**NON-FERROUS METAL INTERMEDIATES UNDER SCC**
**Metal specificities, challenges and examples**

**October 2011**

**Introduction**

*The majority of the intermediates from the (non-ferrous) metals (NFM) industry are* UVCB substances resulting from the metallurgic processing of primary (e.g. ores and concentrates) and secondary sources (recyclables).

Subsequent isolated and/or non-isolated intermediates occur during the smelting and refining steps of these materials to achieve pure substances that are mostly metals in massive form. Intermediates are produced in this respect during the smelting of material mixes (complex concentrates, recycled materials, fluxes) in various batch runs. Typically, by heating under controlled conditions, a bottom layer of matte (a material rich in metals), and a top layer of slag (silicate, poor in metals) are produced. After removal of the slag layer, the molten matte is converted into another intermediate (i.e. blister), and further refined by means of subsequent furnace (smelting) operations. Alternatively, electrochemical or leaching techniques (liquid-liquid extractions) are used as refinement steps.

Extensive *hazard profiles and related hazard classifications* (where appropriate) *are available* for intermediates based on the effects assessment files of their known components.

<u>*A number of general issues critical for assessing SCC of (non-ferrous) metal UVCBs have been identified below, and are illustrated by the attached examples*</u>

1. Metal refining intermediates are ***typically UVCB substances***, and as such they are complex metal-containing materials with known, but variable, composition ranges of main and minor constituents. For example, metal matte is composed primarily of metal sulphides, but also contains some other sulphides and iron oxides in various concentrations. The chemistry and mineralogy of the materials, in combination with the mixture toxicity rules, are applied to define ***detailed and conclusive hazard classifications for each UVCB,*** and different grades based upon the composition and concentration of their ingredients.

2. The mixture entering the initial smelting step is fully characterised (following sampling and assaying) and the composition of the feed is derived/calculated/predicted so that its constituents are known. Subsequently, the hazard of each constituent, documented in the often very extensive effects assessment files, is used to derive/calculate/predict **the overall hazard of the smelted stream.** The rigorous containment design is therefore based on extensive knowledge.

3. While no material-specific DN(M)ELS, or PNECS are usually available for these UVCB materials 'as such'; both hazard profiles and data on exposure and (residual) emissions of the individual constituent metals are available, and are often **covered by registration files (see also points 4 & 5 below).**

4. The manufacturing and use processes are generally highly automated and controlled from air-conditioned control rooms/cabins. Operators are normally physically separated and do

not handle the substance directly. Appropriate local exhaust ventilation is integrated, with partial or full enclosures, based on the effects knowledge level described above. Containment strategies **combine elements from different levels (Hirst levels 2, 3 and 4).**

5. Several UVCB intermediates, and their production process, are characterised by a low emission potential due to the physical form of the intermediate manufactured or used. This includes massive forms or granules, as well as wetted materials (Example 2). In such cases, Rigorous Containment conditions can be reached and proven at lower “containment strategies”, such as Hirst 2 level.

6. Pyrometallurgical and hydrometallurgical techniques are often applied in a sequential way to concentrate and recover the metal from ore concentrates (primary smelters) or from secondary (recovered) materials. Several UVCB intermediates may be temporarily and consecutively formed at various stages of the production process. All steps usually take place at the same industrial site and in the same or connected industrial area(s). The identification, measurement, or determination of occupational exposure or environmental emissions, arising from a single intermediate, is therefore not feasible or relevant, given that a large number of them are smelted in a combined way **(Example 1).** Assessment of worker exposures, arising from the overall process, is common industry practice**.**

7. **Multiple Intermediates are often treated together,** in a single step, certainly at the start of the smelting/refining process. This complicates the ***attribution of monitoring data on potential residual exposure to individual intermediates*** and the attribution of the (high) knowledge level on effects data so that adequate assessments can be made for the resulting intermediates (Example 3). Rigorous containment of installations is specifically designed for this purpose, and monitoring, training and management include strategies for integrated assessments/follow-up.

8. The combined metal exposures of workers and the environment, arising from pyrometallurgical, hydrometallurgical or liquid/liquid extraction processes, have already been documented for **major metal constituents in the relevant Chemical Safety Reports (CSR) and ECHA registration dossiers**. The sector has **monitoring data available** for a variety of process and exposure/emission steps.

9. **Local Exhaust Ventilation (LEV) techniques** applied in metals smelting and refining **are designed for typical production conditions,** in particular high temperature and high air flow volume. This requires different exposure barriers from those often applied in other processes (water curtains, pressurised systems, etc.). These are clearly demonstrated in all examples listed below.

10. **Personal Protective** Equipment (PPE) is used for activities other than cleaning and maintenance because it may be legally mandatory, independent of a demonstrated need for risk management measures. A second reason is voluntary initiative by companies to prevent workers from being exposed during potential accidents/incidents (see Example 4).

**Example 1: Intermediate under SCC: a metal matte**

## *1. Brief description of technological process applied in manufacture of the intermediate*

Metal matte is manufactured during pyrometallurgical metal production from primary and secondary raw materials. Concentrates are complexes of sulphidic and other metal-containing minerals. Smelting of the primary material mix, composed of metal ore concentrates (exempted from REACH), fluxes, internal recycling of slags, flue dusts or secondary metal material, takes place under oxidising conditions.

For the manufacturing of metal matte, there are two distinct steps:

(1) Smelting: concentrates are smelted in a furnace at high temperature (> 1,100°C) to produce a melt that can be separated into a matte and a slag (rich in iron and silica). The relevant smelting process is most often a flash or blast/shaft furnace.
(2) Tapping: Matte is removed from the furnace in **molten state** through a tapping hole and poured through an enclosed launder (tunnel) into a ladle.

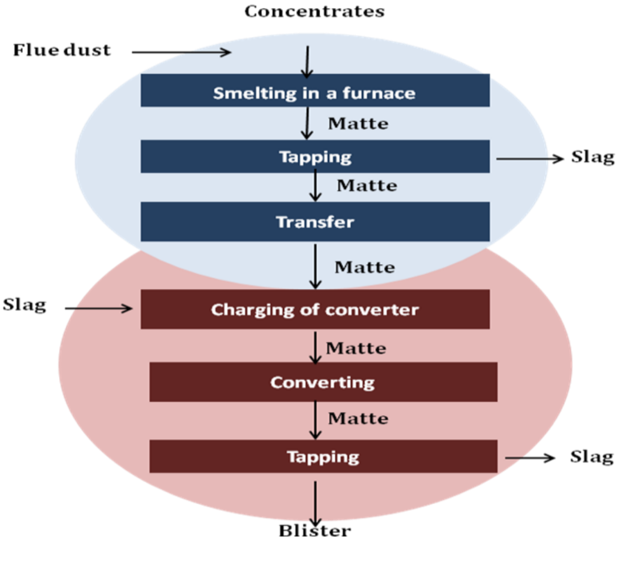
## *2. Brief description of technological processes applied in use of the intermediate*

Matte is **used in a molten state,** at the same site, for the manufacturing of the intermediate blister. The process takes place in converters.

