. We are investigating these differences in more depth.

#### Future Work

A much more comprehensive study is currently underway investigating workplace aerosols obtained at Vale Inco's Sudbury smelter and refinery using XANES spectroscopy.

#### References

1. Toxicological Review of Soluble Nickel Salts, March, 1999. Prepared for the Metal Finishing Association of Southern California, U.S. Environmental Protection Agency and Health Canada by Toxicology Excellence for Risk Assessment (TERA)
2. Zatka, V.J., Warner, S. and Maskery, D. 1991. Chemical speciation of nickel in airborne dusts: Analytical method and results of an interlaboratory test program. Environ. Sci. Technol. 26, 138-144. DOI: 10.1021/es00025a015
3. Bacon, J.R. and Davidson, C.M. 2008. Is there a future for sequential chemical extraction? The Analyst 133, 25-46. DOI:10.1039/b711896a

#### Acknowledgements

The authors would like to acknowledge Joe Sciallo for Zatka measurements at ITSL Vale Inco, Mississauga, ON.