Chapter

Application of X-Ray Diffraction to Study Mineralogical Dependence of Reduction: Disintegration Indices RDI of Blast Furnace Sinters

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Abstract

The aim of this research was to continue an examination of influence of mineral components of blast furnace sinters on their quality. Two of reduction-disintegration indices RDI were taken into account: static resistance to degradation RDI-$1_{+6.3}$ and static susceptibility to degradation RDI-$1_{-3.15}$. X-ray diffraction was used for phase identification and the Rietveld method was applied to study quantitative dependence. Static susceptibility to degradation RDI-$1_{-3.15}$ showed clearly dependence on quantitative mineral composition, namely on quantities of magnetite, silicates and slag phases. Static resistance to degradation RDI-$1_{+6.3}$ was also dependent on fractions of magnetite and silicates.

Keywords: Rietveld method, blast furnace sinters, mineralogy, reduction-disintegration indices RDI

1. Introduction

The history of integrated factory's steel product usually begins from a preparation of a sinter being one of the main component of a blast-furnace charge. In blast-furnace practice a sinter is a product after high temperature treatment of a mixture of iron ores and their concentrates, fluxing agents (dolomite, lime) and coke breeze. Sintering process takes place in a range of 1200–1300°C and causes partial melting of individual grains of all sinter's components, forming a compact product. The temperature has to be lower than a melting point of the mixture. There are some phase transformations and/or degradation of minerals which accompany the sintering processes. As a result, a mineralogy of a sinter is different than a mineralogy of starting components.

Generally, the mineralogy of sinters can be thought as a mineralogy of two types of compounds: oxides and silicates, including also silicate glass. The presence and the amount of individual minerals depend on the properties of and the conditions of technology (practice). One of the most important factor, characterizing a sinter, is its basicity; the value of this parameter is defined as a ratio of a content of calcium (given as calcium oxide) to a content of silicon (given as silicon dioxide).

The basicity of a sinter is the main reason of diversity in observed mineral composition and – consequently – in properties of the sinter.

The identification of mineral components can be done using various experimental techniques from which the X-ray diffraction seems to be the most important. Every crystalline chemical compound (mineral) produces its own, typical X-ray diffraction pattern which can be used in identification of it in a multiphase mixture. The individual patterns are kept in Powder Diffraction File, updated every year by the International Centre for Diffraction Data and having now (2020) more than 400,000 data of inorganic compounds. In many cases, the data for one particular compound contains also information about crystallography of this compound. It means that a calculation of a theoretical pattern of this compound is possible. In X-ray diffraction method, one can assume that the observed pattern of a multiphase powder mixture is a sum of weighed patterns of individual compounds (minerals). This assumption gives the possibility to apply the Rietveld method to study the multiphase mixtures and to calculate the fractions of individual components of the mixture.

The Rietveld method was presented for the first time in 1967 by H. Rietveld to refine crystallographic structure of a crystalline compound, using neutron diffraction [1, 2]. R. A. Young and D. B. Wiles applied the method to X-ray diffraction in 1981 [3, 4] and the next application to quantitative phase analysis was introduced by Hill and Howard in 1987 [5] and Bish and Howard in 1988 [6]. The crucial advantage of the Rietveld method in studying and quantifying mixtures is the ability to analyze the overlapped reflections. Overlapping is the most important problem in mixtures, especially in the case of low symmetry of constituents. The number of reflections can reach some hundreds in a typical 2Theta range of measurements. There is also another problem – a contribution of intensities of many small reflections to an observed intensity of a background of an experimental X-ray diffraction pattern and consequently some difficulties in refining the background. This is also the case of the presence of amorphous component. This matter was solved in the Siroquant software [7] in which the shape and intensity of the background is not refined but manually removed from a pattern. Owing to the above, the Rietveld method gives the unique opportunity for a precise quantitative description of blast furnace sinters.

The quality of sinter's pieces can be described using different indices which have to be determined by some technical tests and experiments, according to international standards [8].

The tests are carried out in conditions which simulate blast-furnace's conditions in upper part of its shaft. A sample of a sinter of 500 g is placed into a furnace heated up to 500÷550°C and is exposed to a reducing gas for 60 minutes. Then the sinter is cooled in an atmosphere of inert gas and is subjected to tumbling. The disintegration sinter's pieces gives grains of various sizes which are screened to three groups. The following indices, according to International Standard ISO 4696-1:2007, are determined:

Static resistance to degradation (the ratio of reduced sinter with size larger than 6.3 mm after tumbling test to reduced sinter)

$$RDI - 1_{+6.3} = \frac{m_1}{m_0} \times 100\% \tag{1}$$

Static susceptibility to degradation (the difference between reduced sinter and the sum of reduced sinter with size larger than 6.3 mm and reduced sinter with size larger than 3.15 mm divided by reduced sinter)

$$RDI-1_{-3.15}=\frac{m_0-(m_1+m_2)}{m_0}\times 100\% \quad (2)$$

Static grindability (the difference between reduced sinter and the sum of reduced sinter with size larger than 6.3 mm, reduced sinter with size larger than 3.15 mm and reduced sinter with size larger than 0.5 mm divided by reduced sinter)

$$RDI-1_{-0.5}=\frac{m_0-(m_1+m_2+m_3)}{m_0}\times 100\% \quad (3)$$

where: m_0 [g] – mass of a sample after reduction before tumbling m_1 [g] – mass of oversize particles remained on a screen of 6.3 mm after tumbling m_2 [g] – mass of oversize particles remained on a screen of 3.15 mm after tumbling.

m_3 [g] – mass of oversize particles remained on a screen 0.5 mm after tumbling.

