

An occupational hygiene assessment of dermal nickel exposures in primary production industries

Graeme W Hughson

Research Report

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Nickel is known to cause contact dermatitis in humans and it is possible that nickel may be absorbed through the skin and contribute to overall systemic dose. However, the permeation rate of metallic nickel is considered to be low, so the main concern is in relation to dermatitis. There is a lack of dermal exposure data for industrial workers and this information was required for a regulatory risk assessment purposes. The object of this study was therefore to measure the levels of nickel in the skin contaminant layer of nickel refinery workers and to facilitate a comparison with analogous data from the zinc industry and predicted exposure levels given by the EASE model.

Workplace surveys were carried out in two different nickel refineries and a range of production tasks were studied. The subjects monitored were involved with processes such as leaching, electro-winning and packaging of the final products. Dermal exposure samples were collected using a removal method, using commercial moist wipes to recover nickel deposits from measured areas of skin. The test procedures were validated by measuring the recovery of known quantities of nickel contamination from surrogate skin media. In addition, background dermal nickel levels were established by studying a group of non-occupationally exposed subjects. The combined nickel recovery efficiency for the sample preparation and analysis procedure was approximately 95% for insoluble nickel and 87% for soluble nickel compounds.

A total of 33 complete sets of dermal exposure measurements were collected from 22 different workers. Of the total 792 dermal exposure measurements, 60 were less than the LOD of 0.02 μ g/cm². The highest actual dermal exposures were recorded for nickel powder packing, where the hands, arms, face and neck all received more surface contamination compared with other tasks. In the case of the powder packers, the median and $95th$ percentile combined hand/arm dermal nickel exposures were 8.40 and 15.37 μ g/cm². The corresponding results for the electro-winning workers were 0.30 and 1.91 μ g/cm². Taking all tasks combined, the corresponding levels were 0.76 and 8.90 μ g/cm². Although the exposure levels for the electro-winning area were much less than in the nickel powder packing plant the solubility of the nickel was higher, thereby possibly increasing the potential health risks.

Overall, the dermal exposures were low, and certainly much less than predicted values generated by the EASE model. In addition, the dermal nickel levels were much lower than levels measured in the zinc industry. It is concluded that this is largely due to the much higher levels of engineering controls applied to the nickel production processes generally, combined with specific hygiene measures such as the consistent use of personal protective equipment.

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1. INTRODUCTION

Nickel, in the form of various alloys and compounds, has been in widespread commercial use for over 100 years. Exposures to nickel and nickel compounds by inhalation, ingestion or skin contact may occur in nickel, nickel compound, and nickel alloy production plants as well as in welding, electroplating, grinding and cutting operations.

Occupational exposure has been shown to give rise to elevated levels of nickel in blood and urine, with inhalation assumed to be the most important route of systemic uptake.

Nickel also causes contact dermatitis in humans, although this mainly occurs through close prolonged contact with nickel metal or nickel plated items e.g. in jewellery, body piercing and clothing fasteners. It is widely recognised that the ability to release nickel ions is an important factor in the potential for a nickel-containing material to cause dermatitis (Lidén *et al.,* 1996; Lidén *et al.,* 2001; Ung *et al.,* 1983). This is also important for systemic uptake through the skin or gut.

The important routes of human systemic exposure to nickel and nickel compounds are from inhalation of dust and fumes and through ingestion of food and drink, which naturally contain nickel. It is also recognised that inadvertent ingestion of nickel may contribute to increased urinary nickel levels in workers (Kiilunen *et al.,* 1997a; Kiilunen *et al.,* 1997b). Consequently, it is usual practice in nickel refineries to implement strict personal hygiene programmes in the workplace in order to minimise the exposure to nickel and nickel compounds.

Dermal occupational exposure to nickel and nickel compounds is not normally considered to be significant. There is anecdotal evidence from nickel producing facilities that there are no excess cases of skin sensitisation in nickel refinery workers (Williams, *personal communication*). This may be due to the fact that the duration and intensity of exposure is not sufficient to induce nickel sensitisation or elicit nickel dermatitis in the workers. Also there is some evidence from human and animal studies that ingestion of nickel, which may occur inadvertently in the workplace, increases the threshold level for skin sensitisation to nickel and may even induce complete immunotolerance to nickel (Artik *et al.,* 2001; Kerosuo *et al.,* 1996; van der Burg *et al.,* 1986; Van Hoogstraten *et al.,* 1991).

The EU regulatory risk assessments carried out as part of the Existing Substances Regulations (CEC, 1993) require that all routes of exposure are assessed for human health risk assessment purposes (ECB, 2003). Where there are no existing exposure data, default levels of exposure are used based either on analogous data sets or from exposure models such as EASE (HSE, 1996).

The Estimation and Assessment of Substance Exposure (EASE) model was developed by the UK Health and Safety Executive (HSE) to assist exposure assessment for new substances. The model is based on a series of logical criteria contained within a computer-based expert system and can be used to predict exposures using task and situation-specific information about the substance and methods of control. The dermal exposure model predicts the potential exposure to the hands and forearms expressed as a mass per unit area of exposed skin per day (mg/cm²/day). This evaluation is based on information about the method and frequency of handling of contaminated objects and assumes an exposed anatomical area of approximately

2,000 cm². The two principal criteria used in the EASE model to predict dermal exposure are: the dermal contact level (possible values *– none, incidental, intermittent and extensive*) and the pattern of use (*closed system, with limited use* – termed *'inclusion into matrix or nondispersive use*' in the model, and *uncontrolled release* – termed *'wide dispersive use*'). The predictions or 'end-points' are expressed as exposure ranges, which can take five different values from 'very low' to $5 - 15$ mg/cm²/day.

A comprehensive review of the EASE model has recently been carried out (Creely *et al.,* 2004). The EASE model has been shown to generate predicted exposures which, in general, are overly conservative. This has been demonstrated for the dermal exposure model in a study concerned with dermal zinc exposure (Hughson *et al.,* 2004). The data from this study was incorporated into the EU regulatory risk assessment for zinc metal (ECB, 2004) and other zinc compounds including zinc oxide and zinc chloride. These exposure data are being used as an analogous data set for default dermal exposure levels for other metal industries including nickel, but this may overestimate exposures because the working practices in the zinc industry are likely to be different from those in the nickel industry.

Therefore, in order to accurately evaluate actual dermal exposure levels within the nickelproducing sector a dermal exposure monitoring survey was designed and implemented for two different European sites producing nickel and nickel metal compounds. One of these was a nickel refinery producing nickel metal powder. The second company was a nickel refinery producing a range of nickel metal and nickel compounds.

The exposure measurements for this study were collected using a wipe sampling method, previously reported for zinc (Hughson *et al.,* 2004) so that the nickel exposure data could be compared with this previous study.

2. AIMS

The main aim of this study was to supplement existing scientific knowledge about the levels of occupational dermal exposure to nickel and nickel compounds in the nickel refining and nickel compound producing industries.

To achieve this aim we addressed the following key objectives:

- To assess occupational dermal exposures to nickel and nickel compounds in primary production industry, taking into account the working practices and conditions within each workplace.
- To collect measurements of actual dermal exposures; defined as the level of contamination on the skin surface, averaged over the relevant exposure period.
- To collect corresponding airborne nickel exposure measurements from each worker monitored.
- To differentiate between soluble and insoluble forms of nickel in the dermal monitoring tests.
- To compare measurements of dermal exposures against exposure predictions produced by the EASE model where applicable.
- To observe and measure task-specific exposures for common industrial tasks, where possible. This included packing and/or bag emptying work as these may be considered to represent the worst case exposure scenarios for EU risk assessment purposes.

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3. METHODS

3.1 SAMPLING STRATEGY

Actual skin exposures were measured using a removal method. In this case, dermal exposures were measured using moist wipes. These wipes were used to remove residual contamination from predetermined skin areas at different intervals over the working shift. Samples were collected before washing so that they were representative of the level of skin contamination during the working day.

It is recognised that there is a wide variability in potential dermal exposures within and between tasks and individuals (Kromhout *et al.,* 1993). It is therefore desirable to monitor as many different workers as possible within each exposure scenario under consideration. However, due to the high level of automation common in modern industrial workplaces, this is not always a practical option. In this case it was necessary to select the process operators with significant potential for dermal exposure and to repeat these measurements over consecutive days, where necessary, in order to ensure a sufficient numbers of measurements.

3.2 DERMAL SAMPLING METHOD

Wipe samples were collected from the skin using a commercial moist wipe (Jeyes 'Sticky Fingers' Wet Ones) and an acetate template with an open aperture of 25 cm² pressed onto the relevant anatomical area at the time of sampling. Each sample comprised three sequential wipes from the anatomical area being sampled.

Wipe samples were collected from the palm and back of each hand and from both forearms prior to leaving the work area. This was done before rest breaks so that contamination was not lost from the skin as a result of washing. Samples of skin contamination were collected at three different intervals over the working day in order to assess contamination while at work.

The wipe samples from the palms and backs of the hands were collected in separate containers. The samples for the left and right forearms were bulked together into a third container. These were kept separate from other samples collected at different times of the day to enable an assessment to be made of the variability of exposure across the working shift.

