XA0201261

Occupational exposure to nickel, uranium and thorium in a nickel mine

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Abstract. The workers involved in mining and milling ores are exposed in the workplace to many hazardous agents that can cause a health detriment. In this work, the measurements obtained in a nickel mineral processing facility in the Brazilian Central-West are presented. One of the most important hazardous agents in this facility is the aerosol present in the air that contains nickel, uranium and thorium. The aerosol is inhaled or ingested, metabolised and deposited in the whole body or in specific organs. The surveillance of internal contamination of workers was performed by analysis of urine, fecal and hair samples. The ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) method was used to analytically determine nickel, uranium and thorium in these biological samples. Additional data were obtained by the collection of air samples in the workplace. A cascade impactor with six stages was used to collect mineral dust particles with an aerodynamic diameter in the range of 0.64 to 19.4 μm. The particles impacted in each stage of the cascade impactor were analysed by PIXE (Particle Induced X ray Emission), which permits the determination of elemental mass air concentration and the MMAD (Mass Median Aerodynamic Diameter). The concentrations of nickel, uranium and thorium were determined in the aerosol samples. All the results were analysed using statistical methods and biokinetical modelling was applied to evaluate the internal contamination and to make a risk estimation.

Introduction

In many regions of Brazil where ores of minerals with commercial importance are extracted, there is also an associated occurrence of the radioactive materials thorium and uranium. In the different steps of mineral processing, the aerosol is formed in the work place. This results in the inhalation of particles containing toxic and radioactive materials. In this work, internal contamination by nickel, uranium and thorium in a nickel extraction and processing facility is investigated. The choice of a nickel mine is supported by the high toxicity of refined nickel, which is classified as group 1 of priority by the International Agency for Research on Cancer [1]. The quantification of the nickel, uranium and thorium in the aerosol samples was made by PIXE (Proton Induced X ray Emission). To evaluate the internal contamination of the workers, biological samples: urine, feces and hair were collected and analysed by ICP-MS (Inductively Coupled Plasma – Mass Spectrometry). To determine the regional contribution due to food consumption, urine, feces and hair of local inhabitants (the worker's wives) were collected. Background values for nickel, uranium and thorium concentrations in urine were obtained by sampling and measuring urine and feces samples in the city of Rio de Janeiro.