From technological point of view, the most important index is a static susceptibility to degradation and a question of dependence of its value on a mineralogical composition of a sinter is still to be answered. Previous examinations showed that there was a connection between quantities of mineral components of sinters and their reducibilities [9] and this work is a continuation of studying a dependence of quantitative mineral composition of blast furnace sinters on their quality.

1.1 Materials

All sinters were prepared from raw materials which were used in Polish steel plants. There were two kinds of iron ores and three kinds of concentrates of other iron ores (**Figure 1**). Six different mixtures were prepared, each one consisted of different combinations of ores and concentrates but with a planned basicity (**Table 1**). Basicity was calculated as a ratio of calcium content recalculated to CaO to silicon content given as SiO_2. Sintering process was carried out in laboratory conditions with application of lime and dolomite in a conventional sinter pot of a diameter of 490 mm [10]. Ten laboratory tests were done for each kind of mixture (**Figure 2**); then three samples characterized by optimal moisture with the highest productivity were selected for further investigations (**Table 2**). The RDI values were calculated according to the procedure given above.

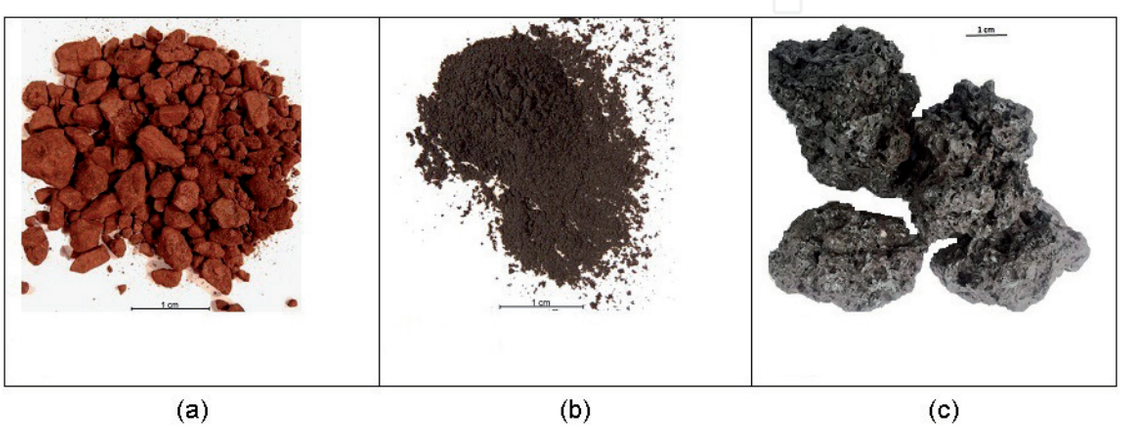

Figure 1.
Samples of hematite lump ore (a), magnetite concentrate (b) and sinter (c).

	Series A	Series B	Series C	Series D	Series E	Series F
Basicity CaO/SiO2	1,20	1,20	1,50	1,50	0,90	1,20

Table 1.
The planned basicity values of each kind of mixtures.

Figure 2.
The experimental site for sintering iron ores and waste products in Sieć Badawcza Łukasiewicz - Instytut Metalurgii Żelaza.

Sinter RDI values	A1	A2	A3	B1	B2	B3	C1	C2	C3
RDI-1+6.3	39,5	40,2	45,9	46,2	50,2	51,5	44,3	51,1	55,8
RDI-1-3.15	29,9	28,7	26,1	26	22,6	22,4	21,3	17,2	18,8
Sinter RDI values	D1	D2	D3	E1	E2	E3	F1	F2	F3
RDI-1+6.3	54,9	55,2	52,8	39,7	36,6	39	51,3	53,7	52,6
RDI-1-3.15	14,3	15,2	14,9	32,4	32,9	33,5	20,8	19	19,1

Table 2.
The RDI values of the chosen sinters.

2. Methods

In XRD method, the first step was to reduce a crystallite size of the sinters, using Fritsch Puverisette 0 mill and also a mortar and a pestle. The measurements of diffraction patterns were carried out using a PANalytical Empyrean diffractometer with a PIXcel solid state detector and filtered Co K_a radiation (Fe filter on a diffracted beam). The range of 2θ was 10°- 100° with step size Δ2θ = 0.02626° and time/step 800 s. The identification of phases was done according to International Centre for Diffraction Data (ICDD) Powder Diffraction File PDF-4+. The quantities of individual phases were calculated by means of the Rietveld

method and Siroquant software [7]. An amorphous component was detected and quantified after adding a small addition of corundum (certified Standard Reference Material SRM No. 676a from National Institute of Standards and Technology NIST, USA) to an initial sample of a sinter, next a homogenization and a repeated measurement.

3. Results

Generally, two groups of minerals can be distinguished in sinters: oxides and silicates. The examined sinters contained two iron oxides: hematite Fe_2O_3 and magnetite Fe_3O_4 and one silicon dioxide – quartz SiO_2. Only traces of wuestite FeO were found. The group of silicates consisted of calcium silicates (larnite β-$CaSiO_4$, γ-$CaSiO_4$, wollastonite $CaSiO_3$), calcium-iron silicates (hedenbergite $Ca_{0.5}Fe_{1.5}Si_2O_6$, kirschsteinite $CaFeSiO_4$), magnesium silicate $MgSiO_3$ and so called silica glass (amorphous component). There were also three so called slag phases identified in the sinters: $Ca_{2.3}Mg_{0.8}Al_{1.5}Fe_{8.3}Si_{1.1}O_{20}$ (SFCA phase), $Ca_{3.18}Al_{1.34}Fe_{15.48}O_{28}$ (SFCA-1 phase) and $Ca_{2.45}Fe_{9.2}Al_{1.74}Si_{0.6}O_{20}$ (SFCA Mg – free phase).

