

IUCLID 5 COMPOSITION AND ANALYSIS GUIDANCE DOCUMENT:

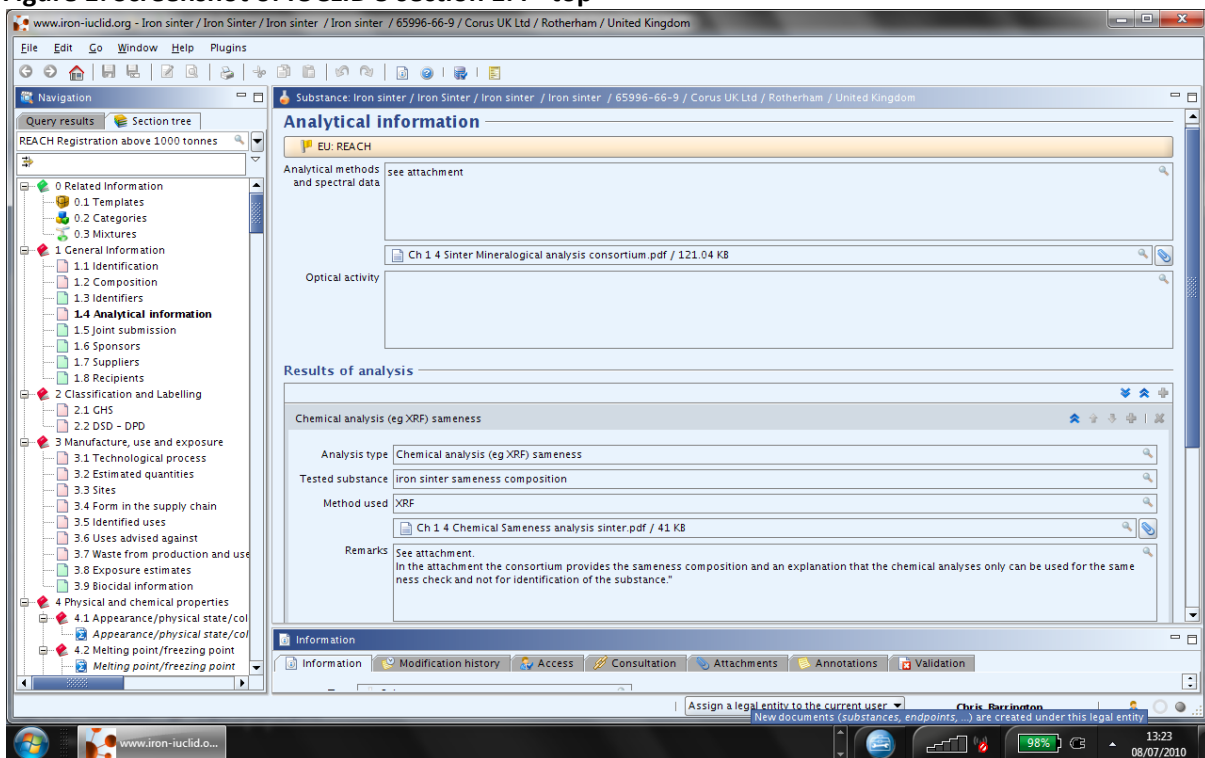
IRON SINTER [EINECS NUMBER 265-997-9, CAS NUMBER 65996-66-9]

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 iron sinter 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