The use includes 3 handling steps:

(1) Transfer to the converter in ladles by overhead cranes
(2) Charging of the converter: the converter is rolled out and the molten matte is poured from the ladle
(3) Conversion/refining of the matte to blister by blowing it with oxygen-enriched air. Converting is a conventional batch process, based on selective oxidisation and removal of impurities. In the first stage, iron and part of the sulphur are oxidised and slag is formed. The slag is skimmed off periodically and further processed to recover residual metals. In the second stage, the remaining sulphide is oxidised to metal blister.

A schematic of the manufacture and use of metal matte:



**3. *Means of rigorous containment and minimisation technologies applied by the registrant during the manufacturing and/or use process***

| *Description of the **technical means to rigorously contain** the substance* |
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Smelting of concentrates to matte

- Closed furnace that contains the molten matte (as well as the concentrate and slag) and prevents emissions
- Operation under negative pressure to prevent fumes escaping (~ 50 Pa)
- Automated processes are operated from a physically separate control room
- Off-gas from smelting is captured completely and cleaned in a sequential gas and post-cleaning system

Tapping of matte from the smelting furnace in **molten** state

- Semi-automated process control
- LEV located above the tapping hole for effective hot air capture
- Matte is transferred from the furnace to the ladle through a enclosed launder/tunnel
- The ladle is placed in an isolator during tapping: housing with a movable door and hood in the ladle loading area
- Furnace and enclosures are maintained under negative air pressure to prevent leakage/ensure optimal exhaust collection efficiency
- Off gas from tapping is captured completely and cleaned in a sequential gas and post-cleaning system

Transfer of **molten** matte to the converter in ladles by crane

- Remote process control from the crane cabin
- During ladle transport the matte is covered by carbon forming a protective cover, thereby minimising emissions from the hot surface
- Short distance transfer between furnace and converter
- Building ventilation captures residual emission and direct them to effective gas and dust cleaning systems

Charging of the converter with **molten** matte via ladle

- Converters are equipped with effective LEV protection to prevent fumes escaping into the working environment
- Hoods are connected with effective local exhaust ventilation and sequential gas and post-cleaning systems
- Automatic process control. The crane and converter movements are remote-controlled from the converter control room and the crane cabin.
- Automatic controls prevent blowing during the periods that the converter is "rolled out" or "rolled in"
- Operation under negative pressure
- Individual hoods are motor driven to the positions that ensure optimal collection efficiency

Matte conversion to blister in converters

- Converters are equipped with effective off-gas collection to avoid fumes entering the workplace
- Hoods are connected with effective local exhaust ventilation and sequential gas and post-cleaning systems
- Automatic process control from a control room
- Automatic controls prevent blowing during the periods that the converter is "rolled out" or "rolled in"
- Operation under negative air pressure
- The individual hoods are motor driven to the positions that ensure optimal collection efficiency

*Identification of* ***residual emissions***

**Due to the nature of the process and complexity of the intermediates, it is technically not possible to identify and assess the exposure to the matte as such. Workers and the local environment are exposed to the metals/metal compounds arising from the production of several intermediates, formed simultaneously and consecutively, at various stages of the process.**

Residual exposures at the workplace and the environment are assessed from regular measurements of metals.

*Workplace*

Monitoring campaigns at the workplace are performed in line with the requirements of occupational health legislation and approved standard sampling/measurement methods.

All workplaces are monitored as relevant: smelting furnace operators, converter operators and crane operators. Measurements typically include SO2, total/respirable dust, and relevant metal concentrations using personal samplers for relevant exposure duration (normally 8 hours).

In addition, biological personal monitoring data are measured in urine or in blood for Cd, As, Cu, Ni and Pb. These data are to be considered as representative for realistic internal exposure patterns.

Measured data represent total exposure to metals related to several intermediates (matte, slag, flue dust and blister) handled at the workplace during a shift (8 hours).

*Environment (air, water)*

Monitoring of emissions to air and water is performed in line with the requirements of environmental legislation, permit conditions and approved standard sampling/ measurement methods. The monitoring is based on authority-approved programmes.

Point source air measurements are performed continuously, or on a regular basis, at every stack, and typically include SO2, dust and relevant metal concentrations. Effective and

sequential gas abatement systems are used to treat process gases from a number of sources together. The measured air emissions data therefore represent total exposure to metals, related to several intermediates, associated with one particular stack or, in some cases, the whole smelter building.
Secondary gases from various points of the smelter (converter secondary hoods, ventilation hoods at flash smelting furnace and electric slag furnace, taphole and launder ventilation of flash smelting furnace, electric slag furnace and anode furnaces, ventilation hoods of anode furnaces, ventilation of reverts handling and screening plant) are collected in a common system.

Emissions to water are typically measured prior to discharge at the outlet of the water treatment plant based on qualified random sample or 24 h composite sample. Effluents are typically treated in one on-site waste water treatment plant. Measured water emissions data therefore represent total exposure to metals related to all products/intermediates produced at the site.

- Water from wet gas cleaning and effluents from other sources, from the whole site, are treated in a multi-stage water treatment plant before discharge
- Run off water from the smelter area is collected and treated in rain water treatment plant

*Description of **procedural and control technologies** in place to minimise emissions and resulting exposures. Quantification of the releases and information on the effectiveness of control techniques.*

*Workplace*

- Exhaust ventilation applied at converter secondary hoods, ventilation hoods at smelting furnace, tapping hole and launder ventilation is integrated with enclosures described in the technical means.
- Variable speed fans are used to provide extraction rates suitable for changing conditions.
- System to operate automatically the fans, valves and dampers to ensure optimal collection efficiency and prevent diffuse emissions.
- Smelting process is fully automated and operated from a closed ventilated control room. Operations in place at the furnace only include short-term observation tasks (visual inspection tour and bath level measurements) to ensure proper furnace operations.
- During tapping operations, workers are generally in air-conditioned cabins. Workers do not directly handle the substance, but need to be in the tapping area to open/close the tapping hole, and for temperature measurement and sampling.
- During ladle transfer and charging of converter (<30 minutes), the operator does not manipulate the substance directly. Operators are physically separated from the substance in air-conditioned crane cabins and converter control rooms.
- Converting process is fully automated and operated from a closed, ventilated control room. Operations outside of the control room include short-term activities like punching and sampling to ensure proper converter operations. Punching of the converter's tuyeres is performed with a remote controlled punching machine.
- Residual exposure to metals (Cu, Pb, As, Cd, Ni) is below the exposure limits and/or biological limit values.

