Europe 600

XRD applications in iron and steelmaking industry: mill scale and sinter product

Introduction

Steel has been the emblem of modern society's development for more than a century, but at a price for our planet. Despite it is one of the most-recycled material in the world with almost 100% recyclability, its production is still resource-demanding: in order to produce 1.7 billion tonnes worldwide, 2 billion tonnes of iron ore, 1 billion tonnes of metallurgical coal and 575 million tonnes of recycled steel are required[1]. Energy requirements and emissions to the environment are of great concern too. Thus, in last decades increased public awareness and sustainability policies have pushed industry to progressively implement the efficient use of natural resources, the valorization of by-products and the development of advanced technology for increased production yields.

As far as raw materials and processing are concerned, iron ore, coal, limestone and scrap steel are the basic ingredients which are used in different amounts either in the Blast Furnace (BF), followed by the Basic Oxygen Furnace (BOF), or in the Electric Arc Furnace (EAF). Currently, the BF-BOF route accounts for 70% of total produced steel, while the EAF for the remaining 30%.

The BF basically converts the iron oxides to molten "pig iron" (reduction), which is further treated in the BOF to become steel. The efficiency of the process relies on several parameters, among which the size and chemical composition of iron bearing minerals. Usually, the ore excavated at the mine is delivered as three basic products characterized by different sizes: 10-40 mm fraction used as lump ore, intermediate fraction between 150 μm and 8 mm for sinter, and fines below 150 μm, which are either rejected or used to make pellets.[2] Sinter, a major feedstock of blast furnaces, consists in a mixture of iron oxides, limestone or dolomite, olivines and coke breeze, which is heated rapidly to a temperature up to 1300 °C, where partial melting occurs. After slower cooling in air, the resulting composite material, made of iron oxides bonded by a silicon and calcium ferrites matrix, is both porous and physically strong, thus suited for the reduction process in the furnace[3].

Sintering product quality is described by several parameters, which are related to its size, chemical and mineralogical composition: for example, FeO concentration and CaO/SiO_2 ratio (basicity) must be within a

[1] Worldsteel association factsheet and figures, www.worldsteel.org

[2] A. Ghosh and A. Chatterjee, Ironmaking and steelmaking: Theory and Practice, 2008, PHI Learning Private Limited, New Delhi.

[3] Webster et al., Powder Diffr., Vol. 32, No. S2, December 2017

defined range for the BF to operate efficiently[4], i.e. 4%< FeO <11% and basicity about 1.7. Thus, monitoring the mineralogical and chemical composition of the blend raw materials is of paramount importance, taking into account the growing utilization of steel production by-products, among which mill scale.

Mill scale is a by-product of the steel hot rolling process: basically, it is the flaky layer formed on the steel surface, which is later removed in order to further process the sheet metal. Depending on the process and the nature of the product, the weight of scale can vary between 20 and 50 kg/t of the hot rolled product.

The main crystalline phases are metal iron and three iron oxides: hematite (Fe_2O_3), magnetite ($FeO{\cdot}Fe_2O_3$) and wüstite (FeO). The total iron content is usually about 70%, which makes it appealing for direct recycling as a sinter blend component[5]. Nevertheless, the presence of other trace metals and residues of lubricants, oils and greases from the equipment is a nuisance: in particular, zinc and alkali elements cause problems in the furnace, while the oily fraction generates dioxins[6]. Generally, mill scale with a particle size of between 0.5 mm and 5 mm and an oil content < 1.0% is considered returnable via sintering without any pretreatment, which is instead necessary if it is above 3.0%. Particles below 0.1 mm (sludge) cannot be recycled via sintering because of high oil level (5.0–20.0%) and so are normally treated as landfill waste.

X-Ray Diffraction is well suited for the analysis of both iron ore blends and sinter products: in fact, it allows to identify and quantify both the crystalline phases and the amount of amorphous content. Moreover, it can indirectly provide an estimation of FeO and basicity parameters[7], which usually are determined through wet chemistry methods. Certainly, a comprehensive characterization can be carried out only by integration with information from other analytical techniques, such as microscopy, XRF, SEM, EPMA[8].

In this note it will be shown how Europe 600 diffractometer can be used effectively to characterize both a mill scale and a sinter product from a steelmaking company.

