

X – RAY DIFFRACTION ANALYSIS OF SLUDGE AND DUST PRODUCED IN STEELWORKS

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Abstract

Before handling, storage, disposal, these wastes need to be analyzed. In many cases, it is not enough to know only their chemical composition, but it is necessary to determine their mineralogical composition, or to know exactly what is their crystallographic structure. This can be well done using X – ray diffraction device. Examples of sludge from Steelshop and Tin Mill, and dust from Sintering and Steelshop demonstrate current opportunities of X – ray diffraction. The analysis was done using programs of "search - match" type with diffraction database PDF2 – 2004 and crystallographic COD database. Diffraction records were refined by Rietveld method in the TOPAS program.

Keywords: X – ray diffraction (XRD), Rietveld method, sludge, dust

1 Introduction

The production of iron processed range of materials such as iron ore, coke, slag additive and etc. Iron ore with 30 % iron content is now considered economically exploitable. Iron ores are rocks which contain a sufficient amount of metal – bearing minerals and other supporting elements. Metal bearing minerals iron ores are the most common iron oxides such as magnetite Fe_3O_4 , hematite Fe_2O_3 , limonite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Less important is ferrous carbonate siderite FeCO_3 . There are also ores containing iron silicates or aluminosilicates such as chamosite which is used only locally. Ore material must be adjusted in agglomeration or pelletisation plant [1-3].

The agglomeration process allows sintering of iron ore, concentrates and various secondary raw materials with sufficiently high content of iron substance. In addition to iron containing material added to mixture also slag additive (calcite, dolomite) in an amount needed to achieve the desired agglomerate basicity. In dedusting technology origin the other products such as sinter dust from electrostatic precipitators and sinter sludge from agglomeration process itself. Both products are recycled depending on their chemical and phase composition or stored at various defined landfills [4-5].

The blast furnace consists of metal bearing materials, slag and fuel. Metal bearing part includes iron and manganese ore, sinter, pellets and also some waste from industrial production. The charge materials must respect the requirements in term of chemical composition, phase composition, physical and metallurgical properties. The large amount of raw material in steel production resulting secondary raw materials sludge, dusts and blast furnace slag. All these secondary materials are recycled in varying degrees, stored and sold [6-7].

In steel processing it is necessary to eliminate undesirable impurity elements such as C, Mn, Si, Al, P, S due to steel respect the required chemical composition which is sufficiently for hot and

cold steel rolling. This process is carried out in oxygen converter blowing technical pure oxygen or in electric arch furnace. Depending on dedusting system, various kinds of sludge and dust are formed which are recycled or stored by different ways. The whole process of production and processing of steel creates a lot of components such as sludge, dust, fly, ash, slag, deposit etc. These different multi-component materials are captured, stored and disposed using the complex techniques.

The first step to waste disposal or regeneration is its knowledge. There are many methods used in this process, among which X – ray diffraction has its legitimate place. This method can, in many cases, determine not only the chemical but also the mineralogical composition of the wastes. Exact knowledge of the crystal structures will assist us in disposing or further processing of waste generated in the production process. This is also applied in the production of steel, where a diverse amount of waste is generated in various technological processes.

The analysis of these products is difficult and besides knowledge and experience it requires also the specific analytical instruments with powerful hardware and software. Analyzing all these materials is very difficult and long process. In further text we will limit the discussion to the X-ray diffraction analysis of steelmaking sludge and different dust [8-13].

2 Experimental materials and methods

2.1 Experimental device

The X – ray diffraction analysis of the investigated materials was done using versatile analytical device URD 3003PTS Seifert, which besides the phase analysis allows measurement of residual stress and texture of steel sheets. Wavelength can be changed by selecting the appropriate X – ray tube – Mo, Cu, Co or Cr. For phase analysis the geometrical goniometer is arranged to bar focal point, and the rapid measurement is done using bar detector type Meteor1D. With this detector, the measurement takes about 15 to 20 minutes. Measured diffraction record is processed and evaluated using packages of programs of “search – match” type like DiffracEVA with PDF2 – 2004 and COD database, and programs refining the Rietveld method like AutoQuan and TOPAS. This powerful software enables to qualitatively and quantitatively refine each measured diffraction record [14-16].