- Exposure to the major metal constituent from metal manufacturing (including manufacture and use of matte) has been assessed and documented in the corresponding metal Chemical Safety Report.

*Environment*

- Collected process gases from the smelting furnace and converters are cooled in waste heat boilers, treated in dust removal systems (electric static precipitator and wet static precipitator), and then converted in the sulphuric acid plant.
- The roof of the furnace reaction shaft, settler and uptake is ventilated and the exhaust gases are cleaned in a gas cleaning system (wet scrubber and bag filter).
- Fumes collected from the local exhaust ventilation of the tapping hole, launder and ladle housing are directed to gas cleaning systems (wet scrubber and bag filter).
- Secondary gases from converters are captured at source, via secondary hoods, and extracted off gas is treated in gas cleaning systems (wet scrubber and dust bag filter).
- Roof ventilation captures residual fugitive emissions and directs them to the gas cleaning system (wet scrubber and bag filter).
- Indirect cooling water for the smelting furnace, launders, hoods and converters is re-circulated.
- Effluents from wet off gas cleaning are treated in waste water treatment plants (physical and chemical treatment) to remove metals and solids.
- Run-off water that washes dust away (from the whole smelter) is collected and treated before discharge.
- Procedures for process control to minimise release/exposure are applied.
- Regular inspection and preventive maintenance of furnaces, ducts, fans and filter systems take place to ensure air tightness and prevent fugitive releases.
- Monitoring systems are established to detect leaks and failures in cleaning equipment.
- Emissions to air from gas cleaning installations are controlled and below permit requirements.
- The levels of metals emitted to water (Cu, Pb, Ni, As, Cd , Zn ) are well below the emission limit values specified in the IPPC permit.
- Metal emissions from the manufacturing of the major metal constituent (including manufacturing and use of metal matte) have been assessed and documented in the corresponding REACH Chemical safety report.

| *Management means and training that contribute to the above-mentioned technical means* |
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- Certified Management systems such as Quality Management system ISO9001; Health and Safety Management System (OSHAS, ..), Environmental Management System (ISO14001, EMAS) are in place.
- Metallurgical processes are in compliance with the applicable legislation, such as the Industrial Emissions Directive (IED), control of accidents under the Seveso Directive, occupational protection under the Chemicals Agent Directive and the directive on carcinogenic agents.
- Installations comply with the Best Available techniques (as described in NFM BREF) and associated low residual emission levels.

- Operations are carried out in compliance with the relevant work place and environmental standards, and all permit conditions as approved by competent authorities.
- Housekeeping procedures - work area, equipment and floors are regularly cleaned by industrial vacuum cleaners.
- Hygiene procedures – ban on eating, drinking and smoking in contaminated areas; changing of contaminated clothes, provision of adequate facilities for washing, changing and storage of clothing.
- Activities are only carried out by specialists or authorised and trained personnel.
- Specific on-the-job training, which includes operation of the process and equipment, procedures for limiting exposure to workers and environment.
- There is regular refresher training and instruction of workers.
- Residual emissions to workplace and the environment are regularly monitored and assessed.
- Health surveillance programmes for all workers in the smelter.

### *4. Means of rigorous containment and minimisation technologies recommended to the user of the intermediate*

Means of rigorous containment and minimisation technologies are the same as those described above, and are typical for hot metallurgical processes. Relevant risk management measures for the handling, storage and melting/refining of metal matte are communicated to the user of the intermediate by means of a Safety Data Sheet.

### *5. Special procedures applied before cleaning and maintenance*

There are special procedures for the cleaning of tapping holes and launders and replacement of brick lining, cleaning of ladles, cleaning of build ups in hoods and cleaning of converter mouth.

Procedures are in place to ensure safe cleaning and maintenance operations – cooling down of equipment, switching off power supply, blocking of the rolling of the converters. Permission for maintenance activities is given once all specified conditions are met (use of checklist). A maintenance permit is issued where specific measures for protection of workers and environment are listed.

Cleaning and maintenance operations are performed in the plant under exhaust ventilation. Special procedures exist for the handling and management of the resulting waste.

### *6. Describe activity and type of PPE in case of accidents, incidents, maintenance and cleaning activities*

PPE (respiratory protection P2 half mask, heat-resistant working clothes, helmet, safety glasses and gloves) is required for routine maintenance and inspection of furnace, converters and associated equipment, furnace bath level measurement, observing the tapping area and preparation of the tapping chutes, sampling, punching of converter’s tuyeres. They act as a precaution in line with the company’s safety performance standards.

Respiratory protection P3 is required for cleaning operations and some repair operations (only conducted by specially trained personnel).

## *7. Waste information*

Sludge from waste water treatment plants is recycled within the process or sent to industrial landfill sites.

Metal-containing waste from cleaning operations (build ups, reverts) is re-used internally for metal recovery. Used oils after maintenance/repair of equipment are collected and sent to authorised companies for recycling.

**Example 2: Intermediates under SCC: slime from electrolytic refining**

*The example provided uses information from the corresponding REACH dossier.*

***1. Brief description of technological process applied in manufacture of the intermediate***

The UVCB slimes and sludges from electrolysis processes are complex combinations of insoluble compounds produced, by precipitation, during electrolytic refining or winning processes. They consist typically of various metals (such as precious metals, copper, antimony, tin, selenium, tellurium, arsenic, lead and nickel), as well as their oxides and/or sulphates.

In electrolytic refining, an electrolytic cell is used. This consists of a cast metal anode and a cathode placed in an electrolyte containing metal salts and acids. The metal is removed from the anode to the extent that the remaining anode is still mechanically strong enough. Other metals contained in the anode are separated, soluble metals like Ni are dissolved in the electrolyte, and insoluble metals, such as precious metals (Ag, Au, Pt, Pd), Se and Te form a slime that settles in the electrolytic cells.

