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Advances in Sintering of Iron Ores and Concentrates

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Abstract

Chapter “Sintering of iron ores and concentrates” is focusing on the study of theoretical, thermodynamic and experimental results in the production of sinters from iron ores and concentrates. The authors of the chapter have long been interested with the production of sinter from iron ores and have recently also focused on the use of biomass as a substitute for a part of coke breeze in the production of iron sinter. Important characteristics of the chapter include the characteristics of iron ores and concentrates used to produce sinter including physico-chemical, mineralogical and metallurgical properties. Predicting the influence of the properties of iron ores and concentrates on the final quality of the sinter and on the production of pig iron is another part of the study. These properties are a key factor in achieving the highest possible agglomerate quality for pig iron production. The sintering process requires mathematical and physical modeling. For this reason, the authors created thermodynamic models of sintering including material-heat balance of sinter production. In the final part of chapter is the use of traditional and alternative carbonaceous fuels in the production of sinters, mainly in the context of replacement of coke breeze with biomass.

Keywords: iron ore, iron concentrate, sintering, coke, biomass, modeling

1. Introduction

Iron ores are very important not only in the production of pig iron in blast furnace, but it also in the production of sinter. These are mainly fine-grained iron ores and concentrates. The sinter is a basic input material for the production of pig iron in the blast furnace and plays an important role in the integrated metallurgical cycle. It is produced by high-temperature sintering of fine iron ore, iron ore concentrates and other ferriferous materials (e.g. secondary materials from iron and steel production). The main criterion of the sintering process is the quality produced sinter while maintaining the ecological nature of the production.

1.1 Characteristics of iron ores and concentrates used to produce sinter

1.1.1 Physical, chemical, mineralogical and metallurgical properties

Iron ore is very important for iron and steel industries. It is therefore elementary for the production of pig iron in blast furnace. Almost all (98%) iron ore is used in

steelmaking. Iron ore is mined in about 55 countries. The five largest countries together produce about three quarters of world production, **Figure 1** [1]. Australia and Brazil dominate the world’s iron ore production. Iron ores are classified according to the nature of the ore mineral and according to the nature of the gangue [1].

From a chemical point of view, iron ores are divided into groups: anhydrous oxides, hydrated oxides, carbonates and silicates. **Table 1** shows the classification of iron ores according to the type of ore mineral [2]. In practice, given this principle, only a few iron ore minerals out of a total of more than 300 types are considered. They are mainly oxide minerals, such as magnetite - Fe_3O_4 (72.36% Fe), hematite or martite (pseudomorphism of hematite after magnetite) - Fe_2O_3 (69.94% Fe), limonite - (62.85% Fe) (mixture of hydrated oxides Fe, mainly goethite with lepidocrocite $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, often with absorbed elements of vanadium, manganese, etc.). Carbonate ores based on siderite - FeCO_3 (48.30% Fe) can also be processed, as well as silicate ores (leptochlorites), e.g. chamosite. The highest natural iron content is in magnetite iron ores. Hematite ores are easily reducible. Chamosite is a

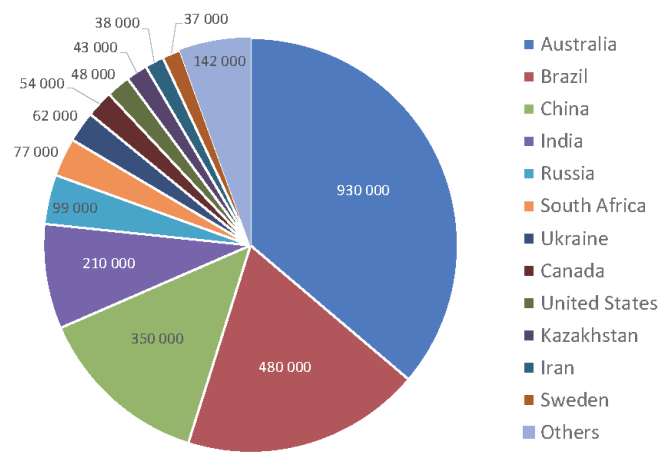


Figure 1.
Global production of usable iron ore (thousand metric tons) in 2019 [1].

