

INCORPORATING DATA ON PARTICLE SIZE AND CHEMICAL COMPOSITION OF AEROSOLS INTO SITE-SPECIFIC EXPOSURE SCENARIOS (WORKERS)

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I. Introduction

The nickel REACH Consortia Secretariat is responsible for drafting the generic exposure scenarios (broad exposure scenarios that describe typical exposure nickel levels and the operational controls and risk management measures relevant to the identified use conditions of each substance) in the joint submission of the dossiers for each of the nickel substances. Individual companies are responsible for checking if they fit within the boundaries of those generic scenarios and proving the safe control of the substance. The site specific parameters (incorporating available data on environmental release and occupational exposure to nickel) and specific information on conditions of use, operational controls and risk management measures, from company sites in the EU have to be checked against the boundaries of the sites, as described in the Generic Exposure Scenarios (GES).

The generic exposure scenarios allow the individual industrial sites to modify the conditions described in the scenarios so they fit those of the actual conditions on site. The modifications need, however, to be in agreement with the guidance provided together with the scenario. Therefore, the goal of this Guidance document is to help the companies assess their compliance with the generic exposure scenarios for workers and provide them with tools to demonstrate that no risks are present in the company-specific operations. This Guidance document will help those companies that wish to incorporate site-specific data on particle size distribution and/or chemical composition of the workplace nickel exposures into the description of the site-specific exposure scenarios.

Please note that the individual companies are responsible for data collection and reporting, including possible refinements to the risk characterization. Therefore, this guidance provides suggestions for possible refinements to exposure scenario descriptions but it does not intend to provide prescriptive protocols. This guidance is equally applicable to downstream users of nickel but it is not the registrants' nor the REACH Nickel Consortium's legal responsibility to ensure that the individual downstream users comply with the generic exposure scenario. Finally, this Guidance document relates to the **Worker exposure part of site-specific exposure scenarios and does not relate to environmental release of nickel and nickel substances.**

II. Workplace Nickel DNELs

The nickel REACH Consortia is using a Derived No Effect Level (DNEL) of 0.05 mg Ni/m³ measured as the inhalable aerosol fraction for long-term, repeated exposure of workers to nickel (all nickel substances) via inhalation. This value is based on the SCOEL (2009) proposed nickel inhalable Occupational Exposure Limit (OEL) value of 0.010 mg Ni/m³ after correction for particle size issues. Please see Appendix C3 of the Nickel substances Chemical Safety Reports for more details on the derivation of the DNEL of 0.05 mg Ni/m³.

In the site-specific exposure scenarios, when inhalable exposures are higher than 0.01 mg Ni/m³ it would be useful if each company could collect information on particle size distribution for their site to justify the use of the inhalable 0.05 mg Ni/m³ DNEL. This information would not be needed if the workplace exposures are below 0.01 mg Ni/m³. The reason is that in the generic exposure scenarios, the assumption, based on published information for the nickel producing and using sectors, is that the particle size distribution of the workplace aerosol is in the inhalable range, with respirable size particles comprising less than 10% of the aerosol (Oller and Oberdörster, 2010; Vincent *et al.*, 1995; 1996; Werner *et al.*, 1996; 1999; Ramachandran *et al.*, 1996; Tsai *et al.*, 1995; 1996a, b).

In the occasional instances where the particle size measurements indicate or predict the presence of very fine workplace aerosols in the respirable size fraction (respirable fraction = aerodynamic equivalent particle diameter

$\leq 10 \mu\text{m}$; 50% penetration at $4.25 \mu\text{m}$), the use of the DNEL of 0.05 mg Ni/m^3 may not be justified. It is recommended that in these cases, the site specific exposure scenarios recognize that additional risk management measures may be needed to protect the workers and keep their nickel exposures lower than 0.01 mg Ni/m^3 .

It should also be recognized that neither the DNEL of 0.05 mg Ni/m^3 nor the SCOEL proposed OEL of 0.01 mg Ni/m^3 are derived based on effects of nanoparticles. Therefore, these values are not necessarily protective for exposure to nickel-containing nanoparticles, which are not covered in the registration.

