

IUCLID 5 COMPOSITION AND ANALYSIS GUIDANCE DOCUMENT:

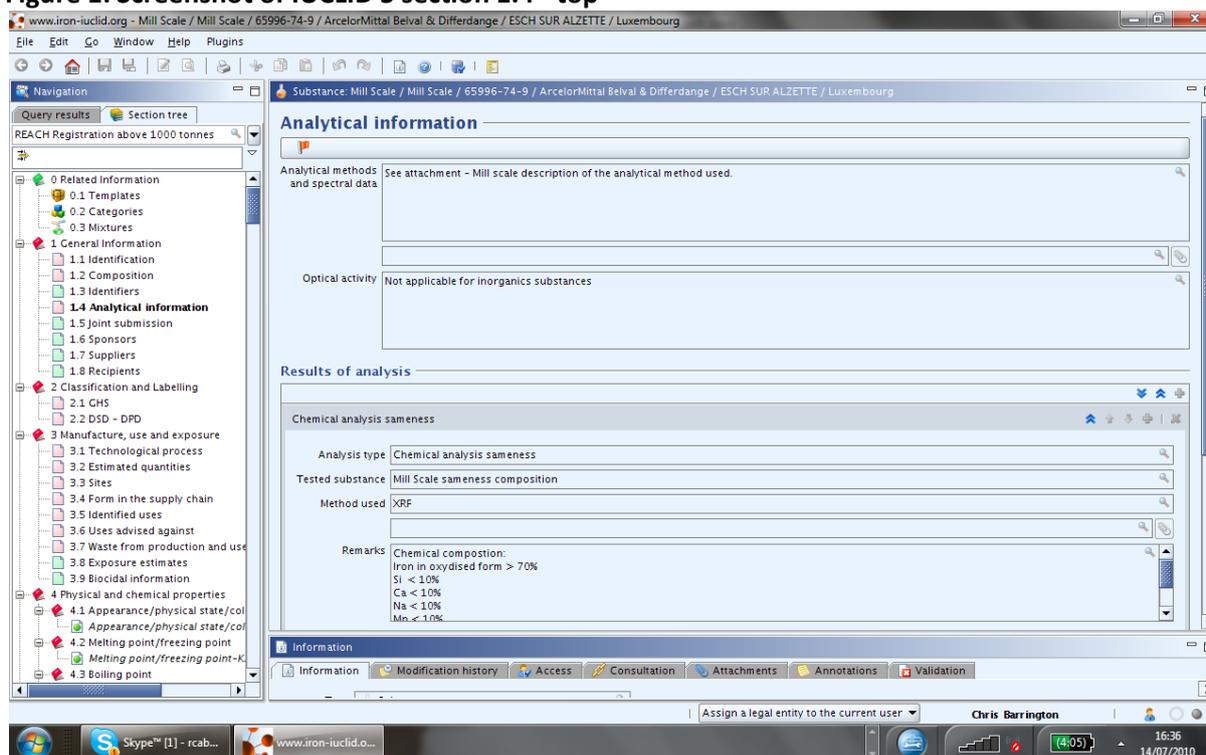
MILL SCALE [EINECS NUMBER 266-007-8, CAS NUMBER 65996-74-9]

INTRODUCTION

Each REACH registrant is required to file its own IUCLID 5 dossier. The IUCLID 5 dossier consists of 14 sections, of which sections 1 and 3 have to be completed by individual registrants [the other sections will be completed by the Lead Registrant and will be linked to the dossiers of all registrants who join the Joint Submission]. *Our guidance document on completion of IUCLID 5 sections 1 and 3 for mill scale will be available soon and will complement this document.*

This document deals with section 1.4 of the IUCLID 5 dossier - see Figures 1 and 2. This information has to be provided by all member registrants.

