



Characterisation of workers' exposure in a Russian nickel refinery

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In support of a feasibility study of reproductive and developmental health among females employed in the Monchegorsk (Russia) nickel refinery, personal exposure and biological monitoring assessments were conducted. The inhalable aerosol fraction was measured and characterised by chemical speciation and particle-size distribution measurements. Unexpected findings were that: (i), pyrometallurgical working environments had significant levels of water-soluble nickel; (ii), significant exposure to cobalt occurred for the nickel workers; (iii), particles of size corresponding to the thoracic and respirable fractions appeared to be virtually absent in most of the areas surveyed. The water-soluble fraction is judged to be primarily responsible for the observed urinary nickel and cobalt concentrations. It is concluded relative to current international occupational-exposure limits for nickel in air, and because of the high nickel concentrations observed in urine, that the Monchegorsk nickel workers are heavily exposed. The implication of this finding for follow-up epidemiological work is alluded to.

Introduction

Alloys of nickel may have been used in China in the Middle Ages and perhaps earlier. Its chemistry allows it to be combined with other elements to form a variety of useful alloys. Nickel comprises approximately 0.009% of the earth's crust and its most prevalent ores are sulfidic or lateritic.¹ The treatments used to recover nickel from these ores differ considerably due to their contrasting physico-chemical properties. Prior to secondary refining, most sulfide ores are subjected to a series of pyrometallurgical processes after crushing/milling operations and mineral separation by either flotation or magnetic procedures. Secondary refining involves either electrolytic, carbonyl separation or hydrometallurgical processes. Nickel from lateritic ores, in which it is present as oxides or silicates, is recovered by pyrometallurgical methods which are often followed by electrolytic purification or by hydrometallurgical steps involving leaching and reduction.² During the production of nickel, a number of nickel species occur in the work-room atmosphere to which workers are exposed. Recently, there has been a research focus on the importance of nickel speciation to the interpretation of toxicological responses in humans. It is recognized that the chemical reactivity and toxicity of inorganic compounds are not only determined by physico-chemical and morphological properties, but also by anatomical structures, biological processes and genetic determinants.³

Cancer risk in the nickel refining industry appears to depend on the nickel species inhaled. The International Committee on Nickel Carcinogenesis in Man (ICNCM)⁴ identified four classes of nickel compounds as having different intrinsic activity or biological availability as cancer causing agents. The specific categories identified were sulfidic, oxidic, metallic and water-soluble nickel. The Committee concluded that epidemiological research was hampered by the scarcity of reliable occupational exposure data, especially speciation information.

Subsequent to the ICNCM Report,⁴ regulatory agencies have intensified their focus on species-specific exposure limits requiring corresponding analytical methods. A parallel development was the adoption of particle size-selective criteria by the International Standards Organisation (ISO)/American Conference of Governmental and Industrial Hygienists (ACGIH)/Comité Européen Normalisation (CEN) guidelines for workplace exposure.⁵ Three health-related aerosol fractions have been defined, namely inhalable, thoracic and respirable. For the exposure to nickel, the ACGIH Occupational Exposure Limits refer to the inhalable particle masses that penetrate anywhere in the respiratory tract, and their numerical values depend on the nickel species (whether it is metallic, water soluble, the subsulfide or insoluble). A fifth species regulated is nickel tetracarbonyl, a volatile compound of extreme toxicity which is an intermediate product in the Mond process of nickel refining.⁶

Few methodologies are currently available for chemical speciation of nickel in work-room air. Air sampling when nickel tetracarbonyl is present in combination with particulate forms of nickel demands unique approaches with separate collection of the nickel carbonyl gas on a suitable adsorbent and filter collection of the particulates.⁷ For speciation of aerosols originating from sulfide ore processing, a sequential leaching scheme has been developed by Zatka *et al.*⁸ for the determination of the four nickel fractions referred to earlier, namely water soluble, sulfidic, metallic and oxidic.

Until recently, reproductive and developmental effects in humans have not been reported in conjunction with exposure to nickel compounds.^{9,10} Chashschin *et al.*¹¹ have expressed concern about an apparent increase in spontaneous abortions among females employed in the Russian nickel refinery at Monchegorsk. The possibility of structural malformation among neonates of these workers was also alluded to.

However, their report was preliminary and did not provide details on worker exposure. Because women are not regularly employed in nickel refineries outside Russia, it was decided to conduct a follow-up study at Monchegorsk to determine whether it was feasible to carry out a detailed epidemiological study including worker exposure assessments. The results of the latter component are described in this paper and includes personal exposure measurements, chemical speciation of the workplace aerosols and their particle-size distribution.

