

<b>1. Title</b>		<b>Version 5, 2014</b>
<b>GES 5 Production of Ni-containing electronic and thermally functioning ceramics</b>		
Life cycle	Formulation – DU of NiO	
Free short title	Production of Ni-containing electronic and thermally functioning ceramics from NiO	
Systematic title based on use descriptor	<p><b>SU:</b> SU 16 Manufacture of computer, electronic and optical products, electrical equipment</p> <p><b>PC:</b> PC 0</p> <p><b>ERC:</b> ERC 2: Formulation of preparations SPERC for the formulation stage of metal compounds</p> <p><b>PROC:</b></p> <p>PROC 0 Other process</p> <p>PROC 1 Use in closed process, no likelihood of exposure</p> <p>PROC 3 Use in closed batch process (synthesis or formulation)</p> <p>PROC 4 Use in batch and other process (synthesis) where opportunity for exposure arises</p> <p>PROC 5 Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact)</p> <p>PROC 22 Potentially closed processing operations with minerals/metals at elevated temperature Industrial setting</p> <p>PROC 24 High (mechanical) energy work-up of substances bound in materials and/or articles</p>	
Processes, tasks, activities covered (environment)	Production of ceramics (ceramics for solid oxide fuel cells; ceramics for thermistor products)	
Processes, tasks, activities covered (workers)	Production of ceramics for solid oxide fuel cells and for thermistor products: The oxides are processed in an industrial setting through a conventional ceramics processing route involving mixing and processing with other materials to form intermediate materials; surface application or forming of these intermediate materials and sintering at high temperatures to form semi-conducting ceramic materials.	
<b>2. Operational conditions and risk management measures</b>		
<b>2.1 Control of environmental exposure</b>		
Environmental related free short title	Production of Ni-containing electronic and thermally functioning ceramics from NiO	
Systematic title based on use descriptor (environment)	ERC 2: Formulation of preparations SPERC for the formulation stage of metal compounds	
Processes, tasks, activities covered (environment)	Production of ceramics (ceramics for solid oxide fuel cells; ceramics for thermistor products)	
Environmental Assessment Method	Estimates based on monitoring local and regional concentrations are used for calculation of PEC. SPERC data for the formulation stage of metal compounds are used in order to estimate releases to air for the generic ES	
<b>Product characteristics</b>		
The tonnage is based on Ni originating from the use of NiO as well as other Ni compounds used at same sites.		
<b>Amounts used</b>		
Maximum daily use at a site	1 kg (50 <sup>th</sup> % emissions days, max tonnage)	
Maximum annual use at a site	ES 1 & 2: 0.29 tonnes (max)	
<b>Frequency and duration of use</b>		
Pattern of release to the environment	304 days per year per site (50 <sup>th</sup> %)	
<b>Environment factors not influenced by risk management</b>		
Receiving surface water flow rate	ES 1 Direct discharge: 567 m <sup>3</sup> /d (Effluent Site: 63 m <sup>3</sup> /d)	
Dilution capacity, freshwater	ES 1 Direct discharge: 10	
Dilution capacity, marine	ES 2 Marine discharge: 100 (default)	
<b>Other given operational conditions affecting environmental exposure</b>		
None		
<b>Technical conditions and measures at process level (source) to prevent release</b>		
None		
<b>Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil</b>		
<b>Waste water:</b>		