All measured diffraction patterns of the examined sinters were characterized by a strong complexity because of many reflexes of individual phases and overlapping of the reflexes. In **Figure 2**, a part of a diffraction pattern of one of the sinters is shown and the positions of reflexes of all crystalline components, according to PDF-4+ standard data, are clearly visible. In a typical experimental range of 2θ (10^o – 100^o2θ) there were about:

- 90 reflexes of larnite β-Ca_2SiO_4
- 105 reflexes of SFCA $Ca_{2.3}Mg_{0.8}Al_{1.5}Fe_{8.3}Si_{1.1}O_{20}$
- 56 reflexes of SFCA-1 $Ca_{3.18}Al_{1.34}Fe_{15.48}O_{28}$
- 77 reflexes of hedenbergite $Ca_{0.5}Fe_{1.5}Si_2O_6$

and also reflexes of other constituents. This was a result of low symmetries of some of the phases forming a sinter. There are all identified phases and their space groups in **Table 3**.

With such a complexity of the diffraction patterns, the only solution was to apply the Rietveld method [1–6]. A model of a sinter file was created, containing all structural data of all identified crystalline components. Two numerical criteria of fit were taken into account: χ^2 and *R-pattern*. The global parameter of the refinement was 2θ- *zero.* Pearson VII was chosen as an analytical profile function. For each phase, the refined parameters were: scale, lattice parameters, full-width-at-half-maximum (FWHM) parameters. The background was removed manually.

The example of the Rietveld refinement is presented in **Figure 3**. The upper line is the experimental pattern (as measured). The higher intensity of the background in the range of lower angles is indicated and it is concerned with a presence of amorphous component. Below, there is the experimental pattern after removing background (points) and the calculated refined diffraction pattern (solid line). At the bottom, a difference plot is shown.

During the refinements, the difference plots were carefully observed. In some cases, the identification of a phase of a small content was possible during the analysis of a shape of a difference plot.

Phase	Space group	Phase	Space group
Magnetite	Fd-3 m	Hedenbergite	C2/c
Hematite	R-3c	Kirschsteinite	Pmnb
Larnite	P21/n	MgSiO3	Pbcn
γ-CaSiO4	Pnma	SFCA phase	P-1
Wollastonite	P-1	SFCA-1 phase	P-1
Wuestite	Fm-3 m	Quartz	P3221

Table 3.
Space groups of sinters' crystalline components.

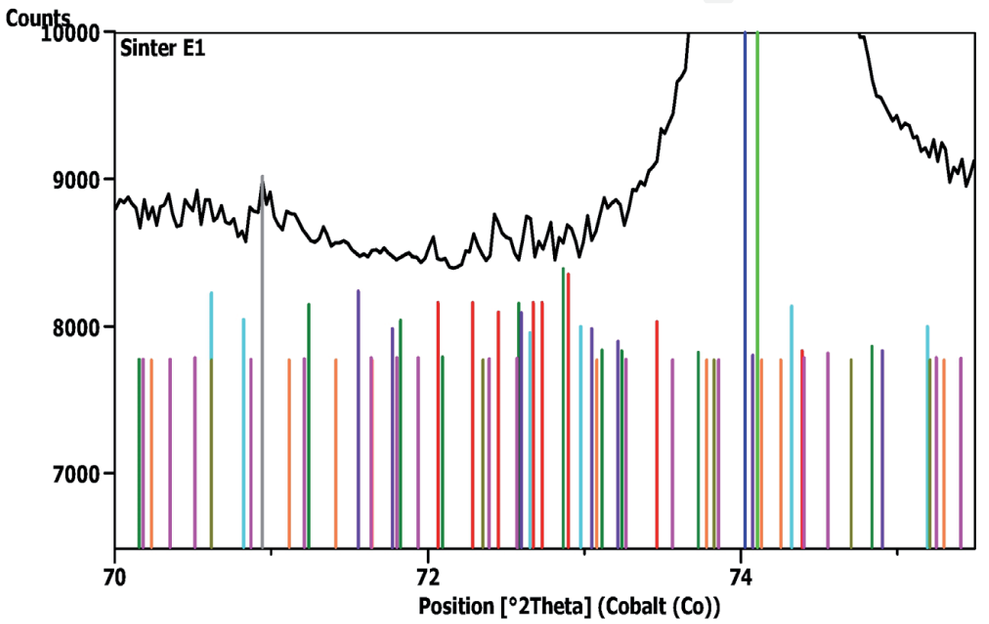

Figure 3.
An example of the Rietveld refinement of a diffraction pattern of one of a sinter. The upper line is the experimental pattern (as measured). Below, there is the experimental pattern after removing background (points) and the calculated refined diffraction pattern (solid line). The higher intensity of the background in the range of lower angles is concerned with a presence of amorphous component. At the bottom, a difference plot is shown.

4. Discussion

No significant differences were observed in the qualitative mineral composition of the sinters. A diversity in some minor components (silicates) was determined, excluding dicalcium silicates which were present in all sinters. The chemical composition and qualitative mineralogical investigations could not provide enough information about any dependence between a mineral composition and the quality indices of sinters. The next step was to apply quantitative phase analysis to check whether – or not – a quantitative dependence existed. The application of the Rietveld method to quantitative phase analysis in sinters was the only possible solution to obtain sensible results. The one of the most important problems in the refinements was the removing of background. The shape of background in sinters is not linear, the presence of amorphous component can influence on both intensity and shape of the background. Moreover, the intensity and shapes of reflexes of minor components (as it can be seen clearly in **Figure 4**, where the positions of