Experimental

Site description

In the Kola Peninsula of Russia (Murmansk Region), nickel refineries are located at Nikel, Zapolyarniy and Monchegorsk. The Monchegorsk refinery was the focus of the present study. Since the early 1970s, ore from Norilsk (Siberia) has been processed at this refinery. Nickel-copper matte is the product of primary refining, which involves the smelting and converting of sulfide ore. Air sampling was conducted in the secondary refining sector of the Monchegorsk nickel refinery, namely in the Roasting/Anode Casting and the Electrorefining Departments. In the Roasting Department, nickel sulfide concentrate derived from nickel-copper matte is fluid-bed roasted to the oxide. Subsequently, the oxide is pre-reduced in rotary kilns and is reduction-melted to anode metal in electric arc furnaces. Two anode-casting units were in operation, one in support of the 'Old' and the other of the 'New' Electrorefining Department. The two main working areas in electrorefining are the tankhouse, in which the electrolysis tanks are located, and the purification circuit. In the electrorefining process, the anode slowly dissolves to yield a solution of nickel sulfate/chloride with copper, cobalt and iron as major impurities. This anolyte is sent to the purification area for removal of the unwanted metals and is returned as the catholyte to the electrolysis tank for the production of pure nickel cathodes.

Subjects

Unlike nickel refineries elsewhere (e.g., in Australia, North America and Western Europe), females constitute a significant proportion of the workforce in the Russian nickel industry. In the Severonickel refinery at Monchegorsk in 1995, 42% of the approximately 13000 workers were female. Eight to twenty-three volunteer workers (mixed gender) were recruited from the roasting/anode casting areas and the electrorefinery tankhouse and were followed for 1–3 eight-hour shifts (morning, 0700–1500; afternoon, 1500–2300). The study group in the present study consisted of 32 females (mean age, 37.9 ± 7.1 yr) and 86 men (30.2 ± 7.6 yr).

Sampling

Strategy. In general, basic worker exposure surveys are designed to identify the variability and quantity of exposure. Since only periodic air-sampling surveys using stationary (area) sampling have been conducted in the Russian nickel industry, no representative personal exposure assessment data were available for the Monchegorsk nickel refinery. Practical problems at the refinery in Monchegorsk did not allow for a sampling strategy that would have made possible an assessment of variability between job function within different departments of the plant. All samples were therefore pooled to obtain a general description of the working environment and to permit areas of high exposure to be identified. Personal environmental monitoring corresponding to a total of 147 shift-samples was conducted using inhalable personal aerosol samplers. This exposure assessment was supplemented by collecting 18 aerosol

samples for nickel speciation measurements (using 25 mm Millipore 'total' samplers), as well as 10 samples for particle-size distribution evaluation. Pre- and post-shift spot urine specimens for nickel and cobalt determinations were also collected from a total of 119 workers.

Air. The inhalable aerosol fraction was assessed by employing IOM inhalable personal samplers (SKC Ltd., Blandford Forum, Dorset, UK); each IOM filter cassette was equipped with a $0.8 \mu\text{m}$ pore-size cellulose-ester membrane filter (25 mm; Millipore, Bedford, MA, USA, AAWP02500). Three-piece Millipore 25 mm 'total' samplers equipped with $0.8 \mu\text{m}$ pore-size Gelman (Ann Arbor, MI, USA) DM Metrical vinyl-acrylic copolymer filters were used to collect samples for the speciation measurements. The IOM personal inhalable dust spectrometer (PIDS) featuring an entry port and 8 impactor stages, while a backing membrane filter at the bottom¹² was used for particle-size distribution measurements; a total of 10 PIDS samples were collected. Although the PIDS used was constructed in-house at NIOH (National Institute of Occupational Health, Oslo) it is commercially available (SKC Ltd., Eighty Four, PA, USA). For each of the 10 stages, the nickel mass collected was determined. The internal surfaces of the PIDS were coated with a silicone spray prior to sampling. For all three types of air samples, the pumps employed were the in-house, pulsation-free units constructed and used routinely at NIOH. They were operated at a constant flow rate of 2.0 L min^{-1} and the flow rate of each pump was measured both at the beginning and at the end of the sampling period as a quality control measure.

Urine. Urine specimens were collected at home (to minimise inadvertent contamination) directly into a clean plastic cup for transfer to containers (Universal Container, volume 25 mL, Nalge Nunc Int. Corp., Rochester, NY, USA), which were tested and found not to contaminate the urine samples ($<0.5 \mu\text{g L}^{-1}$ of Ni or Co). The urines were transported at ambient temperature to NIOH in Oslo within 3 d of collection; on arrival they were frozen and stored at -20°C .

Analytical procedures

Air. All air filters were dissolved in a mixture of 2 mL of *aqua regia* and 0.2 mL of hydrofluoric acid in Teflon autoclaves with microwave assisted digestion (MLS 1200, Teflon Container SV140, 10 bar, Milestone, Sorisole, Italy). The material collected on the inside surfaces of the IOM aerosol cassette was recovered by extraction with 2 mL of 0.5% Triton X-100 in 15% nitric acid, which was added to the filter fraction before digestion. The material collected on the PIDS stages was removed by careful wiping with PVC filters. These filters were treated the same way as the air filters. For the measurements of the elemental composition of the solutions, a Perkin-Elmer Optima Model 3000 inductively coupled plasma atomic emission spectrometer was used (Perkin-Elmer, Norwalk, CT, USA). In-house, commercially-available, reference workroom-air filter material (Batch A-1 and B-1), simulating air concentrations at threshold limit values of individual elements, was used to monitor the accuracy and reproducibility of the measurements. The concentrations found for nickel, cobalt, copper, arsenic, lead and cadmium were in good agreement with the recommended values ($< \pm 5\%$) and the day-to-day variation for the elements were also below $\pm 5\%$.

