

RESPIRABLE CRYSTALLINE SILICA IN IRON ORES

INTRODUCTION

Various emerging international chemical classification and labelling requirements for protection of health and environment require a renewed understanding of the potential hazard associated with ores and concentrates (O&C's), including iron ore. Determining human health and environmental classifications for O&C's using GHS criteria raises unique issues that require special measures for accurate, realistic and consistent classifications.

In the EU a formal review of the classification of bulk iron ores is necessary to comply with EU CLP¹ (which implements GHS) since it requires that substances which meet the criteria for classification as hazardous substances must be notified to the EU classification and labelling inventory within one month of placing on the market from December 1st 2010. It is a legal obligation for each Manufacturer/Importer on the EU market to assess their data, notify if necessary and keep records of the assessment. If a substance is subject to REACH² registration it must be notified even if it is not hazardous.

The REACH Iron Platform includes most of the world's major iron ore producers amongst its membership and the RCS Working Group ("RCSWG") was established to review the hazard assessment for iron ore for the purposes of CLP notification. The group concluded that there were no grounds for notification of any hazards for iron ore, but felt that it would be appropriate to establish a testing programme to ensure that the respirable fraction of crystalline silica ("RCS")³ in bulk iron ores produced in or imported into the EU did not exceed the threshold limit for hazard classification.

CLASSIFICATION OF CRYSTALLINE SILICA

For classification, the EU CLP Article 8.6 specifies that "Tests that are carried out for the purposes of this Regulation shall be carried out on the substance or on the mixture in the form(s) or physical state(s) in which the substance or mixture is placed on the market and in which it can reasonably be expected to be used." In addition, the ECHA Guidance to the CLP Regulation, V 2.0, April 2012 mentions that "for human health, different forms (e.g. particle sizes, coating) or physical states may result in different hazardous properties of a substance or mixture in use" and therefore they may be classified differently. It is therefore justifiable to consider quartz and cristobalite in their respirable form, i.e. RCS.

As indicated above, the key potentially hazardous property of iron ores arises from the presence of crystalline silica. Although there is no harmonised EU classification for this group of substances

¹ European Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of Substances and Mixtures (CLP Regulation), adopting in the EU the Globally Harmonised System (GHS)

² Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

³ The term 'crystalline silica' covers quartz, cristobalite and tridymite.

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under the former European Dangerous Substances Directive, it has been current practice for many years by the industrial minerals producers led by IMA-Europe⁴ to self-classify respirable quartz and respirable cristobalite as Harmful with the label Xn and the risk phrase R48/20⁵. Under the EU CLP the industrial minerals producers led by IMA-Europe now classify respirable quartz and respirable cristobalite as STOT RE 1⁶. The classifications are based on the primary effect of the silicosis hazard and based on evidence that protection against silicosis protects against a carcinogenic affect and better reflect the toxicity in humans. As such, Quartz as respirable fraction (Respirable Crystalline Silica - RCS) has been notified to the EU CLP Inventory as STOT RE 1.

Consequently, mixtures and substances containing RCS, whether in the form of an identified impurity, additive or individual constituent, should be classified (according table 3.9.4, CLP) as:

- STOT RE 1, if the RCS concentration is equal to, or greater than 10%;
- STOT RE 2, if the RCS concentration is between 1 and 10%;
- where the RCS content in mixtures and substances is below 1%, it does not trigger classification.

The Iron Platform decided to follow the IMA-Europe approach for classification under EU CLP and GHS. It has to be noted that a number of organisations regard crystalline silica as a carcinogen, but the most recent IARC⁷ classification recognised that ‘Crystalline silica in the form of quartz or cristobalite dust causes cancer of the lung’ but accepted that effects are no seen in all exposure circumstances. There may be regional specific rules governing the classification of crystalline silica (such as in the US) which are not covered in this document.

DETERMINATION OF LEVEL OF RCS IN IRON ORES

After considerable discussion, both within the RCSWG and with other organisations, it was decided to adopt the Size Weighted potential Respirable Fraction (“SWeRF”) analytical method. The laboratory of RPS Analyse BV at Ulvenhout in the Netherlands was selected to analyse the test samples. This has been adopted by the minerals producers to determine the RCS in bulk materials.