On-site waste water treatment (efficiency: 90%) ES 1 Freshwater direct discharge: Release factor after on-site treatment: 3302 g/T (90P) ES 2 Marine direct discharge: Release factor after on-site treatment: 3302 g/T (90P)	
<b>Air:</b> Exhaust system, fabric or bag filters Release factor is based on SPERC data for formulation of metal compounds (release factor for air 0.01%). ES 1 & 2: Release factor after on-site treatment: 100 g/T	
<b>Organizational measures to prevent/limit release from site</b>	
None	
<b>Conditions and measures related to municipal sewage treatment plant</b>	
<b>Municipal Sewage Treatment Plant (STP)</b>	No
<b>Discharge rate of the Municipal STP</b>	Not relevant
<b>Incineration of the sludge of the Municipal STP</b>	Not relevant
<b>Conditions and measures related to external treatment of waste for disposal</b>	
Hazardous wastes from onsite risk management measures and solid or liquid wastes from production, use and cleaning processes should be disposed of separately to hazardous waste incineration plants or hazardous waste landfills as hazardous waste. Releases to the floor, water and soil are to be prevented. If the nickel content of the waste is elevated enough, internal or external recovery/recycling might be considered.	
<b>Fraction of daily/annual use</b> expected in waste: <ul style="list-style-type: none"> <li>- Nickel producers = 0.05 %</li> <li>- DU: stainless steel and alloy steels = 0.6 %</li> <li>- DU: nickel alloys, copper alloys, foundry, batteries, catalysts, chemicals, dyes and others = 0.5 %</li> <li>- DU: Plating = 3%</li> </ul>	
<b>Appropriate waste codes:</b> 01 03 07*, 02 01 10*, 06 03 13*, 06 03 15*, 06 04 05*, 06 05 02*, 10 08 04, 10 08 08*, 10 08 09, 10 08 15*, 10 08 16, 10 10 03, 10 10 05*, 10 10 07*, 10 10 09*, 10 10 10, 10 10 11*, 11 02 07*, 12 01 03*, 12 01 04, 15 01 04*, 15 01 10*, 16 01 04*, 16 01 06*, 16 01 08*, 16 06 02*, 16 06 05, 16 08 02*, 16 08 03*, 17 04 07*, 17 04 09*, 19 09 04*, 19 10 02*, 19 12 03*	
<b>Suitable disposal:</b> Keep separate and dispose of to either <ul style="list-style-type: none"> <li>- Hazardous waste incineration operated according to Council Directive 2008/98/EC on waste, Directive 2000/76/EC on the incineration of waste and the Reference Document on the Best Available Techniques for Waste Incineration of August 2006.</li> <li>- Hazardous landfill operated under Directive 1999/31/EC.</li> </ul>	
<b>Conditions and measures related to external recovery of waste</b>	
Shredders pre-treating metal wastes should have a maximum release factors to air of 0.0015 after RMM and no releases to water and soil. Qmax, local(shredding)=26kg Ni/day (Note: This Qmax, local for shredders is based on the existing information at the moment of the update. It will be reviewed when new information is available from the BREF for shredding)	
<b>2.2 Control of workers exposure</b>	
Production of Ni-containing electronic and thermally functioning ceramics from NiO	
<b>Workers related free short title</b>	Production of Ni-containing electronic and thermally functioning ceramics from NiO
<b>Use descriptor covered</b>	PROC 0 Other process PROC 1 Use in closed process, no likelihood of exposure PROC 3 Use in closed batch process (synthesis or formulation) PROC 4 Use in batch and other process (synthesis) where opportunity for exposure arises PROC 5 Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact) PROC 22 Potentially closed processing operations with minerals/metals at