Nickel speciation. Chemical speciation by the consecutive leaching procedure devised by Zatka and colleagues¹⁰ was used. Briefly, it involves the preparation of the following leachates in sequence: (i), the soluble fraction with 0.1 M ammonium citrate (pH 4.4) for 90 min at room temperature;

(ii), the sulfidic fraction with 0.067 M ammonium citrate–10% (m/m) hydrogen peroxide for 60 min at room temperature; (iii), the metallic fraction with 2% (v/v) bromine in anhydrous methanol (in the order of seconds) at room temperature; (iv), the oxidic fraction by hot plate digestion in concentrated nitric–perchloric acids. The nickel speciation part of the analytical work was kindly carried out by the J. Roy Gordon Research Laboratory, INCO Ltd., Mississauga, ON, Canada.

Urine. To prevent any risk of laboratory acquired infections and to dissolve urine precipitates, all urine samples were heated for one hour at 95 °C prior to analysis. Nickel and cobalt were measured by electrothermal atomic absorption spectrometry using a Perkin-Elmer SIMAA 6000/THGA System. Due to the high nickel concentrations, the urine samples were diluted 10–50 fold before the measurement of nickel could be performed. This high dilution factor did not permit the simultaneous measurement of both metals; undiluted urine was used for the measurement of cobalt. Spectrometer calibration was achieved with matched, standard-urine solutions. Human urine Seronorm™ trace element quality control material (STE Batch 403125, Sero Ltd., Asker, Norway) was employed throughout to monitor the accuracy and the reproducibility of the measurements. The day-to-day variations of the nickel and cobalt measurements in this quality control material were typically 7 and 6%, respectively. The concentrations measured were in good agreement with the values reported by the manufacturer: Ni found $39.9 \pm 2.9 \mu\text{g L}^{-1}$ ($n=50$), recommended $40 \mu\text{g L}^{-1}$; Co found $10.0 \pm 0.5 \mu\text{g L}^{-1}$ ($n=30$), recommended $10 \mu\text{g L}^{-1}$. The detection limit (DL; $3 \times$ standard deviation, s , of the blank) was $0.3 \mu\text{g L}^{-1}$ for both nickel and cobalt.

Statistical methods

Homogeneity of variance indicated that the air and urinary metal concentrations had a log-normal distribution. Geometric means were tested for differences at the 95% level by a one-way analysis of variance with unequal replications using the F -statistic. Sampled department populations were tested against each other by employing Duncan's multiple range test. Even though large variability in exposure and urinary metal levels were observed between workers, working shifts, job categories and departments, all data points were given equal statistical weight in the calculations. The DL value was substituted for the few results below this concentration. The SPSS statistical software package was employed.

Results

Air measurements

The inhalable air dust and nickel concentrations observed are summarized in Table 1 by working area. Clearly, the roasting/anode casting operations have considerably higher dust, nickel

and cobalt (see Fig. 1) exposures than the electrorefining process. As is illustrated in Fig. 1, there is a strong correlation between the inhalable cobalt and nickel fractions for all samples and thus all the job sites examined, with the nickel concentrations being about 50 times higher than those for cobalt. A linear relationship was also evident for copper and nickel ($r=0.97$; slope, $a=0.08$; $n=147$, not shown).

Nickel speciation results expressed as a percentage of total nickel are provided in Table 2. The predominant chemical form in the Electrorefining Departments (New and Old) workroom air was soluble nickel (55–99%); oxidic and sulfidic nickel constituted, respectively, <0.6–34% and 1–19% with very little in the metallic form. As depicted in Fig. 2, the amount of sulfidic nickel is reduced substantially during matte roasting with a concomitant increase in the oxidic and metallic fractions. It is also noticeable that in the early stages of the roasting process, the amount of soluble nickel is increased and that the workroom air concentration of soluble nickel is higher at the top of the roaster than in the electrolytic department.

The mass distribution of nickel (see Table 3) shows that the largest proportion of the inhalable nickel fraction is deposited in the entry port of the dust spectrometer. Very little nickel mass was collected in stage 5 and beyond for sampling conducted in the electrorefinery tankhouse. By contrast, significant amounts of nickel were found in all spectrometer stages for samples obtained in the roasting/anode casting working areas. Nevertheless, the proportion deposited in stages 5–8 was again marginal. The mass–particle-size distribution curves depicted in Fig. 3 illustrate how the raw data of Table 3 may be transformed. The aerosol impaction and distribution patterns for copper and cobalt (data not presented) were similar to those described for nickel.