Details of the SWeRF method are given in the document embedded below (an IMA document translating the German language [E DIN 33898](#)).



PQdraft_SWeRF__to
_CEN.pdf

Link to IMA RCS dedicated web page

<http://www.crystallinesilica.eu/rcs-measurement.html#595>

The method is based on a liquid sedimentation where the respirable fraction is separated from the bulk material using Stokes’s law. The sedimentation method is optimised for respirable alpha-quartz particles and the sedimentation parameters for the separated fraction are selected to approach the respirable particle size distribution as defined in EN 481 and ISO 7708. The sedimentation is normally performed in water, however, sodium hexametaphosphate was added to ensure adequate deagglomeration.

After separating the liquid portion with the respirable fraction, a volume of this liquid is evaporated and the residue dried. On this residue, which may also contain any dissolved material, the quartz content is analysed with FT-IR using the KBr disk method against SRM 1878a as reference material. XRD analysis can also be used.

⁴ Industrial Minerals Association

⁵ R48/20 -Danger of serious damage to health by prolonged exposure through inhalation

⁶ Specific Target Organ Systemic Toxicant (Repeated Exposure) Category 1.

⁷ *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans* VOLUME 100.Part C: Arsenic, Metals, Fibres, and Dusts. A Review of Human Carcinogens

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Alpha-Quartz and Cristobalite can be analysed separately. Tridymite is normally absent but, if present, would be measured as alpha-Quartz. The crystalline silica content in the respirable fraction is calculated back to a percentage in the bulk sample. Some iron ore samples were tested for recovery by mixing 4 g of the ore with 1 g of very fine Quartz powder (app. 60% respirable). The recovery of respirable Quartz was >97.5 % for Quartz/iron ore mixtures.

The guidance for preparation of samples for RCS determination was as follows:

“Each member will have to prepare their own representative sample material (based on whatever composite is appropriate for the member concerned, e.g. quarterly, monthly, etc.), meaning that the proportion of -1mm material (or -2 mm material) will have to be measured in order correlate RPS’s results to the whole original sample. In taking and preparing the sample, the provisions of ISO 3082 should be observed and care should be taken to ensure that -1 mm (or -2 mm) particles adhering to lumps or larger fine particles are collected, preferably by wet screening. The sample should be dried before dispatch and the moisture content determined.”

ANALYSIS RESULTS

A total of 29 samples were submitted by Iron Platform members. The RCS in every sample was < 0.1% and the range was <0.0013 - 0.049. This indicates that no sample triggers classification under EU CLP or GHS since back calculation to the bulk product results in much lower levels. For competition law compliance reasons these cannot be identified, but the individual results were as follows (%):

0.0049	<0.0016	0.027	0.049
0.017	<0.030	0.024	<0.037
0.025	<0.039	0.0074	<0.037
<0.0017	<0.0020	<0.0014	<0.0018
<0.0017	<0.0014	<0.0013	<0.0020
<0.0014	<0.0015	<0.0026	<0.0015
<0.0021	<0.0015	<0.0026	<0.0021
<0.0014	<0.0026	<0.0027	<0.0038
<0.0023	<0.0078	<0.0089	<0.0040
<0.0040	<0.0085	<0.0084	<0.0092

Each member should then back calculate the content of RCS in its iron ore product(s) as follows:

$$(\%RCS \text{ in bulk}) = (\%RCS \text{ in } <1\text{mm}) \times (\text{mass } <1\text{mm}) / (\text{mass bulk})$$

CONCLUSION

The above results for the -1 mm fraction < 0.1% for each sample and the range was <0.0013 - 0.049. This indicates that all samples are all well below the classification threshold of 1% RCS and thus justify the no classification CLP notification in the EU for bulk iron ore.

Notwithstanding this, determination of the RCS fraction by sedimentation is a method developed primarily for industrial minerals, notably quartz flour. In the metals sector, quartz can be bound to a large range of minerals, including sulphides and other silicates and it appears to be the case that the SweRF approach should be refined on a case-by-case basis. Work on development of the optimum methodology for RCS determination is therefore ongoing across the metals sector. Against this background, whilst the RCS values for iron ore determined by the Iron Platform are well below the classification threshold, the iron ore industry should monitor developments in other metal sectors and be prepared to adjust its approach in case of need.