The dermal exposure level for each worker was taken to be the surface loading of nickel calculated as a mass per unit area of skin. Since the aim of this study was to produce actual exposure measurements for comparison with known levels for elicitation or induction of nickel sensitisation, it was assumed that the best measure of this would be an average value of the three different sample sets collected for the hands and/or forearms. Furthermore, workers were known to regularly wash their hands and forearms as part of their normal hygiene procedure, so an average value of the three sample sets was considered to be representative of what would be present on the skin over the course of the working shift.

Additional samples were collected from the side of the neck, face (perioral region) and chest. The neck and face samples were used to provide an estimate of exposure for the head and also help make informed estimates about the potential for ingestion exposure. The sample from the chest was used to assess the degree of contamination under work clothes. The face, neck and chest samples were collected once, near the end of the shift i.e., before the afternoon break or before showering. It was not possible to use the acetate template for collecting the sample from the perioral region. In this case, the sample was collected by wiping around the mouth, under the nose and above the chin. This area of the face was estimated to be equivalent to 25 cm^2 .

The sampling procedure is summarised in Table 1, below:

Anatomical Region	Sample type	Sampling times			No. of samples
		First break	Mid-shift break	End of shift	
Palms of both hands	Moist wipes		✓		3
Backs of both hands	Moist wipes		✓		3
Forearm (left and right)	Moist wipes				3
Neck (preferred side)	Moist wipes				
Face (perioral region)	Moist wipes				
Chest	Moist wipes				
TOTAL no of samples per subject (excluding blanks)					12

Table 1 Summary of sampling schedule for each subject

A field blank sample was obtained for each subject sampled. This was done in order to check for contamination introduced during the sampling procedure. The field blanks comprised a series of thee wipes which were handled in the same way as the exposed samples but without being wiped over the workers' skin. The nickel level in the field blank was subtracted from the measured values for the corresponding set of samples.

3.3 ANALYSIS

All samples were analysed by inductively coupled plasma atomic emission spectroscopy (ICP/AES) for nickel. The samples were analysed at the IOM analytical laboratory, which holds accreditation for the analysis of nickel and other metals, by ICP/AES. The documented in-house method, based on OSHA method 121 (OSHA 1991) is accredited by the United Kingdom Accreditation Service (UKAS) under UKAS accreditation number 0374.

All wipe samples were transferred to the laboratory in 250 ml glass jars. The wipes contained in each sample jar were analysed to determine the soluble and insoluble nickel content using a variation of a published method (Zatka *et al.,* 1992).

Initially, the wipes in each sample container were covered with 0.1M ammonium citrate and left to soak for three hours in order to recover soluble nickel compounds. This solution was vacuum-filtered through a 1µm membrane filter and then made up to 100 ml using deionised water in a volumetric flask. The filter and remainder of the wipes were then prepared to determine the insoluble nickel content. The samples were covered with 10% nitric acid, heated to near boiling point for three hours, cooled, vacuum filtered, rinsed then made up to 100 ml volume in the same way as before. In each case, 1% anti-foaming agent was added to the sample jars to counter the effects of the detergents contained in the wipes.

Calibration standards were prepared using known weights of analytical grade reagents and the sample masses were determined with reference to these calibration standards. All sample masses were corrected for blank levels and for analytical and sample recovery efficiency using the results from laboratory blanks, spike samples and recovery test samples. Due to the large number of field samples processed it was necessary to prepare fresh laboratory blanks and spike samples for each day's batch of samples processed.

The quantity of nickel in each sample was used to calculate the dermal surface loading for each anatomical area, expressed in terms of mass per unit area $(\mu g/cm^2)$. All field samples were corrected for field blank levels. In the case of the hands and forearms three samples were collected from each of these areas. The skin surface loading for each sample was calculated and an average of each set of three was also calculated.

The results are expressed separately for soluble and insoluble nickel content. Individual measurements were calculated, for each subject, for the hands, forearms, neck, face and chest. In addition, an average value was calculated for the hands and arms combined as this is the relevant metric for comparison with predicted exposures obtained from the EASE model. In doing this the average for the hands and arms combined is weighted to take into account the relative surface areas of the different anatomical areas. The average value is calculated using the mean surface areas for hands (840 cm^2) and the forearms (1140 cm^2) (EPA 1997) as follows:

Average value Hands & forearms = $\frac{(hang \times 840) + (fore arms \times 1140)}{(green to 100)}$ $(840 + 1140)$ $(840) + (fore arms \times 1140)$ + $\frac{hands \times 840 + (fore arms \times 1140)}{(\omega_0 + \omega_1)(\omega_0 + \omega_1)}$ µg/cm²

3.4 METHOD VALIDATION

3.4.1 Compatibility of sample media and quantification of detection limit

for the analytical method. Blank levels and limits of detection were quantified for one wipe only and multiples of 3 and 6 wipes. Each test was carried out three times. Prior to the field surveys, test samples were analysed to check the compatibility of the wipe samples with the laboratory reagents and analytical equipment. The samples were also analysed to determine the background levels of nickel and to establish the limit of detection

3.4.2 Analytical recovery

to 1.0 mg/cm². Since the normal area of sampling is 25cm^2 , samples of nickel were prepared The analytical recovery was determined by preparing a number of spike samples. The spike levels were selected to correspond to surface contamination levels in the range 0.001 mg/cm^2 for approximately 0.025mg, 0.25 mg and 2.5 mg.

consecutive wipes and then placed into a glass beaker. A range of spike masses was chosen in This was done in two ways. Firstly, spike samples were prepared by adding known amounts of nickel onto the surface of the wipes. This was done by weighing out quantities of nickel powder onto plastic boats. The dust samples were removed from the boats using three order to cover the various site conditions expected.

Since it was not possible to accurately weigh out nickel dust samples of less than 0.3 mg, low level spike samples were prepared by adding a known volume of dilute 10 µg/ml stock solution of nickel sulphate hexahydrate in 10% nitric acid. The required amount of nickel solution was deposited onto the test wipes and left overnight to stabilise. These were then acid digested and analysed in the normal way.

The nickel dust used for these tests was INCO Type 123 and 255 nickel powder. According to the technical data sheets for these materials, each of the powders were 100% nickel metal. corresponding figures for the type 255 powder was $2.2 - 2.8 \mu m$. The particle size range for the type 123 powder was quoted as $3 - 7 \mu m$ and the

The nickel sulphate hexahydrate (CAS 10101-97-0) was obtained from Sigma Aldrich (product No. 467901).

3.4.3 Evaluation of soluble nickel species

were soaked in ammonium citrate for ten minutes, filtered, rinsed and the filtrate collected for analysis for nickel by ICP/AES. This was repeated for soak times of 60, 180 and 720 minutes. The average nickel level of the wipe blanks were subtracted from the measured value for each sample. The method described by Zatka was adapted for use with the wipe samples. In this case it was necessary to demonstrate that the recovery of soluble nickel was not influenced by the time of treatment in the ammonium citrate. In order to evaluate this method spike samples were prepared using three wipes per sample, using the two different types of nickel powder (INCO type 123 and 255 powder) and two different spike levels. Three samples of each powder type

3.4.4 Sampling efficiency

exposure assessment work with zinc (Hughson *et al.*, 2004) and antimony (Niven, 1993) showed that this method provided an acceptable level of recovery, but this was re-evaluated Tests were carried out to determine the removal efficiency of the sampling method. Previous for nickel. This is necessary in order to correct for incomplete removal of the skin contamination layer by the wipe sampling method.

were subtracted from the measured value for each recovery sample. The actual recovery This evaluation was made by applying pre-weighed quantities of nickel powder onto the surface of a section of chamois leather glued to a plywood panel. This was intended to act as a surrogate for human skin. The samples of nickel were placed onto the section of surrogate skin and spread out across a defined surface area of 25 cm^2 using a spatula. The spatula was wiped repeatedly on the chamois until it was clean. The contaminated surface was then cleaned using three successive wipes. Each wipe was analysed separately in order to evaluate the relative efficiency of each successive wipe. The average nickel level of the wipe blanks efficiency was calculated based on a ratio of the total mass of nickel recovered from the wipes to the mass of nickel deposited, taking into account any losses from the sample container, etc.

This procedure was repeated using a solution of nickel sulphate hexahydrate in solution, applied to the surrogate skin surface using a pipette. The surface was allowed to dry for three hours and the recovery tests were carried out as described above.

Again, the spike levels were selected to correspond to surface contamination levels in the range 0.01 to 1.0 mg/cm² using approximately 0.25 mg, 2.5 mg and 25 mg samples of nickel as nickel sulphate solution respectively.

3.4.5 Determination of background dermal nickel levels

Background levels of nickel on skin were measured by collecting wipe samples from a number of human volunteers not occupationally exposed to nickel. The average nickel level of the wipe blanks were subtracted from the measured value for each sample. These were used to infer typical background levels for the general population. This was limited to hand and forearm areas only, using the 25 cm^2 acetate template as described previously. In this case, ten male volunteers were obtained from IOM personnel.

3.5 SAMPLING FOR INHALABLE DUST AND NICKEL COMPOUNDS

lay within the breathing zone. The sampling apparatus was fitted to the worker at the start of At the request of the study sponsor, airborne dust sampling was carried out in addition to the dermal sampling previously described. This was done using personal sampling apparatus in accordance with Health and Safety Executive method MDHS 14/3 (HSE, 2000). This involved using an IOM inhalable dust sampler loaded with a preweighed cassette containing a 25mm quartz fibre filter. The sampling flow rate was set to 2.0 litre/min, measured using a calibrated flow meter. The IOM sampler was connected to a battery operated sampling pump, which was worn on a belt, and the sampling head was attached to the subject's lapel so that it the working shift and left running for the majority of the working day. The sampling flow rate was checked at the beginning and end of sampling and periodically over the course of the shift. The start and stop times were recorded so that the sample volume could be calculated.