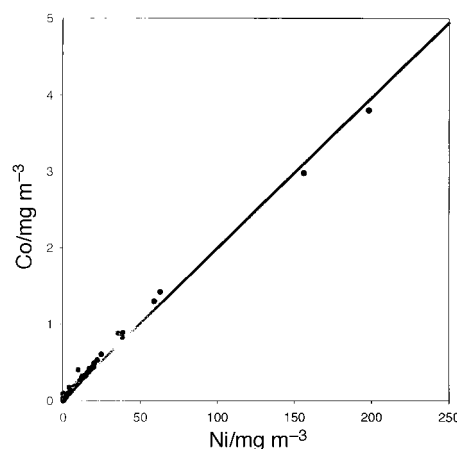


Fig. 1 A comparison of the inhalable nickel and cobalt concentrations for Monchegorsk nickel refinery workers (roasting/anode casting and electrorefinery tankhouse); $a=0.020$, $r=1.0$, $n=47$.

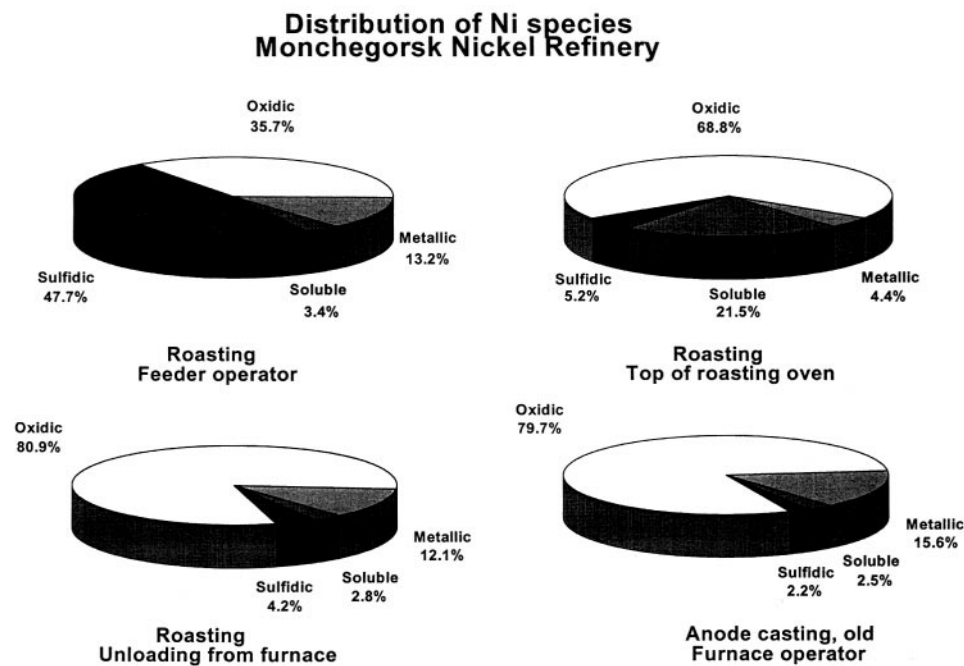
Table 1 Inhalable dust and air nickel concentrations by department of the Monchegorsk nickel refinery

Department	Inhalable dust			Air nickel			Number of filters	Number of workers
	Mean (s)/ mg m^{-3}	Geometric mean/ mg m^{-3}	95% CI/ mg m^{-3}	Mean (s)/ mg m^{-3}	Geometric mean/ mg m^{-3}	95% CI/ mg m^{-3}		
Roasting	42 (68)	$25^{a,c}$	18–34	21 (42)	$11^{a,c}$	7.6–15	32	23 ($F=0$) ^e
Anode casting (old)	31 (30)	$22^{a,c}$	17–29	15 (15)	$10^{a,c}$	7.3–14	31	19 ($F=0$)
Anode casting (new)	10 (11)	$7.2^{a,d}$	4.7–11.0	2.3 (2.6)	$1.5^{a,d}$	0.9–2.4	14	9 ($F=0$)
Electrorefining (old)	3.1 (2.8)	2.7^b	2.2–3.3	0.27 (0.12)	0.25^b	0.20–0.30	21	16 ($F=10$)
Electrorefining (new)	2.7 (1.3)	2.5^b	2.1–3.0	0.34 (0.26)	0.28^b	0.21–0.38	14	8 ($F=5$)
Rinsing (old)	5.7 (16)	2.7^b	2.0–3.7	0.32 (0.77)	0.17^b	0.13–0.23	26	16 ($F=8$)
Rinsing (new)	4.2 (6.2)	2.7^b	2.2–3.3	0.28 (0.35)	0.17^b	0.09–0.32	9	9 ($F=3$)

^{a,b}Significantly different from each other ($p<0.05$). ^{c,d}Significantly different from each other ($p<0.05$). ^e F =Number of female workers.