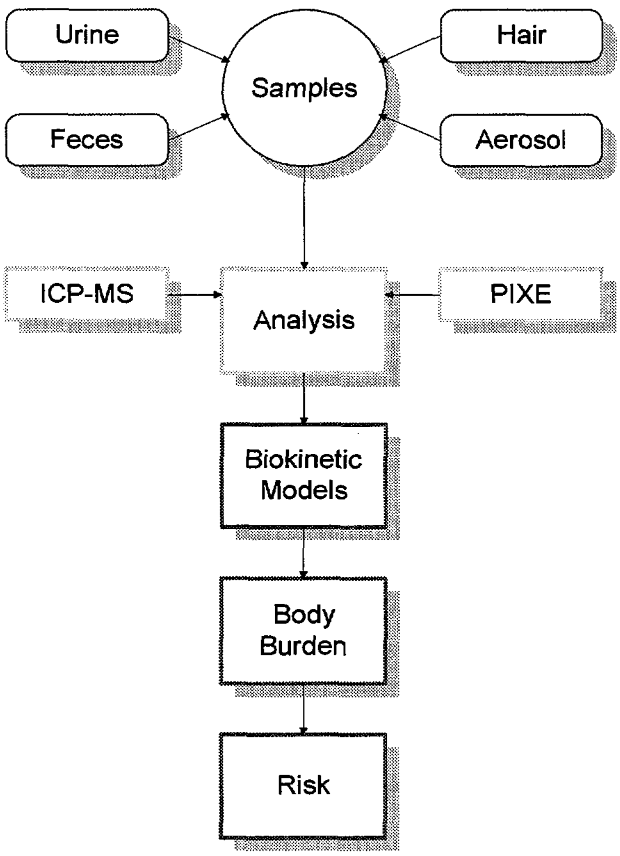
Materials and methods

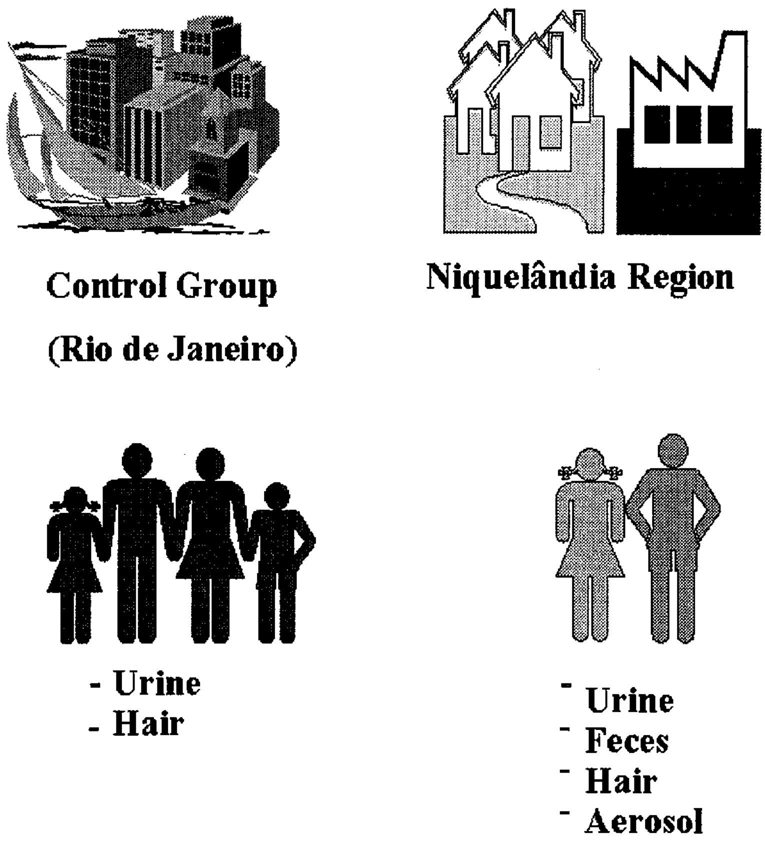
Methodology

The methodology used in this work was to collect samples of urine, feces, and hair of workers at the mining and milling facility and aerosols in the workplaces. Biological samples were also taken from the workers' wives. Biokinetical models were applied to determine the internal deposition and the intake, and the risk was estimated. Figure number 1 shows the applied methodology.

Sample collection
To measure the nickel, uranium and thorium concentrations in biological samples (urine, feces and hair) and in aerosols, a field expedition to the Region of Niquelândia was made, where the most important nickel extraction facilities of Brazil are located. In this expedition, urine, feces and hair samples of the workers occupationally exposed to aerosol in the workplace were collected, and also from their wives to obtain a regional factor for nickel, uranium and thorium excretion and amount in the hair. The collection of aerosol samples was performed with a cascade impactor to evaluate the air concentrations of Ni, U and Th. The results obtained in urine and hair were compared with the values found in the city of Rio de Janeiro. The Figure 2 shows the sampled groups and the samples collected in this work.

Sample preparation and analysis
Aerosol samples
By using a cascade impactor the air samples were collected to determine the aerodinamical behaviour of the aerosol [2]. A thin *Mylar* film covered with an emulsion of Vaseline/toluene was placed in each step of the impactor. The sampling time was adjusted to avoid membrane saturation. The air volume was determined using an integrator placed between the impactor and the vacuum pump. The qualitative and quantitative analysis of nickel, uranium and thorium in each step of the impactor was performed by PIXE (Proton Induced X ray Emission).





Biological samples
In this work, the urine, feces and hair were analysed by ICP-MS [3]. The urine was diluted 1:20 with HNO_3 1N, prepared from hyperpure HNO_3 and H_2O mili *Q*. The fecal samples were dry ashed initially at 400°C, homogenised and then dry ashed again at 600°C. From the residue 0,01g was taken and dissolved in 20 mL of 1N HNO_3 prepared from concentrated HNO_3 hyperpure and H_2O mili *Q*. The hair samples were obtained cutting 100 mg of the hair from the neck of the workers and their wives. The samples were washed in an ultrasound bath and dissolved in concentrated HNO_3 hyperpure in a microwave oven and diluted to 1N. In all the solutions which were analysed by ICP-MS, internal standards of In and Tl were added.