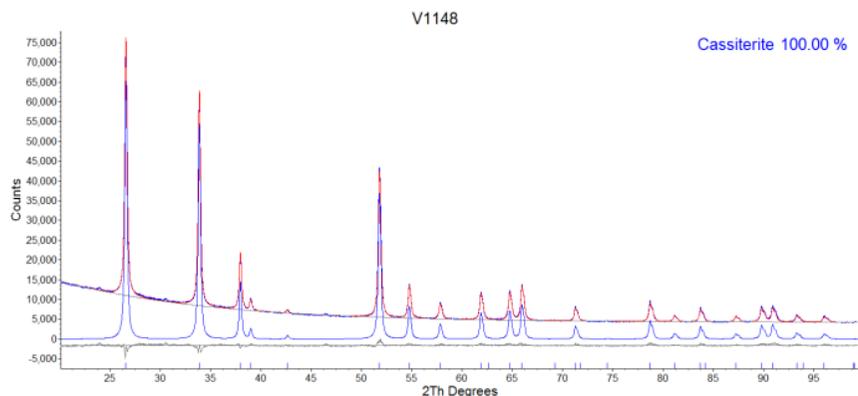
2.2 Solution and experimental material

Samples measured by X – ray diffraction method must be isotropic, therefore they are prepared in the form of fine powders. The optimum powder has particle size of about 10 microns. The powder is prepared using vibratory mill or alumina grinding mortar. Plant sludge and dust samples were prepared in a vibration mill. Milling time was approximately two minutes. To examine the sludge from Steel shop, two samples with different grain size were collected. Sample 1 was designated as gross (thick) sludge, and sample 2 was designated as a fine sludge. Results of the analysis are shown in **Table 1**. All diffraction records were refined by Rietveld method in the TOPAS program. The table shows that they have slightly different chemical and mineralogical composition, which is given by the place and time of sampling. The same applies for the quantitative composition, which is affected in some cases by portion of the amorphous component. These real heterogeneous multi – compact oxide materials contain fine particles of iron, iron oxides – wustite and magnetite, calcite, brownmillerite, and sample 2 also contains portlandite and a considerable amount of graphite. No hematite was found in samples.

Table 1 Identified phase composition of steel sludge

Identified phase composition			Sample 1	Sample 2	Sample 3	Sample 4
Chemical Formula	Mineralogical Name	Space Group	Content [wt%]	Content [wt%]	Content [wt%]	Content [wt%]
Fe	Iron	(229) Im-3m	34.3	10.1	1.4	8.7
FeO	Wustite	(225) Fm-3m	36.3	22.3	56.1	19.7
Fe ₃ O ₄	Magnetite	(227) Fd-3m	15.9	17.2	0.3	10.8
CaCO ₃	Calcite	(167) R-3c	4.2	19.3	5.4	19.8
Ca ₂ FeAlO ₅	Brownmillerite	(062) Pcmn	9.3	3.6	4.6	0.5
Ca(OH) ₂	Portlandite	(164) P-3m1	–	3.7	2.0	3.1
C	Graphite	(167) R-3c	–	23.7	2.4	28.1
CaO	Lime	(225) Fm-3m	–	–	3.5	1.6
Ca ₂ Fe ₂ O ₅	Srebrodolskite	(062) Pnma	–	–	16.1	3.0
MgCaCO ₃	Dolomite	(148) R-3	–	–	2.9	1.3
CaMgSiO ₆	Diopside	(015) C2/c	–	–	2.73	–
MgO	Periclase	(225) Fm-3m	–	–	2.4	0.5
CaFeSi ₂ O ₆	Hedenbergite	(015) C2/c	–	–	–	0.6
ZnFeO ₄	Franklinite	(227) Fd-3m	–	–	–	2.5

At this point, the X – ray analysis could be completed, because the device is not able to detect very small amounts of substances, which may be found in the examined samples. Since the samples contain fine particles of iron and magnetite, they can be separated by the magnet, thereby increasing the portion of non-magnetic components in the samples. This can be done by small magnet wrapped in paper. Sample 3 was formed by separation of sample 1 and similarly sample 4 was formed by separation from sample 2. X – ray diffraction analysis results are presented in **Table 1**. Manual separation failed to completely remove iron and magnetite particles, but their content was reduced. In the case of gross (thick) sludge it was reduced very significantly. Wustite content significantly increased in the sample 3. There were new crystal structures that emerged in the diffraction record, which could be found in the original records. In both samples were found lime, srebrodolskite, dolomite, periclase. In a sample 3 it was of diopside and in sample 4 hedenbergerite and franklinite. Refined diffraction record of gross (thick) Steelshop sludge after magnetic separation is shown in **Fig. 1**.

**Fig. 1** Refined X – ray diffraction record of annealed sludge from the electrolyte of tinning line

Results of X – ray diffraction analysis of the two dust samples are shown in **Table 2**. Analyzed was the Sintering dust – sample 5, and Steelshop dust – sample 6. Their chemical and mineralogical composition is different, which is consistent with the sampling point. Common minerals are iron oxides hematite and magnetite, silica, carbonates, limestone and dolomite, and small amount of baddeleyite. Non – magnetic particles were manually separated from both samples using a small permanent magnet. Sample 7 was formed after separation of sample 5, and sample 8 was formed from sample 6. As shown in **Table 2**, manual magnetic separation in this case was not very successful. Probably cause is the high content of hematite and graphite. Fine particles of magnetite carry away also non-magnetic particles and the presence of hematite with graphite assists in that. In both cases there is increased content of calcite.

