

Does the handling of iron sinter present a potential health hazard from the release of respirable crystalline silica?

IP TWG position paper to support the Iron Sinter REACH dossier

1. INTRODUCTION

Sintering is an agglomeration process that is used in the steel industry to prepare fine-grained iron bearing materials for use in the blast furnace. The product sinter is a hard agglomerate that has high physical strength and which affords high permeability for the reducing gases in the furnace shaft and hence improves furnace efficiency. The purpose of this note is to consider the chemistry of the final product with particular respect to the presence of crystalline silica (e.g., quartz), which may potentially present a health hazard owing to the release of respirable particles of crystalline silica into the atmosphere.

2. THE IRON SINTERING PROCESS

In the sintering process blended iron ore fines, fluxes (e.g., limestone and olivine), fuel in the form of coke breeze, and recycled materials such as dusts and grits from upstream processes, are fused together to produce a clinker-like material. The well-mixed blend is laid upon a slowly-moving continuous grate (sinter strand) as a bed, typically 40 - 60 cm deep and 3 - 4 m wide, see Fig. 1. The moving bed is ignited under an ignition hood and the resulting combustion zone is slowly drawn down through the bed by a strong flow of air induced by powerful fans. The heat generated causes partial fusion of the raw materials and flux resulting in the formation of large pieces of sinter product. When the combustion zone has reached the base of the sinter mix the process is complete, and the resulting sinter cake is tipped from the grate and broken up into smaller pieces. Subsequently, the sinter product is cooled, screened and transferred to the blast furnace. Undersize material is recycled to the strand and added to the raw sinter mixture.

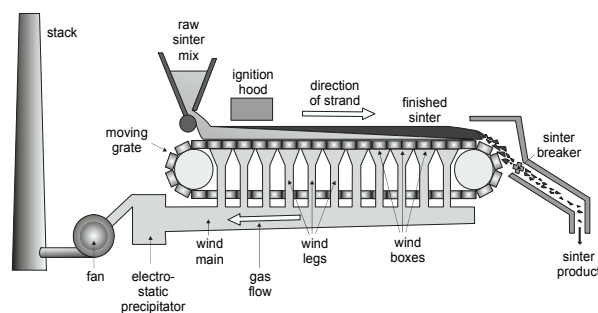


Fig. 1 Schematic of a typical sinter plant

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The composition of the raw sinter mixture is carefully controlled so that the product sinter meets the process requirements of the blast furnace. Among these, the so-called sinter basicity is an important parameter. The sinter basicity is described principally in terms of the lime-to-silica ratio, or as the expanded basicity $(CaO + MgO)/(SiO_2 + Al_2O_3)$. The basicity is adjusted in order to produce the appropriate amount of slag of the required composition for the blast furnace operation. The sinter mix composition is, therefore, controlled very carefully by blending all the raw materials to achieve the required chemistry in the sinter product. While the basicity is essentially controlled by the relative amounts of ores and fluxes used in the blend, the lime, silica, alumina and magnesia contents of the recycled materials are also taken into account. The sinter basicity is dependent upon the blast furnace burden mix but generally ranges between a lime-to-silica ratio of between 0.7 and 2.2.

3. COMPOSITION OF IRON SINTER

Sinter composition is usually expressed in terms of its bulk composition the typical range is shown in Table 1.

Component	% by weight
Total Fe	>38
FeO	<23
SiO ₂	2-11
CaO	4-20
MgO	<5
Al ₂ O ₃	<3
Free moisture	0-6

TABLE 1 SPECIFICATION FOR THE COMPOSITION OF IRON SINTER

It is conventional to represent the bulk composition of oxide materials, such as minerals, ores and refractory products, in terms of the simple oxides of the constituent elements as shown in Table 1. However, this does not imply that the product is composed of such simple compounds it is simply a convenient means of representing the overall composition of the material. Therefore, although the typical analysis shown for iron sinter in Table 1 indicates that it contains 2 to 11% silica this does not mean that the silica is present in the form of crystalline silica. It should also be noted that 'FeO' indicates the amount of Fe(II) present in oxide form but does not imply that this is present in the form of wustite [FeO]. It is more accurately a representation of the amount of iron (II) present in the form of magnetite [Fe₃O₄].

4. CRYSTALLINE FORMS OF SILICA

Silicon dioxide, which is commonly called silica, occurs in 11 crystalline and 2 non-crystalline forms. Of the various polymorphs of silica, quartz is the only stable form under normal ambient conditions (1 atmosphere pressure and 25°C). The other polymorphs are stable under different conditions, mostly at high temperatures and high pressures. The crystal symmetries and equilibrium transformation temperatures of the polymorphs that are stable atmospheric pressure are shown in Fig. 2.