Results and discussion

Aerosol samples
The analysis of the X ray spectrum of the aerosol samples indicated that the uranium and thorium concentration in the respirable fraction of aerosol were below the detection limit of PIXE technique. Therefore the exposure to aerosols in this facility can be characterised as nickel exposure only. Figure 3 shows an X ray spectrum of particles impacted on the surface of the cascade impactor.

The nickel concentration in the respirable fraction of aerosol during the main steps of the facility are shown in table I

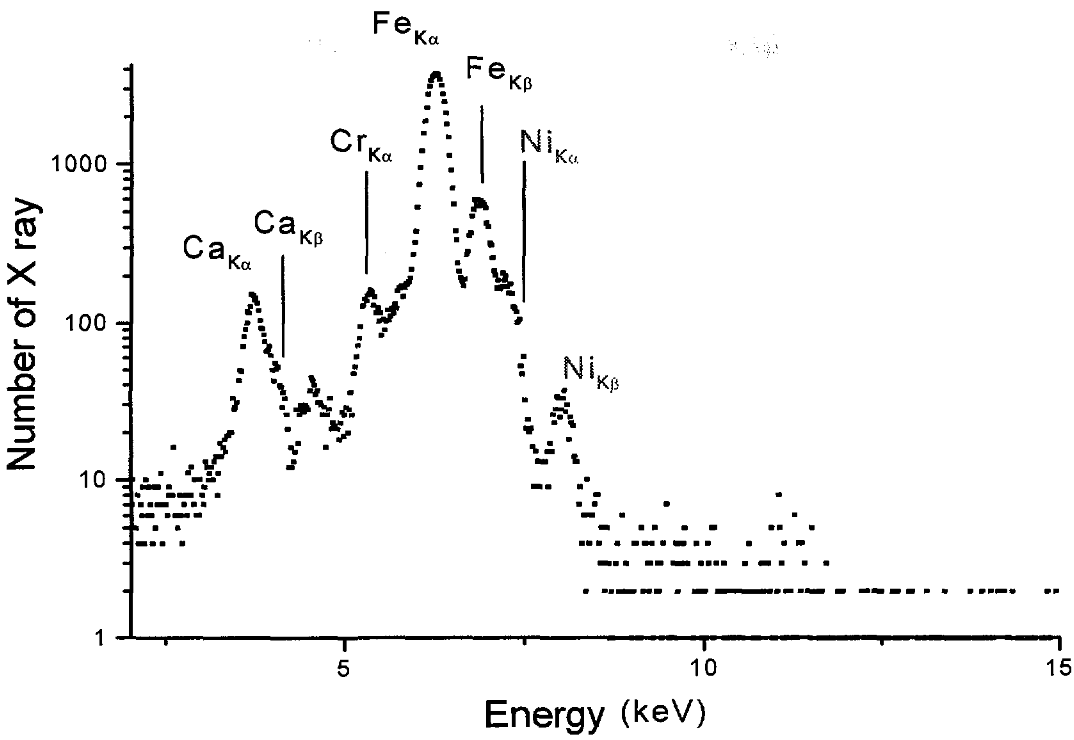


Table I. Nickel concentration in air samples

Step	Ni concentration (μg/ m^3)	MMAD (μm)	σ_g
Pneumatic crushing	0.86	1.0	2.4
Primary crushing	0.23	1.1	2.5
Secondary crushing	0.19	1.2	3.1
Pebbling	0.91	0.6	2.3
Sinter	0.22	1.2	2.3
Refine	0.30	0.9	3.0
Offices	0.02	1.4	2.2

σ_g= geometric standard deviation

The values of MMAD (Mass Median Aerodynamic Diameter) indicate that the particles are in the aerosol respirable fraction.