Figure 1: Screenshot of IUCLID 5 section 1.4 - top

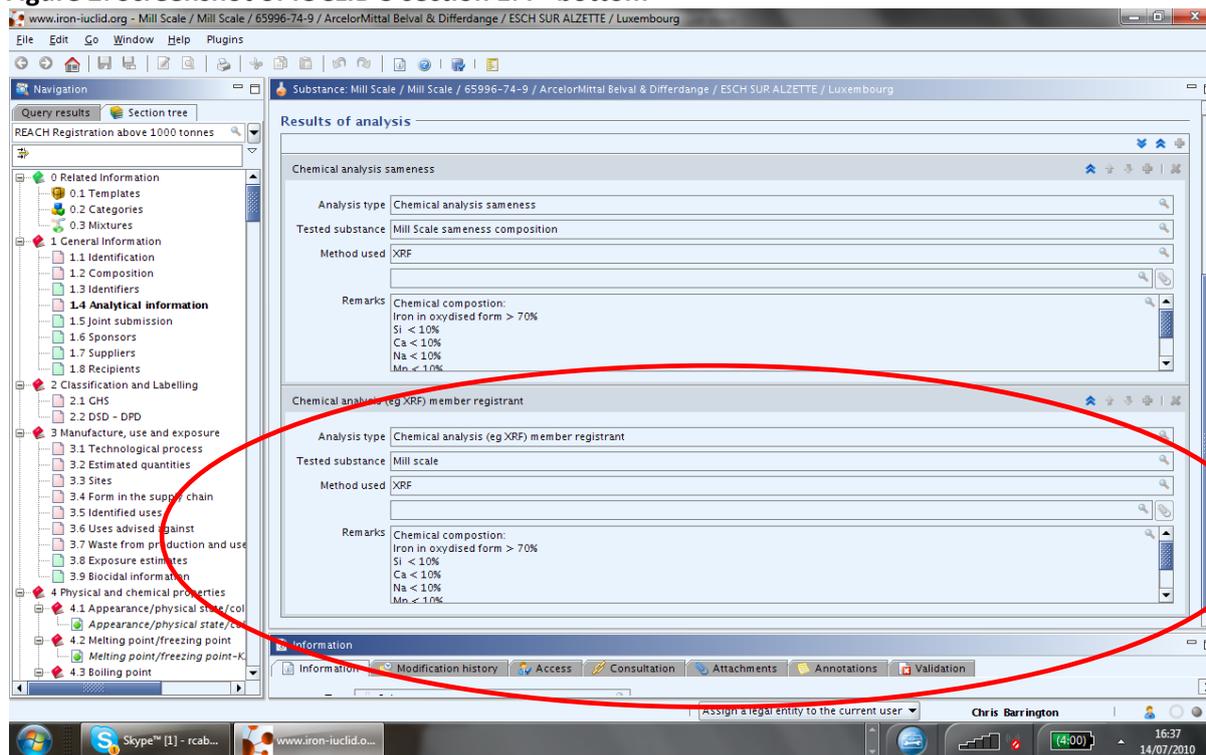


The screenshot displays the IUCLID 5 web application interface. On the left is a navigation tree with sections 0 through 4. The main content area is titled 'Analytical information' and contains the following data:

- Analytical methods and spectral data:** See attachment - Mill scale description of the analytical method used.
- Optical activity:** Not applicable for inorganics substances
- Results of analysis:**
 - Chemical analysis sameness:**
 - Analysis type: Chemical analysis sameness
 - Tested substance: Mill Scale sameness composition
 - Method used: XRF
 - Remarks: Chemical composition: Iron in oxydised form > 70%, Si < 1.0%, Ca < 1.0%, Na < 1.0%, Mn < 1.0%

The bottom of the interface shows a taskbar with the user name 'Chris Barrington' and the date '14/07/2010'.

Figure 2: Screenshot of IUCLID 5 section 1.4 - bottom



It is the responsibility of member registrants to ensure that their substances are in compliance with the sameness specification entered by the LEAD Registrant in its dossier [see Table 1 below]. In simple terms, ECHA needs evidence to be able to assess that the substance in each member registrant's registration dossier is the same as that submitted by the Lead Registrant in the Joint Submission.

Annex VI, Section 2.3 of the REACH legislation specifies certain analytical evidence to be submitted in each individual registration that will generate a "fingerprint" of the substance concerned. This fingerprint will demonstrate that the substance registered is the same as that in the Joint Submission.

Each registrant is responsible for deciding how they are going to satisfy this Analytical Data requirement - this document provides the recommendations of the Iron Platform in this respect.