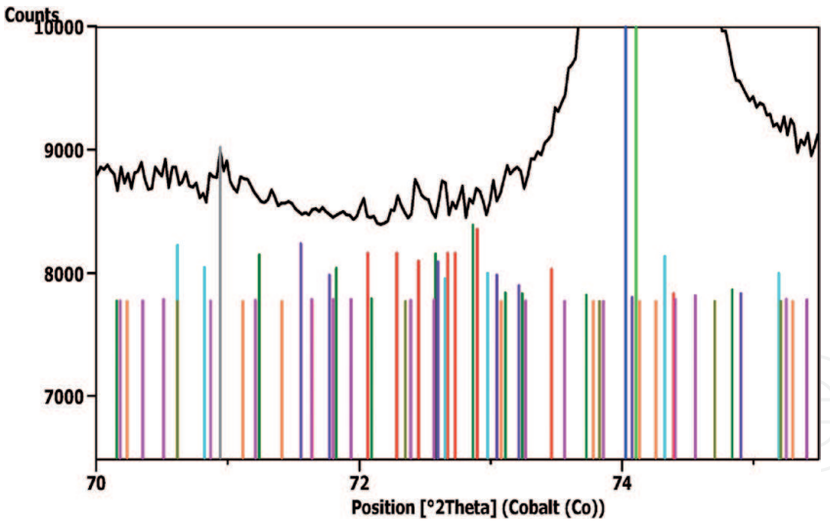

Figure 4.
A small part of a diffraction pattern of one of the sinters. The marks show the positions of reflexes of all components of the sinter, according to their standard data taken from PDF-4+ file. Complexity of the pattern is caused by the number of reflexes.

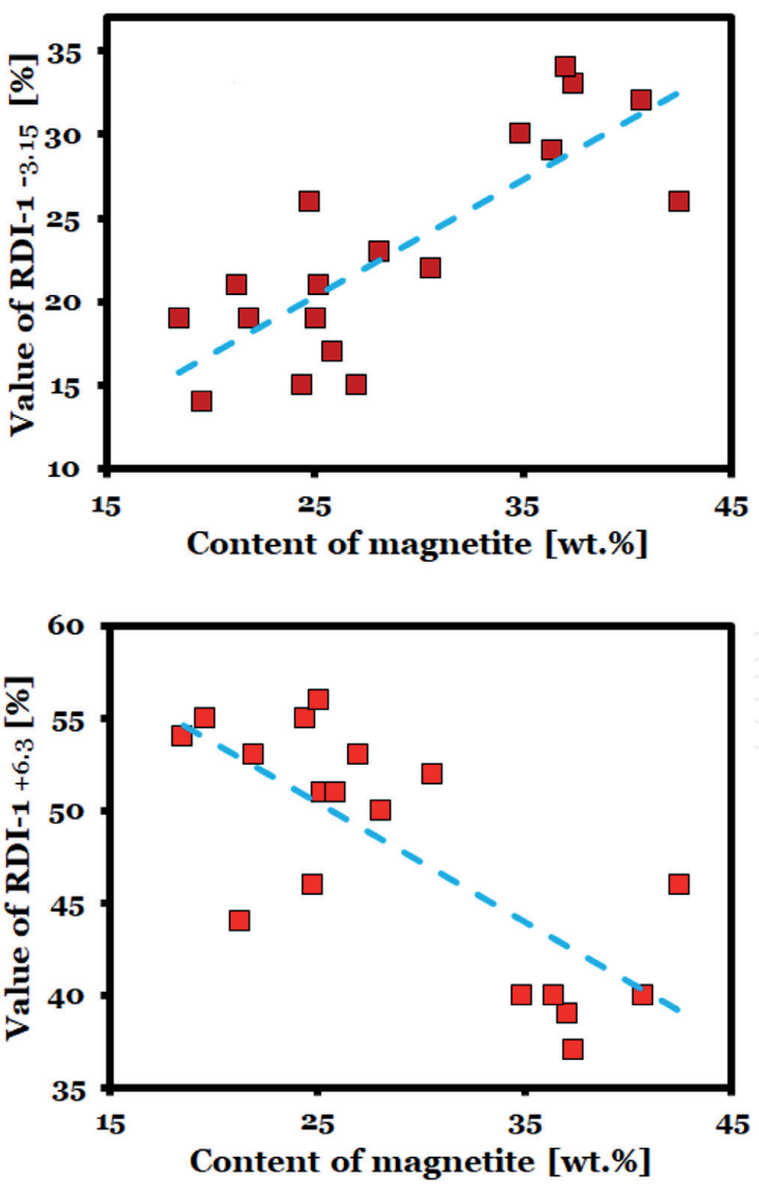

Figure 5.
The RDI-1$_{-3.15}$ (top) and RDI-1$_{+6.3}$ (bottom) dependence on contents of magnetite in the examined sinters. The growing tendency of RDI-1$_{-3.15}$ with growing content of magnetite and the opposite dependence of RDI-1$_{+6.3}$ are shown.

reflexes of all crystalline components are shown in a small range of a diffraction pattern of one of the sinters) also take part in forming the background. In this case, the careful manual removing of background before start of refinements should be used instead of the refinement of background.

The quantitative results show a noticeable dependence of RDI-$1_{-3.15}$ on contents of all kinds of minerals, excluding amorphous component (**Figures 5–9**). The reverse dependence was observed for main components, namely magnetite and hematite.

