FROM IRON ORE TO IRON SINTER – PROCESS CONTROL USING X-RAY DIFFRACTION (XRD)*

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Abstract

Traditionally quality control of iron ore sinter, its raw materials and raw mixtures has relied on time-consuming wet chemistry. The mineralogical composition that defines the properties is often not monitored. XRD analysis in combination with Rietveld quantification and statistical data evaluation using **P**artial **L**east-**S**quare **R**egression (PLSR) has been successfully established to determine the mineralogical composition and process parameters such as the FeO (Fe^{2+}) content and basicity of iron sinter within an analysis time of less than 8 minutes per sample. Both methods take the full XRD pattern into account and can be simultaneously applied on the same measurement. In addition the Rietveld method was used to quantify the phase content of raw mixtures to monitor the composition of blending beds.

Keywords: Iron sinter; X-ray diffraction; Ironmaking agglomeration.

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1 INTRODUCTION

Iron ore sinter materials are an important feedstock material for the steel industry. Since fines cannot be used in conventional blast furnaces because they impair the upward gas flow, they are agglomerated in sinter plants, Gosh & Chatterjee [1].
Most steel plants use coal and iron ores from diverse sites as the major raw material for the sintering process. Both the raw mixtures as well as the sinter material should be controlled carefully to obtain the optimal composition that would lead to a good quality of iron in a blast furnace.
Although FeO in sinter ores is one of the major constituents in making iron and steel, there have been little attempts for the prediction of FeO content in sinter ores using XRD, which has several advantages over conventional analysis methods.
The composition of iron ore sinter according to Patrick & Lovel [2] and Van den Berg [3] includes as main phases hematite (Fe_2O_3), magnetite (Fe_3O_4), ferrites (mostly Silico Ferrite of Calcium and Aluminium, SFCA), a glass phase and dicalcium silicates (C_2S, larnite). Main sources of FeO in iron ore sinter is magnetite. Minor amounts are also present within the SFCA phases.
According to Kwang-Su et al. [4] two different methods are used to determine the amount of FeO in iron ore sinter: a wet-chemical method based on the redox reaction between Fe^{2+} and standard potassium dichromate and an instrumental method based on the magnetic field permeability of Fe^{2+} in sinter ores. The wet-chemical method is accurate but time-consuming (a typical analysis takes 4 hours) and uses chemicals which may have hazardous effects on operators and environment. The instrumental method is rapid and environmentally friendly, but not as accurate as wet chemistry. A rapid, simple, yet accurate determination of FeO content in sinter ores is essential to provide appropriate materials in making iron and steel.
This paper presents how X-ray diffraction data obtained from samples taken at blending beds and the sinter process allow a fast and reliable and environmentally friendly determination of the mineralogical phase composition, the FeO content and basicity without wet chemistry involved.

2 MATERIAL AND METHODS

X-ray powder diffraction (XRD) is a versatile, non-destructive analytical method for identification and quantitative determination of crystalline phases present in powdered and bulk samples. For the studies presented in this paper, a PANalytical *CubiX^3 Iron* industrial diffractometer with a Co anode, incident iron filter and high-speed *X'Celerator* detector was used, featuring measurement times of less than 8 minutes per scan.
Data evaluation was done using the software package HighScore Plus version 4.1, Degen et al. [5]. Two different quantification methods were trialled, Partial Least-Squares Regression (PLSR) and the Rietveld method Rietveld [6].
Modern quantification analysis techniques such as Rietveld analysis are attractive alternatives to classical peak intensity or area based methods since they do not require any standards or monitors the method offers impressive accuracy and speed of analysis.
PLSR is a popular data-mining method with many diverse applications, for example in spectroscopic methods (NIR, FTIR, and NMR). As added in version 4.1 of HighScore, PLSR can be used as a soft-modeling tool to discover and to predict “hidden” correlations directly from the XRD raw scans.

To guarantee a reproducible and constant sample preparation for the XRD measurements, the samples were prepared using automatic sample preparation equipment. All powder samples were milled for 30 seconds and pressed 30 seconds with 10 tons load into steel ring sample holders.

The FeO content of the sinter samples was determined by a wet-chemical procedure in which a portion of ground sinter was dissolved in hydrochloric acid in non-oxidising conditions and the resulting Fe^{2+} in solution was determined by redox titration.