The IOM cassettes were reweighed at IOM to determine the total inhalable dust concentration and the samples were then shipped to an independent laboratory nominated by the sponsor for analysis of soluble/insoluble nickel species. The quartz fibre filter was selected to enable this analysis to be carried out according to the published method (Zatka *et al.,* 1992).

3.6 STATISTICAL METHODS

(ECB, 2003). The associations between exposures for different anatomical areas were investigated by calculating the Pearson correlation coefficient using SPSS for Windows The workplace dermal exposure data for each exposure category were summarised in terms of maximum and minimum values, median and the upper $90th$ percentile level using Microsoft Excel 2002. This is the summary data normally required for EU regulatory risk assessments version 12.01. In addition, correlations between dermal exposure and inhalable dust concentrations were investigated in the same way. Since the data was log-normally distributed, it was log transformed prior to analysis.

In order to summarise the data properly it was necessary to adjust data values that were below the limit of detection. For samples which were less than the limit of detection, the exposure value was set to a level of $\frac{1}{2}$ the limit of detection, in accordance with the approach suggested by Rajan-Sithamparanadarajah *et al.,* 2004.

3.7 EVALUATION OF TASK-BASED DERMAL EXPOSURES USING THE EASE MODEL

EASE model and this provided predicted exposure levels for each category of task. The The various observed tasks in each of the workplaces were categorised in terms of the EASE model, so that the exposure measurements could be compared with the EASE predictions. Information about the working practices and control measures were used as inputs to the categorisation was done after consideration of the dermal contact level and pattern of use, and is a matter of professional judgement, assisted by on-line help embedded in the EASE computer program. The categorisation was done by an experienced user (GWH) of the EASE model, before the results of the dermal exposure results were known.

4. WORKPLACE DESCRIPTIONS

The following sections describe the observed workplace conditions and working practices for each of the two companies included in this assessment. Also, the various tasks or jobs included for sampling are described, together with any exposure controls used by the workforce. Each task is categorised in terms of the EASE model and the predicted dermal exposures are included to enable comparison with the measured results.

4. 1 NICKEL REFINERY 1

This nickel refinery produced nickel metal and nickel compounds by recovering elemental nickel from nickel matte using an electrolytic process. The granulated nickel matte from the smelter was ground in ball mills in a wet grinding process. The ground matte was leached in a sulphate-based liquor recycled from the nickel electro-winning process. Nickel sulphide matte was leached in an atmospheric leaching stage using oxygen or air-sparged in leaching vessels with the aid of copper ions. Dissolved iron was oxidised to form iron oxide, which precipitated out and was removed from the process.

The residue from the atmospheric leaching was passed to a pressure leaching stage where the nickel content was dissolved and copper precipitated out as copper sulphide.

The nickel solution from the atmospheric leaching process was purified by solvent extraction to remove cobalt and other impurities. The purified solution was pumped to the three different production areas: the electro-winning process, the hydrogen reduction plant and the chemical plant.

Each of these areas produced different nickel products as detailed below:

The workplace conditions and working practices are described in detail for the main process areas in the following sections:

4.1.1 Leaching plant

In the leaching plant, nickel was leached into a solution of nickel sulphate using sulphuric acid and the purified solution was pumped to the three different production areas. The operation of the leaching plant was highly automated. Approximately three full time operators were involved with controlling the process, mainly from within a control room. It was necessary for the operators to carry out routine inspection of the plant and carry out various cleaning tasks. One such task was checking the filter press area. The filters were part of the purification process and removed suspended particulate matter. These filters required regular checks and manual clearance of the deposited material, e.g. by tapping the filter elements to remove the cake. The area around the filter press was regularly hosed down to remove any residual contamination from the floor and work surfaces.

There were hygiene procedures in place for accessing the control room, involving changing of footwear, outer clothing and hand-washing before re-entry to the clean areas.

In view of the high level of automation for this process, the tasks involved with this work are categorised in terms of EASE as non-dispersive use with intermittent direct contact. The predicted exposure level for this task is $0.1 - 1$ mg/cm² per day.

4.1.2 Electro-winning plant

There were three interlinked halls containing the electrolytic tanks used to recover nickel from solution. There were approximately 10 workers per shift within the tank room area directly involved with the electro-winning process.

In simple terms, the process can be divided into two sections: (a) production of starter sheets and (b) production of the main nickel cathodes. Starter sheets were produced using tungsten sheets as cathodes, which were placed into electrolytic tanks containing nickel sulphate solution. Nickel was deposited onto the cathodes and after two days the plated tungsten sheets were removed. Loading and unloading of the cathodes was done using a travelling crane, with the assistance of two to three operators who manipulated the load as it was being loaded or unloaded. The plated starter sheets were washed down with water and transferred to the stripping machine which separated the nickel plate from the tungsten sheet. This was a semiautomatic process and involved two workers who supervised the loading and unloading of the machine conveyors. The tungsten sheets were re-used and the nickel plates were transferred to the main process area where they were used as starter sheets for electrolytic recovery of nickel in the main tank room area. The workers who handled the starter sheets were known as cathode 'strippers'. It was usual practice to rotate around the various tasks in this area so that the time in the tank room area was reduced.

The starter sheets were configured as nickel cathodes on the cathode machine. This was another automatic process, supervised by one or two workers. The machine trimmed the nickel plates to size and fixed a copper electrode bar to one end of each plate. The resultant cathodes were loaded onto racks and then placed into the process tanks using an overhead crane in a similar manner as the stripping area. The workers in this main tank house area were known as cathode 'lifters'. Again, it was usual practice for workers to rotate around tasks in order to limit the time spent in the tank area. The cathodes were left in the tanks for seven days and were removed, washed down and then transferred to the cathode cutting area in a different part of the plant.

The tank house was provided with forced ventilation comprising a series of fresh air input vents mounted along the walls on either side of the central part of the tank house. The ventilation for the other areas was provided by under-floor fresh air input vents. This arrangement depended on the incoming fresh air to dilute the airborne nickel aerosol and to induce an upward flow of contaminated air which was discharged via passive roof vents.

There was no local exhaust ventilation applied to the electrolytic process tanks. Instead, potassium lauryl sulphate (CAS 4706-78-9) was added to the electrolyte, which formed a foam blanket over the surface of the tank. This was intended to suppress emission of nickel aerosol into the workplace. Nevertheless, there was a visible haze and a strong odour in the tank room environment.

All workers in the tank house were required to wear an air-assisted filtering visor with P3 filter element (Willson Turbovisor). The workers wore cotton overalls and coated rigger gloves. New gloves were worn at the start of each shift. Gloves were worn continuously in this area due to the risk of cuts from contact with sharp metal surfaces and also due to the corrosive nature of the process liquor.

The tasks in this area were categorised in terms of EASE as non-dispersive use with extensive direct contact, which has a predicted exposure level of $1 - 5$ mg/cm² per day.

4.1.3 Cathode cutting plant

The nickel metal cathodes were transferred from the tank house to the cathode cutting area on pallets by fork-lift trucks. The cathodes were cut up into small squares, which was the final product and these were packed into steel drums for dispatch to the customer. This work was done by three workers per shift using two different cutting machines. One worker operated the auto-cutting machine and two workers operated the manual cutting machine. In both cases the machines were fitted with lifting apparatus which loaded the cathode plates onto the input conveyors for the machines. The machines first cut the cathode sheets into strips and the operator manually lifted these out of the first stage and threw them into the next section of the cutting machine where they were chopped into squares. The output conveyors carried the nickel squares from the machine and automatically fed them into the drum containers. The manual cutting machine required additional manual involvement and the operators were mainly involved with removing waste material and troubleshooting the process. Other tasks included the transferral of stock by forklift trucks and capping of the drum containers. The process was noisy, and the operators wore hearing protection. Rigger gloves and cotton overalls were also worn. No RPE was required for work in this area.

The tasks involved in this process were categorised in terms of EASE as non-dispersive use with intermittent direct contact. This has a predicted exposure level of $0.1 - 1$ mg/cm² per day.

4.1.4 Hydrogen reduction plant

The task of interest in this area was nickel briquette production. Nickel powder was produced by adding ammonia and ammonium sulphate to the purified nickel sulphate solution in an enclosed process. The mixture was reduced in an autoclave using a hydrogen atmosphere. Nickel briquettes were then produced by a totally automated sintering process, which used the nickel powder as a feedstock.

The nickel briquettes were transferred from the output stage of the sinter machine while they were still hot, on a series of conveyors to the packaging area. This was supervised by two workers per shift and their main function was to monitor the process from a control room and carry out movement of stock by forklift truck. The briquettes were packed into 1000 kg flexible intermediate bulk containers (FIBC) known as 'big bags', or 200 kg drums, and the workers were simply involved with loading the fill point with the empty container and waiting until it was filled. The full containers were sealed and transferred to the warehouse area using a forklift truck.