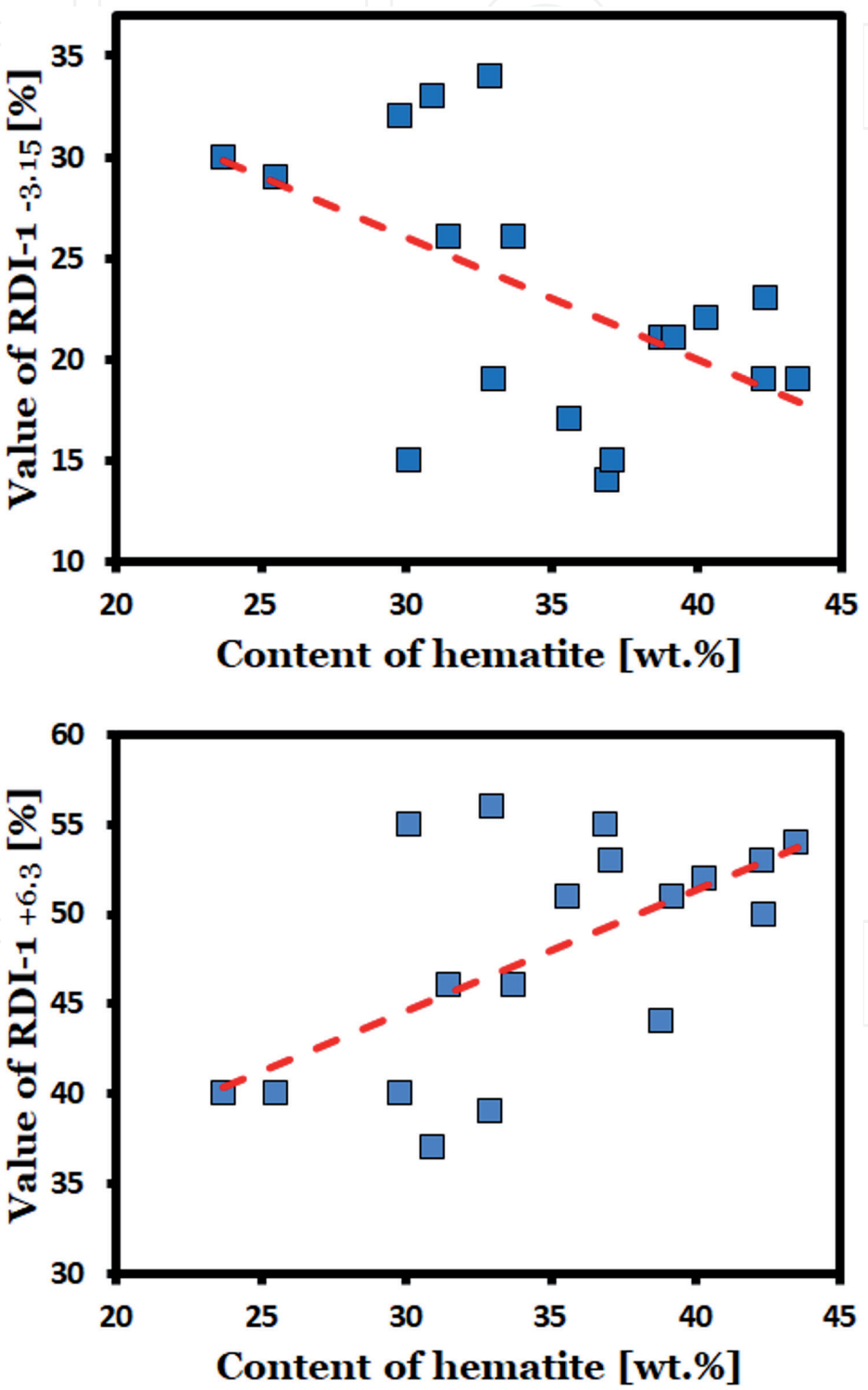

Figure 6.
The RDI-$1_{-3.15}$ (top) and RDI-$1_{+6.3}$ (bottom) dependence on contents of hematite in the examined sinters. The lowering tendency of RDI-$1_{-3.15}$ with growing content of hematite (in a range of values of RDI-$1_{-3.15}$ from 20 to 30) and the opposite dependence of RDI-$1_{+6.3}$ are shown in ***Figure 7****.*

