COMPARISON OF IRON ORE SINTER MINERALOGY QUANTIFICATION

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Abstract

At present, the powder XRD is widely used analytical method for iron ore sinter mineralogy determination. In many types of research, diffraction data for SFCA and SFCA-I phases were not available, and diffraction data for other calcium ferrites were used instead. Therefore, the aim of this paper is to bring a comparison between the evaluation of diffractograms, when SFCA/SFCA-I, and, other calcium ferrites, respectively, are considered. As a result, the quantification of phases is quite comparable, when minerals are collected into groups, i.e. hematite, magnetite, calcium ferrites, silicates and non-assimilated non-ferrous phases. Only in the case of silicates, a comparison tends to be dissatisfactory.

Keywords: calcium ferrite; sinter mineralogy; X-Ray Diffraction

1 Introduction

Powder X-Ray diffraction (XRD) is the fastest analytical method to evaluate an iron ore sinter mineralogical composition – the overall process takes only several minutes, just the sample must be grinded to a fine powder before the measurement [1,2]. On the other hand, this method has some disadvantages, which result from the nature of the technique. Because the XRD is based only on the physical parameters of the minerals and their structures, similarities in crystal lattice parameters of different phases can cause an incorrect identification. To avoid this, the knowledge of analyzed microstructure is necessary.

Nowadays, the research in the field of iron ore sinter mineralogy is concentrated on one group of the bonding phases – complex calcium ferrites (designated as SFCA, an acronym for silico-ferrite of calcium and aluminum), which accumulate besides Fe_2O_3 and CaO also SiO_2, Al_2O_3 and other minority components [3-5]. In industrially produced sinters, there are 2 types of SFCA-s according to the chemical composition: low-Fe SFCA and high-Fe SFCA-I [6].

Before advanced study of SFCA/SFCA-I, calcium ferrites $CaFe_4O_7$ and $CaFe_3O_5$ were considered as the main ferrite phases in lime-fluxed iron ore sinters [7, 8].

Despite the fact, that diffraction patterns for complex calcium ferrites are known since 1989 and 1998 for SFCA [9] and SFCA-I [10], respectively, the diffraction databases of research centres are updated gradually, and in many cases, the data for mentioned phases are absent. For this reason, the rate of calcium ferrites in iron ore sinters is expressed through other, mostly ternary calcium ferrites, which can fit the measured diffraction pattern. Of course, this applies to older studies as well. In the current literature [11-16], it is common to substitute SFCA and/or SFCA-I

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with $CaFe_2O_4$ (CF), $Ca_2Fe_2O_5$ (CF2), $Ca_3Fe_{15}O_{25}$ (C3WF7), $Ca_4Fe_9O_{17}$ (C4WF4), $CaFe_3O_5$ (CWF), $Ca_2Fe_{15.57}O_{25.56}$ (non-stoichiometric) $Ca_2Fe_9O_{13}$ (C2W5F2), $Ca_2Fe_{22}O_{33}$ (C2W4F9), $Ca_2(Fe,Al)_2O_5$ (C4FA), $CaFe_5O_7$ (CW3F), where abbreviations in brackets denote: C – CaO, W – FeO, F – Fe_2O_3 and A – Al_2O_3, respectively. Also, an earlier defined calcium ferrite with formula $Ca_5Si_2(Fe,Al)_{18}O_{36}$ is known [17].

The main aim of the article is not to propose the replacement of diffraction patterns of mineral phases in sinters by others, but show the changes in phase quantification, which can occur when diffraction patterns of SFCA/SFCA-I are used instead of other calcium ferrites.

2 Materials and methods

The five sinter samples for this study were chosen from previous work [12].

Powder X-Ray diffraction analyses of iron ore sinter samples were performed using diffractometer SEIFERT XRD 3003/PTS. The parameters of measurements were as follows: generator at 35 kV and 40 mA, Co – line focus, Fe filter, measuring range 10 to 120° 2θ by scan step of 0.02 θ, input slits 3 mm, 2 mm, and PSD detector Meteor1D. The measured diffraction patterns were analyzed using DIFFRAC.EVA (Search-Match) software with the database PDF2 and by program TOPAS that uses the Rietveld method.