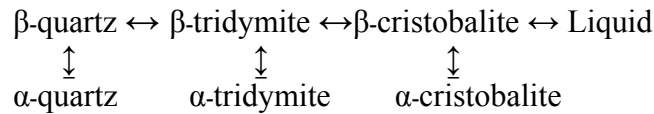


Fig. 2 Inter-relationships between the main crystallographic forms of silica that are stable at atmospheric pressure

The low temperature trigonal α -quartz will transform into hexagonal β -quartz at 573°C, which upon further heating transforms into hexagonal β -tridymite at 870°C, and this polymorph subsequently transforms into β -cristobalite at 1470°C, which finally melts at 1705°C. In metallurgical processes, such as sintering in the steel industry, these are the only relevant polymorphs, since the other polymorphs are only formed at high pressures not found in steelmaking processes.

The interconversion of quartz, tridymite and cristobalite is a complex process and requires the breaking and reforming of Si-O bonds; the activation energies required for these processes are high and consequently they occur only very slowly. Provided the temperature is increased very slowly the whole process is fully reversible, but if the temperature is increased or decreased more rapidly then the thermodynamically stable phase at a given temperature may not have time to form. Thus, β -tridymite and β -cristobalite occur in nature even though only α -quartz is thermodynamically stable at ordinary temperatures. If α -quartz is heated rapidly, it still transforms to beta-quartz but the transformation of beta-quartz into β -tridymite and β -cristobalite is by-passed and the β -quartz melts at the lower temperature of 1550°C. However, the process is not reversible and if the liquid is cooled quickly its liquid structure is preserved resulting in an amorphous silica glass. If the silica glass is subsequently re-heated it transforms to β -cristobalite at $\sim 1000^\circ\text{C}$ and this melts at 1705°C. When the polymorphs β -tridymite and β -cristobalite are cooled rapidly below their respective transition temperatures their crystal structures are preserved but they ultimately transform into the low temperature polymorphs α -tridymite and α -cristobalite at 114 and 270°C, respectively. These transformations, just like that of α -quartz into β -quartz, are fully reversible even at relatively high heating or cooling rates. Thus it may be seen that the transformation of a given α -polymorph into its corresponding beta polymorph takes place reversibly regardless of heating rate. This occurs because related α - and β -polymorphs have similar structures and the transformations do not entail the massive structural changes and high activation energies that are involved in the transformation of quartz into tridymite and tridymite into cristobalite. The sintering process is characterised by a rapidly moving heat zone through the bed of sinter mix so that there is insufficient time in the sintering process for quartz to be transformed sequentially into tridymite and then cristobalite.

5. CONSTITUTION OF IRON SINTER

Sinter product consists essentially of three types of constituent:

- Original mineral components in the raw mix that have remained unchanged in the process.
- Original mineral components that have changed their structure and shape by solid phase recrystallisation.

- Secondary constituents resulting from material that undergoes fusion or melt dissolution during the process. These constituents comprise two groups i.e., constituents that remain mutually dissolved and consolidate as a vitreous (or glassy) phase and those that crystallise from solution.

In addition to the phase transformations that silica can undergo with increasing temperature, it may also react with other constituents of the raw sinter mix, such as limestone or lime, to form silicates such as dicalcium silicate. Silica can also be dissolved by molten phases, such as calcium ferrite, formed in the sintering process. Consequently, any crystalline silica present in the raw materials tends to be assimilated into more complex silicate phases. Published data on sinter mineralogy show quite conclusively that there is little crystalline silica remaining after the sintering process is completed. Extensive work was carried out by the former British Steel's Research Organisation (now Corus UK Ltd) to characterise iron sinter on the basis of its phase analysis. The principal mineral phases present in iron sinter are summarised in Table 2.

Mineral phase	Formula	Typical amount, wt%
Hematite	Fe ₂ O ₃	25-45
Magnetite	Fe ₃ O ₄	12-35
Wustite	FeO	<1
Silicoferrite of calcium and alumina	Ca(FeAl) ₆ O ₁₀ – Ca ₅ Si ₂ (FeAl) ₁₈ O ₃₆	10-40
Calcium diferrite	CaFe ₄ O ₇	0-10
Dicalcium ferrite	Ca ₂ (FeAl) ₂ O ₅	0-5
Dicalcium silicate	Ca ₂ SiO ₄	2-7
Silicate glass	-	2-7

TABLE 2 PRINCIPAL MINERALS IN CORUS IRON SINTER

Other minor phases that may be present include anorthite [CaAl₂Si₂O₈], calcium-magnesium-iron silicates, while other minerals, such as quartz, free lime [CaO], olivine [(MgFe)₂SiO₄] and periclase [MgO] are present only in residual amounts.

The silicate glass and crystalline silicates form a matrix to the main iron-bearing phases, with dicalcium silicate being the most common. Other silicates such as calcium-magnesium-iron silicates, kirschsteinite [CaMgSiO₄], melilite [(CaNa)₂(AlMgFe^{II}){(AlSi)SiO₇}], merwinite [Ca₃MgSi₂O₈] and anorthite occur rarely. Silicate glass, representing the final liquid residuum on cooling, is common as a mesotasis.