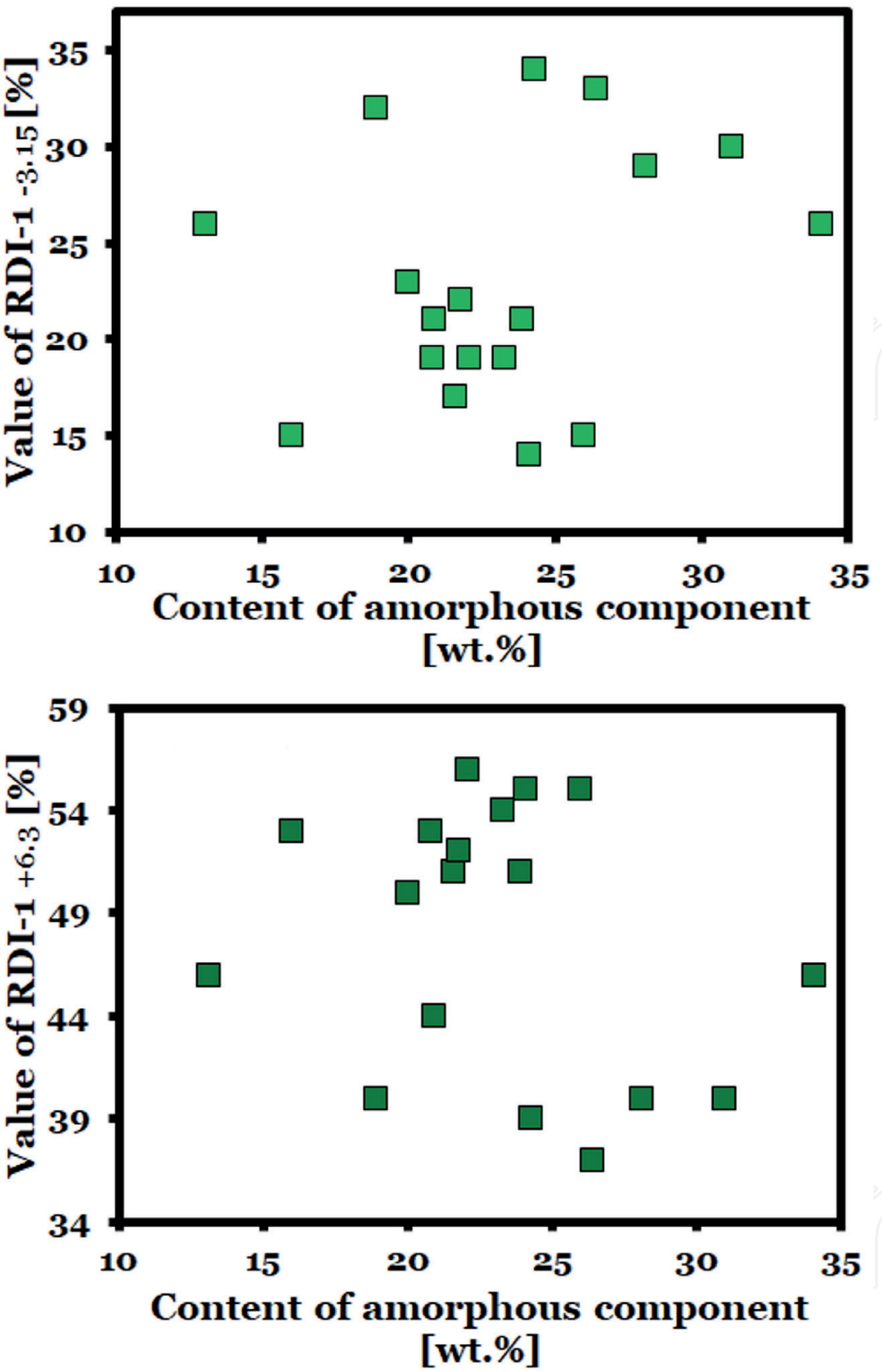

Figure 7.
The RDI-$1_{-3.15}$ (top) and RDI-$1_{+6.3}$ (bottom) dependence on contents of amorphous component in the examined sinters. No tendency is observed for both indices.

The lower value of RDI-$1_{-3.15}$ (the lower means the better) corresponded with higher values of content of hematite (but not in a full range of values of RDI-$1_{-3.15}$) and with lower values of magnetite. No clear tendency was noticed for amorphous component. Unexpectedly the quite high content of dicalcium silicates and also slag phases accompanied the lowest values of RDI-$1_{-3.15}$. As an explanation of the results, one could assume that both, silicates and slags, could form a kind of binder among grains of other minerals and because of it had an effect on obtaining the low values of RDI-$1_{-3.15}$.