3 RESULTS AND DISCUSSION

3.1 Determination of the Mineralogy of Raw Mixtures in Blending Beds

Producing a target quality iron sinter requires accurate charging of the raw materials (ores, coal, additives, etc.). To modify the raw mix recipe at the blending beds, the coke addition, sinter basicity, raw material analysis and their influence on sinter parameters must be taken into consideration.

The purpose of the analysis of the mineralogical composition of the raw mix is to establish a raw mix composition that achieves the assigned target values for coke addition, sinter basicity, FeO, Fe_{tot}, SiO_2 etc.

About 20 kg of sample material from 6 different blending beds were split, ground and pressed into 55 mm steel ring sample holders. Aim of this study was to proof the fast and accurate analysis of the mineralogy of raw mixtures that are fed into a sinter plant. Future process control will require multiple samples per sampling point in order to overcome the inhomogenity of the blending beds.

Figure 1 shows the Rietveld quantification of one raw mixture. Seven different phases could be identified and subsequently quantified. Main phase is hematite besides reasonable amounts of the iron phases goethite and magnetite.

Calcite as additive can be quantified besides the impurities quartz, forsterite and wuestite.

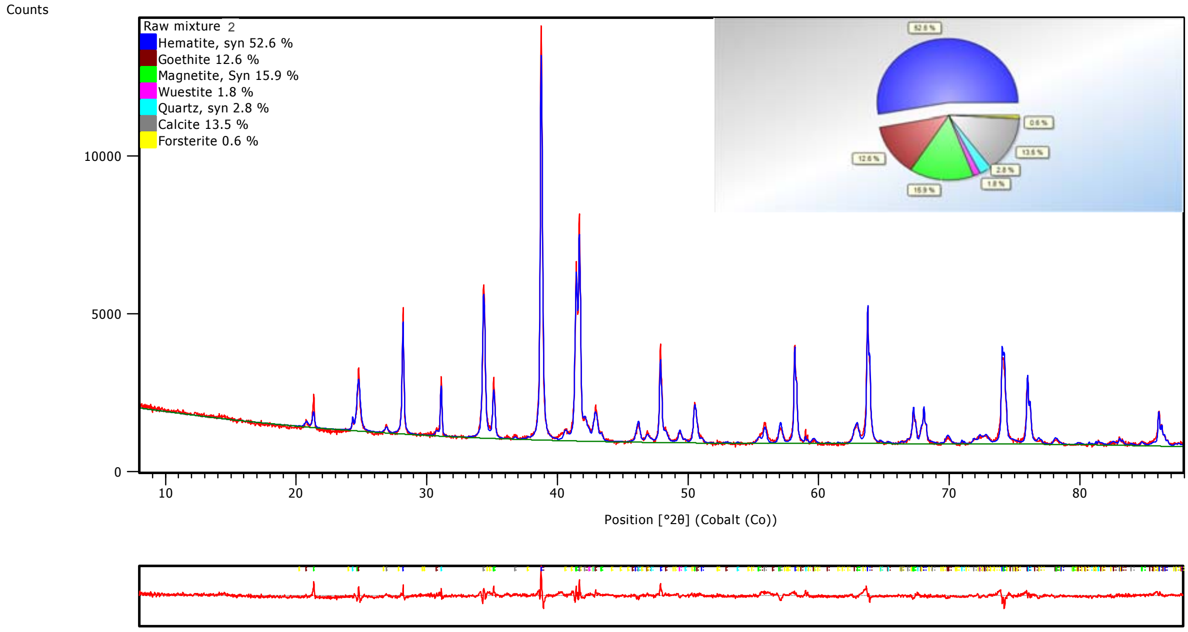

Figure 1. Quantification of an iron sinter raw mixture using the Rietveld method.

Fast and frequent analysis allows a continuous monitoring of the blending beds before the raw mixtures are sintered. Deviations from optimal process conditions can be detected early. Counter actions can be applied in time to correct the process conditions at an early stage. Figure 2 and table 1 give an overview about the different composition of six samples, representing different blending beds. Differences in the flux (limestone) to ore ratio can be clearly monitored.