First, measured diffraction patterns were evaluated without data for SFCA and SFCA-I using patterns for other calcium ferrites – this set of evaluations is denoted here as “set A”. Then, diffraction patterns for SFCA and SFCA-I replaced calcium ferrites from the set A – this set of evaluations is denoted as “set B”.

In all cases, the final XRD results were supported by microscopic examinations, as reported earlier [12].

3 Results

3.1 Diffractogram solution

In the evaluation of diffractogram of an iron ore sinter, the aim is to fill out the vacant spaces of the measured diffraction pattern with calculated diffraction patterns of compounds present in the sinter. As an indicator of the accuracy, a difference curve is used. This curve is the more regular, the more the calculated diffraction patterns match the measured diffraction pattern.

For demonstration, the evaluation of the diffractogram of sample 4 is presented in **Fig 1**. First, the evaluation with binary and ternary calcium ferrites was realized (**Fig. 1 a)**), then the XRD patterns of SFCA/SFCA-I replaced ferrites as well as some other phases from the first case (**Fig. 1 b)**).

As can be seen, the difference curve is well balanced in both cases, only on the sites of magnetite and hematite, there are some deviations.

In XRD of iron ore sinters, a common problem is magnetite phase, which has a spinel structure and exists in sinters in a relatively wide range of chemical compositions because of the isomorphic admixtures. They cause slight shifts of diffraction peaks, which must be taken into account in the processing of the diffraction pattern.

Although dicalcium ferrite and dicalciumaluminoferrite are both described as the precursor phases in the SFCA phases formation process, they are quantified in much larger amounts in the sinter, when SFCA/SFCA-I calculated diffraction patterns are not present. This means that diffraction peaks of $Ca_2Fe_2O_5$ fill out also a part of the non-filled measured diffraction pattern.

A part of the diffraction peaks of $Ca_2Fe_{22}O_{33}$ phase is often situated on the sites of SFCA, or SFCA-I, respectively. This is the reason, why it is possible to fit a part of the diffraction data for

$Ca_2Fe_{22}O_{33}$ to data of complex ferrites without an obvious conflict, which could be seen on the diffractogram.

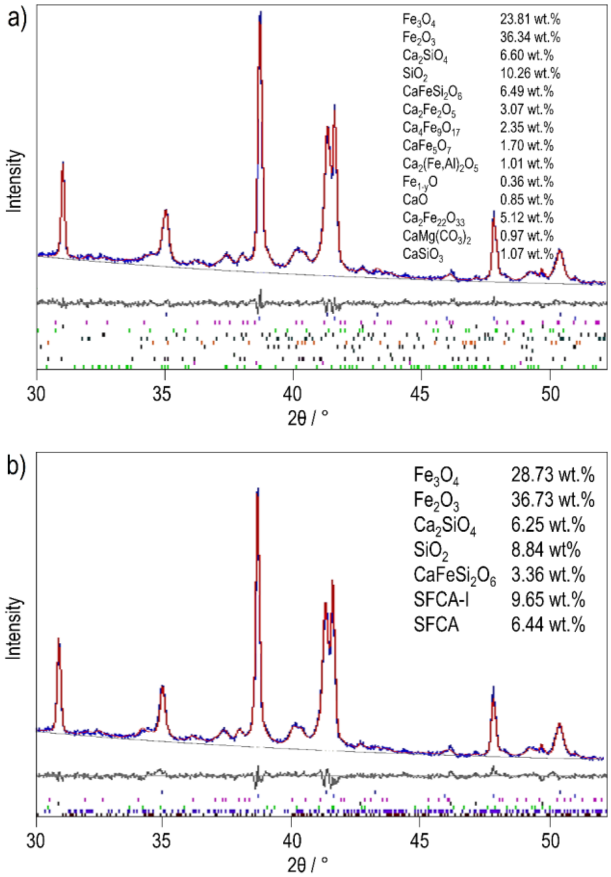

Fig. 1 Diffractogram of sample 4 within a) set A and b) set B in the range $30° \leq 2\theta \leq 54°$. Blue, red, and grey lines represent the measured diffraction pattern, calculated diffraction pattern, and the difference curve, respectively. The list of identified phases corresponds to the order of Braggre reflection markers (online version in color).