Table 2 Nickel speciation results for selected departments of the Monchegorsk nickel refinery

Department	Operation or job	Soluble (%)	Sulfidic (%)	Metallic (%)	Oxidic (%)	Total/ mg m ⁻³
Roasting	Unloading from furnace	2.8	4.2	12	81	7.9
Roasting	Top of roasting oven	22	5.2	4.4	69	3.1
Roasting	Feeder operator	3.4	48	13	36	7.9
Anode casting (old)	Furnace operator	2.5	2.2	16	80	11
Anode casting (new)	Plumber	2.9	1.0	22	74	1.5
Anode casting (new)	Welder	1.5	0.1	19	80	7.9
Anode casting (new)	Furnace operator	19	8.1	26	46	0.19
Electrorefining (old)	Crane operator	97	1.2	<1.1	2.3	0.086
Electrorefining (old)	Crane operator	84	1.0	<1.0	15	0.10
Electrorefining (old)	Tankhouse	99	1.3	<0.6	<0.6	0.16
Electrorefining (old)	Tankhouse	86	1.3	<0.7	13	0.15
Electrorefining (old)	Tankhouse	95	1.8	<0.6	3.6	0.17
Electrorefining (new)	Crane operator	60	19	4.4	17	0.090
Electrorefining (new)	Crane operator	87	6.7	<2.0	6.7	0.045
Rinsing of electrolyte (new)	Tankhouse	55	5.4	5.4	34	0.074 ^a
Rinsing of electrolyte (new)	Tankhouse	92	3.7	1.0	3.7	0.30
Rinsing of electrolyte (new)	Tankhouse	77	7.7	<1.0	15	0.013

^aMinimum values, pump flow rate dropped during sampling.**Fig. 2** Pie charts showing the proportions of oxidic, sulfidic, metallic and water soluble nickel from Monchegorsk nickel workers involved in roasting/anode casting.**Table 3** Particulate masses of nickel on the various stages of the IOM personal inhalable dust spectrometer (PIDS) by department of the Monchegorsk nickel refinery

PIDS no.	Department	Operation or job	Air volume/ m ³	Stage: Cut point /μm	Entry	1	2	3	4	5	6	7	8	Filter
				Mass of nickel/μg	26	18.2	14.4	10.6	6.0	4.8	3.3	1.7	0.9	0
1	Electrorefining (new)	Tankhouse	0.692	118	15.3	4.8	3.0	7.9	0.7	4.4	<0.2	<0.2	<0.2	<0.2
2	Rinsing (new)	Tankhouse	0.590	30.0	10.8	2.9	1.0	0.5	<0.2	<0.2	<0.2	<0.2	<0.2	0.4
3	Electrorefining (old)	Crane operator	0.626	19.3	12.6	8.0	5.2	4.1	<0.2	0.5	<0.2	<0.2	<0.2	<0.2
4	Rinsing (old)	Tankhouse	0.722	12.8	7.1	2.9	4.1	1.2	1.4	<0.2	<0.2	<0.2	<0.2	0.8
5	Roasting/anode casting (old)	Crane operator	0.870	6031	678	627	349	593	51.8	142	133	91.6	120	
6	Electrorefining (new)	Crane operator	0.662	12.1	6.2	5.6	4.1	0.8	<0.2	<0.2	6.3	<0.2	<0.2	<0.2
7	Rinsing (old)	Tankhouse	0.666	3.7	4.1	1.2	1.1	0.9	<0.2	0.2	<0.2	<0.2	<0.2	0.2
8	Roasting/anode casting (old)	Furnace operator	0.738	8367	1589	476	147	280	70.2	54.2	18.8	8.5	24.7	
9	Roasting/anode casting (old)	Crane operator	0.698	1642	495	209	94.3	136	22.7	18.7	109	33.8	53.0	
10	Anode casting (new)	Furnace operator	0.620	370	118	32.9	15.1	17.5	2.9	4.2	0.2	<0.2	0.8	

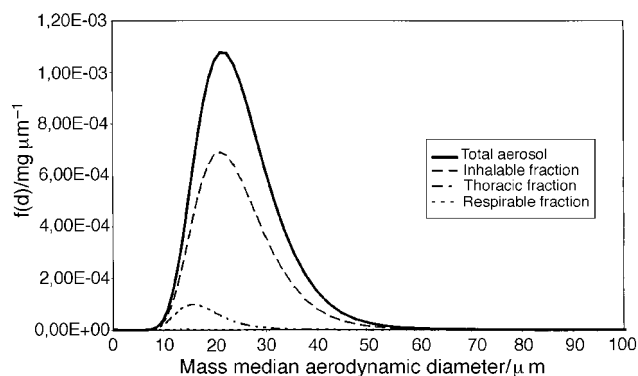


Fig. 3 Particle-size distributions curves for total airborne nickel, the inhalable fraction, the thoracic fraction and the respirable fraction for a sample taken in the tankhouse of the Monchegorsk Nickel Electrorefinery (Old). Mathematical 'data inversion' of the raw data in Table 3 (sample PIDS 7) has been carried out employing special software provided by J.H. Vincent. To achieve these mathematical manipulations, detailed knowledge is required of the particle size-dependent entry efficiency of the sampler and the collection efficiency characteristics of each of the eight stages of the PIDS instrument.²¹ The fitted distribution function is denoted by $f(d)$.

The geometric means for arsenic, cadmium and lead inhalable air concentrations ($\mu\text{g m}^{-3}$) in the roasting and anode casting areas were, respectively, 7.7, 0.15 and 12.2; the corresponding values in the electrorefinery were: 0.70 (As), 0.06 (Cd) and 0.59 (Pb). In the 'New' Anode Casting Department only, the cadmium concentration was $25 \mu\text{g m}^{-3}$ ($n=14$).