As mentioned above, the nickel REACH Consortia is using (for all the nickel substances) a DNEL of 0.05 mg Ni/m^3 to protect workers from repeated inhalation exposure. Using the same approach to nickel OEL derivation as outlined in the SCOEL/SUM 85 background document and applying the appropriate corrections to take aerosols particle size and sampler efficiencies differences, as well as differences in toxicological properties of various forms of nickel into account, the following inhalable DNELs, based on data for four reference substances, can be supported by the available data: 0.05 mg Ni/m^3 for water soluble nickel compounds (*e.g.*, nickel sulphate), 0.05 mg Ni/m^3 for sulfidic nickel (*e.g.*, nickel subsulfide), 0.2 mg Ni/m^3 for oxidic nickel (*e.g.*, green, high-calcining temperature nickel oxide¹), and 0.2 mg Ni/m^3 for metallic nickel (*e.g.*, nickel metal and alloys). See Chemical Safety Reports for Nickel Substances, Appendix C3 for more details. **However, in the absence of speciated nickel exposure information, the lowest DNEL needs to be applied.** This is why in the exposure scenarios included in the joint submission we compare the measured/estimated nickel exposures to the DNEL of 0.05 mg Ni/m^3 .

III. Overall Strategy for Site-Specific Refinement of Exposure Scenarios for Workers

Currently, under the header of “Guidance to DU to evaluate whether he works inside the boundaries set by the ES” the nickel GESs include the following text:

Collect process monitoring data. Use aerosol particle size information, when available, to confirm the appropriate use of an inhalable DNEL (*e.g.*, $\leq 10\%$ of Nickel mass in respirable fraction). Chemical speciation data showing that only Ni metal and/or Ni oxides are present in the workplace air can be used to indicate RCR < 1 at inhalable exposure levels between 0.05 and 0.2 mg Ni/m^3 .

Figure 1 describes a framework for assessing at the site-specific level whether compliance with the long-term inhalable DNELs of 0.01 mg Ni/m^3 , 0.05 mg Ni/m^3 or 0.2 mg Ni/m^3 is warranted.

¹ Although chronic inhalation studies are only available with green nickel oxide, recent acute inhalation studies with black nickel oxide (EPSL, 2010) and bioaccessibility data in synthetic lung fluids (KMHC, 2010) predict that black nickel oxide will have the similar inhalation toxicity (acute and chronic) as green nickel oxide.

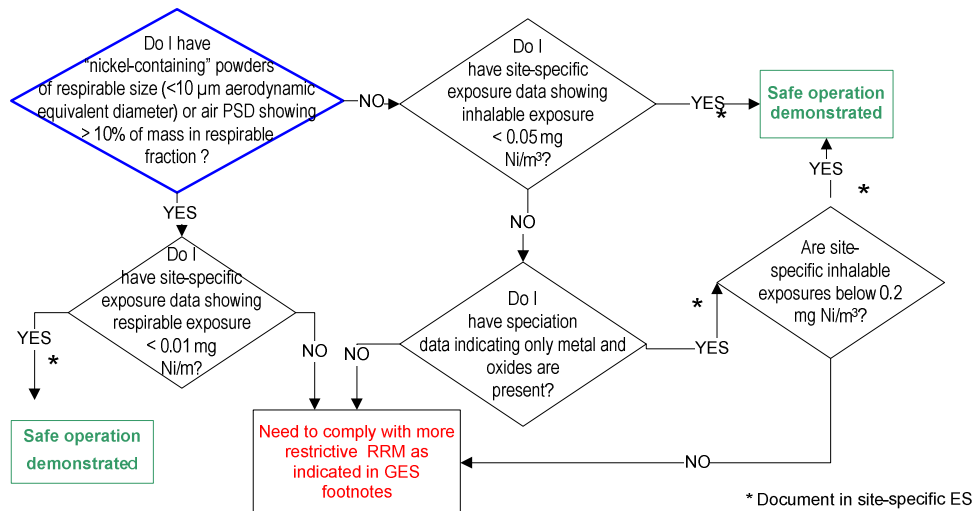


Figure 1. Overall Strategy for Site-Specific Refinement of Exposure Scenarios for Workers

When to comply with DNEL of 0.01 mg Ni/m³?

Independent of the forms of nickel present at the site, if the exposures are to respirable size powders (particles $\leq 10 \mu\text{m}$ aerodynamic equivalent diameter; 50% penetration at $4.25 \mu\text{m}$) of nickel substances or measurements of workplace nickel particle size distribution indicate that $> 10\%$ of the aerosol nickel mass is in the respirable fraction, compliance with 0.01 mg Ni/m^3 would be warranted.