(1) The settled slimes are periodically removed from the cells (using vacuum equipment) and pumped into decantation tanks.

(2) After decantation, the material is pumped mechanically into a leaching tank, where electrolyte is added and refining takes place by blowing with air.

(3) From the tank, the material is pumped into a filter press, washed and pressed.

(4) From the press, the slime is transferred to containers (or drums, depending on amount).

(5) The containers are closed and stored, before being transported by forklift and/or trucks.

***2. Brief description of technological processes applied in use of the intermediate***

Valuable metals will be recovered through further metal refining processes.

The closed containers are transported to the precious metals plant, where additional refining operations take place to remove precious metals, such as Ag, Au, etc (similar leaching and/or furnace operations).

***3. Means of rigorous containment and minimisation technologies applied by the registrant during the manufacturing and/or use process***

| *Description of the **technical means to rigorously contain** the substance* |
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- Electro-refining is a batch process. During electrolysis, the settled slime remains isolated from the environment and worker by means of the overlying electrolyte (constant temperature of the cells).A polypropylene cover is placed on top of the cell, to control temperature and prevent evaporation of electrolytic liquid. In addition, adapted LEV systems are placed in the tank house.

- Automated processes are operated from a physically separate control room.
- The slime is removed from the bottom of the electrolytic cell by means of an automated sucking system (sludge remover), with automated transfer via pumping through closed pipes to an acid remover and sludge tanks for centrifugation and/or pressing.
- Sludge remover, acid remover, and decantation tanks are closed and connected by pipes.
- Electrolysis room is equipped with a vapour collection system (with wet scrubbers) and filters.
- The pressed/filtered cake (water content ca. 20%) is periodically removed from the device and automatically transferred to containers. As the slime is filtered, the filter opens automatically and the cake falls into a container.
- Liquids collected from centrifugation and washing operations are collected and recycled as electrolytes in the system.
- Unloading of solid, massive raw materials, using a crane equipped with a closed cabin (dedicated unloading area with restricted access).
- Periodic maintenance tasks (see Point 6, below), carried out by workers (wearing acid protection clothes (tyvek suit), acid protection shoes or boots and gloves and precautionary PPE designed for corrosive conditions (closed goggles, P3 masks or autoflow full mask and helmet), are minimised due to automatic control systems and carried out with minimal manual handling (optimised process control system).

*Identification of* ***residual emissions***

- Residual emissions are measured in various workplace areas.
- Residual emissions to ambient air in the tank house (outside of the control room) arise from acid vapours carrying some metals. Regular measurements are performed above cells and around tanks.
- **Fugitive emissions from the UVCB, as such, are not expected, due to its handling in a closed system, and the fact that filtered/pressed cake, once isolated, has a water content of 20 to 30%.**

*Workplace:*

The UVCB intermediate remains isolated from its surroundings (by means of liquid electrolytes and/or pumping through closed systems and pipes) until removed from the centrifuge/press by means of automatic equipment (no direct handling by workers). The pressed slime (cake) falls into a container, which is stored in a separate and closed room.

The isolated slime cake (water content of 20 to 30%) is of <u>low dustiness</u> (measurements on totally dry samples show density of ca. 4 to 5 g/cm$^3$). It is stored in a wind- and temperature- protected environment.

The UVCB contains highly valuable materials – at all stages of manufacturing and use, it is obvious that extreme care must be taken so that no UVCB substance is lost.

**Workplace air monitoring:** Personal sampling measurements are taken, complemented by static sampling, in order to confirm the lack of exposure **(**values relate to several activities).

*Environment*:

- Air from filter bag cleaning installations from the whole plant is controlled on a regular and systematic basis and in line with permit requirements.

- For the major metal constituents, the measured emissions were assessed under the Chemical Safety Reports (and EU Risk Assessment), concluding that they did not cause a risk.

- The gas cleaning waters are handled as process waters that are treated in a physico-chemical WWTP before being discharged to the receiving water. Emissions are regularly controlled, in some cases on a continuous basis. The general levels are well below the permit conditions and were evaluated by the aforementioned Safety and Risk Assessment reports as "not causing a risk".

- All emissions to sea, air and ground are reported annually and made available to the public.

**Environmental monitoring (values relate to all materials processed at the site, including raw materials)**

*Management means and training that contribute to the above-mentioned technical means*

**Management means and training** particularly contributing to the functioning of the technical means described above:

Plant is certified for ISO 9001 and 14001

Other existing legislations implemented: IPPC permit, Carcinogens Directive, SEVESO II Directive

The plant is compliant with REACH Occupational & Environmental Safety levels of the major metal constituents of the UVCB processed and handled simultaneously on site such as nickel, lead, copper, zinc, tin, antimony, and arsenic. In addition, the plant is compliant with national/local OELs.

Detailed standard operating procedures exist.

A central control centre exists for the tank house; historical operating data are available.

Internal audits, health surveillance, exposure measurements, and incident investigations are regularly performed.

***4. Means of rigorous containment and minimisation technologies recommended to the user of the intermediate***

Similar to the manufacturing stage. Material composition, handling and storage procedures are communicated to the (external) user of the intermediates by means of a Safety Data Sheet. For internal users, a SDS, a Safety & Health card and specific training documentation are available.

### *5. Special procedures applied before cleaning and maintenance*

Several control measures need to be taken care of before the electrolytic cells or any other tanks can be opened and/or entered. To enter an electrolytic cell, the automated pumps and valves must be turned off or closed, and a maintenance switch turned on. In next steps, the slimes are removed and the anodes, cathodes and electrolyte removed from the cell (via track-bound crane, worker in cabin). Tanks, settlers and caustic towers can only be entered if 2 operators work together and unlock the manhole. A checklist must be followed to lock and unlock the cells, pumps, tanks, settlers and caustic towers. All operators are trained on the procedure and the hazards of the materials. Maintenance access under these strict conditions is only granted to specifically trained personnel and under specific supervision conditions.

### *6. Describe activity and type of PPE in case of accidents, incidents, maintenance and cleaning activities*

Workers have observational tasks and control activities to ensure proper operations, which requires them to leave the control room. During these **periodical activities (placing of equipment to suck in the settled UVCB, cleaning and recharging cells, loading cells, switching valves between tanks, etc.),** due to the corrosive nature of the material, the operators wear acid protection clothes (tyvek suit), acid protection shoes or boots, and gloves and precautionary PPE (closed goggles, P3 mask or autoflow full face mask and helmet).