Summary

The iron and steelmaking industry effort to both exploit by-products and increase operational efficiency requires a careful characterization of the iron-bearing blends from which the basic metal is extracted. X-Ray diffraction analysis is well suited for mineralogical analysis, quantifying both crystalline and amorphous fractions. Additionally, it provides important quality parameters of sinter products, allowing to optimize furnace operations. In this note the capabilities of Europe 600, configured for iron bearing samples, will be showcased by characterizing a mill scale and sinter product from a steelmaking company.

[4] D. Fernández-González et al., MINERAL PROCESSING AND EXTRACTIVE METALLURGY REVIEW 2017, VOL. 38, NO. 4, 254–264

[5] M I Martín, F A López & J M, Ironmaking & Steelmaking, 39:3, 155-162

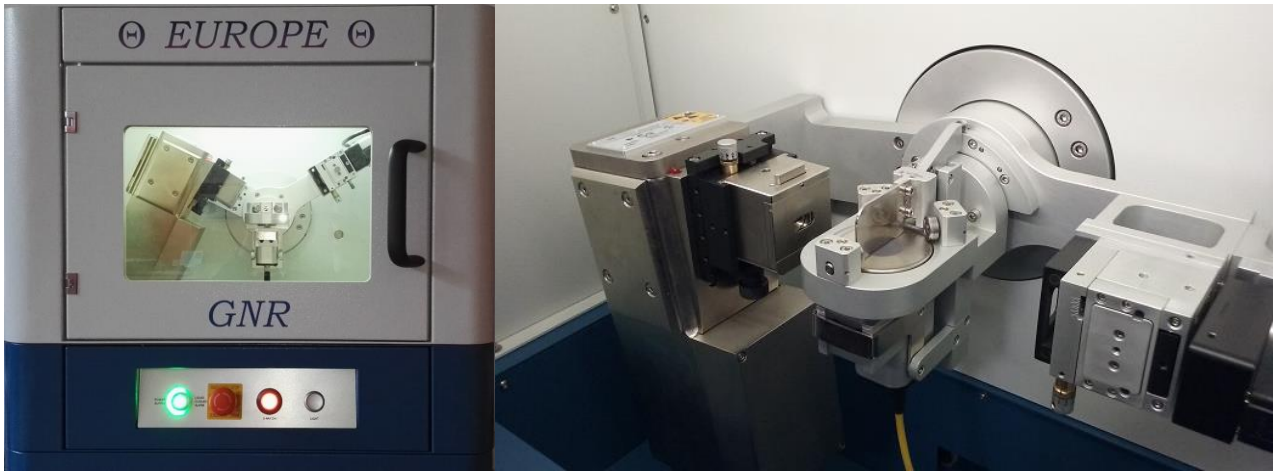
[6] V. Freire de Oliveira, M. Covcevich Bagatini, Journal of Materials Research and Technology, 8, 6, 2019, 5781-5789, https://doi.org/10.1016/j.jmrt.2019.09.047.

[7] König U., Gobbo L., Reiss C. (2012) Quantitative XRD for Ore, Sinter, and Slag Characterization in the Steel Industry. In: Broekmans M. (eds) Proceedings of the 10th International Congress for Applied Mineralogy (ICAM). Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-27682-8_46

[8] T. Honeyands et al., Minerals 2019, 9, 333; doi:10.3390/min9060333

Product Specifications

Europe 600 is a benchtop X-Ray Powder Diffractometer for qualitative and quantitative XRD analysis of polycrystalline materials. It is available in both Theta-2Theta and Theta-Theta configurations.
Its compact size and robust design enable installation and operations in a small space, with low cost of ownership and maintenance.
Thanks to the wide offer of configurations and accessories, such as scintillation counter, secondary monochromator, high-speed detector, spinner, spinning multi-sample holder and variable knife edge, EUROPE is a cost-effective instrument for fast-paced routine industrial quality assurance analysis and for teaching XRD at academic level.



Experimental

Configuration:	Theta-Theta	Sample stage:	Spinner (30 rpm)+ variable knife edge
Goniometer radius [mm]:	160	Anti-scatter slit [mm]:	5.1
X-Ray Source:	Co FF, Line focus	Detector:	MYTHEN 2 R 1D
Power settings[kV, mA]	40, 15	Active area[°]:	2
Filter (source side)	Fe, 0.02 mm	Measurement range 2θ [°]:	10-90
Divergence slit[°]:	0.8	Measurement time [min]:	25
Div. optics soller slit [°]:	2.3		
Div. opt. Anti-scatter slit [°]	1		

In order to reduce the particle size to a value compatible with XRD, as received samples were ground by means of a Retsch MM400 vibratory mixer mill equipped with stainless steel jars and balls.