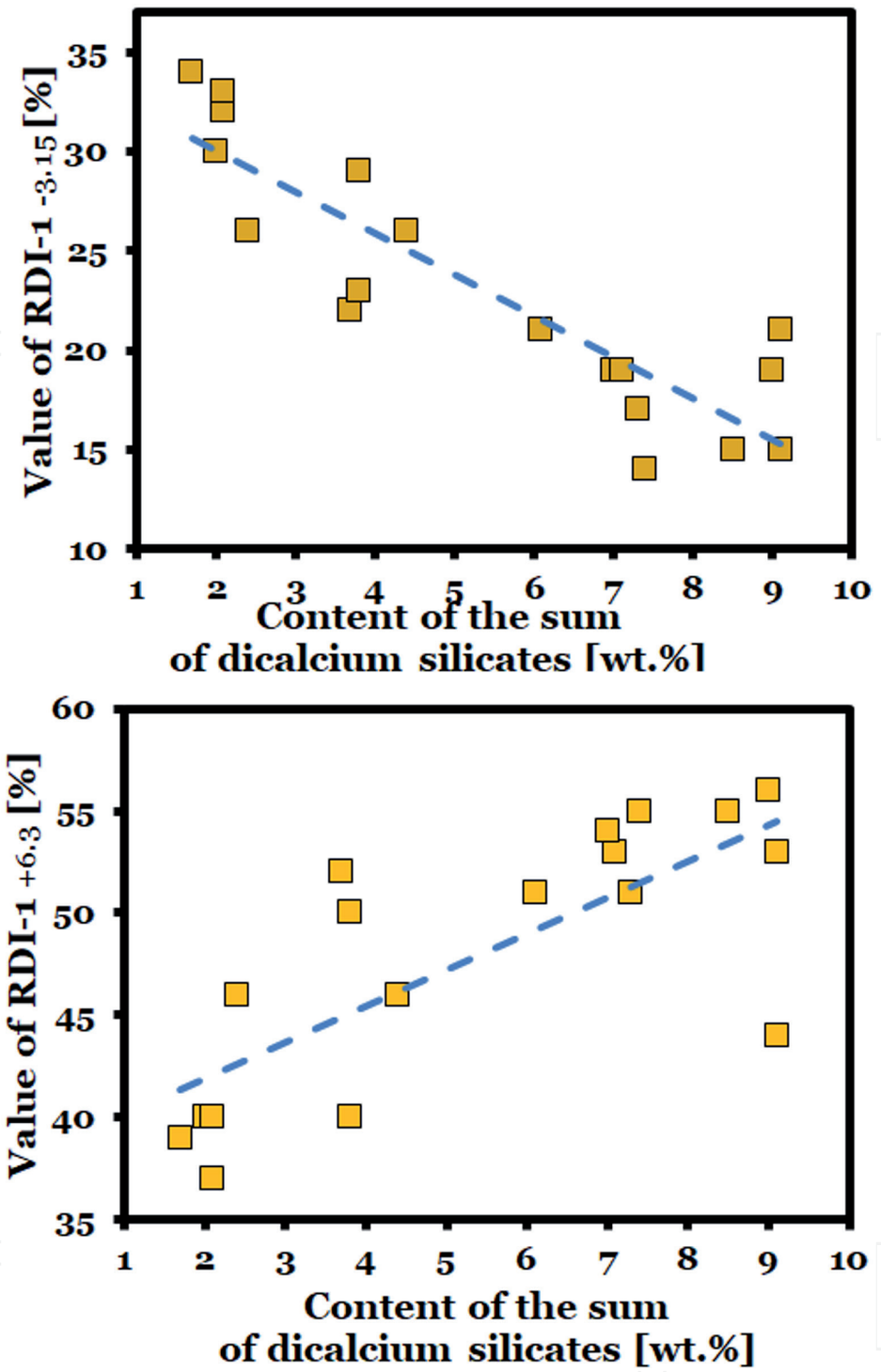

Figure 8.
The RDI-$1_{-3.15}$ (top) and RDI-$1_{+6.3}$ (bottom) dependence on contents of a sum of dicalcium silicates in the examined sinters. The linear, lowering tendency with increasing content of dicalcium silicates is seen for RDI-$1_{-3.15}$ No tendency is seen for RDI-$1_{+6.3}$.

The dependence of RDI-$1_{+6.3}$ values on fractions of mineral components of sinters was also considered (**Figures 5–9**). As in of RDI-$1_{-3.15}$ case, magnetite and hematite contents showed a linear dependence from RDI-$1_{+6.3}$ values; the increasing values of RDI-$1_{+6.3}$ were related with lower values of magnetite contents and higher values of hematite fractions. The other minerals did not show so clear regularities.

The observed dependencies of RDI-$1_{-3.15}$ on basicity is shown in **Figure 10** - the higher value of basicity the lower RDI-$1_{-3.15}$ was obtained what can be thought as

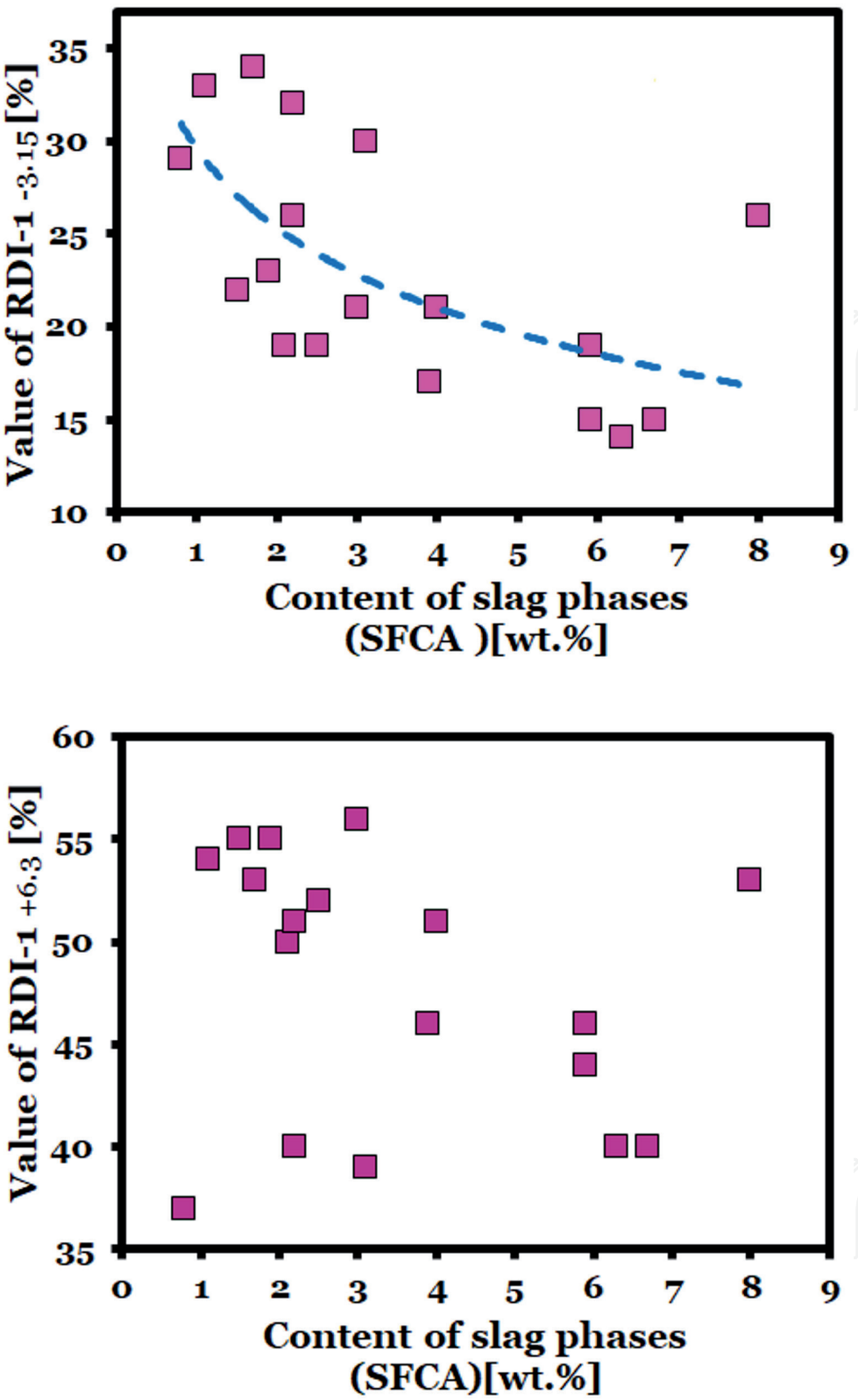

Figure 9.
The RDI-$1_{-3.15}$ (top) and RDI-$1_{+6.3}$ (bottom) dependence on contents of a sum of slag phases in the examined sinters. It can be seen that higher content of slag phases lowers the value of RDI-$1_{-3.15}$.