The remaining gap between measured diffraction pattern and missing SFCA calculated diffraction patterns is filled with calculated diffraction patterns of other calcium ferrites: $Ca_4Fe_9O_{17}$, $CaFe_5O_7$.

By replacement of calculated diffraction patterns with SFCA/SFCA-I, not only calcium ferrite types but also other phases like carbonates or wüstite were no more fittable.

The choice of complex calcium ferrite patterns was based on the previous careful microscopic observation, which exactly confirmed the occurrence of SFCA and SFCA-I in studied sinters.

3.2 Phase quantification

The comparison of XRD measurements results of 5 samples without (set A) and with the use of diffraction patterns of SFCA/SFCA-I (set B) is presented in **Fig. 2**. In each graph, the first column (white) represents an evaluation within the set A, the second (grey) an evaluation within the set B, respectively. Because of the different phases, they were in both cases collected into 5 groups: hematite, magnetite, total calcium ferrites, total silicates, and non-assimilated non-ferrous phases (NANP). Note that the magnetite group includes also the share of wüstite $Fe_{1-y}O$ and the NANP group involves besides quartz also lime CaO and dolomite $CaMg(CO_3)_2$, when occur. In addition to the visual comparison, the differences between 2 evaluations are expressed in numbers on the top of second (grey) columns, as well.

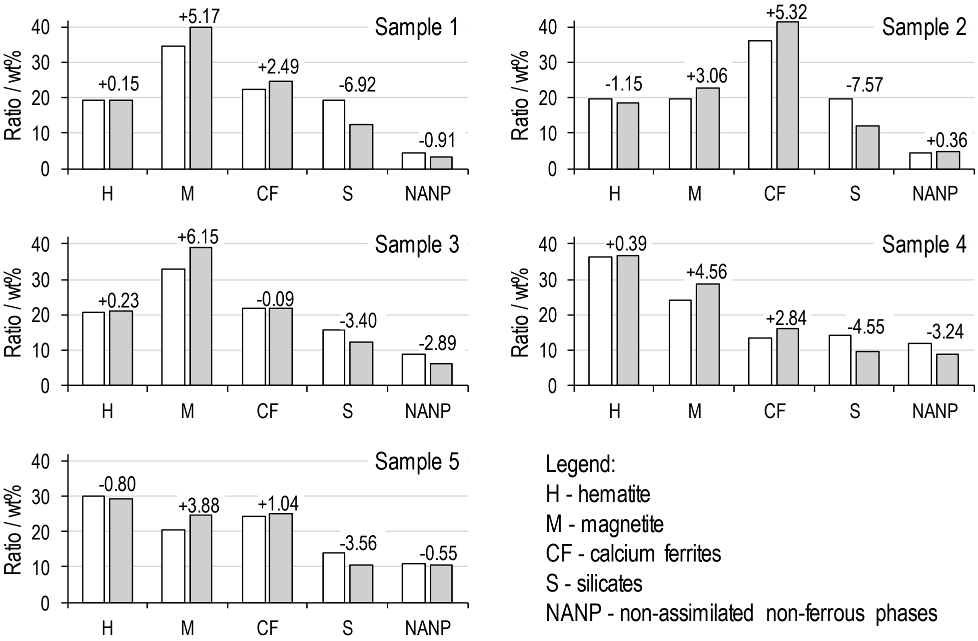

Fig. 2 Comparison of mineral phases quantification. White and grey columns represent set A and set B, respectively

When "substitute" calcium ferrites were replaced with SFCA/SFCA-I, changes in phase quantification appeared: the share of magnetite always increased, and the share of silicates always decreased.