When to comply with DNEL of 0.05 mg Ni/m³?

When 1) the exact chemical forms of nickel present at the site are not known or the presence of nickel compounds other than metallic nickel and oxides cannot be excluded, and 2) measurements of workplace nickel particle size distribution indicate that $\leq 10\%$ of the aerosol nickel mass is in the respirable fraction, compliance with 0.05 mg Ni/m^3 would be warranted

When to comply with DNEL of 0.2 mg Ni/m³?

When nickel exposures 1) are only to powders of metallic nickel or nickel oxides and 2) measurements of workplace nickel particle size distribution indicate that $\leq 10\%$ of the aerosol nickel mass is in the respirable fraction, compliance with 0.2 mg Ni/m^3 would be warranted

IV. Tiered approach to Collection of Workplace Aerosol Particle Size Distribution for Site-Specific Exposure Scenarios

Information on workplace air particle size can be measured directly using a personal cascade impactor as recommended by IOM (IOM Report 1, Attachment 1 to Appendix D7). Alternatively, other methods can be used to predict the particle size distribution of the workplace air with different degrees of confidence (IOM Report 2, Attachment 2 to Appendix D7). A tiered approach to collecting site-specific particle size information (going from more precise to less precise data) is described below.

Tier 1 Particle Size Distribution of Workplace Aerosols Using Cascade Impactors.

If possible, collect particle size distribution information of workplace aerosol using a personal cascade impactor as described in IOM Report 1 (Attachment 1 to Appendix D7). Calculate Mass Median Aerodynamic Diameter (MMAD) and geometric Standard Deviation (GSD), and the fraction of the aerosol mass that is present in the inhalable, thoracic and respirable fractions. The presence of a respirable size fraction $\leq 10\%$ of total aerosol mass can provide strong support for the use of the DNEL of 0.05 mg Ni/m^3 . Attachment 1 to Appendix D7 provides information on cascade impactors, data collection and analysis, cost and suppliers of cascade impactors. Information on a few laboratories that conduct these kinds of measurements is also included.

Tier 2 Particle Size Distribution of Materials/Products Using Dustiness Tests.

Conduct dustiness tests of the materials handled at the plant following guidance provided in IOM Report 2 (Attachment 2 to Appendix D7). These tests allow calculation of the fraction of the aerosol mass expected to be present in the inhalable and respirable fractions and in some cases (where a cascade impactor is attached) it allows estimation of the MMAD and GSD of the suspended dust. As indicated

in Tier 1, the presence of a respirable size fraction $\leq 10\%$ of total aerosol can provide additional support for the use of the DNEL of 0.05 mg Ni/m^3 .

Tier 3 Particle Size Distribution of Materials/Products Using Granulometry or SEM.

Suitable granulometry methods that can also be applied to materials handled at the plants are described in IOM Report 2 (Attachment 2 to Appendix D7). Methods such as sedimentation and electrozone sensing do not allow determination of MMAD but allow the assessment of respirable and inhalable fractions of dry powders and granules. The presence of a respirable size fraction $< 10\%$ of total aerosol can provide additional support for the use of the DNEL of 0.05 mg Ni/m^3 .

Sometimes information from Scanning Electron Microscopy (SEM) analysis of particles of plant materials exist. SEM analyses provide information on the number size distribution and may report the mean particle diameter of the sample. For example, if the data indicate an average particle diameter of $5 \mu\text{m}$, this could be equivalent to $15 \mu\text{m}$ aerodynamic equivalent diameter, if particles are spherical and the density of the particles is 9 g/cm^3 . This kind of results would strongly suggest that most of the mass of the airborne particles will be associated with the non respirable fraction and this could justify the use of the inhalable DNEL of 0.05 mg Ni/m^3 . SEM will yield a very conservative estimate of the respirable fraction mass.

In the occasional instances where the particle size measurements indicate or predict the presence of very fine workplace aerosols in the respirable size fraction (aerodynamic equivalent particle diameter $\leq 10 \mu\text{m}$), or workplace measurement indicate that the $> 10\%$ of the nickel mass is in the respirable fraction, the use of the DNEL of 0.05 mg Ni/m^3 may not be justified. It is recommended that in these cases, the site specific exposure scenarios recognize that additional risk management measures may be needed to protect the workers and keep their nickel exposures lower than 0.01 mg Ni/m^3 .