The Lead Registrant will include the following information in section 1.4 of its IUCLID % dossier:

- Chemical sameness criteria based upon the bulk chemical composition of mill scale.
- X-ray diffraction data to demonstrate the typical mineralogical phases present in mill scale.
- Results of a transformation dissolution test in accordance with ECHA guidance.

The Lead Registrant will make its XRD data and transformation dissolution data available to member registrants for the purposes of proving sameness.

SAMENESS

Mill scale is composed mainly of iron oxides and may contain varying amounts of other oxides and spinels, elements and trace compounds. The oxidised surface of steel produced during re-heating, conditioning, hot rolling and hot forming operations. This substance is usually removed by process

waters used for de-scaling, roll and material cooling and other purposes. It is generally subsequently separated from the water by gravity techniques.

Table 1: Identity of mill scale

Chemical name	Mill Scale [ferrous metal]
IUPAC name	
Other names (usual name, trade name, abbreviation)	Each registrant can provide its own information in section 1.1. [see our guidance document on completion of IUCLID 5 sections 1 and 3 for mill scale]
EINECS No.	266-007-8
CAS name and CAS No.	65996-74-9
Minerals of identical or similar composition	hematite; magnetite; wüstite

The sameness specification for mill scale as agreed by the SIEF is given in Table 2 below.

Table 2: Sameness specification for mill scale

Constituent	Typical range, % m/m
Iron oxides [Fe_2O_3 , Fe_3O_4 , FeO]	>70%
C, Si, Ca, Na, Al, Mn and other metal oxides	<10% each [components are listed in elemental form, but are actually present in other oxidation states]
No hazardous substances present in the group "other metal oxides" in excess of the CLP [Classification, Labelling and Packaging of Substances and Mixtures] Regulation (EC) No. 1272/2008 limits for classification such as to render Mill Scale as hazardous [hazardous substances are defined in accordance with the current legally binding ATP (Adaptation to Technical Progress) of the CLP regulation]	
Oil content	<1% for all uses except batteries and melting charge for which <3% applies

ANALYSIS TECHNIQUES

It is conventional to represent the bulk composition of complex oxide materials, such as mill scale, iron ore pellets, iron sinter, minerals, ores, and refractory products, in terms of the simple oxides of the constituent elements, as shown in the chemical analysis in Table 2. However, this does not imply that the product is composed of a mixture of such simple compounds. It is simply a convenient means of representing the overall elemental composition of the material with each element concentration expressed in the form of its stable oxide. Therefore, although the typical analysis shown for mill scale may indicate that it contains silicon or calcium in oxide forms [SiO_2 or CaO], this does not mean that silica is actually present in free crystalline form, such as quartz or cristobalite, nor does it imply that the calcium oxide is present as free lime.

The bulk chemical compositional analysis of mill scale is normally carried out using X-ray fluorescence [XRF] spectrometry by the fused bead technique or with the original substance. For the fused bead method, typically, a 0.5 to 1-g portion of finely ground and ignited mill scale is mixed with alkali borate [e.g. lithium metaborate] in the ratio 1:10 (sample:borate) and the mixture is fused and cast into a circular glass bead. When the original substance is used, it is finely ground and mixed with a binding agent. The resultant test sample is subsequently subjected to multi-element analysis by XRF spectrometry using well established calibration.

The FeO content is determined separately by a wet chemical procedure in which a portion of finely ground mill scale is dissolved in hydrochloric acid in non-oxidising conditions and the resulting iron (II) in solution is determined by redox titration, e.g. with potassium dichromate.

Metallic iron content is determined by dissolution of the metallic iron in bromine-methanol and, after evaporation of the solvent mixture the residue is dissolved in sulphuric acid and the iron is determined by redox titrimetry after reduction of iron (III) to iron (II).

There are no existing EN standards for the multi-element analysis of mill scale by XRF spectrometry or for the determination of FeO by redox titrimetry. However, there is a related ISO standard [ISO 5416:2006] for the determination of metallic iron in direct reduced iron that may be applied to mill scales. Ideally, laboratories undertaking analyses of mill scales should hold accreditation to ISO 17025 or ISO 9001.

Multi-element analysis of mill scale provides the overall concentrations of the main constituents of the product, but does not give any indication of the identity of the individual compounds or chemical phases present, i.e. the mill scale mineralogy. Quantitative phase analysis of all the major chemical phases present in mill scale can be achieved only by means of X-ray diffraction [XRD] analysis combined with Rietveld data analysis. The identified mineralogical phases present in mill scale are summarised in Table 3.