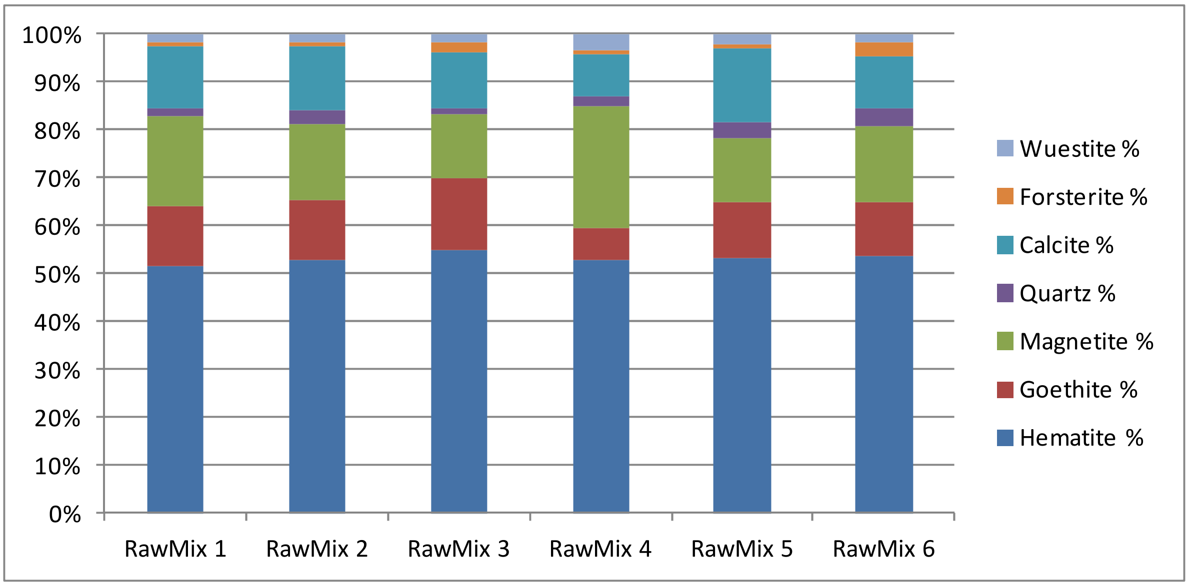

Figure 2. Comparison of the mineralogy of 6 different iron sinter raw mixtures.

Table 1. Comparison of the phase quantities of 6 different iron sinter raw mixtures

Sample ID	Hematite %	Goethite %	Magnetite %	Quartz %	Calcite %	Forsterite %	Wuestite %	RProfile
RawMix 1	51.7	12.3	18.8	1.8	12.8	0.9	1.7	3.5
RawMix 2	52.6	12.6	16.0	2.9	13.5	0.7	1.8	3.8
RawMix 3	54.8	15.1	13.3	1.4	11.8	1.9	1.8	4.2
RawMix 4	52.9	6.5	25.5	2.3	8.7	0.7	3.5	5.0
RawMix 5	53.2	11.8	13.5	3.1	15.4	0.9	2.2	3.9
RawMix 6	53.6	11.2	15.8	3.8	11.0	2.8	1.7	4.0

3.2 Determination of FeO and Basicity in Iron Sinter

The analysis of the FeO content and the basicity of 48 iron sinter samples was trialed with PLSR as well as the Rietveld method. The results were compared with the contents obtained by wet chemistry.

3.2.1 Rietveld Method

Since the amount of ***FeO*** in the samples cannot directly be analyzed with the Rietveld method, a back calculation from the mineralogical phase content was applied. Prior to these calculations, ***all crystalline phases*** present were identified and quantified. In addition the amorphous content of the samples was determined.
Main components present in the analyzed sinter samples are hematite ($Fe_2^{3+}O_3$), magnetite ($Fe_2^{3+}Fe^{2+}O_4$), larnite (Ca_2SiO_4, also known as belite or C_2S), silico ferrites of calcium and aluminium SFCA and SFCA-I, according to Hamilton [7] and Mumme [8].
Figure 3 illustrates an example for a full pattern Rietveld refinement of one sinter sample in the measured range from 10 to 88 ˚2θ. Measured and calculated patterns

are shown as well as the difference plot between both. Agreement indices of $R_{wp} < 2.6$ were found. Besides the crystalline phases the amorphous content was determined using the external standard approach, O'Connor et al [9].