The phase analysis of sinter shows that most of the silica is present in complex silicate forms and as a vitreous phase rather than in the form of crystalline silica. Even in instances where crystalline silica is present it is likely to be physically trapped within the bulk of the material rather than freely available at the surface, and hence not readily released into the air.

More recently, phase analyses have been carried out at Corus IJmuiden in support of the REACH programme. The analyses were performed by means of X-ray diffraction with

quantification of the phases by use of Rietveld analysis. The average phase composition results are summarised in Table 3.

Mineral phase	Formula	Amount, wt%
Calcium magnetite	-	25
Magnetite	Fe ₃ O ₄	12
Hematite	Fe ₂ O ₃	11
Wustite	FeO	2
Metallic iron	Fe	0.1
Calcium ferrites (SFCA)	-	44
Larnite	Ca ₂ SiO ₄	5
Iron forsterite	-	0.7
Free lime	CaO	0.5
Crystalline silica	SiO ₂	Not detected

TABLE 3 AVERAGE PHASE ANALYSIS OF IRON SINTER AT CORUS IJMUIDEN SINTER PLANT

As may be seen from Table 3 free crystalline forms of silica were below the limit of detection, which are shown in Table 4.

Crystalline form of silica	Limit of detection, wt%
Quartz	0.2 – 0.3
Tridymite	0.3 – 0.5
Cristobalite	0.3 – 0.4

TABLE 4 LIMITS OF DETECTION FOR THE DETERMINATION OF QUARTZ, TRIDYMITE AND CRISTOBALITE IN IRON SINTER BY X-RAY DIFFRACTION.

The overall limit of detection for the three main forms of crystalline silica can therefore be taken to be 0.5 wt%.

6. POTENTIAL FOR EXPOSURE TO CRYSTALLINE SILICA

The mineralogical studies carried out on iron sinter show that crystalline forms of silica are not present above the limit of detection. However, it is not possible to state that there is no crystalline silica present at all. To assess the potential health hazard from crystalline silica it is necessary to consider the potential for respirable particles to be released into the atmosphere from the handling of the sinter product.

Iron sinter is strong and hard clinker-like material that is not easily abraded or crumbled into a fine powder. For example, preparation of sinter for chemical analysis requires the material to be reduced in particle size to <106 µm and to achieve this the material must first be pulverised in a hammer mill and then ground in a ring-and-puck type grinding mill equipped with silicon carbide parts. Under normal handling conditions, therefore, sinter may be regarded as a material that does not easily release respirable particles of any type into the atmosphere. The potential for exposure to crystalline silica from the handling of iron sinter must be regarded as

insignificant. In the UK and many parts of the EU the general occupational exposure limit (OEL) for respirable dusts is 4 mg/m^3 , while that for respirable crystalline silica is 0.05 mg/m^3 (the strictest OEL in Europe). Thus, if exposure to respirable sinter dust is maintained below 4 mg/m^3 it follows that exposure to respirable crystalline silica would be less than 0.02 mg/m^3 , if crystalline silica were present in the sinter at a concentration of 0.05 wt%. In practice airborne concentration respirable dust concentrations $< 1 \text{ mg/m}^3$ are considered more likely so that respirable crystalline silica concentrations are more likely to be $< 0.005 \text{ mg/m}^3$, and hence exposure to crystalline silica from iron sinter is considered to present a negligible risk to health.

7. CONCLUSIONS

It is conventional to represent the bulk composition of oxide materials, such as minerals, ores and refractory products, in terms of the simple oxides of the constituent elements. This does not imply that the product is composed of such simple compounds it is simply a convenient means of representing the overall composition of the material. Therefore, although the typical analysis shown for iron sinter indicates that it contains 4 to 6.5% silica (SiO_2) this does not mean that the SiO_2 is present in the form of crystalline silica.

Owing to the thermal conditions occurring in the sintering process, any crystalline silica present in the raw materials is converted into complex silicate phases such as calcium and alumina diferrite, dicalcium silicate or a vitreous (glassy) silicate phase in the product sinter. In these silicate phases the silica is locked into a complex oxide matrix with other elements such as iron, calcium and aluminium. Any crystalline forms of silica, such as quartz, tridymite or cristobalite, are present at concentrations below the detection limit of 0.5 wt%.

Iron sinter is strong and hard clinker-like material that is not easily abraded or crumbled into a fine powder. Under normal handling conditions, therefore, sinter may be regarded as a material that does not easily release respirable particles of any type into the atmosphere. The potential for exposure to crystalline silica from the handling of iron sinter must be regarded as insignificant. It is estimated that exposures to respirable crystalline silica from the handling of iron sinter are likely to be $< 0.005 \text{ mg/m}^3$, i.e. one-tenth of the occupational exposure limit of 0.05 mg/m^3 (strictest European limit).

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