Table 3: Mineralogical phases present in mill scale

Phase name	Assumed chemistry for XRD refinement
Hematite	Fe ₂ O ₃
Magnetite	Fe ₃ O ₄
Wüstite	FeO

The principal variation in mill scale mineralogy is in the relative proportions of iron oxide phases, such as hematite, magnetite and wüstite, the relative concentrations of which may vary dependent upon the thermal history (holding time, heating rate, final temperature, oxygen potential etc) of the steel substrate. The concentrations of other elements in mill scale are dependent upon the composition of the steel substrate with regard to alloying elements.

Stainless steel producers

In the case of mill scale derived from stainless steel production, it is recommended that the XRD analysis include Ni and Cr in order to demonstrate that the contained Cr and Ni are bound up in the metallic matrix and are not present in a classified form. A leaching test should also be carried out in order to demonstrate that there are no water-soluble toxic species present. A suitable leaching test has been developed by Jackson et al [2010, Corus R, D & T Report No. 150388 - attached as Appendix 1] wherein a 1-g portion of finely ground sample is sonicated with 30 ml of water for 6 hours at 70°C. The mixture is filtered and the filtrate is diluted to 50 ml with water and submitted to multi-element chemical analysis by ICP-MS.

Other techniques

As mentioned above, the principal methods of analysis used for characterisation of mill scale are XRF spectrometry for bulk chemical analysis, and XRD for individual phase analysis. Since mill scale is an inorganic material, analytical techniques such as nuclear magnetic resonance (NMR) spectroscopy, infra-red spectrometry [IR] and ultra-violet absorption spectrophotometry [UV] are not suitable, since these techniques are used to investigate the molecular bonding states of organic compounds

that contain essentially covalent bonds. They are not appropriate methods for the identification of inorganic structures where the bonds are principally ionic or metallic in character.

Gas chromatography [GC] is also an inappropriate analytical technique for inorganic solids since it can only be applied to organic [covalent] substances that are vaporised at temperatures below ~320°C. Similarly, high-performance liquid chromatography [HPLC], which is applicable principally to organic compounds, is not a suitable method for identification of inorganic substances. Mass spectrometry can only be applied if high energy excitation techniques, such as spark discharge or laser ablation, are used to vaporise the sample for introduction into the mass spectrometer. However, these techniques essentially provide the same information as XRF spectrometry, which is highly developed and widely applied for product and process control purposes. Thermo-chemical methods of analysis, such as differential thermal analysis [DTA], differential scanning calorimetry [DSC] or thermo-gravimetric analysis [TGA] may be applied for specific investigations on chemical phase changes and chemical reactions that occur when iron or iron oxide materials are heated, but the data provided by these techniques are not generally sufficient for identification of these materials.

ICP-AES [inductively coupled plasma - atomic emission spectrometry, ICP-MS [inductively coupled plasma-mass spectrometry] or AAS [atomic absorption spectrometry] methods may be used for the analysis of mill scale, but they are generally more time-consuming and laborious techniques than XRF spectrometry techniques. Moessbauer spectroscopy is a useful technique for the identification and quantification of iron-bearing phases [FeO, Fe₃O₄, Fe₂O₃, Fe₃C, metallic iron, calcium ferrites, FeSiO₄ etc.] in mill scale products, however, the technique is not commonly applied in industry since the instrumentation required is specialised and generally only available in research institutions. The technique is less useful than XRD since it does not provide information on non-ferrous phases such as silicates and aluminosilicates.