	elevated temperature PROC 24 High (mechanical) energy work-up of substances bound in materials and/or articles
Processes, tasks, activities covered	<p>Thermistor production</p> <p>NiO powder from a production batch is measured out using manually operated balances. The NiO is milled and then mixed with other ingredients including cobalt oxide and manganese oxide. This intermediate product is transferred to a furnace and calcined. The calcined powder is then mixed with deionised water and additives, formed and sintered to produce the semiconducting ceramic. This ceramic slab is cut into 'chips' of sintered ceramic. The thermistors are then assembled into the temperature sensing probe and packed into individual boxes by hand. Mixing and forming machines are wet washed and cleaned on a daily and twice weekly basis respectively. All extraction equipment is under a planned maintenance schedule.</p> <p>Fuel cell production</p> <p>Anodes for solid oxide fuel cells (SOFC) are made of either a nickel/yttria-stabilised zirconia (Ni-YSZ) or of nickel oxide/yttria-stabilised zirconia (NiO-YSZ). These anodes are produced by using powder technology methods in one of three ways namely 1) a Ni slurry is applied to the cell substrate and yttria-stabilised zirconia is deposited by electrochemical vapour deposition and sintered 2) Ni-YSZ slurry is applied to the cell substrate and sintered or 3) NiO-YSZ paste is applied to the cell substrate by screen-printing and sintered. During cell application in stack environment NiO is reduced to particulate Ni.</p>
Assessment Method	<p>Estimation of inhalation exposure based on measured data.</p> <p>Estimation of dermal exposure based on Tier 1 model.</p>
<b>Product characteristic</b>	
Nickel Oxide in the form of green powder PSA D50 = 0.3micron	
<b>Amounts used</b>	
0.29 tonnes per year	
<b>Frequency and duration of use/exposure</b>	
11.2 hours per day [1 shift], 7 days per week [2 shifts 4 days on/4 days off]	
<b>Human factors not influenced by risk management</b>	
Respiration volume under conditions of use	Not relevant
Room size and ventilation rate	Not relevant
Area of skin contact with the substance under conditions of use	480 cm <sup>2</sup>
Body weight	Not relevant
<b>Other given operational conditions affecting workers exposure</b>	
<p>The production line is manned by five operators who carry out the weighing of raw and intermediate materials, transfer operations <i>e.g.</i> bagging the intermediate product from the mixer and transferring it to the calciner, mixing, cutting chips from the semiconducting ceramic strips, inspecting the mechanised parts of the process (milling, mixing, calcining, sintering and sieving) and assembling the probe (article) from the thermistor and packaging the probe.</p> <p>Maintain clean workplace to prevent accumulation of powders and dusts on surfaces.</p> <p>Oral: Good workplace hygiene practice.</p>	
<b>Technical conditions and measures at process level (source) to prevent release</b>	
<p>Transfer operations before and after the calcining step (to contain/bag and move the calcined product through process), weighing out raw and intermediate materials and charging/unloading processing equipment are manual operations and not fully enclosed.</p> <p><b>Inhalation:</b> Enclosure during milling, mixing, calcining, sintering and sieving is not likely to give rise to significant exposures to inhalable NiO.</p> <p>Operations not under complete enclosure <i>e.g.</i> manual NiO-containing powder transfer operations in bags, weighing out NiO raw and intermediate material and cutting chips from the semiconducting ceramics are likely to give rise to significant exposures to inhalable and dermal NiO</p> <p><b>Dermal:</b> Automation of processes should be used where possible to eliminate dermal contact.</p>	
<b>Technical conditions and measures to control dispersion from source towards the worker</b>	
LEV system with filtration is required for process steps that are not fully enclosed and involve NiO powder or are other vice	

likely to give rise to Ni containing dust e.g. roll mill and dicing machine.

**Organisational measures to prevent /limit releases, dispersion and exposure**

None

**Conditions and measures related to personal protection, hygiene and health evaluation**

**Inhalation:** RPE (FFP2) (approved with regard to EN 149) is required for unenclosed processes involving powders e.g. non contained powder transfer processes and weighing out NiO powder raw materials

**Dermal:** Gloves suitable for handling powders e.g. Nitrile and other suitable protective clothing are required where direct contact with NiO could occur e.g. non contained powder transfer processes, weighing out NiO powder raw materials and picking/grinding chips from the semiconducting ceramic strips .

**3. Exposure and risk estimation**

**Environment**

ERC 2: Formulation of preparations, SPERC – formulation stage of metal compounds  
Production of ceramics (ceramics for solid oxide fuel cells; ceramics for thermistor products)

Compartment	Unit	PNEC	PEC <sub>Regional</sub>	C <sub>local</sub>	PEC	RCR	Methods for calculation of environmental concentrations
ES 2: Freshwater direct discharge							
Freshwater	µg Ni/L	7.1	2.9	3.59	6.49	0.91	Measured values, Tier 3-RWC
Sediment	mg Ni/kg	136	33.5	94.3	127.8	0.94	
Terrestrial	mg Ni/kg	29.9	16.2	< 0.01	16.20	0.54	Estimated values (SPERC)
ES 3: Marine direct discharge							
Marine water	µg Ni/L	8.4	0.3	0.36	0.66	0.08	Measured values, Tier 3-RWC
Sediment	mg Ni/kg	136	16.1	9.4	25.5	0.19	
Terrestrial	mg Ni/kg	29.9	16.2	< 0.01	16.20	0.54	Estimated values (SPERC)