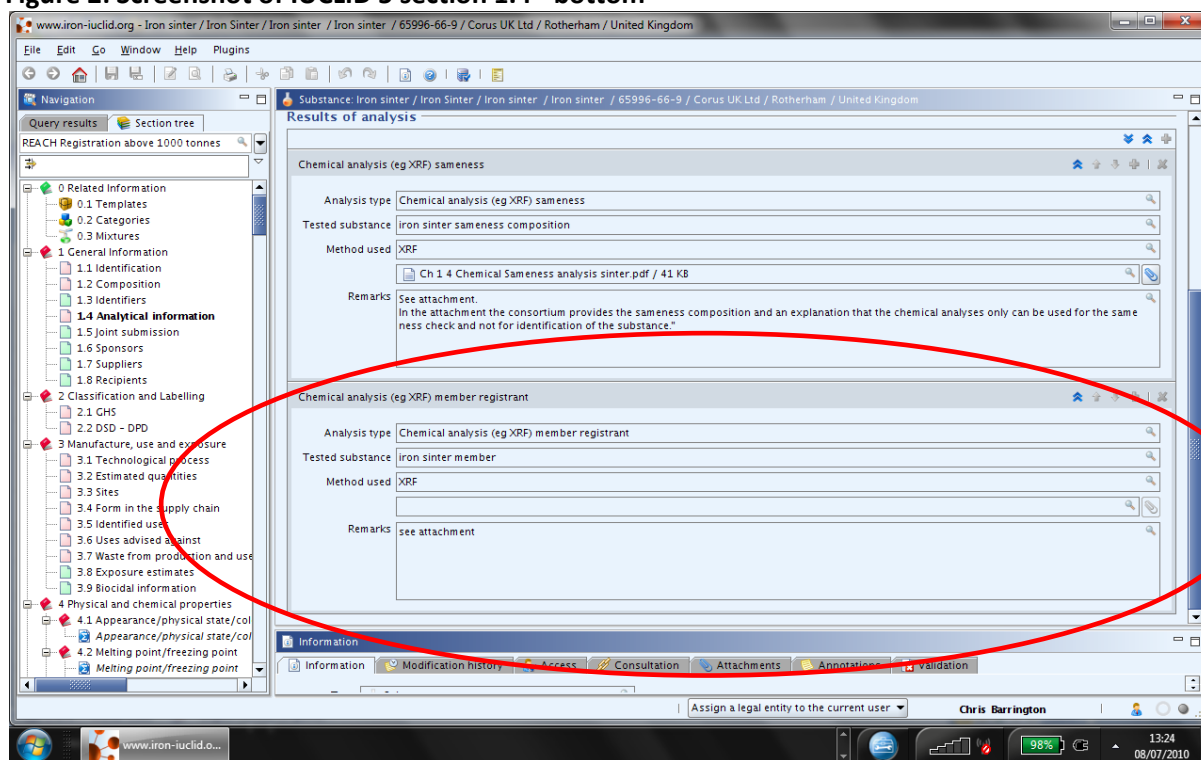


The screenshot displays the IUCLID 5 web application interface. On the left is a navigation tree with sections 0 through 4. The main content area is titled 'Analytical information' and contains a section for 'EU: REACH' with 'Analytical methods and spectral data' and 'Optical activity' fields. Below this is the 'Results of analysis' section, which includes a table for 'Chemical analysis (eg XRF) sameness'. The table contains the following data:

Analysis type	Tested substance	Method used	Remarks
Chemical analysis (eg XRF) sameness	Iron sinter sameness composition	XRF	See attachment. In the attachment the consortium provides the sameness composition and an explanation that the chemical analyses only can be used for the sameness check and not for identification of the substance.

The bottom of the interface features a toolbar with buttons for 'Information', 'Modification history', 'Access', 'Consultation', 'Attachments', 'Annotations', and 'Validation'. The system tray at the bottom right shows the date as 08/07/2010 and the time as 13:23.

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 iron sinter;
- Particle size sameness criteria for iron sinter;
- X-ray diffraction data to demonstrate the typical mineralogical phases present in iron sinter.

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

SAMENESS

Iron sinter is the thermally agglomerated substance formed by heating a variable mixture of iron ores, finely divided coke, limestone, blast furnace dust, steelmaking dust, mill scale and other miscellaneous iron-bearing materials in the temperature range 1315 to 1480°C. The product iron sinter is used exclusively as a burden material in the production of iron in the blast furnace. The

identity of iron sinter is summarised in Table 1. The typical [sameness] specification for Iron Sinter is given in Table 2.