a beneficial result. In comparison, the rise of FeO content (not as a mineral, but as Fe^{2+} recalculated to oxide) gives higher values of RDI-$1_{-3.15}$ (**Figure 10**) what is an unfavorable tendency. This result is in accordance with the results for magnetite ($FeO.Fe_2O_3$) (**Figure 5**) which is the main source of Fe^{2+} in sinters

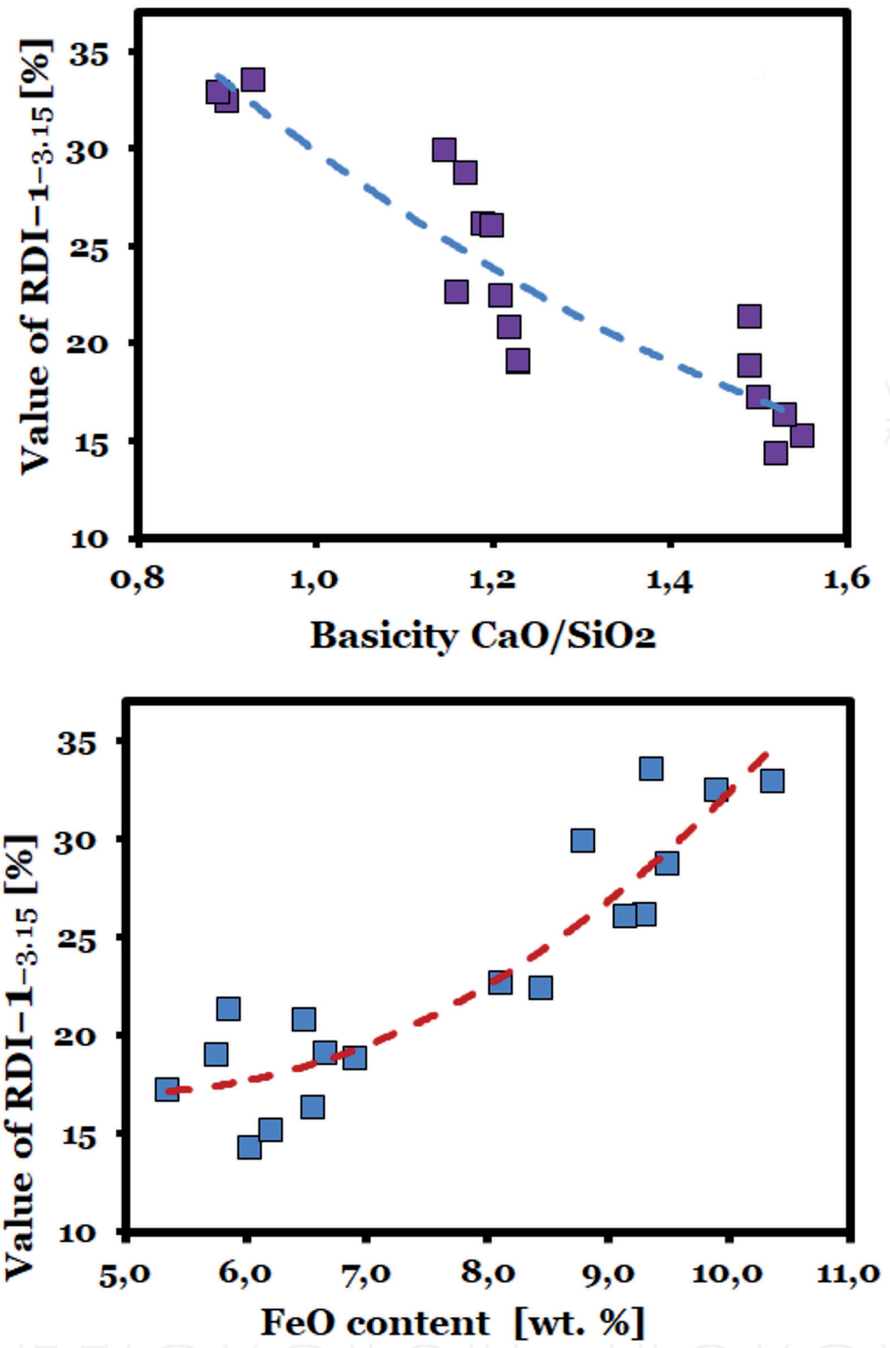

Figure 10.
The dependence of RDI-1$_{-3.15}$ on basicity CaO/SiO$_2$ (top) and on FeO content (bottom) in sinters with calculated tendency lines.

5. Conclusions

- The identification procedure showed no significant differences in qualitative phase composition of the examined sinters. There were only small discrepancies in occurrence of some silicate components (as e.g. magnesium silicate), but their contents were about 1 wt.%, so their influence on properties of the sinters was not crucial.

- There is a clear dependence between static susceptibility to degradation RDI-1$_{-3.15}$ and quantities of mineral components of the sinters. This is not observed for all minerals - amorphous component do not show any kind of correlation with values of RDI-1$_{-3.15}$. The correlation of the content of hematite

and corresponding values of RDI-$1_{-3.15}$ is not evident – it can be seen only in a range from 20 to 30 of values of RDI-$1_{-3.15}$. and in this range is decreasing with growing contents of hematite.

- The growing dependence of values of RDI-$1_{-3.15}$ with higher contents of magnetite is easily seen and it is in a good agreement with the results of studies of influence of FeO content (Fe^{2+} recalculated to oxide) on values of RDI-$1_{-3.15}$ as the main source of Fe^{2+} in sinters is magnetite.

- The reverse tendency can be observed for dicalcium silicates and also for slag phases. The increasing content of these minerals is accompanied with lowering values of RDI-$1_{-3.15}$. It can be correlated with basicity values – the Ca^{2+} atoms are mostly present in the above mentioned type of minerals.

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