**Workers**

**Whole process**

	Unit	DNEL NiO	Exposure concentration	RCR	Methods for calculation of exposure
<b>Dermal</b>					
Acute systemic	mg Ni/kg/day	-	NR	-	
Acute local	mg Ni/cm <sup>2</sup> /day	-	NR	-	
Long-term systemic	mg Ni/kg/day	-	NR	-	
Long-term local	mg Ni/cm <sup>2</sup> /day	0.012	0.0005	0.041	90 <sup>th</sup> percentile from MEASE modelling (PROC 8b, 14, 22, automated with manual intervention, partly enclosed, LEV, gloves)
<b>Inhalation</b>					
Acute systemic	mg Ni/m <sup>3</sup>	520	0.06	0.00012	Estimated as 3 x the long-term value (highest of 7 measurements). A factor of 3 was considered sufficient as a worst case estimate.
Acute local	mg Ni/m <sup>3</sup>	3.9	0.06	0.015	
Long-term systemic and local	mg Ni/m <sup>3</sup>	0.05	0.02	0.4	

NR: Not Relevant

Acute local inhalation  
DNEL based on respirable size aerosols. Equivalent inhalable fraction levels expected to be at least 3-fold higher

**4. Guidance to DU to evaluate whether he works inside the boundaries set by the ES**

**Environment**

Scaling tool: Metals EUSES IT tool (free download: <http://www.arche-consulting.be/Metal-CSA-toolbox/du-scaling-tool>)

Scaling of the release to air and water environment includes:  
Refining of the release factor to air and waste water and/or and the efficiency of the air filter and wastewater treatment facility.

Scaling of the PNEC for aquatic environment by using a tiered approach for correction for bioavailability and background concentration ( $C_{local}$  approach).

Scaling of the PNEC for soil compartment by using a tiered approach for correction for bioavailability and background concentration ( $C_{local}$  approach).

#### Workers

Scaling considering duration and frequency of use

Collect process monitoring data with an inhalable sampler. The simultaneous use of a respirable sampler is encouraged. Use aerosol particle size information, when available, to confirm the appropriate use of the inhalable DNEL of 0.05 mg Ni/m<sup>3</sup>. Respirable fraction exposure levels should be kept below 0.01 mg Ni/m<sup>3</sup>.

For further information and guidance on exposure scenarios, available tools, and scaling options, please visit the Nickel Consortia exposure scenario library at the following link: <http://www.nickelconsortia.eu/exposure-scenario-library.html>

### Man via Environment exposure and risk characterisation assessments for the use of NiO for the production of nickel-containing electronic and thermally functioning ceramics

Inhalation is the critical exposure pathway for humans via the environment. The PEC for air at site neighbouring residential areas should be lower than the chronic inhalation DNEL for the general public of 20 ng Ni/m<sup>3</sup> as annual average in PM<sub>10</sub> in order to demonstrate adequate control of risk (RCR < 1) for Man via the Environment (MvE).

Hereto a Generic safe use Exposure Scenario for MvE was developed based on the EUSES model. The MvE GES is defined as the product of tonnage (T) and emission factor to air (EF) being lower than 18000 g Ni/year. The value of 18000 g Ni/year is derived by using EUSES model to back-calculate the product of T and EF that results in a local air concentration ( $C_{local}$ ) of 13.8 ng Ni/m<sup>3</sup>. The value of 13.8 is derived from the difference between the DNEL of 20 ng Ni/m<sup>3</sup> and the EU regional background concentration ( $C_{regional}$ ) of 6.2 ng Ni/m<sup>3</sup> (P90 annual concentration for 2007-200).

#### Generic safe use ES for all sectors according to Tier 1 (EUSES model)

Sector	Tonnage (Ni T /year)	Emission factor (g Ni/T)	Tonnage × emission factor (g /year)	$C_{local}$ (ng/m <sup>3</sup> )	$C_{regional}$ (ng/m <sup>3</sup> )	PEC <sub>local</sub> (ng/m <sup>3</sup> )	RCR = PEC/DNEL (DNEL= 20 ng/m <sup>3</sup> )
All	T	EF	T × EF < 18000	<13.8	6.2*	<20	<1

\*: EU average of country P90 annual Ni concentrations (2007-2009)

If a site is not compliant with these conditions, meaning that the product of tonnage and emission factor is above 18000 g Ni/year, a tiered approach including site-specific modelling can be applied to demonstrate safe use.