Table 1: Identity of Iron Sinter

Chemical name	Iron, sinter
IUPAC name	
Other names (usual name, trade name, abbreviation)	Iron sinter
EINECS No.	265-997-9
CAS name and CAS No.	65996-66-9
Other identity code: Related CAS No.	Hematite (Fe ₂ O ₃) 1317-60-8
Molecular formula	Fe ₂ O ₃
Structural information (Crystal lattice)	
Minerals of identical or similar composition	Hematite
MW (g/mole)	159.69

Table 2: Sameness Specification for Iron Sinter

Constituent	Typical range, % m/m
Fe ₂ O ₃	>55
FeO	<23
SiO ₂	3-11
Al ₂ O ₃	<3
CaO	4-20
MgO	<4.5
Other elements [Zn, Ti, K, Cr, Mn, S]	<5
Free moisture content	≤ 6
Grain size distribution	
-8 mm	≥16%
-10 mm	≥26%
-20 mm	≥60%
-30 mm	≥75%
-50 mm	≥90%
-70 mm	≥99%
overall	≥ 85% in the range 5-70 mm

It is conventional to represent the bulk composition of complex oxide materials, such as iron sinter, iron ore pellets, 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 iron sinter indicates that it contains silica [SiO₂] and lime [CaO], this does not mean that silica is actually present in free crystalline form, such as quartz or cristobalite, nor does the calcium oxide exist as free lime. In addition, the reference to 'FeO' in Table 2 should not be taken as the concentration of the wüstite phase [FeO] in iron sinter since the analysis given for 'FeO' is a measure of the amount of iron (II) present in sinter, most of which is present in the form of iron (II,III) oxide or magnetite, Fe₃O₄. Similarly, 'Fe₂O₃' represents the total iron content expressed as Fe₂O₃, not the actual Fe₂O₃ concentration.

ANALYSIS TECHNIQUES

The bulk chemical compositional analysis of iron sinter 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 sinter 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. In either instance 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 sinter 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.

There are no existing EN standards for the multi-element analysis of iron sinter by XRF spectrometry or determination of FeO by redox titrimetry, but laboratories undertaking such analyses should hold accreditation to ISO 17025 or ISO 9001.

Multi-element analysis of iron sinter 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 sinter mineralogy. Quantitative phase analysis of all the major chemical phases present in iron sinter can be achieved only by means of X-ray diffraction [XRD] analysis combined with Rietveld data analysis.

Table 3: Mineralogical phases present in Iron Sinter

Phase name	Assumed chemistry for XRD refinement	Density (g/cm ³)	Comments / references
Hematite	Fe ₂ O ₃	5.3	Webmineral: http://www.webmineral.com/data/Hematite.shtml
Magnetite	Fe ₃ O ₄	5.2	Webmineral: http://webmineral.com/data/Magnetite.shtml
Ca-Magnetite	Fe _{1.7} Ca _{0.3} FeO ₄	5.1	Calculated; used in Rietveld refinement
Wuestite	FeO	5.88	specific gravity. 5.7 g/cm ³ is bulk density; http://euromin.w3sites.net/mineraux/WUSTITE.html
SFCA I	Ca _{7.12} Fe _{0.88} (2+) Fe _{23.82} (3+) Al _{8.18} O ₅₆	4.16	Arakcheeva, A.V., Karpinskii, O.G., Lyadova, V.Ya., Kristallografiya, volume 36, page 603 (1991)
SFCA II	Ca _{2.8} Fe _{8.7} Al _{1.2} Si _{0.8} O ₂₀	4.13	Hamilton, J.D.G., Hoskins, B.F., Mumme, W.G., Borbidge, W.E., Montague, M.A., neues Jahrbuch fuer Mineralogie. Abhandlungen (Band-Nr) (1950-), vol 161, p1-26 (1989)
CF2 mkl	Ca _{3.6} Fe _{14.4} O _{25.2}	4.57	Millon, E., Malaman, B., Bonazebi, A., Brice, J.F., Gerardin, R., Evrard, O., Mater. Res. Bull., volume 21, pages 985-994 (1986)
CF2 hex	Ca _{2.00} Fe _{15.57} O _{25.56}	4.63	Arakcheeva, A.V., Karpinskii, O.G., Doklady Akademii Nauk SSSR, vol 273, p1127-1129 (1983)
CF	CaFe ₂ O ₄	4.85	Apostolov, A., Bassi, G., Godishnik na Sofiiskiya Universiteit, Fizicheski Fakultet, vol 63, p177-187 (1971)
CWF	CaFe ₃ O ₅	4.94	Evrard, O., Malaman, B., Jeannot, F., Courtois, A., Alebouyeh, H., Gerardin, R., J Solid State Chem., volume 35, page 112 (1980)
C2W4F9	Ca ₂ Fe ₂₂ O ₃₃	4.67	Arakcheeva, A.V., Karpinskii, O.G., Kristallografiya, vol 35(N), p1105-1109 (1990)
C2F	Ca ₂ Fe _{1.4} Mg _{0.3} Si _{0.3} O ₅	4.051	Colville, A.A., Acta Crystallogr., Sec. B, volume 26, page 1469 (1970)
Larnite	Ca ₂ SiO ₄	3.28	Webmineral: http://webmineral.com/data/Larnite.shtml
Forsterite	Mg ₂ SiO ₄	3.21-3.33, average 3.27	Webmineral: http://webmineral.com/data/Forsterite.shtml
Metallic Iron	Fe	7.874	
Lime	CaO	3.345	Webmineral: http://webmineral.com/data/Lime.shtml