The two workers wore the standard cotton overalls with rigger type gloves, when required. No RPE was required for work in this area.

The tasks for this work were categorised in terms of EASE as non-dispersive use with intermittent direct contact. This has a predicted exposure level of $0.1 - 1$ mg/cm² per day.

4.1.5 Chemical plant

The chemical plant used nickel sulphate solution to produce nickel sulphate hexahydrate and nickel hydroxycarbonate. The chemical reactions and transfer of compounds to the packing area was entirely automatic and completely enclosed. The packing area was highly automated with modern robotic packing and bag handling equipment. The nickel compounds (nickel sulphate hexahydrate and nickel hydroxycarbonate) were packed into 25 kg sacks using this equipment and there was no manual involvement with the bag filling operation. The 25 kg sacks were automatically stacked onto pallets by robotic arm and the pallets were automatically shrink-wrapped before being conveyed through to the warehouse area. The workers were required to supervise the machinery and correct any faults that developed. There were four workers on one day shift, involved with supervising the process. All of these workers were monitored.

One of the workers had some involvement in machine repair work, involving replacement of a pneumatic cylinder and considerable time was spent preparing the machine for production. Otherwise, the remaining packing lines were relatively trouble free and the workers had only incidental contact with the packing equipment and final products.

Nickel hydroxycarbonate in powder, paste or granular form was also packed into big-bags at a number of fill points. The big-bag filling operation was a fully contained system, with tight fitting joints to the bag spouts. The powder products were allowed to settle in the bags before they were uncoupled from the system and each unit was fitted with extract ventilation as a means of controlling dust emissions into the workplace. One operator was involved with this work. The work involved removing the spout of the big-bag from the filling nozzle, which was tied up with the cord provided. An empty bag was attached to the filling nozzle and the full bag was transferred to the warehouse area by forklift truck. The forklift truck had an enclosed cab. During the bag replacement task, there was some noticeable spillage of powder onto the surface of the container, but this was a minor amount.

All of the workers in the chemical plant wore air assisted filtering visors, cotton overalls and rigger type gloves. The workers returned to the main control room area when they were not required to directly observe the process. There were hygiene procedures in place for entering the control room, involving removal of work footwear and outer clothing, with hand-washing prior to accessing the clean areas.

Due to the high level of control in this area the tasks carried out are categorised in terms of EASE as non-dispersive use with intermittent direct contact, which has a predicted exposure level of $0.1 - 1$ mg/cm² per day.

4.2 NICKEL REFINERY 2 (NICKEL POWDER PRODUCTION)

This nickel refinery produced nickel metal and nickel powder products using the Mond process, i.e. by decomposition of nickel from nickel carbonyl gas. This study relates only to the nickel powder production area.

The company produces a variety of nickel metal powders. At the time of survey, three types of nickel powders were being produced. These were known as type 123, type 210 and type 255 powders. Type 123 Powder is a high purity nickel with fine, discrete particles in the size range $3.0 - 7.0 \,\mu$ m. The type 210 powder was an extra-fine nickel filamentary metal powder with a three-dimensional chain-like network of extra-fine particles in the range of $0.5 - 1.0$ µm. The type 255 powder is also a chain-like filamentary powder, but with larger individual particles, which were in the size range $2.2 - 2.8$ um.

Nickel carbonyl was produced by heating the nickel concentrates in the presence of carbon monoxide in a series of rotary kilns. The nickel carbonyl was maintained in gaseous phase and by controlling the thermal conditions the gas was decomposed to form nickel powders of a uniform particle size range. The nickel carbonyl production and decomposition processes were all fully contained due to the highly toxic nature of the gaseous chemicals. The chemical decomposition of nickel carbonyl occurred in a series of reaction chambers known as decomposers. The process conditions for the decomposers were monitored by one operator, who was also responsible for some powder packaging work in a separate area. The main duties for this worker mainly involved routine inspection of control panels, and actuator valves etc. When the decomposers discharged to hoppers, it was necessary for this worker to sound the side of the cone to ensure that all of the powder inside was being properly discharged. This operator also packed type 123 nickel powder into FIBC. The packing operation for type 123 powder was highly automated and well controlled. All that was required for this task was to remove the fill point of the FIBC from the packing machine and secure the bag by tying it up with the cord provided. A fork lift truck was used to move the full bag to a warehouse area. The operator then installed an empty FIBC onto the fill station and then left the area. This changeover was done two to three times per shift.

The nickel powder was transferred from the decomposer hopper to the powder packing stations through a series of conveyors to storage and automatic weigh-cells. At the powder packing area one operator (per shift) was involved with packing type 255 nickel powder into drums. In a second area known as the Dec 2 powder packer, a second worker was involved with packing type 210 nickel powder, also into drums.

The tasks for each operation mainly involved ensuring the semi-automatic powder packing stations were supplied with the necessary empty drums. The workers took the drums from storage and placed them onto the input conveyors for each of the packing machines. At the 255 powder packer, the drums would move through the packing machine, which would dispense a measured quantity of nickel powder into the container. The operator checked the drum weights using the scale built into the conveyor. If the drum weight needed to be adjusted, the operator removed excess powder using a hand scoop and placed the surplus material into a storage bin located at the workstation. If any of the drums needed to be topped up, the operator used the scoop to transfer powder from the storage bin to the drum. Each packing station was provided with local exhaust ventilation at the filling points so that any airborne dust generated was effectively controlled.

Each drum was fitted with a lid which had a small diameter aperture (approximately 100mm), through which it was filled. As the drums passed through the packing machine they entered an enclosed booth where a robot arm was used to perform a quality control test. The drums then backed up onto the end of the conveyor system where the operator would fix the sealing cap onto the open aperture. The tops of the drums were then vacuum-cleaned to remove any residual dust and then they were lifted off the conveyor by fork lift truck and transferred to storage.

The task performed by the Dec 2 powder packer was similar in nature to the main packer except that this worker was only involved with supervising one drum packing machine. The packing machine for this area was contained in a semi-enclosed booth, having local exhaust ventilation applied to it in order to prevent emissions to the general workplace area.

RPE was provided in the form of air assisted filtering visor fitted with P3 filter. While it was a mandatory requirement to use the RPE during packing work, this was not always adhered to. All packing operators wore cotton overalls, safety boots and rigger-type gloves. Glove use was regular, but generally only when carrying out manual handing tasks, e.g. lifting drums onto the conveyors. There was potential for skin contact with contaminated surfaces when touching handrails, driving the fork lift truck and operating buttons on control panels.

The tasks relating to the powder packaging work may be categorised in terms of EASE as non-dispersive use with extensive direct contact, for which EASE gives a predicted exposure level of $1 - 5$ mg/cm² per day.

5. RESULTS

The results for the method validation and workplace exposure measurements are included in the following sections.

5.1 METHOD VALIDATION

5.1.1 Determination of limit of detection and recovery efficiency

Three types of moist wipes were checked to determine their compatibility with the analytical reagents. These were Boots Travel Wipes, Jeyes Family Size Wet Ones and Jeyes 'Sticky Fingers' Wet Ones. All of the types tested were considered to be acceptable on the basis that they did not cause unacceptable foaming when treated with the nitric acid.

Initial spike samples were prepared by adding a known volume of nickel sulphate hexahydrate solution onto a selection of clean wipes. The results of these tests are detailed in Table 2. This showed that the analytical procedure gave good recovery for the Boots wipes, with an overall average value of 1.013. However, these particular wipes were very thin and did not appear to be very absorbent. They also proved to be difficult to source. The Sticky Fingers wipes were thicker and appeared to be more absorbent and their packaging was more convenient for the intended application. The average recovery for the Sticky Fingers was 0.743, but this was heavily biased by one unusually low value, which may have been erroneous. Ignoring this value, the average recovery of the remaining two Sticky Fingers tests was 0.996. On balance, the Jeyes 'Sticky Fingers' wipes were identified as the best dermal sampling media for this study, due to a combination of their physical characteristics (tough and absorbent), availability, suitability of the packaging, acceptable recovery of the analyte and compatibility with the analytical procedure.

Table 2 Initial tests of recovery for three different types of moist wipe

Additional tests were carried out to determine blank levels for varying numbers of wipes and to establish a detection limit for the analytical method. The results of this procedure are detailed in Table 3.

Table 3 Blank levels for varying numbers of blank wipe samples

These results in Table 3 show there was very little variability in the blank levels for varying numbers of wipes. If an average of all the samples is taken, then the limit of detection (LOD) for the analytical procedure can be determined using three times the standard deviation (SD), which in this case is equivalent to 0.5 µg. Assuming a sample area of 25 cm², the sample LOD is calculated as $0.018 \mu g/cm^2$.

This experiment was designed to determine the typical blank level for samples comprising varying numbers of these wipes. In practice, when field samples were being analysed separate blank samples were used for each batch of samples being processed. The values for these blanks were subtracted from the measured values for each occupational scenario.