It also seems that the most affected were magnetite and silicate phases. But the magnetite phase was in all samples present in much higher amounts than silicates, so the differences cannot be taken equally. For example, in sample 1, by changing the evaluation, the amount of magnetite increased from 34.65 wt% to 39.82 wt%, so the difference is +5.17 wt%; but expressing the difference in simple %, the amount of magnetite phase has grown by 14.92 %. At the same time, the number of silicates decreased from 19.52 wt% to 12.60 wt%, so the difference is -6.92 wt%, but the ratio of silicates has dropped by 35.45 %.

The least affected tend to be the ratio of hematite: the highest difference was the decrease in sample 2, only -1.15 wt% (-5.78 %). The changes in ratios of calcium ferrites and NANP were variable. The differences in the quantification of all phase groups as described above are summarized in **Table 1**.

Table 1 Differences of phase quantification between set A and set B

sample	difference	H	M	CF	S	NANP
1	diff. / wt%	+0.15	+5.17	+2.49	-6.92	-0.91
	diff. / %	+0.78	+14.92	+11.14	-35.45	-21.21
2	diff. / wt%	-1.15	+3.06	+5.32	-7.57	+0.36
	diff. / %	-5.78	+15.55	+14.72	-38.49	+7.83
3	diff. / wt%	+0.23	+6.15	-0.09	-3.40	-2.89
	diff. / %	+1.11	+18.68	-0.41	-21.85	-32.40
4	diff. / wt%	+0.39	+4.56	+2.84	-4.55	-3.24
	diff. / %	+1.07	+18.87	+21.43	-32.13	-26.82
5	diff. / wt%	-0.80	+3.88	+1.04	-3.56	-0.55
	diff. / %	-2.66	+18.80	+4.30	-25.32	-4.95

The very important question is if the sinters are comparable by phase ratios when the patterns for SFCA/SFCA-I are missing. As shown in **Table 2**, there were absolute matches in comparison of magnetite and ferrites' orders; only slight differences were in orders of hematite and NANP. However, although the same diffraction data for silicates in both sets were used, the order of phases in first and second evaluations was not comparable.

Table 2 Comparison of sinters according to mineral phases' ratio
(designations a and b are for evaluation within set A and set B, respectively)

mineral group	order of samples	agreement
hematite	1a<2a<3a<5a<4a	3 matches
	2b<1b<3b<5b<4b	
magnetite	2a<5a<4a<3a<1a	absolute match
	2b<5b<4b<3b<1b	
Ca-ferrites	4a<3a<1a<5a<2a	absolute match
	4b<3b<1b<5b<2b	
silicates	5a<4a<3a<1a<2a	no match
	4b<5b<2b<3b<1b	
NANP	1a<2a<3a<5a<4a	3 matches
	1b<2b<3b<4b<5b	

4 Discussion

Nowadays, the distinguishing between low-Fe and high-Fe SFCA phases becomes very important; however, when the diffraction data for these phases are not available, their quantification is practically impossible. Nevertheless, the image processing techniques based on the evaluation of the shades of grey are also limited to dividing the minerals in examined sinter samples just into main groups, i.e. hematite, magnetite, Ca-ferrites, silicates and pores [15,18-20]. This means that the distinction between calcium ferrite types is also not involved. Therefore, the XRD evaluation from studies working without complete XRD database can be usable only when phase groups are considered rather than individual phases. In spite of this, the evaluation of samples in this study showed, the quantification of silicates seems to be problematic, and this must be taken into account.

Conclusions

When diffraction patterns of SFCA/SFCA-I are used instead of other calcium ferrites, changes in phase quantification appear. The XRD evaluation from studies working without complete XRD database can be usable only when phase groups (i.e. hematite, magnetite, total calcium ferrites, total silicates, and non-assimilated non-ferrous phases) are considered rather than individual phases. In comparison presented in this paper, the quantification of phases was quite comparable except for the silicates, that were most affected by changing the patterns.

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