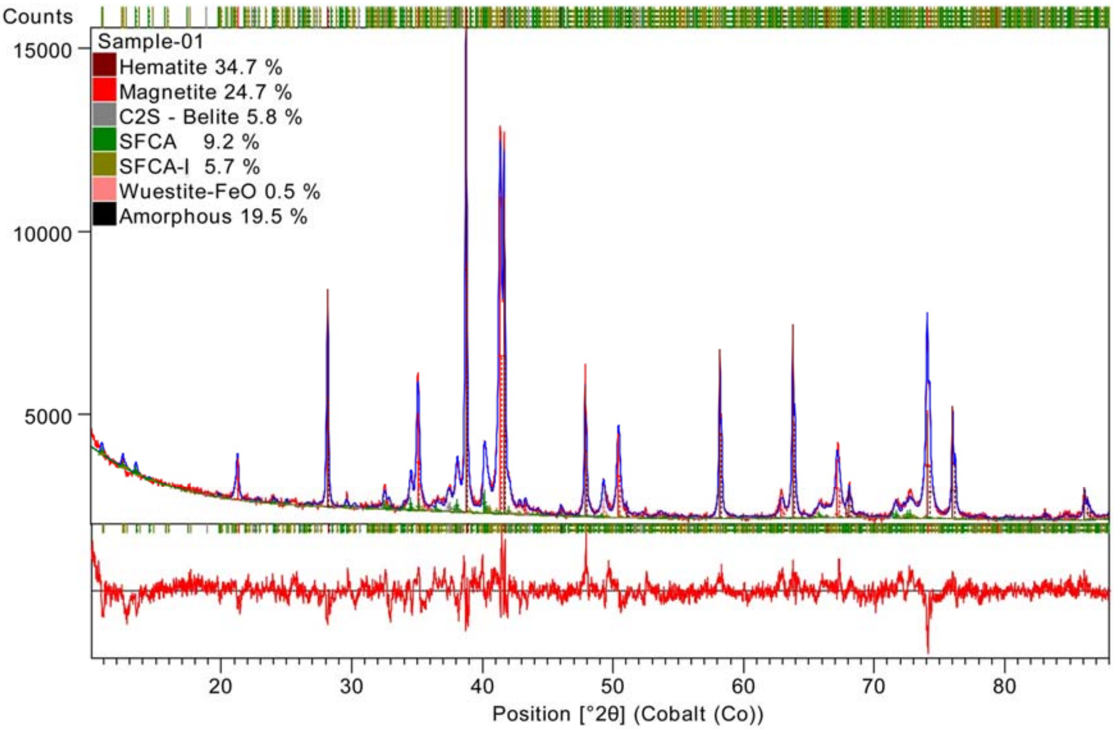

Figure 3. Example of a Rietveld quantification of one iron sinter sample. Measured scan, calculated pattern, difference plot and quantitative phase composition

Advantage of the Rietveld analysis is the simultaneous quantification of all mineral phases. This valuable information can be used in addition to other process-relevant parameters to optimize the quality of the sinter and the sintering conditions.

The ratio of the iron-containing phases in the samples can be used to optimize the reducibility of the material. The SFCA phases and the C_2S (larnite) content are indicators for the sinter strength since the SFCA phases act as a glue in the sinter whereas C_2S causes cracking of the material due to hydration and volume increase. By monitoring these phases the reduced fines rate can be optimized and subsequently the efficiency improved and energy can be saved.

Based on the Rietveld results of all samples the FeO contents were calculated and compared with the results from wet chemistry, figure 4. Generally the match of the results demonstrate that the Rietveld method can be used to determine not only the phase composition of iron sinter but also the FeO content. The information gained with this method gives the possibility to monitor the sinter process more frequently and increase the efficiency by saving energy.