### *7. Waste information*

Any waste arising from cleaning the cells, tanks and trucks is collected and re-used in the metallurgical system. Used PPE equipment is collected and disposed of.

**Example 3: Intermediates under SCC: Smelting, converting and refining of complex base and precious metals-containing UVCB streams**

***Introduction***:

Process description: The smelting of a very varying material mix (complex copper lead concentrates, a wide variety of recovered by-products from the non-ferrous industry, a series of recyclable products, all containing a variable content of precious metals (PM), and flux materials) is performed in batch runs. Heating under controlled oxidising conditions, produces a copper matte, rich in precious metals, and a lead silicate slag, poor in precious metals. After removal of the slag, the copper matte is converted to impure copper blister, under controlled oxidizing conditions in the same furnace. The impure blister is transferred, in liquid form, to a refining furnace, where it is further refined to copper blister.
The example described covers the first step, in which a varying combination of intermediates are melted together to form two new type of intermediates - slag and matte.

***1. Brief description of technological process***

The “manual’ interventions referred to below are carried out by fully trained personnel. The workplace is monitored and PPE is used to protect workers against unforeseen incidents.

***a. Loading of the smelter***

The wet material mix, consisting of a series of intermediates, fed to the smelter is prepared in an entry restricted area, following detailed material mass balance instructions. It is loaded from a covered storage box, by a wheel loader on a closed conveyer belt, through loading bins equipped with a local LEV creating an under pressure barrier. The mix is charged through a covered feed port located at the top of the furnace.

The furnace is equipped with a central pipe to inject large amounts of air and fuel in the molten phase, resulting in a high temperature (~ 1,050°C) and an intensive bath mixing, which assures that quick chemical reactions with high recovery yields can occur. Liquid raw materials are loaded directly into the furnace through the injection pipe. Massive materials such as alloy ingots, etc. can be fed manually into the furnace via the feeding port.

***b. Smelting phase***

During the smelting stage, a copper lead sulphide phase, known as “matte”, and a lead silicate slag, are formed. The PM are preferentially collected in the copper phase, whereas elements, less noble than copper (Fe, Ni, Cd, As, Sb, etc.), are carried by the slag phase.

After the material has been fed into the furnace, the feeding and blowing is stopped and a decantation stage is started, followed by the tapping of the molten slag into large pouring pots, disposed in cascade and equipped with under pressure LEV systems. The tap hole is opened and closed automatically. After solidification of the upper layer of the slag, preventing emissions during handling, the pouring pots are transported by a crane, equipped with a closed cabin, to a covered storage area and cooled down for 24 hours. The solidified slags are then removed by tilting the pots, by crane, under continuous water sprinkling, forming a further barrier to limit residual emissions occurring in the cooling process.

The “smelting – decantation - slag tapping” sequence is repeated several times per run. Following this, the converting step can be carried out on the material that was not removed from the smelter, i.e. the copper matte (see Example 1

### *c. Collection and treatment of process and other gases*

The process gases from the smelter and refining furnace, rich in SO2, are effectively collected and cooled in a radiation chamber, subsequently de-dusted in an electrical precipitator, cooled down in a quenching tower, and finally sent via a pipe track to the sulphuric acid plant. The dust slurry collected in the precipitator is recovered as a wet filter cake and reused in the feed mix entering the smelter. This sequential gas cleaning effectively eliminates all residual metal emissions.

Workplace LEV installations, eliminating potential workplace exposures, are treated in a separate baghouse filter. The collected dust is sent pneumatically to a closed reactor, mixed with water and finally recovered as a wet filter cake, also reused in the feed mix to the smelter. The cleaned residual gases are released to the atmosphere through a stack.

## *3. Means of rigorous containment and minimisation technologies applied by the registrant during the manufacturing and/or use process*

| *Description of the technical means used to rigorously contain the substance.* |
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- During storage, potentially powdery or dusty materials are regularly sprayed with water, creating a physical barrier that prevents dust formation and erosion of stock piles.
- The smelting step is a batch process performed in a furnace maintained continuously under negative pressure to prevent leakage and exposure.
- Fully automated processes are operated from physically separate control rooms.
- Local LEVs designed for high temperature processes are installed at all relevant potential emission sources.
- Gases and other exhausts are treated in sequential steps before release to the atmosphere.
- Dry, dusty materials are re-pulped in water, in a closed mixing tank, and filtered before processing to prevent dust formation.
- Materials are handled (liquids and solids) using a crane, equipped with a closed cabin, on a dedicated unloading area with restricted access.

| *Identification of residual emissions to Workplace and the Environment* |
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- Potential residual emissions at the workplace are measured at regular time intervals.
- Residual emissions to the ambient air through the stacks are measured at regular time intervals.
- Process waters are treated in an onsite physico-chemical, BAT compliant wastewater treatment plant before discharge.

*Workplace:*

- Installations operate with "state of the art" technologies and computer automated systems. Areas where residual exposures may occur have restricted access for trained personnel only.
- Process parameters (temperature, pressure, valve position, flow rates, etc.) are continuously monitored and stored in a computerised database. Alarms are reported on screens in the control room whenever conditions might cause accidental exposures.
- Daily control and maintenance tasks are carried out by trained workers wearing heat protective clothes, face shields, shoes or boots, and gloves and precautionary PPE (closed goggles, P3 masks or auto-flow full mask and helmet). The number of these interventions is minimised by means of automatic control systems.
- Periodic maintenance tasks are performed monthly, during a short shutdown of the installation, where the furnaces are kept warm. Long-term maintenance tasks are only performed after complete shutdown and cleaning of the installation. Risk assessments, which include safety and protective measures, are performed for each maintenance task.
- Dust emissions in the building are continuously monitored, with exceedance alarms reported directly in the control room. **Extensive workplace air-monitoring data for all relevant metal components are available and well documented** at the plant site.

***Environment*:**

- **Air from filter bag cleaning installations from the whole plant is controlled** well below permit requirements based on BAT.
- All stack emissions to ambient air are monitored on a regular and systematic basis.
- All process water is treated in a physico-chemical, BAT applicable WWTP prior to discharge. Emissions into the receiving surface water are controlled by continuous monitoring, with general levels well below permit requirements.
- All emissions to water, air and ground are reported annually, and are available to the public.
- **Environmental monitoring data for all relevant metal components are available and well documented** at the plant site.

**<u>Management means and training that particularly contribute to the functioning of the technical means described above</u>**.