Ground powder was put into a back loading sample holder and finally mounted on the spinner sample stage of Europe diffractometer. Spinner speed was set to 30 rpm.

The choice of Co anode X-Ray tube was driven by the need of reducing:
-the detrimental X-Ray absorption and fluorescence from large amount of iron in the sample, largely present when traditional Cu X-Ray tube is used;
-the microabsorption issue, related to particle size and large differences in Mass Absorption Coefficient (MAC) among phases[9].

Methods and results

Search & Match procedure was performed using Match! software and PDF-4 database , after background determination, Kα2 removal and peak searching and fitting. Quantitative Rietveld analysis was performed by using PROFEX software[10], where preferred orientation is taken into account through spherical harmonics functions.
The amorphous fraction was estimated by the external standard method[11]: basically, the weight amount (%) of a crystalline phase *i* in a sample is given by

$$w_i = \frac{S_i(ZMV)_i}{K}\mu_s \qquad (1)$$

where S is its Rietveld refinement scale factor, Z the number of its unit formulas per cell, M the unit formula mass, V its cell volume and μ_s the mass attenuation coefficient (MAC) of the whole sample. K is a constant related to the instrumental setup only, which can thus be determined by analyzing a well-known sample, e.g. NIST 640 silicon powder, for which w_i=1 and μ_s= μ_i. Once K is determined and the unknown sample MAC is estimated, e.g. through XRF[12], each identified phase can be quantified by applying equation 1. The difference between unity and the sum of identified phases' weights gives the amount of amorphous and unidentified phases present in the sample. If only the relative amount of phases in the crystalline fraction is of interest, the analysis is simplified by assuming that their sum is equal to 1:

$$\sum_i w_i = \sum_i \frac{S_i(ZMV)_i}{K}\mu_s = 1 \Rightarrow \qquad w_i = \frac{S_i(ZMV)_i}{\sum_j S_j(ZMV)_j} \qquad (2)$$

As regards the sinter quality parameters, FeO content and basicity, they were estimated by performing a molar calculation for the quantified crystalline phases only.

[9] N. Scarlett et al., J. Appl. Cryst. (2002). 35, 383-400
[10] Döbelin, N., Kleeberg, R., Journal of Applied Crystallography 48 (2015), 1573-1580. https://www.profex-xrd.org/
[11] Ian C. Madsen, Nicola V. Y. Scarlett and Arnt Kern, Z. Kristallogr. 226 (2011) 944–955 / DOI 10.1524/zkri.2011.1437
[12] B. H. O'Connor and D. Raven, Powder Diffraction, Vol. 3, No. 1, March 1988

Mill scale sample

The sample was measured after grinding, without any further treatment. It is likely that oil and grease contamination was present. Results are reported in Figure 1 and Table 1: two different non-stoichiometric FeO phases were identified, which account for more than half of the crystalline fraction of the sample.