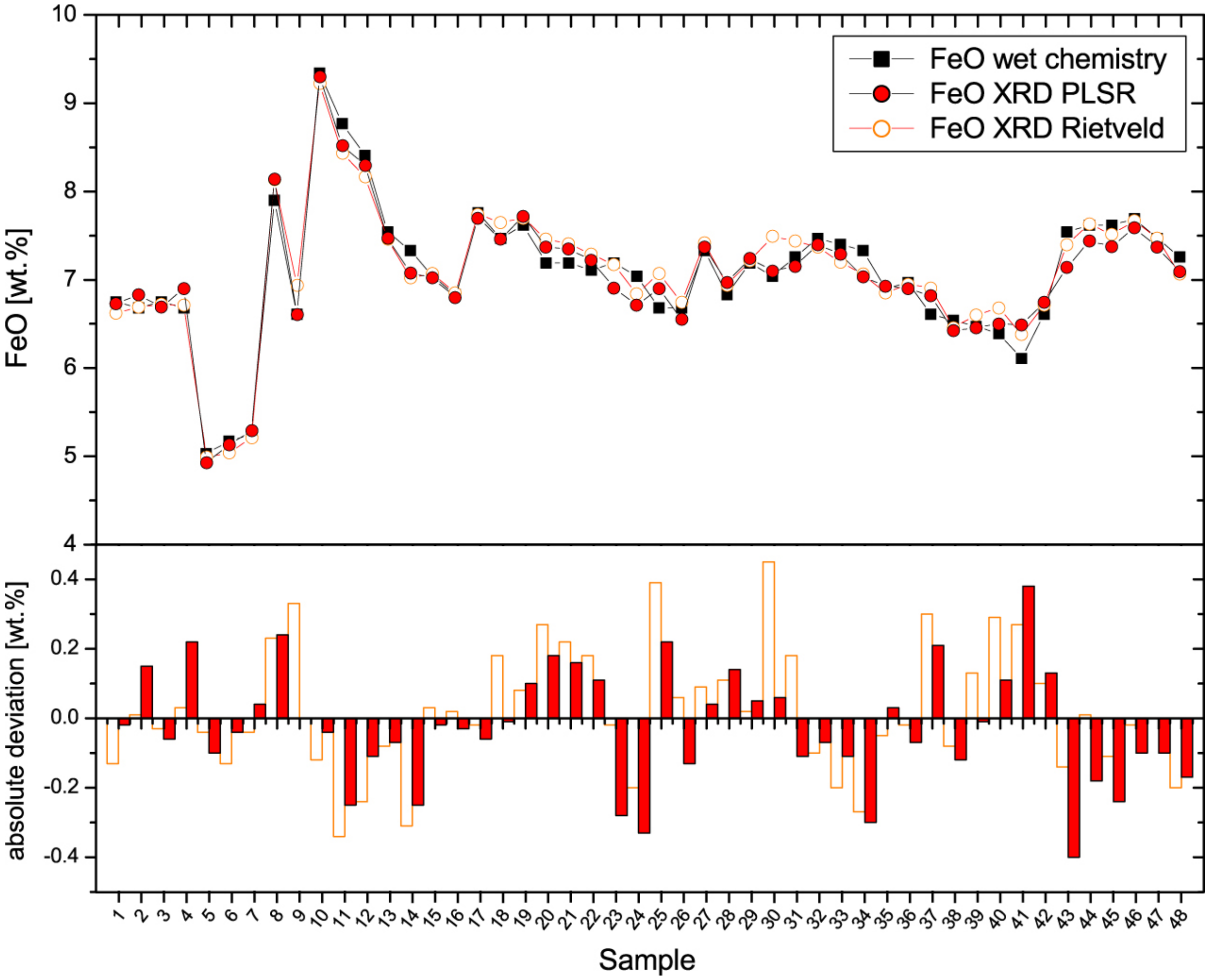

Figure 4. Comparison of reference values (wet chemistry) and the results from XRD-Rietveld and XRD-PLSR for the FeO content of 48 iron sinter samples

3.2.2 Partial least squares regression (PLSR)

PLSR was applied to determine the ***basicity*** and the total ***FeO*** content directly from the XRD raw data. Owing to the fact that PLSR is a statistical method, the number of reference samples (in this case study 21) is the most limiting factor for the development of a reliable and accurate calibration model.

Input for the PLSR analysis were the measured XRD scans (range 10 to 88 °2θ) and the FeO results from wet chemistry. All samples were used as standards to develop the PLSR model. An optimal regression model was found automatically using the optimization routine of the PLSR tool in the software HighScore Plus version 4.1.

Cross-validation (set of 4 samples, 10 repetitions) was applied to estimate the errors of the PLSR calibration model. It is integrated in the software and can be performed automatically by entering the number of test sets and the required repetitions.