The analytical recovery was tested in more detail using five spike levels. The spike samples were prepared by making a 10 μ g/ml stock solution and adding known volumes of solution by pipette onto the wipes. Three wipes were used for each spike sample and the prepared wipes were left overnight to stabilise. The samples were then covered in 10% nitric acid, heated to near boiling point for three hours, cooled, filtered and then analysed by ICP/AES as before. The results of this procedure are detailed in Table 4

Spike sample	Spike mass	Actual Mass Ni	% Recovery	
	Ni (µg)	recovered (μg)	efficiency	
Sp01	2.765	ND	$<$ 1	
Sp02	2.765	ND	$<$ 1	
Sp03	2.765	15.8	572	
Sp04	11.06	5.8	53	
Sp05	11.06	4.6	41	
Sp06	11.06	5.0	45	
Sp07	27.65	36.9	134	
Sp08	27.65	31.3	113	
Sp09	27.65	31.6	114	
Sp10	276.5	220.3	80	
Sp11	276.5	208.8	76	
Sp12	276.5	220.2	80	
Sp13	2765	2064	75	
Sp14	2765	2056	74	
Sp15	2765	2168	78	

Table 4 Results of analytical recovery tests at five different sample spike levels

Note: $ND = Not detected$, based on detection limit of 0.5 µg nickel.

This analysis showed that there was poor recovery at the lowest spike level of 2.765 µg. However, this is not unexpected given the overall blank levels of approximately 4 μ g for the wipes used. The recovery efficiency at the 11.06 μ g spike level was in the range 41 – 53%, which although being relatively low, is more consistent than the lowest spike range available. The recoveries improved at the higher spike levels, with the best recovery apparent at the 27.65 µg spike level. Since the sample area used for exposure measurements is 25 cm^2 , the measured recovery of approximately 113% shows that analytical recovery is reliable for typical dermal exposure of about 1 μ g/cm².

It was noted that the results from the daily spike recovery samples prepared for each batch of field samples showed a higher level of recovery than for the test results detailed in Table 4. These sample recovery tests were therefore repeated, for soluble and insoluble forms of nickel and the results are detailed in the following section.

5.1.2 Evaluation of soluble nickel recovery

Spike samples were prepared using nickel powder applied onto clean wipes. This was done in order to evaluate the soluble fraction of the nickel powder and also to test the efficiency of the sample preparation and analytical procedures. While it was expected that the commercial nickel powder would have low water solubility, the purpose of this exercise was to show that the sample preparation procedure did not affect the rate of dissolution of nickel into the test solution.

The results of the soluble nickel evaluation are summarised in Table $5(a)$. This shows the average soluble nickel content for the two types of nickel powder samples tested at each spike range and for each of the soak times. The solubility of the nickel powder in the test solution was approximately 5% over all soak times and all spike ranges. It is clear from this analysis that the length of the soak time had no significant effect on the recovery of soluble nickel species, at least for the nickel powders tested. The detailed results relating to this procedure are contained in Appendix A: Tables A1 and A2.

However, this analysis showed only the soluble portion of the nickel dust, so this was repeated to evaluate both the soluble and insoluble nickel fractions and hence the total practical recovery efficiency of the preparation and analytical procedure. This was done in the same way as before, by adding known quantities of nickel powder onto wipe samples at three different spike levels. This was repeated using a solution of nickel sulphate hexahydrate for comparison. The results of this analysis are summarised in Table 5(b), with the detailed results contained in Appendix A: Tables A3 and A4.

(The detailed results of this analysis are contained in Tables A1 and A2, in Appendix A)

Table 5(b) Evaluation of soluble and insoluble nickel content of test material by nickel type.

Note: $ND = Not detected (based on detection limit of 0.5 µg nickel)$

(The detailed results for this analysis are contained in Tables A3 and A4 in Appendix A)

The results from the above analysis showed that the combined nickel recovery efficiency for the sample preparation and analysis was approximately 95% for insoluble nickel and 87% for soluble nickel compounds. Again, this shows a good recovery at the lowest spike range of 25 μ g, corresponding to a dermal exposure level of about 1 μ g/cm², based on a sample area of 25 cm^2 .

The detailed results relating to Tables 5(a) and 5(b) are contained in Appendix A. All field samples were corrected for analytical recovery using sets of spike samples prepared for each batch of samples processed.

5.1.3 Determination of sampling efficiency

The sampling efficiency was established by analysing the mass of nickel on each wipe used to remove a known mass of nickel applied to a surrogate skin media. This was done by applying a known amount of nickel powder or a solution of nickel sulphate hexahydrate onto separate sections of chamois leather mounted onto plywood board. The sampling efficiency was calculated as the ratio of total recovered nickel to the amount deposited.

The results of the recovery tests carried out using nickel powder are detailed in Table 6(a). These results show that the majority of the nickel powder deposits were removed on application of the first wipe, with small remaining percentages being removed by the second and third wipes. The average recovery efficiency for nickel powder using this test was 92%. Due to the high level of recovery with this method the field samples were left uncorrected for sampling efficiency.

The results of the tests carried out for the nickel sulphate solution are detailed in Table 6(b). This shows that recovery of nickel solution from the surrogate skin media was poor, with an average value of 16% at the higher spike levels. However, it was apparent during these tests that the solution applied to the chamois leather was being quickly absorbed through the matrix and onto the underlying support material. It was therefore considered that this particular media was not representative of natural human skin, at least in terms of permeation of liquids. This experiment was repeated using a different cured soft leather product as a surrogate skin and the results from this procedure are detailed in Table $6(c)$. This showed that the recovery of nickel was much better, due to the greater retention of nickel on the surface of the surrogate skin media and removal by the sequential wiping process. The average sampling efficiency using the alternative skin media was an average of 97% using the results from the $25 - 2500$ µg spike range. Since the sample recoveries for these tests were high, the results of the field sample analysis were left uncorrected.

Table 6(a) Results of wipe sampling recovery tests using nickel powder

Note: Nickel dust (type 255) weighed in plastic boats and applied to the surrogate skin medium, removed using 3 sequential wipes for each spike sample. Individual samples digested in 10% nitric acid and analysed for total nickel content. Sampling efficiency determined by ratio of mass nickel recovered to mass nickel deposited onto surrogate skin media.

These results show that the majority of the nickel deposits were removed on application of the first wipe, with small remaining percentages being removed by the second and third wipe. This demonstrates an acceptable recovery of dust from the surrogate sampling media.

The results of the tests carried out for the nickel sulphate solution are detailed in Table 6(b).

Table 6(b) Results of wipe sampling recovery tests using nickel sulphate hexahydrate solution

This clearly showed that recovery of nickel solution was poor. However, by observation it was apparent that the solution applied to the surrogate skin was immediately absorbed through the matrix. It is unlikely therefore that this was representative of natural human skin where the liquid may run off, dry on the surface or be absorbed. This experiment was therefore repeated using a cured soft leather product as a surrogate skin and the results from this procedure are detailed in Table 6(c).

In the repeat experiment, the recovery efficiencies were much higher, due to the greater retention of nickel on the surface of the surrogate skin media and removal by the sequential wiping process. At the lowest spike level of 2.5 µg, the recovery was poor, although this was expected from the previous tests at this level. At spike levels of 25 µg and above the recovery efficiency was better than 92%, which provides reassurance that exposure levels of 1 μ g/cm² and above are valid.

Table 6(c) Results of wipe sampling recovery tests using nickel sulphate hexahydrate solution

(Repeat test using alternative surrogate skin media)

Note: $ND = Not detected$, based on detection limit of 0.5 µg nickel

Nickel sulphate hexahydrate added by pipette onto surrogate skin (cured soft leather on cardboard base) and left to dry overnight. Nickel deposits recovered by three sequential wipes analysed separately for total nickel content

5.1.4 Background dermal nickel levels for control group

The results of the background levels of nickel on the skin of non-occupationally exposed volunteer subjects are detailed in Table 7. The table contains the results for the analysis of all individual samples for the palms, backs of the hands and the forearms. The surface loadings for each anatomical area are calculated using the sample area for each anatomical area sampled i.e. 50 cm², based on two 25 cm² template areas from each limb.

For each subject, the average values for hands, arms and hands and arms combined are calculated.

Out of a total of 30 samples collected, 12 were below the limit of detection for the method, which was calculated as $0.019 \mu g/cm^2$. For the purposes of the analysis, samples less than the LOD were set a value of half the LOD, equivalent to $0.01 \mu g/cm^2$.

The results of this analysis show that the background nickel levels for the hands only were in the range $0.01 - 0.09 \mu\text{g/cm}^2$, with a median value of 0.03 $\mu\text{g/cm}^2$. The upper 90th percentile value for these measurements was $0.05 \mu g/cm^2$. The results for the forearms were in the range $0.01 - 0.06 \,\mu$ g/cm², with a median value of 0.01 μ g/cm². The upper 90th percentile value for the forearm samples was $0.03 \mu g/cm^2$.

There was some evidence to suggest that the nickel levels were marginally higher on the palms of the hands than on the backs of the hands. However, there was very little difference in the levels on the backs of the hands compared to the forearms.

Table 7 Background nickel levels on skin of non-occupationally exposed volunteers

*Note – sample loading based on sample surface area of 2 x $25 \text{cm}^2 = 50 \text{ cm}^2$ areas (both palms, both backs of hands, both forearms)

Surface loadings <LOD set to $\frac{1}{2}$ of LOD, equivalent to 0.01 μ g/cm².

5.2 RESULTS OF DERMAL SAMPLING IN THE WORKPLACE

A total of 396 samples (including field blanks) were collected for nickel analysis. Each sample was analysed for soluble and insoluble nickel content, making a total of 792 dermal exposure measurements. There were 33 complete sets of exposure measurements with one partial set, collected from 22 different workers. There were 11 workers that were sampled twice, i.e. on consecutive days.