Urine measurements

The most obvious feature of the data in Tables 4 and 5 is that comparable urinary nickel and cobalt concentrations were found for workers in both the tankhouse and roasting/anode casting areas. The relationship in Fig. 4 between urinary cobalt and nickel was only observed for the roasting/anode casting workers. Because both males and females were monitored, only creatinine uncorrected results are reported in Tables 4 and 5 and Fig. 4. Although female workers ($N=105$) and male

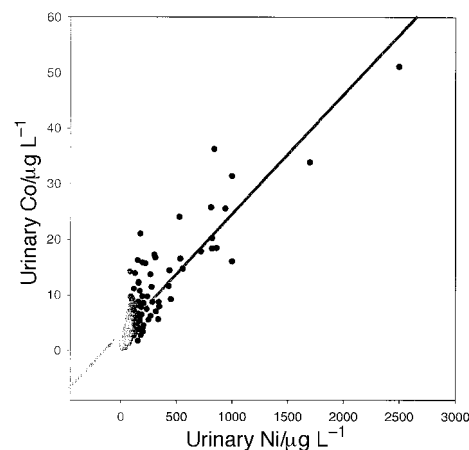


Fig. 4 A comparison of the urinary nickel and cobalt concentrations for Monchegorsk nickel-roasting and anode-casting workers; $a=0.022$, $r=0.87$, $n=156$.

workers ($N=85$) in the electrorefinery had similar air nickel exposures, female urinary nickel concentrations were significantly lower ($p<0.02$) than for the males (geometric means of 93 and $132 \mu\text{g L}^{-1}$, respectively). Such a difference was not observed for cobalt.

Discussion

Environmental monitoring

Inhalable dust, nickel and cobalt concentrations. The observation that higher exposures are associated with pyrometallurgical processes compared to other operations in nickel refining is well documented.^{4,13} Before the present air concentrations can be compared to other published values, an inter-sampler correction needs to be applied. The reason for this is that the sampling efficiency of the IOM sampler used in the present study complies with the ISO/ACGIH/CEN inhalable-fraction criterion, while the three-piece 37 mm 'total' sampler measures a non-specified component of the total aerosol.

Table 4 Urinary nickel concentrations by department of the Monchegorsk nickel refinery

Department	Mean (s)/ $\mu\text{g L}^{-1}$	Geometric mean/ $\mu\text{g L}^{-1}$	95% CI	Number of urines	Number of workers
Roasting	121 (127)	87 ^{a,c}	71–106	61	25 ($F=0$) ^e
Anode casting (old)	268 (427)	159 ^{a,d}	122–208	47	20 ($F=0$)
Anode casting (new)	337 (787)	131 ^{a,d}	92–186	48	11 ($F=0$)
Electrorefining (old)	293 (380)	179 ^{a,d}	140–230	61	23 ($F=12$)
Electrorefining (new)	191 (188)	127 ^a	96–169	40	10 ($F=6$)
Rinsing (old)	123 (114)	88 ^{a,c}	71–109	57	18 ($F=8$)
Rinsing (new)	77 (88)	53 ^{b,c}	40–71	32	12 ($F=6$)

^{a,b}Significantly different from each other ($p<0.05$). ^{c,d}Significantly different from each other ($p<0.05$). ^e F =Number of female workers.

Table 5 Urinary cobalt concentrations by department of the Monchegorsk nickel refinery

Department	Mean (s)/ $\mu\text{g L}^{-1}$	Geometric mean/ $\mu\text{g L}^{-1}$	95% CI	Number of urines ($n=346$)	Number of workers ($n=119$)
Roasting	5.8 (5.7)	4.0 ^{a,c,e}	3.1–5.0	61	25 ($F=0$) ^g
Anode casting (old)	8.4 (9.0)	5.7 ^{a,c}	4.4–7.4	47	20 ($F=0$)
Anode casting (new)	14 (37)	6.1 ^{a,c,f}	4.6–8.2	48	11 ($F=0$)
Electrorefining (old)	2.9 (4.8)	1.6 ^{a,d}	1.2–2.1	61	23 ($F=12$)
Electrorefining (new)	2.7 (2.4)	1.8 ^{a,d}	1.2–2.4	40	10 ($F=6$)
Rinsing (old)	8.7 (11)	4.2 ^{a,c}	2.9–5.8	57	18 ($F=8$)
Rinsing (new)	16 (19)	10 ^{b,c}	7.2–14	32	12 ($F=6$)

^{a,b}Significantly different from each other ($p<0.05$). ^{c,d}Significantly different from each other ($p<0.05$). ^{e,f}Significantly different from each other ($p<0.05$). ^g F =number of female workers.

Recent comparisons between 'total' and inhalable aerosol sampling results indicated that inhalable exposures were, on average, nearly twice as high as corresponding 'total' aerosol measurements for dust, nickel and several other elements in the nickel refining industry.^{14,15} A perusal of the environmental data presented in the Doll Report⁴ suggests that the exposure conditions in the Roasting and 'Old' Anode Casting Departments resemble the experience in non-Russian nickel refineries during the 1960s or earlier. The observed mean or median inhalable nickel concentrations for the 'New' Anode Casting and the Electrorefining Departments are comparable in magnitude, after adjustment for differences in personal sampler efficiency, to exposures reported for similar operations in the 1970s and early 1980s in nickel refineries in the western world.^{13,16} A comparison of the observed exposure levels with the current ACGIHs inhalable Threshold Limit Values—Time Weighted Averages (TLV-TWAs) of 0.10 mg m⁻³ (for soluble compounds and the subsulfide), 0.20 mg m⁻³ (for insoluble compounds, mostly oxides, silicates and other sulfides) and 1.5 mg m⁻³ (metal) clearly indicates that the workers studied are heavily exposed.