Urine samples

In this work the nickel concentration in urine samples was determined for a group composed by workers from the nickel mine, and another group composed of inhabitants of the mine region, the workers' wives. To situate the magnitude of the obtained values was necessary obtaining nickel data in urine of a control group. The control group chosen was composed of 68 people from Rio, of both sexes and with ages from 7 to 51 y. The nickel concentration in urine was found to be in the interval of 2–16 μg/L. The concentration in the control group was compared to the international value of 7.9 μg/L [4]. The *t*-Student test was applied and no difference between the urine concentration in Rio de Janeiro and the international reference was found ($p>0.05$) [5, 6]. In the table II was represented the medium concentration of nickel in urine obtained in the three groups sampled: (a) group of Rio de Janeiro; (b) group of Niquelândia inhabitants (wives of mine workers); and (c) mine workers.

Table II. Nickel concentration in urine samples

Group	Age (y)	Ni concentration ± sd (μg/L)
Rio de Janeiro (n=68)	07–51	7.1 ± 3.1
Niquelândia inhabitants (n=26)	33–34	16.0 ± 6.5
Mine workers (n=24)	24–58	15.6 ± 5.7

sd= one standard deviation
n= sample size

As it can be seen, the average Ni concentration obtained in Rio de Janeiro (control group) was lower than the other two. The variance analyses showed that the three groups are different ($p<0.05$). The application of the *t*-Student test indicated that the Rio de Janeiro group is different from the others ($p<0.05$), and that there is no difference between the groups of local Niquelândia inhabitants and the mine workers.

The air sampling results also showed an absence of uranium and thorium, however the urine samples were analysed by ICP-MS and a concentration of uranium and thorium was measured. To situate the magnitude of the obtained values was necessary determining uranium and thorium data in urine of a control group. The control group sampled was the same as above. The results obtained for uranium excretion for the control group were in the interval 0.01–0.12 μgU/L The average value obtained of the group formed by the nickel mine workers was 0.10 ± 0.02 μgU/L. The application of the *t*-Student test indicated that is no significant difference between these groups ($p>0.05$) [5, 6]. Using the same methodology, the results obtained for thorium excretion for the control group were in the interval 0.08–0.28 μgTh/L. The average value obtained for the group formed by the nickel mine workers was 0.18 ± 0.04 μgU/L. The application of the *t*-Student test indicated that there is no significant difference between these groups ($p>0.05$) [5, 6]. The urine measurements therefore confirmed that the exposure to uranium and thorium in this nickel mine is not significant.

Fecal samples

To evaluate the nickel concentration in feces, two groups were sampled and compared: (a) group of Niquelândia inhabitants (wives of mine workers); and (b) mine workers. Table III represents the mean results obtained for the groups.

Table III. Nickel concentration in feces samples

Group	Age (y)	Ni concentration ± sd (μg/g)
Niquelândia inhabitants (n=26)	33–44	95 ± 28
Mine workers (n=24)	24–58	141 ± 51

sd= one standard deviation
n = sample size

The two groups were compared applying the t-Student test, and the result indicates that there is a significant difference ($p<0,05$). However the statistical test showed that the average fecal excretion of Niquelândia inhabitants (382 μg Ni/day) is not different ($p>0.05$) from the reference value (370 μg Ni/day) reported for reference man [4]. The comparison between the two Niquelândia groups didn't show differences in the urine excretion. However there is an increment of nickel concentration in the fecal excretion of mine workers. This is due probably to nickel present in the air as insoluble compounds and the principal path of intake is probably the ingestion through mouth breathing.

Hair samples

The samples of hair from two groups were analysed in this work: (a) group of Niquelândia inhabitants (wives of mine workers); and (b) mine workers. The table IV represents the mean results obtained for the groups.

The *t*-Student test indicates that these groups are statistically different ($p>0.05$). The same statistical test was applied to compare each group with the reference value (0.06 µg/g) from people from Rio de Janeiro. The magnitude of the difference between the groups and the reference value makes it possible to conclude that this result comes from external sources rather than from systemic contamination. This idea is reinforced by the results of nickel concentration in urine that are 2 or 3 times the reference value, while the hair concentration is more than 100 times this value. A hypothesis of external hair contamination is reinforced by the good correlation obtained through the multiple regression between nickel content in feces and hair [5, 6].