- Certified management systems such as ISO 9001and 14001 and OHSAS 18000 are in place
- Other existing legislations implemented: IPPC permit, Carcinogens Directive, SEVESO II Directive
- Plant is compliant with REACH Occupational & Environmental Safety levels of the major metal constituents of the UVCB processed and handled simultaneously on site, e.g. Ni, Pb, Cu, Zn, Sn, Sb, As
- In addition, plant is compliant with the national/local/EU wide OELs
- Centralised control centre exists for the installation, with historical operating data available
- Internal audits, health surveillance, exposure measurements and incident investigations are regularly performed

***4. Means of rigorous containment and minimisation technologies recommended to the user of the intermediate***

Material composition, handling and storage procedures are communicated to the personnel by means of Safety Data Sheets and Safety & Health Cards, freely available in the control room. Training documents also include general safety procedures.

***5. Special procedures applied before cleaning and maintenance***

Several actions need to be taken before the installation can be opened and/or entered. A checklist must be followed to lock and unlock the cells, pumps, tanks, conveyors, etc. and all operators are trained on the procedure and the hazards of the materials.

***6. Describe activity and type of PPE in case of accidents, incidents, maintenance and cleaning activities***

The whole installation is split into three safety levels, based on the results of regular risk assessments. Access to each area is restricted, and the minimum mandatory safety protection requirements for each area are clearly stipulated.

Workers have observational tasks and control activities, ensuring proper operations, which requires them to leave the control room.

During periodic maintenance (placing of locks to secure safety devices, cleaning and manual feeding tasks, etc.), the operators wear protective clothes, safety shoes and gloves, and precautionary PPE (closed safety goggles, P3 mask or auto flow full face mask and helmet).

***7. Waste information***

Any waste arising from production activities is collected and re-used in the metallurgical system. Used PPE equipment is collected and disposed of.

**Example 4: Intermediates under SCC: metal dross**

The metal dross example is to show that the intermediate is manufactured and used under strictly controlled conditions, evaluated against the conditions in Article 18 (4). The metal dross is produced during metal refining steps. This particular example represents only one step of the dross life cycle and does not address the entire metal refining process. Rigorous containment is achieved through the technical design of a process that aims to prevent releases in combination with procedural and control technologies.

Metal dross is a solid phase formed during the removal of impurities from molten metal during the pyrometallurgical refining of both primary and secondary metal bullion. The dross consists of variable amounts of lead, copper and other metals in either alloy form or as compounds such as oxides. This substance is considered to be a UVCB.

***1. Brief description of the technical processes used in the manufacture of the intermediate***

Pyrometallurgical metal refining consists of a series of kettles where the metal bullion is fed into a kettle, melted, and given sequential treatments to remove specified impurities. Firstly, it is heated to 350 - 450 °C, whereupon impurities are separated out as sulphidic dross. Automatic stirring is applied. Dross is removed from the metal surface by a closed mechanical conveyer and discharged into a closed container. The conveyor is placed in the kettle by a crane through two small openings in the lid. During the refining process, where dust is liable to be produced, the refining kettle is covered with a lid that is not opened.

***2. Brief description of the technical processes used in the use of the intermediate***

The metal dross rich is used for metal recovery, which is not discussed in this example.

***3. Means of rigorous containment and minimization technologies applied by the registrant during the manufacturing and/or use process***

*Description of technical means of rigorously containing the use of the substance*

- The refining kettle is covered with a lid that remains closed during the process.
- A mechanical skimmer is either lowered through a hole in the lid, with the system remaining closed with a fume exhaust and collection system, or there could be a mechanical skimmer on a “bridge” where the lid is removed, but where rim extraction is in place.
- Enclosed conveyer and connection hoses.
- Closed container for interim storage of the metal dross

*Identification of sources of residual emissions both to the workplace and the environment (air, on-site waste streams)*

Due to the nature of the process and complexity of the intermediate, it is technically not possible to identify and assess exposure to metal dross. Workers and the local environment are exposed to the metals/metal compounds arising from the production of several intermediates formed simultaneously and consecutively at various stages of the metal refinement process.

Residual exposures at the workplace and the environment are assessed from regular measurements of metals.

*Workplace*

- Monitoring campaigns are performed in line with the requirements of occupational health legislation and approved standard sampling/measurement methods.

- Measurements include inhalable/respirable dust and lead concentrations based on personal samplers for relevant exposure duration (normally 8 hours). It is important to note that all steps usually take place at the same industrial site and in the same or connected industrial area(s). Consequently, workers' exposure to metal arising from one intermediate is neither feasible nor relevant. **Assessment of workers' exposures to metal arising from the overall process is common practice.**

- Lead biological personal monitoring data are measured in blood. Some companies also measure for Cd, As, Pb and Hg in blood and urine. These data are to be considered as representative for realistic internal exposure patterns.

*Environment*

- Monitoring of emissions to air and water is performed in line with the requirements of environmental legislation, permit conditions and approved standard sampling/ measurement methods. Point source air lead measurements are taken on a regular basis at the stack. Some other metal elements, such as Cu, As, Cd and Hg, may also be measured.
- A gas abatement system bag filter, or other technology conforming to BAT described in the Non-ferrous Metals BREF Note, is used for the extraction of lead and/or other metals.
- Fugitive emissions from the roof openings of the lead refinery building are measured. Metal loads (Cu, Pb, As, Cd and Hg) are controlled and reported.
- Air emissions are below the permit requirements.

*Description of the procedural and control techniques in place to minimise emissions (workplace and environment).*

*Workplace:*

- The metal dross removal process takes place indoors. During the process there is no direct handling of the substance.
- Exhaust ventilation is in place on the kettle from which emissions are released.
- The workers remain in a control room for the majority of the shift during the process on the work floor during the refining process.
- There are procedures and instructions for process control.
- Automatic process control during metal refining.
- Crane operations in the refining kettles area are remotely controlled by a worker.
- There are regular inspections of conveyer and connection hoses to prevent damage and to ensure tightness.
- A monitoring system is installed to detect potential leaks in the bag filter.

- Good housekeeping is practised by shop cleanliness, which is maintained by measures that may include frequent vacuuming, and/or the floor is kept wet to prevent dust formation.
- Personal hygiene - No eating, drinking or smoking is permitted in any area contaminated with lead. Contaminated clothing is changed daily. Adequate facilities are available for the washing, changing and storage of clothing. All work clothing is cleaned.
- Blood lead monitoring is carried out on a regular basis, covering all lead refining activities throughout workers' shifts. The blood lead levels of workers are below the "action level", that is typically 5 µg/dL below the exposure limit deemed to be safe (DNEL 40 µg/dL).
- Exposure to major metal constituents from the metal dross has been assessed in the corresponding metal Chemical Safety Report and safe use has been demonstrated.