Out of the total 792 dermal exposure measurements, 60 were less than the LOD of 0.02 μ g/cm². For the purposes of the statistical analyses, these measurements were set at a nominal level of $\frac{1}{2}$ of the LOD, i.e. 0.01 μ g/cm².

The results of the dermal nickel sampling survey are detailed in Tables 8 - 10. The results are expressed as the dermal nickel loading $(\mu g/cm^2)$ for the hands, forearms, hands and arms combined, face, neck and chest. The data for the hands are averages of the separate samples collected for each subject monitored as previously explained in Section 3.2. All of the results are expressed in terms of soluble nickel (Table 8), insoluble nickel (Table 9) and total nickel (Table 10).

The individual measurements for the hands and forearm results used to calculate the average exposures referred to in Tables $8 - 10$ are provided in Tables 11 – 13. Again, these are presented in terms of soluble (Table 11), insoluble (Table 12) and total nickel (Table 13) and are expressed as a skin surface loading in μ g/cm².

Additional information about the tasks performed for each subject monitored is detailed in the job activity records contained in Appendix B (Tables $B1 - B5$). This shows the types of activities carried out immediately before each of the three separate sets of dermal exposure measurements were collected.

It should be noted that the value for the hands and arms combined is weighted to take into account the relative surface areas of the different anatomical areas. The average value is calculated using the mean surface areas for different anatomical areas (EPA, 1997) as explained in Section 3.3.

All samples were corrected for blank levels, field blanks and for analytical recovery efficiency. The results were not corrected for background skin levels, with reference to the control group. The sample results were also left uncorrected for sampling efficiency as this was judged to be sufficiently high on this occasion.

Table 8 Dermal nickel exposures for various tasks in primary nickel production

Soluble Nickel Species

area and workers rotate between these tasks so exposures are a combination of both jobs.
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 The two different jobs specified are the primary job of the workers measured, but workers rotate between these tasks so exposures are a combination of both jobs.

N/A – Not available, not sampled.

Table 9 Dermal nickel exposures for various tasks in primary nickel production

Insoluble Nickel Species

area and workers rotate between these tasks so exposures are a combination of both jobs.
[¥] The two different jobs specified are the primary job of the workers measured, but workers rotate between these tasks so exposures are a combination of both jobs.

N/A – Not available, not sampled.
Table 10 Dermal nickel exposures for various tasks in primary nickel production

area and workers rotate between these tasks so exposures are a combination of both jobs.
[¥] The two different jobs specified are the primary job of the workers measured but to

 The two different jobs specified are the primary job of the workers measured, but workers rotate between these tasks so exposures are a combination of both jobs.

Table 11 Individual sample results for the hands and forearms (soluble nickel)

area and workers rotate between these tasks so exposures are a combination of both jobs.
[¥] The two different jobs specified are the primary job of the workers measured, but workers rotate

between these tasks so exposures are a combination of both jobs.

Table 12 Individual sample results for the hands and forearms (insoluble nickel)

area and workers rotate between these tasks so exposures are a combination of both jobs.
[¥] The two different jobs are if we are the second workers with the second was a combination of both jobs.

 The two different jobs specified are the primary job of the workers measured, but workers rotate between these tasks so exposures are a combination of both jobs.

Table 13 Individual sample results for the hands and forearms (total nickel)

area and workers rotate between these tasks so exposures are a combination of both jobs.
[¥] The two different jobs specified are the primary job of the workers measured, but workers rotate

between these tasks so exposures are a combination of both jobs.

5.3 ANALYSIS OF DERMAL EXPOSURE DATA BY TASK AND EASE CATEGORY

The summary exposure data detailed in Tables $8 - 10$ were analysed for each anatomical area sampled by job title/task to determine the number of samples per category (N), the exposure range (minimum and maximum values), median and the upper $90th$ percentile value.

Exposure results are provided for the hands (average of three separate measurements per subject), forearms (average of three separate measurements), arms and forearms combined (weighted average of hands and arms), neck, face and chest. In addition, the total number of samples, minimum, maximum, median and $90th$ percentile values is calculated for all exposure measurements within each task category.

These are sorted by task category in process order from leaching plant workers (Table 14), electro-winning (Table 15), cathode cutting (Table 16), briquette packing (Table 17), nickel sulphate hexahydrate and nickel hydroxycarbonate packing (Table 18), nickel powder packing (Table 19) and then for all categories (Table 20).

All jobs fell within two different EASE task categories. These were non-dispersive use with intermittent direct contact or non-dispersive use with extensive direct contact. The predicted values for these categories of exposure are $0.1 - 1$ mg/cm²/day and $1 - 5$ mg/cm²/day respectively. The justifications for including the data in the different EASE categories were previously given in the relevant subsections of Section 4.

For the purposes of this assessment, all the workers in the electro-winning plant (cathode lifters and strippers) were considered as a similarly exposed group. This is because the work areas are not segregated and the workers tended to rotate around the various tasks over the day or cover for others during rest breaks. The workers involved in packing nickel hydroxycarbonate and nickel sulphate hexahydrate were also considered as one similarly exposed group for similar reasons.

Comparisons of dermal exposure for each anatomical area are illustrated graphically for each task category in the box-plots shown in Figures $1 - 6$. A similar comparison is provided for all jobs combined in Figure 7. In these plots, the boxes include data from the lower $5th$ and the upper $95th$ percentiles. Outlying data points are indicated by excursions outside the box. The notch in each of the boxes indicates the position of the median.

From the results shown in Figures $1 - 6$, it is clear that all measured exposures were much lower than the predicted exposures given by EASE. For example, the electro winning process was assessed as non-dispersive use with extensive direct handling, for which EASE gives a predicted exposure of $1 - 5$ mg/cm². The measured dermal nickel exposures for the workers in this area were approximately $0.2 - 3.2 \mu g/cm^2$, which is approximately three orders of magnitude less than the predicted range

Table 14 Summary of dermal nickel exposures by industry/task and allocated EASE task category

(Leaching plant operators)

Table 15 Summary of dermal nickel exposures by industry/task and allocated EASE task category

(Electro-winning operators)

Table 16 Summary of dermal nickel exposures by industry/task and allocated EASE task category

(Cathode cutting operators)

Table 17 Summary of dermal nickel exposures by industry/task and allocated EASE task category

(Briquette packing operators)

Table 18 Summary of dermal nickel exposures by industry/task and allocated EASE task category

(Nickel compound packing operators)

Table 19 Summary of dermal nickel exposures by industry/task and allocated EASE task category

(Nickel powder packing operators)

Table 20 Summary of dermal nickel exposures for all task categories included in measurement programme

5.4 ANALYSIS OF DERMAL EXPOSURE BY NICKEL SPECIES

The exposure measurements detailed in Tables $8 - 10$ were analysed together to determine the ratio of soluble nickel to total nickel content for each individual sample collected. The results of this analysis are shown in Table 21. This shows that there were some differences in nickel solubility between the different task categories and also some variability with task categories. Using the median values for each task category, the solubility ratios were relatively high overall. The tasks with the lowest nickel solubility levels were in the briquette packing area and nickel powder packing plant, although there was a high outlying value for the latter category. These results are broadly consistent with the expected pattern that lower nickel solubility compounds would be present in nickel metal product handling areas rather than in upstream nickel refining processes, such as the electro-winning area where soluble nickel compounds were being used.

Table 21 Ratio of soluble nickel to total nickel content of dermal sample measurements

(All anatomical areas by plant area)

The solubility ratios for each task category are illustrated using a box-plot, as shown in Figure 8. This illustrates the wide spread in the results for each category, particularly for the leaching plant workers. It is also clear that the overall ratios are affected by large outlying values, particularly for the nickel packers, chemical plant and cathode cutting workers.

5.5 RESULTS OF INHALABLE DUST MONITORING

Measurements of inhalable dust exposures are presented for each worker included in the dermal sampling survey. A technical problem with sampling equipment prevented collection of inhalable dust samples at the Nickel refinery 2 at the time of dermal sampling. However, samples were collected by the company occupational hygienist at a later date. This was done using the same sampling strategy and using the same sampling instruments. The samples were returned to IOM for analysis and were treated in the same way as for all other inhalable dust samples. In addition, the working conditions at the time of sampling were considered to be broadly similar to those observed when the dermal measurements were collected. Repeat samples were also collected for each worker.

A total of 36 inhalable dust samples were collected and these were analysed gravimetrically to determine inhalable dust concentrations. The results of this analysis are provided in Table 22.

In general, airborne concentrations of inhalable dust at nickel refinery 1 were low, except for one sample measurement of 5.9 mg/m³ (QF-09) obtained from an operator who was involved in packing big-bags of nickel hydroxycarbonate. Sample concentrations for the nickel powder packing work at nickel refinery 2 were variable. The type 255 powder packer recorded dust exposures of 5.0 and 4.2 mg/m³, while another worker who did this job recorded an exposure of 1.6 mg/m³. The Dec 2 operators were packing type 210 powder during the dermal survey but were packing type 110 powder when they were monitored for inhalable dust. These two nickel powder products have very similar physical properties so the fact that type 110 powder was being packed at the later time is not considered to represent a material difference to the exposure assessment. Three measurements were collected during normal packing work and the dust exposures were in the range $0.3 - 0.9$ mg/m³. One additional measurement was collected when there was a breakdown and the operator was involved with clearing blockage in the plant. The dust exposure recorded during this work was 2.3 mg/m³. Two samples were collected for the decomposer operator and these were recorded as 0.7 and 1.2 mgm/m³.