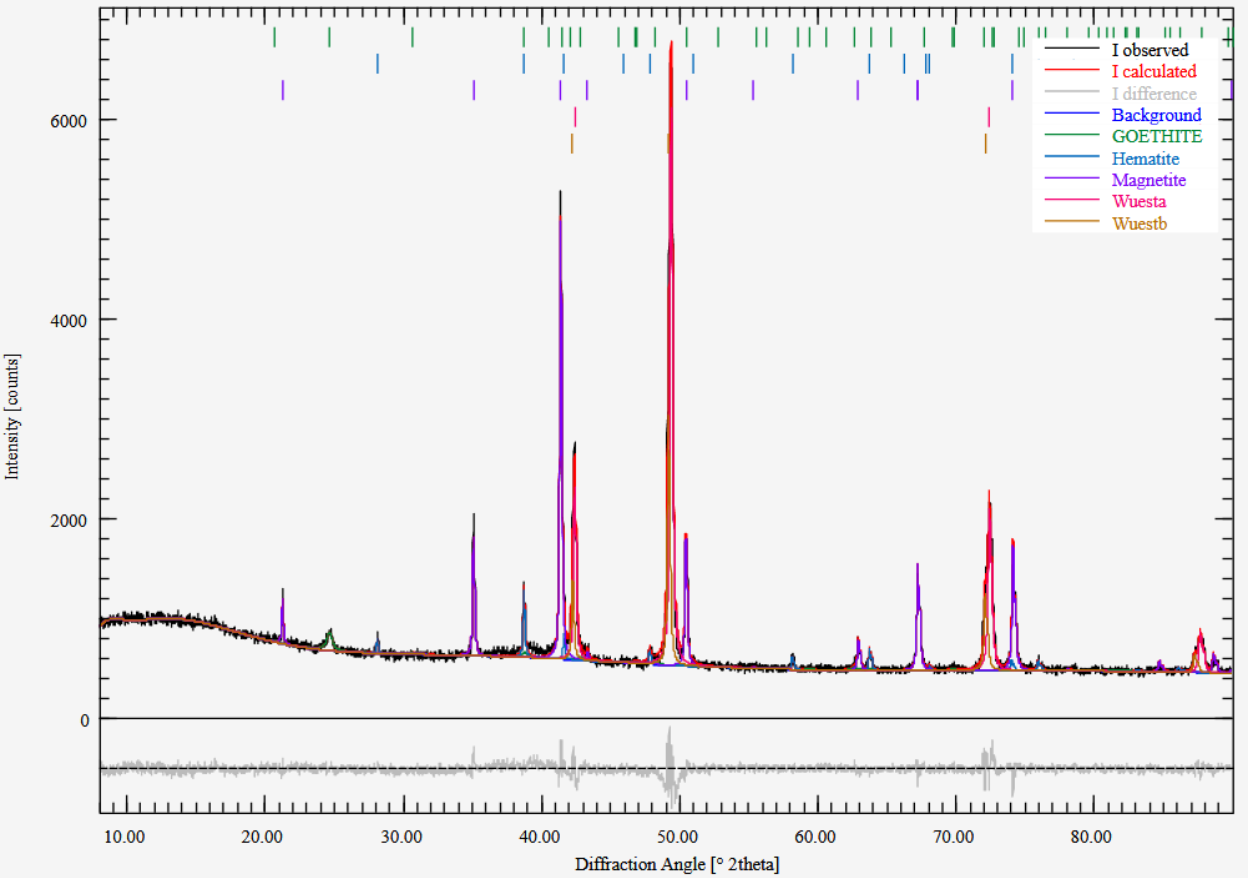


Figure 1. Mill scale diffraction pattern with its Rietveld refinement profile.

Table 1. Identified crystalline phases, weight amount estimation and quality parameters for mill scale.

Phase	Formula	PDF 4 card	weight (%)	
			crystalline fraction	whole sample
Wüstite (a)	$Fe_{0.925}O$	04-008-0276	41.0 ± 0.5	19.5 ± 0.2
Magnetite	Fe_3O_4	04-008-4511	31.5 ± 0.2	15.0 ± 0.2
Wüstite (b)	$Fe_{0.91}O$	04-004-3816	18.0 ± 0.5	8.6 ± 0.2
Hematite	Fe_2O_3	04-015-6947	5.8 ± 0.2	2.8 ± 0.1
Goethite	FeO(OH)	04-015-8332	3.7 ± 0.3	1.7 ± 0.1
Sum			100	47.6
Amorphous and unidentified phases				52.4
Scale quality parameters				
FeO (Fe^{2+})[13]			57.6 (44.8)	27.1 (21)
Total Fe			74	34.8

[13] FeO content for wüstite was determined according to Hazen, R. M., and R. Jeanloz (1984), Wüstite (Fe1-x O): A review of its defect structure and physical properties, Rev. Geophys., 22(1), 37–46,

Sinter sample

The sample was measured after grinding, without any further treatment. Quartz, silicate and carbonate phases could be identified together with iron oxide ones (Figure 2). Quantitative analysis results are reported in Table 2.