For the FeO content of the 21 reference samples, a root-mean-square error of prediction (RMSEP) of 0.23 % was obtained from the cross validation. The RMSEP value is an estimate for the prediction quality. It represents ±1 σ error of the predicted values. This value has the same unit as the prediction values, in this example it is in wt.% of predicted FeO. For testing the model, 48 samples (including the 21 references) were prepared, measured and analyzed as unknowns. The results are plotted in figure 4 together with the FeO values from the Rietveld quantification and the reference values from wet chemistry.

In addition to the FeO content it was trialed to correlate other process parameter directly with the XRD data. Figure 5 shows a comparison of the reference values of the ***basicity*** from all 48 samples with the results obtained with PLSR on the XRD raw data.

Both parameters FeO and basicity were determined simultaneously and the results for all samples were reported automatically.

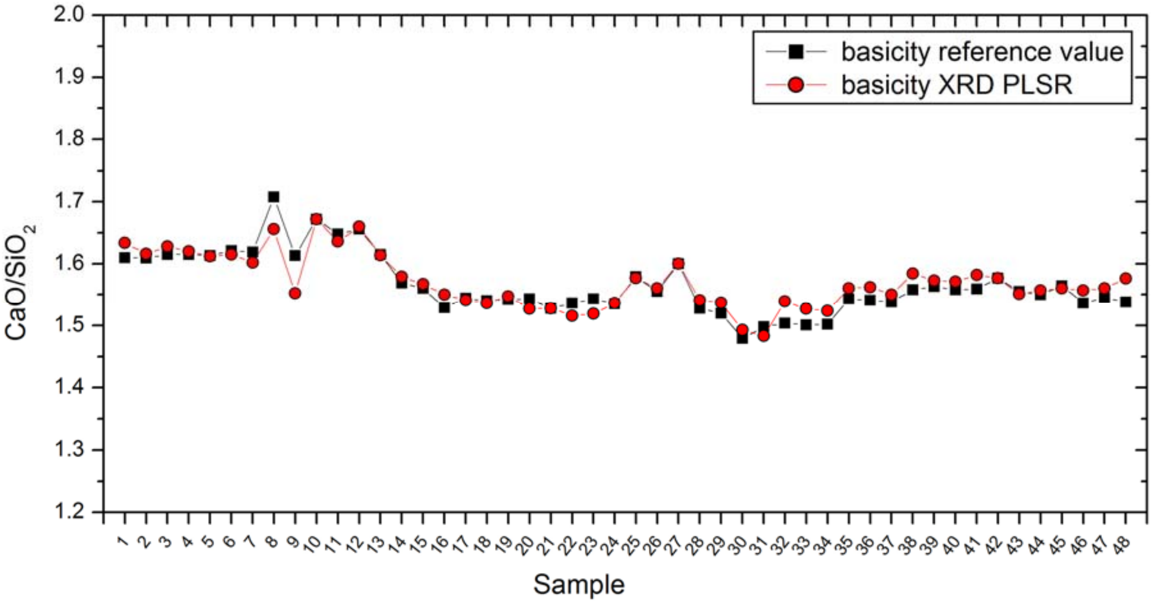

Figure 5. Comparison of reference values (wet chemistry) and the results from XRD-PLSR for the basicity of 48 iron sinter samples.

4 CONCLUSION

The results prove that XRD is a robust and fast alternative to time and cost consuming wet-chemical methods during the iron sinter process. The examples demonstrate the great potential of XRD for controlling and monitoring ironmaking processes and material properties. The technique can be used for

a) quality control of raw materials from different suppliers (iron ore, coal, limestone etc.),
b) monitoring raw mixtures in the blending beds; and
c) control of process parameters of the sinter plant.

High frequency analysis and no use of any chemicals are the main differences between traditional wet-chemical methods and fast characterization with XRD. Today's optics, detectors, and software can provide rapid (< 10 minutes) and accurate analyses, suitable for process control environment. The complete analysis is ready for automation and can be easily included in full automation lines.

Fluctuations in raw materials and raw mixtures can be detected and the composition of the blending beds can be optimized immediately. Obviously this proactive compensation of raw material fluctuations is much faster than waiting to see effects in the produced sinter.

However, the usage of an optimized iron sinter with stable quality in the blast furnace results in a further reduction of the blast furnace fuel consumption. Therefore, a frequent analysis of the mineralogy and the process parameter such as FeO and basicity are important to increase the productivity of the sinter plant.

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