Table IV. Nickel concentration in hair samples

Group	Age (y)	Ni concentration ± sd (µg/g)
Niquelândia inhabitants (n=9)	33–44	0.55 ± 0.34
Mine workers (n=11)	24–58	3.06 ± 1.36

sd= one standard deviation

n = sample size

Nickel exposure

The distribution of nickel in the organism of workers was estimated through the urine excretion using the metabolic model for nickel from ICRP publication 67 [7], together with the respiratory model of ICRP 66 [8]. The ratio urine/feces determined experimentally for the group of mine workers and Niquelândia inhabitants were compared to results obtained from 4 models for nickel entrance in the organism: (a) ingestion; (b) inhalation of type S (slow pulmonary clearance) compounds; (c) inhalation of compounds type M (medium pulmonary clearance); and (d) inhalation of compounds type F (fast pulmonary clearance). Table V resumes the values for the ratio urine/feces for nickel calculated experimentally and theoretically. The theoretical values are for the first and last days worked in a week. The experimental values are averages.

Table V. Theoretical and experimental ratio urine/fece

	Ratio urine/feces				
Group	Ingestion	Inhalation (type S)	Inhalation (type M)	Inhalation (type F)	Experimental ±sd
Mine workers	1.08×10^{-1}	1.20×10^{-1}	7.42×10^{-1}	5.70	$(3.85 \pm 2.03) \times 10^{-2}$
	4.77×10^{-2}	7.05×10^{-2}	3.52×10^{-1}	2.30	
Niquelândia inhabitants	1.08×10^{-1}	1.21×10^{-1}	8.35×10^{-1}	6.72	$(5.86 \pm 2.94) \times 10^{-2}$
	4.77×10^{-2}	7.49×10^{-2}	4.13×10^{-1}	2.80	

sd = one standard deviation

The analysis of the obtained values suggests that for the workers and the Niquelândia inhabitants, the most probable path of nickel intake is the ingestion. The hypothesis of inhalation of type S compounds is also possible.

Through the ingestion model using the average excretion for workers and inhabitants of 15 µg Ni/L and 21 µg Ni/L, the daily intake of 0.47 mg Ni/day was estimated. This value is compatible with the 200–600 µg Ni/day suggested by ICRP 23 [4]. Using the inhalation model (type S) the expected excretion for workers would be 7.65 × 10^{-2} mg Ni/day for men and 5.27 × 10^{-2} mg Ni/day for women. These values are far from the 21 and 22 μg Ni/day determined experimentally. Applying the ingestion model over a time of 35 years, the total amount of nickel body burden will be 9.11 mg for workers and Niquelândia inhabitants.

To risk estimation was made using the oral reference dose (R_fD) for metallic nickel of 2.00 × 10^{-2} mg/kg/day [9, 10]. The reference dose was compared to the daily intake (D_E) of 0.47 mg/day. For the workers, it is acceptable to consider the weight of the reference man as 70 kg. For these individuals, the R_fD is 1.4 mg/day. The potential risk quotient (QR), defined as D_E/R_fD, then 0.34. This result indicates that for the workers, the appearance of adverse effects is unlikely due this exposure.

For the Niquelândia inhabitants, the group was composed of women, so the body weight of 58 kg was considered. For the risk estimation the oral reference dose (R_fD) was used for metallic nickel of 2.00 × 10^{-2} mg/kg/day [9, 10]. The reference dose was compared to the daily intake (D_E) 0.47 mg/day [11]. For these individuals, the R_fD is 1.16 mg/day. The potential risk quotient (QR), defined as D_E/R_fD, is then 0.41. This result indicates that for the Niquelândia inhabitants, the appearance of adverse effects is unlikely due this exposure.

Conclusions

In this nickel mine the coupled exposure due to radioactive and stable elements was not characterised, since uranium and thorium are present in background levels. On the other hand, Nickel is an element classified by the International Agency for Research on Cancer [1] in the first priority group due its high toxicity. It was verified that the mineworkers and the Niquelândia inhabitants have a nickel concentration in urine higher than Rio de Janeiro inhabitants, probably due to a dietary intake, through food and water consumption. The workers have an additional intake of aerosols predominantly through the gastrointestinal system and with a contribution of inhalation of nickel compounds with slow pulmonary clearance. Using the biokinetical model proposed by ICRP 67 [7] the nickel incorporation was calculated, and these values were compared to the nickel reference dose [9]. The potential risk coefficient calculated was low.

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