*Environment:*

- Emission control measures are complemented by an integrated management system, e.g. ISO 9000, ISO 14001, ISO 18001.
- Effective abatement systems ensure that emissions hazardous to the environment are far below the permitted levels.
- Metal emissions from metal refining operations have been assessed in the **corresponding metal Chemical Safety Report,** and safe use has been demonstrated.
- No water effluents are produced during this process. Water is only used for indirect process cooling and is re-circulated.
- Run-off water from the metal refinery area is collected and treated in a chemical rainwater treatment plant. Clean water after treatment is re-used as indirect cooling water or discharged.
- No soil or ground water emissions take place during this process.

| *Specify management and training that particularly contributes to the functioning of the above-mentioned means.* |
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- Certified management systems such as ISO 9001, ISO 14001, EMAS, and OSHAS 18001) are in place.
- Activities are only executed by specialised and authorised personnel.
- There is area separation to prevent exposure to non-authorised people.
- Personal monitoring and biological monitoring of operators is regularly performed.
- Detailed training is provided for new workers on the risks of lead exposure and the procedures for protection.
- Instructions are provided on specific lead exposure risks for workers undertaking new tasks.
- Refresher courses are provided for all employees on the risks of metal exposure and the procedures for protection.
- Regular training and instruction of workers, which includes training on personal hygiene and good housekeeping.
- Management of maintenance of respiratory protective devices and their correct use is in place.
- The metal refining processes are carried out in full compliance with all applicable legislation, such as the Industrial Emissions Directive (IED), Chemical Accidents (Seveso II) Directive, occupational protection under the Chemical Agents Directive and country-specific legislations.

- Installations comply with the Best Available Techniques (BAT) (as described in NFM BREF) and associated residual emission levels.
- The operations are carried out in accordance with the national workplace and environmental standards.
- All permit conditions are approved by competent authorities

| *Specify whether these or other procedures are communicated to the user of intermediates* |
| --- |

Yes.

***4. Means of rigorous containment and minimisation technologies recommended to the user of the intermediate***

See above.

***5. Special procedures applied before cleaning and maintenance, such as purging and washing applied before the system is opened and entered for cleaning and other maintenance work***

All equipment is intensively cleaned prior to the maintenance. Dust is removed by vacuum cleaner, and metal build-up is removed by heating or manually by hammering.

Workers who will come into contact with the equipment are given instructions on the safe manipulation and handling of the substance.
An exhaust/off-gas system is in place for any maintenance that may be carried out in the plant area. If a central workshop has to be used, this is carried out in a closed area.

***6. Describe the activity and type of PPE in case of accidents, incidents, maintenance and cleaning activities***

Work involves operations to prepare and deploy dross removal equipment, preparation of the container for the removed dross, observation of the kettle, skimming of dross, and removal of the container in a safe manner to the designated storage or processing area(s).

- PPE is legally required to protect the workers from combined exposure to metals, molten metal and heat that may occur in the kettle area – related to the production of main metal and several intermediates associated with various metal refining steps.
- It is important to note that PPE is required for workers not just because they are exposed to this particular intermediate. The same workers are involved in all metal refining operations during an 8-hour shift, where there is a potential of exposure to that metal from other sources. Suitable effective respiratory protection, such as P2/P3, or P2 forced air helmet is used to minimise corresponding exposure.
- The use of PPE is also legally mandatory in some EU countries for all lead refining operations for an 8-hour shift, irrespective of the risk management measures in place (for example in Germany according to TRGS 505 (Technical guidance for hazardous substances - lead, Article 4.2.2 and Annex 2). For the above reasons, a medical surveillance programme is in place, and workers' lead blood levels are controlled. For human health, exposure (as measured blood lead levels) is below the DNEL of 40 µg/dL for male workers.
- Formal mask cleaning and filter changing strategies are in place.

- PPE, including heat resistant coveralls, safety shoes/boots, safety glasses or face shield, head protection, air filtration, hand protection and hearing protection, are deployed in every location where they are required.
- Additionally, standard "personal hygiene" measures are in place, such as washing hands and face on leaving area of potential contamination and showering at the end of shift.
- Workers involved in cleaning and maintenance activities are also provided with all necessary PPE as described above.

*Specify if these or other procedures and suitable PPE are communicated to the user of intermediates*

Yes.

***7. Waste information***

No waste is discarded, as metal dross is invariably processed to recover metal values.

**Example 5: Intermediates under SCC: Storage, Handling and loading of Doré metal to TBRC furnace**

***1. Brief description of the technical processes used in the manufacture of intermediates***

Dore metal is produced by melting and refining of anode slime from copper circuit in a Top Blown Rotary Converter (TBRC). Not discussed in this example

***2. Brief description of the technical processes used in the use of the intermediates***

Melting and refining of dore and other silver rich materials (like silver rich bullion from lead refining) take place in a Top Blown Rotary Converter (TBRC) at high temperature ( ~1100 C), The feed material (dore metal in massive large blocks (up to 2 t) is transported, stored and handled in a manner which takes account of the form, low or no-dustiness and weight. The blocks are charged to the converter through charging door by crane. The block is carefully placed on the floor of the converter. Subsequently the converter is heated and melt is formed.

***3. Mean of rigorous containment and minimization technologies applied by the registrant during the manufacturing and/or use process***

*Description of technical means of rigorously containing the use of the substance*

- Massive metallic dore blocks with stable and heavy structure, no possibility to create inhalable dust particles
- Dore blocks are stored on a sealed surface in a covered building for safety reasons (ensure blocks are not wet) and security reasons.
- Blocks are handled via forklift, front loader and overhead crane. They are transferred in moulds, in barrels or by crane directly to be fed into the furnace
- The lid of the furnace is a hood.
- In- house containment solution : the whole furnace is placed inside a large enclosure
- Hood is connected to exhaust ventilation

*Identification of sources of residual emissions both to the workplace and the environment (air, on-site waste streams)*

*Workplace*

- Monitoring campaigns at the workplace are performed in line with the requirements of the occupational health legislation and approved standard sampling/measurement methods.
- Measured data represent the total exposure towards metals related to silver metal and several intermediates handled at the workplace during shift (dore, different streams of slags from precious metals refining, silver rich bullion from lead refining)
- Measurements include: total/respirable dust, silver and lead concentrations based on personal samplers for relevant exposure duration (normally 8 hours).
- Biological personal monitoring data are measured in urine or in blood for As, Pb, Cd and Hg. These data are to be considered as representative for realistic internal exposure pattern.