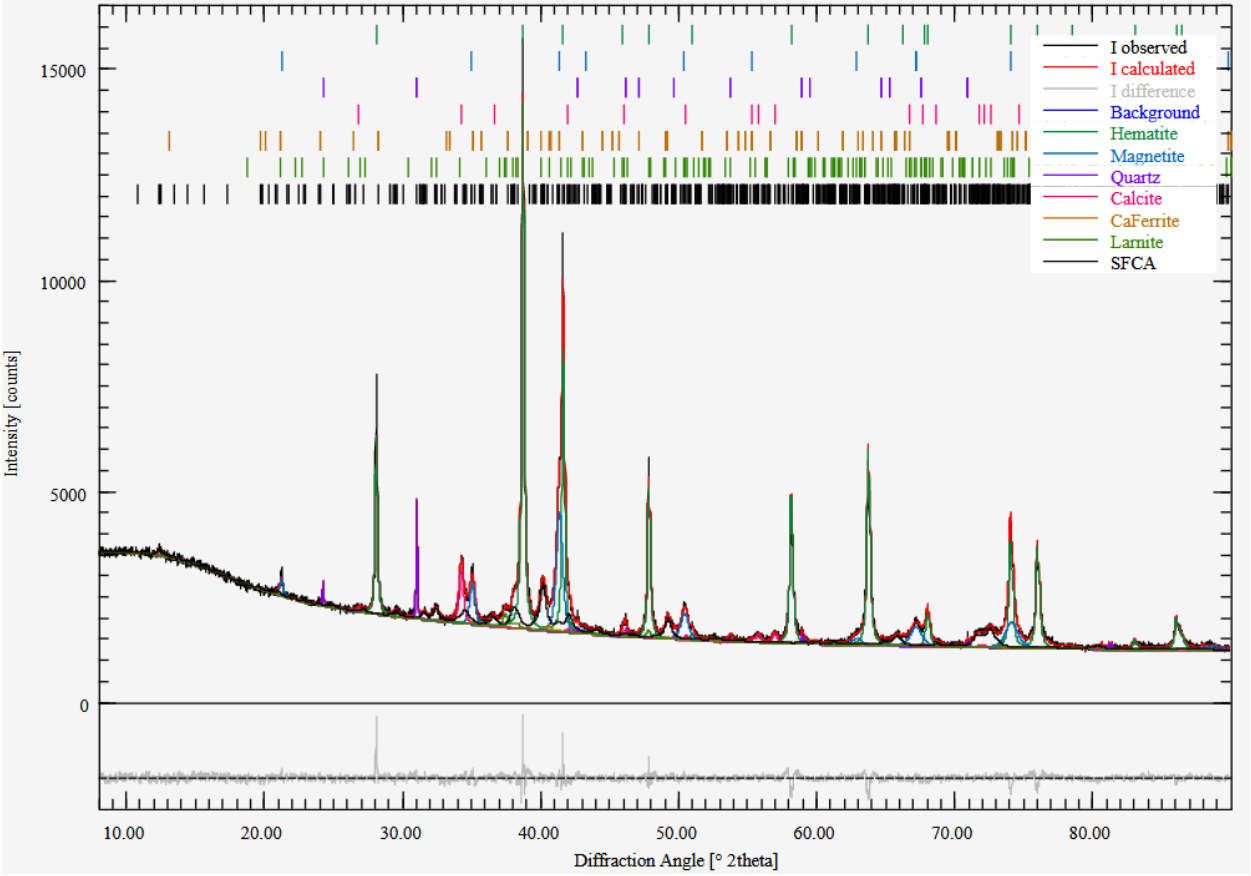


Figure 2. Sinter sample diffraction pattern with its Rietveld refinement profile.

Table 2. Identified crystalline phases, weight amount estimation and quality parameters for sinter.

Phase	Formula	PDF 4 card	weight (%)	
			crystalline fraction	whole sample
Hematite	Fe_2O_3	04-015-9752	53.2± 0.3	33.8 ± 0.2
Magnetite	Fe_3O_4	04-007-1427	15.7 ± 0.2	9.9 ± 0.1
SFCA	$Ca_{2.8}Fe_{8.7}Al_{1.2}Si_{0.8}O_{20}$	01-080-0850	18.8 ± 0.3	12.0 ± 0.2
Quartz	SiO_2	01-086-1560	2.9 ± 0.1	1.8 ± 0.1
CFF	$Ca_2Fe_{15.588}O_{25}$	01-078-1184	1.3 ± 0.2	0.8 ± 0.1
Larnite	$Ca_2(SiO_4)$	04-007-9746	3.1 ± 0.3	2.0 ± 0.2
Calcite	$Ca(CO_3)$	01-083-3288	5.0 ± 0.2	3.2 ± 0.1
Sum			100	63.5
Amorphous and unidentified phases				36.5
Scale quality parameters				
FeO (Fe^{2+})			4.85 (3.77)	3.1 (2.4)
Total Fe			58.8	37.3
Basicity (CaO/SiO_2 ratio)= 1.64				

Conclusions

Europe 600, equipped with Co X-Ray tube, spinner, variable knife edge and linear detector, allowed to effectively collect XRD patterns of mill scale and sinter products coming from steelmaking industry. Both the crystalline and amorphous fractions were quantified by means of Rietveld refinement coupled with the external standard method. Moreover, sinter quality parameters, such as FeO and basicity, were estimated through a molar calculation.

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About GNR SRL

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