At the time of writing, it is not possible to say what proportion of the total inhalable dust comprised elemental nickel or other nickel compounds. The speciation analysis of these samples will be done in a separate study by NiPERA.

Table 22 (a) Results of air monitoring at primary nickel production sites

(Inhalable dust concentrations)

Table 22 (b) Results of air monitoring at primary nickel production sites

(Inhalable dust concentrations)

Note: Airborne dust samples collected at Refinery 2 were collected at a different time than the dermal measurements. Also, type 110 nickel powder was being packed at the time of air sampling rather than type 210 nickel powder which was being produced when dermal survey was carried out. However, working conditions were broadly similar to those observed during the dermal sampling survey and the two types of dust have very similar physical properties.

5.6 CORRELATION OF EXPOSURE DATA BY ANATOMICAL AREA

The dermal exposure measurements for each anatomical area (hands, arms, neck, face and chest) were compared with each other to identify any associations. In addition, the dermal exposure measurements were compared with the inhalable dust concentration measurements in order to identify any association between these measurements. However, it should be noted that the amount of nickel in the dust is not yet known and will be quantified in a separate NiPERA study.

The exposure data used for this comparison is detailed in Table 23 and the results of the Pearson correlations are detailed in Table 24. The work locations and subjects are identified as, for example, Leaching plant operator 1, 2, and 3. In the case of the Electro-winning process, Reduction plant, Chemical plant and Nickel powder plant, there were repeat measurements collected from the same subjects over consecutive days. No more than one repeat set of samples was collected from any one subject.

The average of all the sample results for each subject is provided as a general indication of nickel skin surface loading for each worker. This average value is calculated using all three sets of samples from the hands and forearms and one of each from the neck, face and chest.

The results of the inhalable dust samples collected at Refinery 2 were obtained during slightly different operating conditions, but these were not considered to be significant and are therefore included for comparison. In the case of these measurements, where two air samples were collected for a particular worker, the average of the two measurements is included.

The results of the Pearson correlation tests (Table 24) showed a high level of correlation between the hands and forearms $(r=0.660)$, hands and neck $(r=0.796)$, hands and face (0.800) , and between the hands and chest $(r=0.679)$. All p values were highly significant, with p=<0.001. These comparisons are presented as scatter plots, as shown in Figures 9 – 12.

All upper body exposure measurements (neck, face and chest) were highly correlated with each other. The highest correlation was for neck and chest (r=0.820), with face and chest next $(r=0.812)$ and then face and neck $(r=0.798)$. Again, these associations were all highly significant ($p = < 0.001$).

However, when the dermal exposure data were compared with the inhalable dust concentrations, the correlations were less obvious. The highest correlations were for the hands $(r=0.466)$ and face $(r=0.407)$. The correlations are illustrated graphically for the hands, forearms, neck, face and chest in Figures 13 – 17 respectively.

Table 23 Comparison of dermal nickel exposures with inhalable dust concentrations

(Total nickel or total dust)

Notes:

¹Average is calculated using all measurements from each subject, i.e. three individual hand samples, three different forearm samples, neck, and one each from the neck, face and chest. 2 NHC= Nickel hydroxycarbonate

N/A – Not sampled, not available

³ Results of inhalable dust samples obtained for nickel power packing were collected during type 110 powder packing work and are included for comparison.

⁴ Average of two separate measurements.

Table 24 Correlations between dermal exposures between different anatomical areas and airborne dust concentrations

Total nickel or total dust (log-transformed data)

6. DISCUSSION

The sampling method used for this study was a removal method using moist wipes to remove surface contamination from the exposed skin, or skin areas beneath protective clothing. As such, the results obtained may be considered to be measurements of the average nickel skin surface loading over the working shift. These average exposures were calculated using the results of three separate measurements for the hands and forearms. This is a relevant metric for risk assessment purposes as the main interest is in relating the surface contamination levels with known threshold levels for elicitation or induction of nickel sensitisation. While it is recognised that this method has certain limitations including concerns about removal efficiency (Brouwer *et al.,* 2000), this method was validated for nickel compounds and the sampling protocol was designed to be comparable with previous work carried out for zinc compounds (Hughson *et al.,* 2004), the data from which has been used for regulatory risk assessments for zinc metal (ECB 2004), zinc oxide and other zinc compounds. This method is suitable and appropriate for assessing dermal occupational exposure levels to nickel and nickel compounds.

The validation showed that there was a low background nickel level in the sampling media and there was good recovery efficiency and an acceptable limit of detection for the analytical technique. There was also good sampling recovery efficiency for solid nickel particles, although there was poor recovery for water soluble nickel salt in solution when applied to the surrogate skin test substrate. This would be expected given the highly absorbent nature of the chamois leather used as the surrogate skin. When this test was repeated using a less permeable surrogate material, the recovery efficiency was much better. The former test highlights one of the potential drawbacks of removal sampling methods for assessing dermal exposure: namely that it is not possible to quantify the amount of contamination that has permeated through the skin by the time of sampling. This is unavoidable, but alternative methods using sampling patches as surrogate skin can result in unrealistically high exposure estimates due to the higher retention properties of the patch materials compared to that of human skin (Soutar *et al.,* 2000).

While average exposures were calculated from the separate samples, the individual sample results are presented separately to provide an indication of variability across the working shift. This means that the exposure data may be used to calculate a cumulative daily exposure, if it is assumed that the nickel is completely absorbed through the skin. However, the dermal absorption of soluble nickel and metallic nickel have been shown to be low, at 2% and 0.2% respectively (Hostynek *et al.,* 2001, Tanojo *et al.,* 2001), so it is not likely that a significant amount of nickel was absorbed between sampling times.

Additional samples collected from a control group of non-occupationally exposed subjects showed that there were low background nickel skin surface loadings for this group, with a typical value of approximately 0.1μ g/cm² or less This provides a useful comparison with the occupationally exposed workers in the industry groups and shows that the dermal nickel skin loading of the nickel exposed workers were at most 400 times greater than the control group.

It is clear from the results that nickel skin surface loadings in the primary nickel production industries included in this survey were very low for most jobs, with powder packers having higher levels, even for the hands and exposed skin areas of the face and neck. This indicates that emission of nickel substances into the working environment is being well controlled in both refineries, confirmed in part by the generally low airborne dust concentrations.

The highest actual dermal exposures were recorded for nickel powder packing, where the hands, arms, face and neck all received significantly more surface contamination in comparison with other task categories included in the study. This would be expected given the highly mobile nature of this nickel product, although it is interesting to note that the nickel compounds produced in this particular area were one of the least soluble forms of nickel in use. In the electro-winning area, the actual dermal exposures were much less than in the nickel powder packing plant but the solubility of the nickel was higher, thereby increasing the potential health risks. This illustrates the importance of considering the physical properties of the nickel species, rather than just the overall skin contamination levels in any health risk assessment.

The dermal nickel exposures for briquette packing showed surprisingly similar levels to the nickel powder packers, although this was biased by one or two high measurements from one individual. This was unexpected since this particular process appeared to be reasonably clean and highly automated. One possible reason for the slightly elevated levels for this task is that the briquettes are manufactured by sintering nickel powder, and while nickel powder is not actually produced as a final product at this particular company, there was evidence of nickel powder residues in the manufacturing areas and workers would conceivably come into contact with contaminated surfaces during their normal work.

There was some variability in dermal exposure levels within task categories, but probably less than would be expected taking into account the measured data from the zinc industry. This is probably due to the more systematic use of protective clothing and other occupational hygiene control measures in the nickel production industry. It is also very likely that the high level of automation in the chemical plant area is a key factor in reducing the potential for skin contact. These various factors are reflective of the skin problems associated with direct skin contact with nickel. For example, the lowest spread of results were within the leaching plant and cathode cutting operators, although there were relatively few subjects monitored in these locations. Most exposures for these task categories were within $0.1 - 3 \mu$ g/cm². There was a slightly greater range of measurements observed for the electro-winning workers, with levels over $0.04 - 4 \mu$ g/cm², taking all measurements into account. For other tasks such as briquette or nickel compound packing the overall levels were higher but the ranges of measurements were mainly within one order of magnitude.

The various tasks identified in this study could be grouped into two different exposure scenarios as defined by the EASE model. These would be categorised as either non-dispersive use with extensive direct handling (for nickel powder packing and electro-winning) and nondispersive use with intermittent direct handling (leaching plant, cathode cutting, nickel compound packing and briquette packing). When the measurements are compared with the EASE predictions for these categories $(1 - 5 \text{ mg/cm}^2 \text{ and } 0.1 - 1 \text{ mg/cm}^2)$ respectively, it is clear that the predicted exposures are very much higher than the measured levels, by a factor of about 1000. However, the predicted exposure levels produced by EASE are intended to be estimates of potential exposure and do not therefore take into account the attenuating effect of gloves and other protective clothing. Nevertheless, one would not expect gloves or other standard work wear to provide such a high level of protection (Brouwer *et al.,* 2001). This indicates that EASE tends to over-estimate exposure for these workplace scenarios, which is in line with previous evaluations of the EASE model (Creely *et al.,* 2004; Hughson *et al.,*

2004). However, it should be noted that the observed jobs are not easily categorised according to the EASE criteria and other users may select different options for the same workplace and thereby produce different estimates. This highlights other weakness in the EASE model, i.e., that it is not always possible to consistently categorise real-world tasks according to the EASE criteria.