In summary:

- **Member registrants will need to enter their own chemical analysis data into their dossiers in order to demonstrate that they meet the analytical sameness criteria - such analysis is recommended to be carried out in accordance with this document, XRF spectrometry being the preferred method;**
Member registrants will need to provide their own XRD analysis
- **Those with mill scale derived from stainless steel production should in addition carry out a leaching test - recommended method per Appendix 1.**
- **The Lead Registrant will provide its XRD and transformation dissolution data to member registrants.**

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APPENDIX 1: LEACHING TEST PROCEDURE¹

1. INTRODUCTION

The EU REACH Regulations (Registration, Evaluation, Authorisation, and Restriction of Chemical) entered into force on the 1st June 2007. REACH [1] places an onus on industry to manage the risks from chemicals and to provide guidance on their safe use. Accordingly, manufacturers and importers of chemicals are required to gather information on the properties of chemical substances that will afford their safe use, and to register the information in a central database operated by the European Chemicals Agency (ECHA) in Helsinki. The information required for the dossiers on the properties of the substances includes physicochemical data for the substances that are registered. The list of physicochemical properties that must be considered is quite extensive and includes melting point, boiling point, vapour pressure, aqueous solubility, flammability, explosive properties etc. For pure chemical substances the relevant data are generally available from standard reference sources, but for more complex substances, such as iron sinter, these data are not readily available. One of these properties for which data are not readily available for iron sinter is its aqueous solubility.

Solubility is an important determinant in metal toxicology [2]; the greater the solubility, the greater the bioavailability. A readily soluble substance increases the risk of leachate entering natural water systems therefore potentially polluting and hazards to aquatic life.

This report details an investigation into the aqueous solubility of iron sinter. Chemical equilibrium modelling performed by Professors Peter Campbell (University of Quebec) and Ronny Blust (University of Antwerp) has demonstrated iron to be highly insoluble at pH 6 and above via the determination of iron's limit of solubility (decreasing solubility with increasing pH) [3]. Sequential extraction methodology has previously been applied to a Corus sinter product by K. Jackson [4] for the investigation of multi-element fractionation within steelmaking raw material samples. Results demonstrated that only a few elements (calcium, barium, potassium, zinc, magnesium and manganese) were susceptible to extraction using a mild acid (0.11 M acetic acid), remaining elements were held with greater affinity to the sample matrix and were only removed using harsh acidic conditions.

The results of this study are to be used with estimated solubility results based on thermodynamic modelling to demonstrate a lack of aqueous solubility of iron sinter and therefore conclude there to be minimal risk to both human health and the environment.

2. MATERIALS AND METHODS

2.1 Samples

The aqueous solubility of three Corus sinter products was investigated. Sinter was collected from three Corus Sinter Plants in 2009; Port Talbot (09/L/Z/0820), Scunthorpe (09/L/Z/0549), and Redcar Sinter Plants (09/L/Z/0914). Samples were ball-milled, homogenised, and stored in light-sensitive containers prior to analysis.

2.2 Aqueous extraction procedure

Samples were extracted in accordance with method ENV PES 104, accredited to UKAS 17025. For each sinter product, approximately 1 g of sample was weighed (Sartorius LA1200S) directly into a

¹ Extracted from a Corus paper entitled Investigation of the Aqueous Solubility of Iron Sinter, Jackson et al [2010, Corus R, D & T Report No. 150388]

50ml polypropylene sample tube to which 30 ml of high purity water (Millipore AplhaQ 18.2 MΩ.cm) was added. The samples were sonicated in an ultrasonic bath (Branson 5510) at 70°C for 6 hours. Following sonication, samples were allowed to cool to room temperature and diluted to 50 ml with high purity water.

2.3 Sample preparation

Extracted samples were shaken vigorously for several minutes and filtered through 25 mm diameter, 0.45 µm pore sized syringe filters. Prior to filtration, syringes were washed with their respective sample. The filtered samples were then introduced directly into the inductively coupled plasma mass spectrometer for simultaneous multi-elemental quantification.

2.4 Inductively coupled plasma mass spectrometry (ICP-MS) analysis

Filtered iron sinter extract samples were analysed by inductively coupled plasma mass spectrometry (ICP-MS). Prior to analysis, the ICP-MS was tuned giving satisfactory precision and sensitivity, also ensuring that interfering species were minimal across a wide isotopic mass range. Isotopic masses of interest were quantified using both no-gas mode and helium mode. The ICP-MS (Agilent 7500ce) was calibrated using matrix matched calibration standards (0, 10, 50, 100, 200 and 500 µg/l) prepared from a 10 mg/L multi-element stock solution obtained from Ultra Scientific. An external QC (50 µg/l) sample was analysed for the clarification of satisfactory instrumental calibration and performance during analysis. Regular blank samples were analysed to ensure there was no element carryover between samples.