Exposure to cobalt of nickel workers has been reported infrequently, although data are available for cobalt refinery and hard-metal workers.¹⁷ Relative to the 'total' ACGIH TLV-TWA for cobalt (element and inorganic compounds) of 0.02 mg m⁻³, the workers in the roasting and the anode casting areas experienced significant exposures. This conclusion is still valid if one were to consider other international exposure limits for cobalt,¹⁷ which fall in the range of 0.05 to 0.10 mg m⁻³.

The strong relationship observed between inhalable cobalt and nickel concentrations is not unexpected, since the cobalt-to-nickel mass ratio may be assumed to remain constant throughout the process, *i.e.*, in the roaster feed, the roasting product, the cast anode and the tankhouse anolyte. Corroboration for this interpretation is provided by a similar relationship between inhalable nickel and copper ($r=0.97$, $a=0.08$, $n=147$).

Arsenic and copper were present at or just above the current ACGIH TLV-TWAs only in the Roasting and 'Old' Anode Casting Departments, depending whether or not an intersampler correction factor comparable to that used for nickel aerosols was applied. Lead and cadmium air levels were inconsequential in all departments. This knowledge is relevant to a consideration of confounding factors in the interpretation of epidemiological data pertaining to the Monchegorsk workers.

Aerosol speciation and particle-size distribution. None of the work areas examined is characterised by a single nickel contaminant. In the roasting and anode casting facilities all the four nickel fractions measured are represented, whether expressed in concentration units or as a percentage of total nickel. Similarly in the tankhouse, in addition to the expected dominance of soluble nickel, half of the samples had 13–34% of the total nickel present in the oxidic form, although the actual concentrations were relatively low. This is important as mixed exposures to soluble and insoluble particulate nickel compounds are suggested to pose a specific high cancer risk.^{4,18} Based upon the roasting process description, the lowering of the sulfidic content and the increase in oxidic nickel might have been predicted as the matte feed proceeds along the roaster to the anode casting unit. However, the surprising observation is the significant amount of water-soluble nickel at the top of the roasting oven and around the 'new' anode casting. In fact, the highest concentration of soluble nickel was observed at the top of the roaster and not in the electrorefinery. Recently, Andersen *et al.*¹⁹ reported similar

findings for nickel-matte roasting workers and they suggest that the sulfate salt of nickel accounts for this. Thus, sulfation appears to occur during roasting. Traditionally, pyrometallurgical workers were believed to be exposed only to sulfidic and oxidic nickel.^{4,13}

Even though the efficiency of the 'total' sampler is at least a factor of two lower than the IOM inhalable sampler, we expect the species distribution to be applicable to the inhalable fraction since Vincent *et al.*²⁰ showed that the distribution of nickel species did not vary significantly between the inhalable and 'total' samplers. This extrapolation still ignores a possible particle-size dependence of nickel speciation, since the IOM sampler collects a greater proportion of larger particles. Further, it should be emphasized that the Zatka *et al.*⁸ speciation protocol does not identify individual nickel species. It constitutes an operational determination of speciation. The soluble fraction includes all nickel salts (*e.g.*, sulfate and chloride). Although for the refining processes monitored the sulfidic fraction is primarily made up of nickel sulphides, any minor amounts of arsenides, selenides and tellurides present are concurrently leached and determined. Nickel alloys are also determined as part of the metallic fraction. Finally, oxidic nickel comprises a family of nickel oxides, as well as complex oxides (*e.g.*, NiFe₂O₄) and nickel silicates if they are present.

Complex mathematical algorithms are required to convert the raw cascade-impactor mass-deposition data into particle-size distribution curves.²¹ A new extended version of this algorithm has been applied in the present study. Consistent with the observed dust-spectrometer mass-distribution pattern, very little of the nickel is judged to be present in the Monchegorsk refinery area surveyed as small particles corresponding to the thoracic or respirable fraction. In fact, the respirable fraction was nearly non-existent in both the electrorefinery and the roasting and anode casting aerosols. The extrathoracic aerosol fraction is thus largely responsible for the actual nickel exposure experienced by the workers. The mass particle-size distribution described for nickel also applies to cobalt and copper.