A group of iron ores	Mineral	Chemical formula	Color	Density (g.cm ⁻³)	Fe content in pure state (wt.%)
Magnetite ore	Magnetite	Fe ₃ O ₄	Dark gray	5.17	72.4
Semimartite ore	Magnetite	Fe ₃ O ₄	Black	5.1–5.2	—
Martite ore	Hematite	Fe ₂ O ₃	Dadrk red	—	70.0
Hematite ore	Hematite	Fe ₂ O ₃	Red	5.26	70.0
Limonite ore	Hydrohematite Goethite Lepidocrocite	Fe ₂ O ₃ ·nH ₂ O	Dark red Light red Dark brown	3.1–4.4	63.0–69.0
Siderite ore	Siderite	FeCO ₃	Gray	3.9	48.3
Chamosite ore	Chamosite	Fe ₄ Al (Si ₃ AlO ₁₀). (OH) ₆ ·nH ₂ O	Green Black	3.03–3.19	38.0

Table 1.
Classification of iron ores [2].

very difficult to reduce iron ore. Oxidation of magnetite creates varieties of hematite-martite and semimartite (according to the degree of oxidation). Most of the world's production of pig iron - 90%, is produced from iron ores of an oxidic nature, of which 5% from magnetite ores and 85% from hematite ores.

Figure 2 shows some known iron ores from world. The samples come from the Atlas of iron ores, which was created at the VUHŽ Dobrá (Czech republic) research institute [3] and with which the authors of this chapter have collaborated in the past.

The evaluation of the properties of iron ores shows that the best ores are from Brazil, Australia and Venezuela, **Table 2** [3]. They have a suitable particle size distribution, excellent chemical and mineralogical composition, they are well reducible and stable after temperature tests. The optimal piece size of raw iron ore for blast furnaces is 10–40 mm and it is necessary to completely exclude dust fractions below 5 mm. Kryvyi Rih ore has an unsatisfactory chemical composition - low Fe content and high SiO₂ content, which is unsuitable for the blast furnace process. On the other hand, this ore has good physical properties (eg. strength and stability) and metallurgical properties (reducibility and plasticity). Ore Algeria has a high proportion of large grains (above 40 mm) and lower strength, reducibility is average and plasticity is unsuitable (high temperature range). Indian ore has worse metallurgical properties - lower reducibility and higher plasticity temperature range. The softening onset temperature and the softening interval characterize the plasticity and also affect the position and height of the plastic zone in the blast furnace. The course of softening depends on the type of ore and cannot be influenced. The blast furnace charge should therefore contain a minimum number of different iron ore raw materials.

Sinter grade ores and concentrates are characterized as iron ore raw materials with the required granulometry, composition and properties. The following



Figure 2.
Iron ores (the photographs were created from atlas of ores [3] by the authors of this chapter).