Table 1. Summary of methods available under each tiered approach, as described in IOM Reports 1 and 2.

	Method allows determination of mass in various fractions or estimation of MMAD				Method can be applied to:	
	Respirable Fraction	Thoracic Fraction	Inhalable Fraction	MMAD, GSD	Workplace exposure	Materials/products
Tier 1						
Cascade Impactors	√	√	√	√	√	√ ¹
Tier 2						
Dustiness tests	√		√			√
- Rotating drum	√		√	√ ¹		
- Single Drop						
- Continuous drop	√		√	√ ¹		
- Fluidization						
Tier 3						
Granulometry	√		√			√
- Sedimentation	√		√			
- Coulter, Electrozone sensing	√		√			
- Phase Doppler Analyzer	√		√			

¹. The cascade impactor can be coupled to the outlet of these methods allowing data on the MMAD and GSD of the suspended dust to be collected.

V. Tiered Approach to Collection of Workplace Aerosol Nickel Speciation Data for Site-Specific Exposure Scenarios

As indicated in section III, for those site-specific Exposure Scenarios where only exposure to inhalable size aerosols of nickel oxides and nickel metal are known to be present ($< 10\%$ of mass in respirable fraction), it could be indicated that these scenarios may not necessarily be operating at increased risk when the nickel exposures are above 0.05 mg Ni/m^3 but below 0.2 mg Ni/m^3 . Information on speciation of workplace exposure showing that no other nickel compound is present could strengthen the case in favor of justifying that sufficient worker protection is afforded by the higher DNEL. Again, as discussed in Section IV a tiered approach to

reporting site-specific chemical speciation information (going from more precise to less precise information) is described below.

Tier 1 Speciation.

There are many physical and chemical methods that can be applied to complex workplace exposures to assess nickel speciation (Zatka *et al.* 1992; Andersen *et al.*, 1998; Höflich *et al.*, 2000; Füchtjohan *et al.*, 2001; Weinbruch *et al.*, 2002; Conard *et al.*, 2008; Oller *et al.*, 2009). A description of these methods is beyond the scope of this Guidance document. Because physical and chemical methods have strengths and weaknesses, a combination of both types of methods is highly recommended. Alternatively, in exposure scenarios where only one kind of nickel material is used/handled, and this material does not undergo chemical transformation (*e.g.*, nickel powders), this information would be sufficient to justify that sufficient worker protection is afforded by the higher DNEL.

Tier 2 Speciation.

Alternatively, a thorough description of the process with detailed information on the composition of the material present in each of its steps may be sufficient to provide support for less stringent risk reduction measures in cases where exposures (inhalable fraction) are solely to nickel metal or nickel oxides and are below 0.2 mg Ni/m³.

VI. Combining Information on Particle Size and Chemical Speciation

There could be particular situations where exposures are mainly to powders of nickel metal or nickel oxides in the respirable size range ($\leq 10 \mu\text{m}$ aerodynamic equivalent diameter). The absence of water soluble, sulfidic or other nickel compounds would suggest that exposures below 0.2 mg Ni/m³ would be safe; however, the small particle size of the powder would indicate that exposures should be kept $\leq 0.01 \text{ mg Ni/m}^3$. In these cases, the current recommendation from the REACH Secretariat is to keep the exposure of all respirable size powders of nickel metal or nickel compounds below $\leq 0.01 \text{ mg Ni/m}^3$. We do not have solid data (at this time) on which to base other adjustments.

VII. References

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Please Note: Attachment 1 and 2 to this appendix (D7) are not included but can be requested from the Nickel Institute

Attachment 1. IOM Report 1. Guidance for collection of relevant particle size distribution data of workplace aerosols-Cascade Impactor Measurements. TM/ 09/04. A Sánchez-Jiménez, KS Galea, RJ Aitken

Attachment 2. IOM Report 2. Guidance for collection of relevant particle size distribution data of workplace aerosols: Dustiness and Granulometry Tests. TM/ 10/02. A Sánchez-Jiménez, RJ Aitken