Biological monitoring

Our exposure and urinary nickel data (as geometric means) roughly conform to the somewhat historic and generalised relationships for group measurements shown in eqn. (1) and (2),^{22,23} when taking into account differences in sampler efficiency (see below), discounting outliers and comparing predicted with observed concentration ranges.

$$U_{\text{Ni}} (\mu\text{g L}^{-1}) = 700 \text{ Ni}_{\text{air}} (\text{'total'}^\dagger, \text{mg m}^{-3}) + 2 \text{ (electrolytic workers)} \quad (1)$$

$$U_{\text{Ni}} (\mu\text{g L}^{-1}) = 85 \text{ Ni}_{\text{air}} (\text{'total'}, \text{mg m}^{-3}) + 2 \text{ (pyrometallurgical workers)} \quad (2)$$

The explanation for the different slopes in eqn. (1) and (2) has been that relatively insoluble nickel compounds such as sulfidic and oxidic nickel are considerably less bioavailable than water-soluble compounds. The dissolution half-times of nickel sulfides in serum are known to be considerably shorter (values of 20–30 d) than for oxides (≥ 1 yr), suggesting some differential bioavailability.^{24,25} A perusal of the available animal data suggests that indeed nickel subsulfide is more readily cleared from lungs than high temperature (green) nickel oxide and also appears to be more bioavailable.¹⁸ However, low temperature (black) nickel oxide, to which roaster workers are likely also exposed, appears to be more water-soluble and biologically active than green nickel oxide.²⁴ By contrast, and as outlined below, our speciation results imply that the main

[†]'Total': mass of nickel measured by conventional aerosols samplers.

factor responsible could be the difference in the water-soluble aerosol fraction the workers are exposed to.

Based solely on the magnitude of the air concentrations, one might have expected the urinary nickel concentrations to be higher for workers in the Roasting and Anode Casting Departments. A review of published data indicates that the highest nickel concentrations in urine have consistently been reported for nickel plating and electrorefinery workers.^{16,22,23} It is tempting to explain the comparable urinary nickel concentrations for the Electrorefining and Roasting/Anode Casting Departments by similar exposures to water-soluble nickel since, as indicated, the bioavailability of sulfidic and oxidic nickel compound (as well as nickel dust) may be expected to be considerably lower. Interestingly, Werner *et al.*²⁶ have recently shown for nickel-matte roasting workers that the water-soluble aerosol fraction, but not the sum of the three other fractions, correlated with urinary nickel. From this perspective, the lower excretion of nickel among workers in the Roasting Department suggests that, on average, these workers are exposed to somewhat lower soluble nickel air levels than those observed among electrorefinery workers. Similar arguments appear to be relevant to the interpretation of the urinary excretion of cobalt data in Table 5. Indeed, different urine cobalt/air cobalt slope factors have been reported for hard metal workers exposed to cobalt metal powder and those primarily exposed to dissolved cobalt.¹⁷

There is considerable evidence that variability in urinary nickel due to differential urinary flow rates can be minimised by adjusting the concentrations to a standard creatinine concentration or specific gravity.^{15,23} Of these two parameters, only creatinine was measured in the present study. We chose not to normalise with creatinine because our worker population involved both males and females. Because urinary creatinine excretion is dependent on gender,²⁷ we worried about introducing additional variability in our results. Clearly, the lower urinary nickel concentrations found in females need to be investigated more rigorously, which will require knowledge of urine flow rates (*i.e.*, 24 h specimens) and donor morphometric measurements.

Concluding remarks

It may be concluded from our study that the working conditions in the Monchegorsk nickel refinery correspond to exposures encountered in the 1980s or earlier in similar departments of nickel refineries outside of Russia. A novel finding was the presence of relatively high water-soluble nickel concentrations for workers involved in the pyrometallurgical refining of nickel matte, which may well have bearing on the rationalisation of known process-specific or species-specific respiratory cancer risks^{4,18,28} and likely has regulatory implications.

Accidental and experimental exposures to water-soluble nickel^{29,30} suggest that reversible perturbations of eyesight, heart rhythm and renal function may occur for individuals whose urinary nickel concentrations exceed 400–500 $\mu\text{g L}^{-1}$. Since a small number of the workers in the Monchegorsk refinery had nickel concentrations of this magnitude, there may be some basis for medical concern. Further, and as already indicated, high nickel exposures in both electro- and pyrometallurgical refining have been associated with an excess of nasal and lung cancers.^{4,18,28} The high occupational exposures found are of special concern for women of reproductive age, since nickel freely passes the placental barrier. In fact, since urine nickel is proportional to serum nickel,^{22,23,29} it may well serve as an index to fetal exposure. As animal studies suggest that cobalt may also impact on reproduction and development,^{17,31} the cobalt exposures documented are an important issue for any reproductive/development epidemiological follow-up work.

Since very little of the nickel was found in the thoracic or respirable fraction, significant gastrointestinal absorption appears to occur. The reason for this is that aerosol clearance of the extrathoracic nickel may be expected, resulting in swallowing.^{3,32} Absorption studies of water-soluble nickel in humans indicate that 10–40% is absorbed, depending on the nature of any concomitant food intake.^{23,30}

Because the chemical speciation of the inhalable aerosol fraction is clearly important it is recommended that speciation measurements be a routine component of exposure assessments of nickel workers. Extension of the chemical-speciation leaching scheme to cobalt would be helpful from this perspective. Although not addressed in the present study, a possible dependence of species distribution on particle size should be explored. It is conceivable that sulfation during the roasting process of nickel matte is particle-size dependent.

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Paper 8/07771A