*Environment*

- Monitoring of emissions to air and water is performed in line with the requirements of the environmental legislation, permit conditions and approved standard sampling/measurement methods. The monitoring is based on authority approved monitoring programs.
- Point source air measurements are performed on regular basis at the stack and include dust, Ag, Cu, Pb, As and Zn concentrations.
- Fugitive emissions from the roof openings of the whole building (where other processes take place) are measured. Metal loads (Cu, Ag, Pb, As and Zn are controlled and reported.
- Gas abatement system (bag filter) is used to treat process gases from the converter as well as secondary gases. The measured air emissions data represent the total exposure towards metals related to production of silver metal and several intermediates (dore, different streams of slag precious metals refining, flue dust, precious metals refining)

*Description of the procedural and control techniques in place to minimize emissions (workplace and environment).*

*Workplace:*

- There is no direct handling of the substance
- Inhalation and dermal exposure are not relevant because of the physical form – massive large metal blocks.
- Semi-automatic loading operation
- Crane operations are remote controlled
- No fine particulate materials are processed in the furnace
- In-house containment solution: furnace is sucked off over the lid, diffuse emissions are captured by the large exhaust hood
- There are procedures and instructions for storage, transport, loading and process control.
- The workers are physically isolated from the material (in the carrier, in a control room), and spend some time at the floor.
- Good housekeeping is practiced – storage and converter area as well as transport equipment are regularly cleaned by industrial vacuum cleaner to prevent diffuse emissions.
- Personal hygiene - No eating, drinking or smoking is permitted in any contaminated area. There is daily changing of clothing. Adequate facilities are available for the washing, changing and storage of clothing. All work clothing is cleaned by the company on a daily basis and may not be taken off site.
- Measured exposure levels are below the relevant exposure limits. The blood lead levels of workers are below the “action level” that is typically 5 µg/dL below the exposure limit deemed to be safe (DNEL 40 µg/dL).

- Exposure to silver from silver refining operations (including loading of dore metal to the converter) have been assessed in the Silver Chemical Safety Report and safe use is demonstrated.

*Environment:*

- Process gases from the converter as well as exhausted secondary emissions are treated in dust removal equipment – bag filter
- Regular inspection of storage area, converter, hood and ducts to prevent damage and ensure tightness
- Monitoring system is established to detect leaks in the bag filter
- Air emissions levels after the bag filter (Ag, Pb ,Cu, As and Zn ) are far below the permitted levels.
- Silver emissions from silver refining operations (including loading of dore metal to the converter) have been assessed in the Silver Chemical Safety Report and safe use is demonstrated.
- No water effluent during this process. Indirect cooling water is used for the furnace lid; the inner circle is re-circulated and reused in the process
- Run off water from the plant area is collected and treated in a chemical rain water treatment plant. Clean water after treatment is re-used as indirect cooling water or discharged.
- No soil and ground water emissions take place during storage, handling or the subsequent process step.

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| *Specify management and training that particularly contributes to the functioning of the means describe above* |

- Certified management systems (ISO 9001, ISO 14001, EMAS, and OSHAS) are in place.
- Activities are only executed by specialized and authorized personnel.
- There is area separation to prevent exposure to non-authorized people.
- Personal monitoring and biological monitoring of operators is regularly performed.
- Detailed training is provided for new workers on operational procedures and procedures for protection of human health and environment.
- Refresher courses are provided for all employees on the risks of exposure and the procedures for protection.
- Regular training and instruction of workers which includes training on personal hygiene and good housekeeping.
- Management of maintenance of respiratory protective devices and their correct use are in place.
- The silver refining processes are carried out in full compliance with the Industrial Emissions Directive (IED), Chemical Accidents (Seveso II) Directive, occupational protection under the Chemical Agents Directive, and country-specific legislation.

- Installations are compliant to the Best Available Techniques (BAT) (as described in NFM BREF) and associated residual emission levels.
- The operations are carried out according to the national workplace and environmental standards.
- All permit conditions as approved by competent authorities

*Specify whether these or other procedures are communicated to the user of intermediates*

Yes.

***4. Means of rigorous containment and minimization technologies recommended to the user of the intermediate***

*See above*

***5. Special procedures applied before cleaning and maintenance such as purging and washing applied before the system is opened and entered for cleaning and other maintenance work***

All equipment has to be intensively cleaned prior to the maintenance of any equipment. Dust is removed by a vacuum cleaner, and metal build-up is removed by heating, or manually by hammering.

Workers who will come into contact with the equipment wear appropriate PPE and are given instructions on the safe manipulation and handling of the substance. For this process a special maintenance information system is used, which is connected directly to the order for the repair.

An exhaust-/off-gas-system is in place for any maintenance that may take place in the plant area, if possible; otherwise, if a central workshop has to be used, it has to be cleaned intensively by blasting, which is carried out in a closed area.

***6. Describe the activity and type of PPE in case of accidents, incidents, maintenance and cleaning activities***

- Work involves preparation of the equipment, placement of the dore blocks in the converter, observation of refining process, and slags skimming.
- Respiratory protection (P2 half mask or air stream helmet with P2 Filter) during storage, handling and loading operations is used to prevent exposure in the event of unforeseen incidents.
- PPE is used to protect the workers from combined exposure of metals, molten particle and heat that may occur in the converter area – related to the production of silver metal and several intermediates associated with different refining steps – dore, slags precious metals refining, flue dust precious metal refining, silver rich bullion from lead refining.
- The same workers are involved in all refining operations with the TBRC furnace during an 8-hour shift
- The respiratory protection (P2 mask or air stream helmet) is legally mandatory for operations with lead-containing substances in Germany according to TRGS 505 (Technical guidance for hazardous substances – lead, article 4.2.2 and annex 2. This is not particularly relevant for dore metal, but is applicable to the TBRC furnace area because of other handled substances (slags, silver rich bullion from lead refining)
- Formal mask cleaning and filter changing procedure are in place.

- Heat resistant coveralls, safety shoes, and safety goggles/glasses are required.
- Workers involved in cleaning and maintenance activities are equipped with P2 half mask, helmet, working clothes, safety glasses and leather gloves.

*Specify if these or other procedures and suitable PPE are communicated to the user of intermediates*

Yes.

***7. Waste information***

There is no waste, since the dore metal as such is used for metal recovery.