Iron ore							
		Brazil MBR	Kryvyi Rih (H)	Australia	Algeria	Venezuela	India
Analysis (wt.%)	Fe	68.13	47.59	67.20	59.50	65.09	65.50
	FeO	1.12	2.00	0.49	0.24	1.08	0.53
	Fe ₂ O ₃	96.16	65.82	95.50	84.81	91.81	93.08
	Mn	0.04	0.05	0.05	1.28	0.26	0.08
	SiO ₂	0.53	24.30	1.77	2.85	4.49	2.81
	Al ₂ O ₃	1.61	3.25	1.33	0.65	1.14	2.07
	CaO	0.23	0.22	0.28	1.31	0.15	0.35
	MgO	0.03	0.20	0.10	0.72	0.19	0.06
	P	0.05	0.05	0.02	0.02	0.03	0.03
	S	0.01	0.03	0.01	0.03	0.01	0.02
	Na ₂ O	0.07	0.14	0.01	0.08	0.07	0.09
	K ₂ O	0.04	0.95	0.02	0.06	0.06	0.07
Grain (mm)	< 1	1.55	2.74	1.92	0	8.03	6.34
	< 5	5.64	4.75	5.85	0	13.22	10.30
	> 10	81.13	91.40	70.54	98.70	64.16	85.04
	> 25	30.18	49.54	14.03	97.15	0.80	47.18
	> 40	5.36	23.04	0	84.19	0	16.80
	d _A	20.46	28.60	16.30	59.85	11.89	25.84
Apparent density (g.cm ⁻³)	ρ _A	1.99	1.78	2.22	1.45	2.42	2.15
Real density (g.cm ⁻³)	ρ	5.21	3.85	4.82	4.11	4.95	4.73
Porosity (%)	P	18.6	7.8	16.2	33.6	12.1	20.9
Surface (m ² .g ⁻¹)	S	1.22	0.96	1.63	5.00	0.44	6.55
Drum strenght (%)	+ 6.3 mm	78.99	84.63	89.42	75.12	88.94	77.62
Heat test (%)	+ 6.3 mm	76.62	73.04	69.42	85.70	69.32	62.26
Reducibility (%)	R _i	40	35	42	33	43	30
Reducibility (min)	R _{i60}	101	110	95	121	100	170
Plasticity (°C)	Pl ₆₀	1174–1320	1150–1483	1380–1423	990–1390	1265–1490	1210–1480
Mineralogy	XRD	Hematite, goethite	Martite, hydrogoethite quartz	Hematite, goethite, quartz	Limonite, goethite, hydrogoethite, quartz	Hematite, martite, goethite, quartz	Martite, goethite, hydrogoethite, quartz
Reducibility is according ISO 7992.							

Table 2.
Properties of iron ores (according [3]).

Tables 3, 4 provide a basic chemical analysis of some, also used in Slovakia, sinter grade ores and concentrates for the production of sinter [4].

The authors of this chapter used in their research mainly such iron-bearing raw materials as sinter grade ores supplied from Kryvyi Rih and Brazil and concentrates from Michailovsky and Inguletsky MBCs (Mining-Benefeciation Combines), **Figure 3**. The grain size of the sinter grade ores is 90% below 10 mm, the grain size of the iron concentrates is 90% below 0.04 mm. Iron ores and concentrates before sintering are pretreated in the granulation process. The values of specific surface of the granulated materials should not be lower than 2000 cm².g⁻¹, which corresponds to 100% portion of the size fraction below 0.15 mm, from which 75% of the size fraction below 0.04 mm.

Table 5 shows the chemical composition of iron-bearing raw materials, where the difference in the richness of ores can be seen. **Figure 4** shows the structure of the samples and Energy Dispersive X-Ray Analysis (EDX), **Table 6**. The larger

Iron ore	Fe	Mn	SiO ₂	Al ₂ O ₃	CaO	MgO	P	S	Na ₂ O	K ₂ O	Zn	H ₂ O
	(wt.%)											
Krivbas	64.04	0.02	6.24	0.68	0.05	0.05	0.035	0.014	0.183	0.046	0.002	3.9
Sucha Balka	59.86	0.02	12.10	0.77	0.06	0.14	0.026	0.011	0.148	0.043	0.004	3.8
Zaporozska	62.70	0.06	7.38	0.84	0.52	0.23	0.023	0.020	0.055	0.027	0.004	4.6
Brazil MBR	65.00	0.08	3.50	0.90	0.08	0.06	0.042	0.005	0.005	0.008	0.003	7.4
CVG-Venezuela	65.66	0.31	1.16	0.89	0.10	0.05	0.074	0.014	0.013	0.024	0.003	6.8
Liberia	64.50	0.16	6.73	0.96	0.10	0.05	0.047	0.004	0.013	0.015	0.003	7.5
CIL Trinidad	67.57	0.01	1.48	0.47	0.70	0.52	0.001	0.003	0.001	0.001	0.001	4.0
Hope Downs	64.79	0.02	1.36	0.77	0.03	0.07	0.057	0.007	0.016	0.001	0.006	5.5

Table 3.
Chemical analysis of selected sinter grade ores in the delivered state [4].