The measured dermal exposure levels in this study are also significantly lower than the dermal exposure levels used in the current nickel metal and nickel compound draft risk assessment documents, which were based on measured dermal exposure data from the zinc and zinc compound risk assessments. The values used in the current draft risk assessment documents range from 25 - 600 μ g/cm² for typical exposure, compared to 0.04 - 4 μ g/cm² measured in this study.

The high level of correlation between dermal exposures to the hands, arms, face, neck and chest is interesting and corresponds with the results of other dermal exposure research (Vermeulen *et al.,* 2000). This high level of correlation is useful when designing future sampling protocols, as it may be possible to extrapolate exposure levels for the main anatomical areas from a relatively limited number of actual exposure measurements. The low correlation between dermal exposure and airborne dust levels is also to be expected given the dissimilar analytes. This will need to be reassessed once the nickel analysis has been completed for the airborne dust samples.

The pattern of dermal nickel deposition combined with observed working practices shows that there is potential for inadvertent ingestion of nickel and nickel compounds, either through hand to mouth contact or from deposition into or around the perioral region. The significance of this route of exposure needs to be investigated in more detail.

7. CONCLUSIONS

A monitoring programme to assess dermal nickel exposures was carried out for six different nickel production processes in two different European nickel refineries. A total of 33 complete sets of dermal exposure measurements were collected from 22 different workers. In all cases, the production and activity levels within each workplace were considered to be typical of normal production, so the measured exposures can be considered representative of normal production conditions. In doing this, we have achieved the main aim of this study, which was to expand the existing scientific knowledge of dermal nickel exposure in this industry sector.

The survey programme used a removal method for dermal sampling, with proven reliability. Although it is not possible to state with confidence how much nickel was bound to or was absorbed through the skin prior to sampling, this is not considered to be significant since the rates of dermal absorption of soluble nickel and metallic nickel have been shown to be low, at 2% and 0.2%, respectively.

Overall, the dermal exposures were low, and certainly very much less than predicted values generated by the EASE model. In addition, the dermal nickel levels were much lower than levels of exposure previously obtained from the zinc industry. It is concluded that this is largely due to the much higher levels of engineering controls applied to the nickel production processes generally, combined with specific hygiene measures such as the consistent use of personal protective equipment.

Nevertheless there were measurable nickel deposits on the hands, arms, face, neck and chest areas of all workers monitored and there was a high degree of correlation between the different anatomical areas.

8. STATEMENT OF QUALITY

IOM recognise and adopt accepted UK guidelines for good survey practice

This project was carried out under the IOM project management system, which includes preparation of a written protocol for the research and periodic auditing of the work by experienced senior scientists not actively involved in the study.

IOM has UKAS accreditation for several measurement techniques. While the laboratory analysis of all samples collected under this study is covered by the UKAS accreditation, the sampling protocol is a non-standard research procedure and cannot easily be accredited. However, the sampling procedures followed the general quality procedures required by the overall quality management system. Sampling and analytical quality assurance included appropriate calibration checks, replicate analyses and blank samples

Data processing and reporting was subject to the internal data processing control procedures. Raw data is stored for five years and can be audited by the sponsor.

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Figure 4 Dermal (total) nickel exposures for refinery workers Includes inhalable dust concentrations (Briquette packing workers)

Figure 5 Dermal (total) nickel exposures for refinery workers Includes inhalable dust concentrations (Chemical plant packing workers)

Figure 6 Dermal (total) nickel exposures for refinery workers Includes inhalable dust concentrations (Nickel powder packing workers)

Figure 7 Dermal (total) nickel exposures for refinery workers Includes inhalable dust concentrations

Figure 8 Ratio of soluble nickel/total nickel content for dermal samples by work department (All anatomical areas)

Figure 9 Correlation of hand and forearm nickel exposures for all workers

Figure 10 Correlation of hand and neck nickel exposures for all workers

Figure 11 Correlation of hand and face nickel exposures for all workers

Figure 12 Correlation of hand and chest nickel exposures for all workers

Figure 13 Correlation of hand exposures and inhalable dust concentrations

Figure 14 Correlation of forearm exposures and inhalable dust concentrations

Figure 15 Correlation of neck exposures and inhalable dust concentrations

Figure 16 Correlation of face exposures and inhalable dust concentrations

Figure 17 Correlation of chest exposures and inhalable dust concentrations

APPENDIX - A DETAILED RESULTS OF VALIDATION TESTS FOR EVALUATING ANALYTICAL RECOVERY OF SOLUBLE AND INSOLUBLE NICKEL COMPOUNDS

Type 255 Ni Powder						
Actual mass Ni (μg)	Soak time (mins)	Mass Sol Ni recovered (μg)	%Soluble Ni	Average % Sol Ni for soak time	Average % Sol Ni for spike level	Average % Sol Ni for powder type
219	10	17.3	7.9			
261	10	36.7	14.1			
236	$10\,$	13.3	5.6	9.2		
245	60	17.3	7.1			
288	60	10.2	3.5			
528	60	12.4	$2.4\,$	4.3		
227	180	8.7	3.8			
234	180	11.4	4.9			
406	180	25.0	6.2	4.9		
311	720	22.5	7.2			
288	720	16.3	5.7			
334	720	27.9	$\ \, 8.4$	$7.1\,$	6.4	
1101	10	46.0	4.2			
995	$10\,$	70.6	7.1			
1285	10	25.9	$2.0\,$	4.4		
1249	60	23.2	1.9			
1392	60	56.9	4.1			
1112	60	39.1	3.5	3.2		
1496	180	60.9	4.1			
1751	180	47.4	2.7			
1783	180	71.2	4.0	3.6		
1798	720	119.0	6.6			
1221	720	115.2	9.4			
1604	720	68.7	4.3	6.8	4.5	5.4

Table A1 Evaluation of analytical recovery of soluble nickel content of wipe samples spiked with known amounts of nickel powder Tests carried out at two spike levels and by varying soak times in ammonium citrate

Table A2 Evaluation of analytical recovery of soluble nickel content of wipe samples spiked with known amounts of nickel powder Tests carried out at two spike levels and by varying soak times in ammonium citrate

Table A3 Detailed results of recovery efficiency of soluble and insoluble forms of nickel from spike samples

Samples prepared using nickel powder at two different spike levels, treated in ammonium citrate for different times

Table A4 Detailed results of recovery efficiency of soluble and insoluble forms of nickel from spike samples

Samples prepared using nickel sulphate hexahydrate solution at three different spike levels, treated in ammonium citrate for different times

Table A4 (continued) Detailed results of recovery efficiency of soluble and insoluble forms of nickel from spike samples Samples prepared using nickel sulphate hexahydrate solution at three different spike levels, treated in ammonium citrate for different times

APPENDIX B JOB ACTIVITY RECORDS RELATING TO DERMAL EXPOSURE SURVEY

Table B1 - Job activity record

Refinery 1

Table B2 – Job activity record

Refinery 1(continued)

Table B3 – Job activity record

Refinery 1 (continued)

Table B4 – Job activity record

Refinery 1 (continued)

Table B5 – Job activity record

Refinery 2

Applying science for a better working environment

The Institute of Occupational Medicine

The IOM is a major independent centre of scientific excellence in the fields of occupational and environmental health, hygiene and safety. We aim to provide quality research, consultancy and training to help to ensure that people's health is not damaged by conditions at work or in the environment. Our principal research disciplines are exposure assessment, epidemiology, toxicology, ergonomics and behavioural and social sciences, with a strong focus on multi-disciplinary approaches to problem solving.

Our beginnings

Our first major research programme began in the 1950s, on respiratory health problems in the coal mining industry. Major themes were quantification of airborne dust concentrations in different jobs, characterisation of types and constituents of the dusts, measurement of health effects, relationships between exposure and disease, and proposals for prevention. This research became an international benchmark for epidemiological studies of occupational health, and was the primary influence on dust standards in mines in the UK, US and other countries.

Current themes

Our current work spans many other industries including asbestos, MMMF, pesticides, chemicals, energy, telecoms, metals, textiles, construction, agriculture as well as the environment. While diseases of the respiratory tract remain a major interest, our scope now extends to many other health outcomes such as mortality, cardiovascular effects, cancer, back pain, upper-limb disorders, hearing loss, skin diseases, thermal stress and psychological stress. Related work includes the development and application of measurement and control systems, mathematical models and survey methods.

Who we work for

Our work in these areas is conducted for a wide range of organisations in the UK, the EU, and the US, including Government departments, international agencies, industry associations, local authorities, charitable organisations, and industrial and commercial companies. The IOM is a World Heath Organisation (WHO) collaborating centre and is an approved institute of the Universities of Edinburgh and Aberdeen, enjoying collaborative research links with NIOSH, IARC, and many other institutes throughout the world.

Publication

We believe that our research findings should be publicly available and subject to the scrutiny of the international scientific community. We publish our findings in the peer reviewed scientific literature and through our own series of Research Reports.

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