Table 2 Identified phase composition of sinter and steel dusts

Identified phase composition			Sample 5	Sample 6	Sample 7	Sample 8
Chemical Formula	Mineralogical Name	Space Group	Content [wt%]	Content [wt%]	Content [wt%]	Content [wt%]
Fe ₂ O ₃	Hematite	(167) R-3c	34.9	60.3	12.6	16.4
Fe ₃ O ₄	Magnetite	(227) Fd-3m	36.4	5.3	22.9	29.4
ZnFe ₂ O ₄	Franklinite	(227) Fd-3m	–	–	21.1	24.4
SiO ₂	Quartz	(152) P3121	6.8	6.9	4.3	0.9
C	Graphite	(186) P63mc	–	–	18.2	0.4
CaCO ₃	Calcite	(167) R-3c	4.9	10.2	6.9	14.6
MgCaCO ₃	Dolomite	(148) R-3	7.3	10.2	2.4	2.6
MgCO ₃	Magnesite	(167) R-3c	–	–	4.9	5.9
CaFeSi ₂ O ₆	Hedenbergite	(015) C2/c	–	–	3.6	2.9
CaO	Lime	(225) Fm-3m	1.8	0.1	–	–
KCl	Sylvite	(225) Fm-3m	3.7	2.9	–	–
NaCl	Halite	(225) Fm-3m	2.6	2.4	–	–
CaF ₂	Fluorite	(225) Fm-3m	–	–	1.3	1.0
ZrO ₂	Baddeleyite	(014) P21/c	1.7	1.6	1.3	1.0
ZnO	Zincite	(186) P63mc	–	–	0.4	0.2

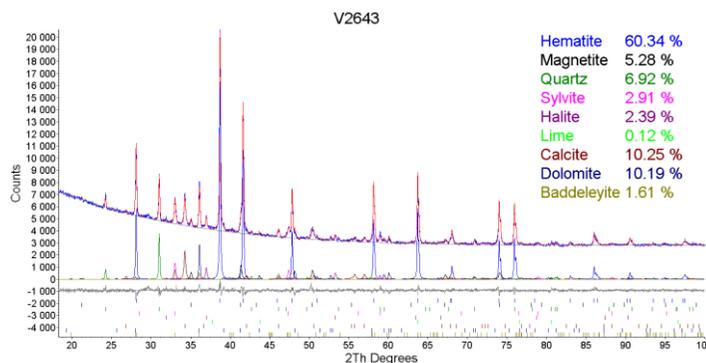


Fig. 2 Refined X-ray diffraction record of sinter dust after manual magnetic separation

In samples 5 and 7 of Sintering dust were found sylvite and halite salts, which were not found in samples 6 and 8 of Steelshop dust. In samples of Steelshop dust was found fluorite, magnesite, hedenbergite and very small amount zincite. Diffraction records were refined by Rietveld

method using TOPAS program. **Fig. 2** and **3** show fitted refined record of Steelshop dust sample.

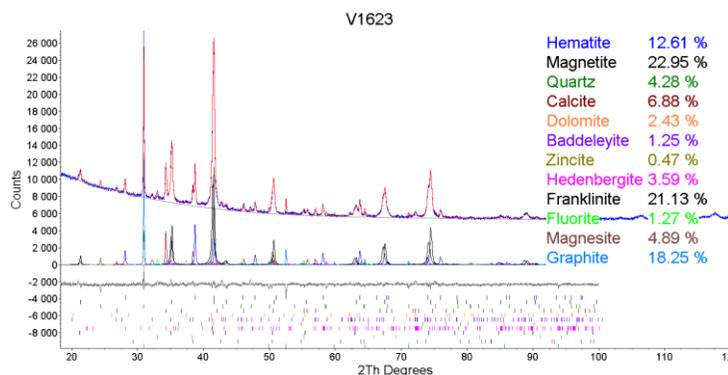


Fig. 3 Refined X-ray diffraction record of steel dust after manual magnetic separation

3 Conclusions

Samples of sludge from Steelshop and Tin Mill and samples of dust from Steelshop and Sintering were analyzed by X-ray diffraction method. All diffraction records were refined by Rietveld method using TOPAS program.

- To achieve the best quality results, non-magnetic particles were separated from samples by simple manual way. This effect was strongly felt in the sludge samples, which contained iron and magnetite particles and where no hematite particles were detected. Magnetic particles could not be effectively separated from the dust samples with high portion of hematite.
- The amorphous sample of sludge from the electrolyte of tinning line was annealed in a furnace in order to crystallize. The oxide of tin cassiterite was identified in the sample.
- Following minerals were found in the sludge samples with non-magnetic particles: lime, srebrodskite, diopside, periclase, hedenbergite and franklinite, which were not found in the original samples.
- Steelshop and Sintering dust commonly contain following minerals: hematite, magnetite, quartz, calcite and dolomite. Sintering dust differs from the Steelshop dust by small amount of lime and salts: sylvite and halite, which were found in the Steelshop dust. The Steelshop dust contains graphite, magnesite, hedenbergite and small amounts of fluorite, baddeleyite and zincite.

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