Iron concentrate	Fe	Mn	SiO ₂	Al ₂ O ₃	CaO	MgO	P	S	Na ₂ O	K ₂ O	Zn	H ₂ O
	(wt.%)											
Southern MBC	67.50	0.023	5.90	0.15	0.12	0.35	0.010	0.027	0.059	0.014	0.003	10.2
Central MBC	64.90	0.032	8.49	0.31	0.19	0.35	0.015	0.073	0.038	0.042	0.003	9.3
Stoilensky MBC	66.36	0.041	6.78	0.18	0.21	0.44	0.014	0.035	0.045	0.049	0.003	8.8
Inguletsky MBC	65.68	0.027	7.28	0.25	0.23	0.29	0.013	0.066	0.032	0.042	0.003	9.4
Lebedinsky MBC	67.79	0.025	4.92	0.14	0.16	0.33	0.011	0.044	0.062	0.035	0.002	9.5
Kovdor MBC	64.74	0.430	0.42	1.78	0.23	5.49	0.038	0.269	0.026	0.032	0.034	2.7
LKAB magnetic fines	70.78	0.050	0.61	0.25	0.16	0.33	0.021	0.008	0.041	0.045	0.003	2.7
Venezuela	69.65	0.056	0.97	0.78	0.24	0.13	0.075	0.020	0.011	0.022	0.005	7.0

Table 4.
Chemical analysis of selected iron ore concentrates, as delivered [4].



Figure 3.
Iron raw materials for sintering process.

Iron ore material	Fe	FeO	Fe ₂ O ₃	Mn	SiO ₂	Al ₂ O ₃	CaO	MgO	P	S	Na ₂ O	K ₂ O
	(wt.%)											
Sinter grade ore Krivbas	57.86	0.72	81.94	0.05	15.17	0.74	0.15	0.25	0.05	0.01	0.08	0.05
Sinter grade ore Brazil	65.23	0.14	93.12	0.57	2.21	1.32	0.10	0.10	0.05	0.01	0.05	0.05
Concentrate Inguletsky MBC	67.91	28.45	65.57	0.07	4.92	0.18	0.59	0.49	0.02	0.09	0.06	0.07

Table 5.
Chemical analysis of selected iron ore materials, as delivered.

grains of Brazil sinter grade ore are practically free of impurities and have a relatively homogeneous structure. In addition to iron oxides, the smaller sinter grade ore Brazil grains also contain impurities in the form of silicon and aluminum oxides.

In general, the richness of concentrates is in the range of 65–70%, while sinter grade ores have this interval wider and shifted slightly lower (55–67%).

Taking a closer look at the chemical composition of iron commodities, we can see a fundamental difference in the FeO content of sinter grade ores and concentrates (**Table 5**), which is related to the enrichment processes of concentrate production and mainly the hematite character of the sinter grade ores used, **Table 7**.

The SiO₂ content (in the form of quartz) is desirable at a minimum level and depends on the specific ore resp. concentrate. Manganese is also a welcome ingredient and increases the utility value of ore along with titanium and vanadium. Undesirable impurities are mainly sulfur, phosphorus, zinc, lead, arsenic, copper, sodium, potassium, which are chemically bound in the minerals of the ore part of the burden, as well as in the agglomeration fuel.

The form of occurrence of harmful elements in iron ores is as follows [5–7]:

- Arsenic is present in arsenopyrite or arsenolite.
- Zinc is present in the form of smithsonite or sphalerite.
- Lead occurs in the form of galena.
- Copper can be present in the form of chalcopyrite or chalcocine.
- Phosphorus forms phosphite, which is a part of apatite.
- Sulfur is present in the form of sulphides such as FeS₂ and FeS and of sulphates such as CaSO₄, MgSO₄, BaSO₄.