Mineralogically iron sinter comprises, essentially, relict [original surviving] particles of iron ore, silicate and former carbonate, bound within a matrix of secondary phases formed only during sintering. This secondary matrix between relict particles comprises a mixture of iron oxides, diverse calcium ferrites, calcium silicate and less abundant minor crystalline silicate phases and silicate glass. On rare occasions traces of metallic iron are observed, as are unburned coke particles and diverse revert materials. The calcium ferrite types consistently identified in XRD patterns and verified by microscopy and EDS [energy-dispersive X-ray spectrometry] microanalysis are listed in Table 3 above.

The principal variation in sinter mineralogy is in the relative proportion of iron oxides [sum total of hematite, magnetite and Ca-magnetite] and calcium ferrites, while only relatively subtle variations

are seen in the fraction of calcium and magnesium silicates. Although the phase proportions observed may vary from one sinter plant to another, dependent upon the sinter mix composition and the sinter strand operating conditions, iron sinter is rather consistent in terms of its constituent phase assemblage - i.e. the same collection of phases are generally present, and only extremely minor phases appear or disappear altogether one from sample to another.

Other techniques

As mentioned above, the principal methods of analysis used for characterisation of iron sinter are XRF spectrometry for bulk analysis, and XRD for phase analysis. Since iron sinter is an inorganic material, analytical techniques such as nuclear magnetic resonance (NMR) spectroscopy, infra-red spectrometry [IR] and ultra-violet absorption spectro-photometry [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 $\sim 320^{\circ}\text{C}$. 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 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 iron sinter, but these techniques are generally more time-consuming and laborious than XRF spectrometry. Moessbauer spectroscopy is a useful technique for the identification and quantification of iron-bearing phases [FeO, Fe₃O₄, Fe₂O₃, Fe₃C, calcium ferrites, FeSiO₄ etc.] in iron sinter 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.

As far as particle size distribution is concerned, this should be verified by means of a sieve test in compliance with an internationally accepted standard [ISO, ASTM, etc.]. For the purposes of sameness, despite the detailed particle size distribution in the sameness specification, if the substance complies with the "overall" particle size distribution of $\geq 85\%$ in the range 5 -70 mm, then sameness can be considered to have been demonstrated.

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;
- Particle size distribution analysis should be carried out using a method that complies with the relevant standard [ISO, ASTM, etc.];
- The Lead Registrant will provide its XRD data to member registrants for reference purposes, but member registrants should carry out their own XRD analysis and enter it into their dossiers.

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