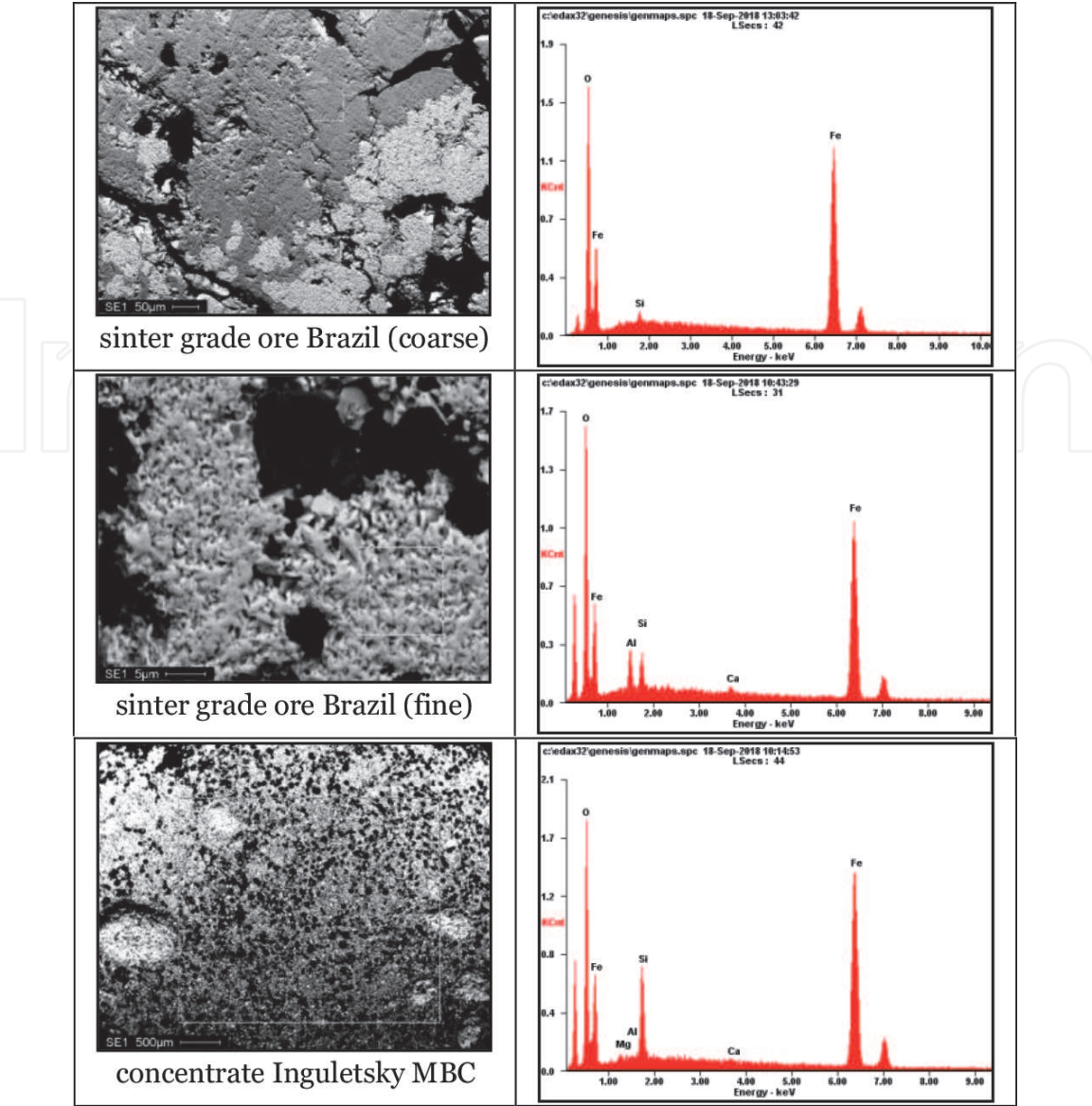


Figure 4.
EDX analysis of Brazil iron ore and Inguletsky iron concentrate.

Element	Sinter grade ore Brazil (coarse)		Sinter grade ore Brazil (fine)		Concentrate Inguletsky MBC	
	Wt%	Atom %	Wt%	Atom %	Wt%	Atom %
O	18.45	44.13	17.56	41.15	14.49	35.33
Fe	81.55	55.87	75.40	50.62	78.21	54.61
Mn	—	—	1.56	1.06	—	—
Si	—	—	3.00	4.01	5.77	8.02
Al	—	—	1.85	2.57	0.25	0.36
Ca	—	—	0.64	0.59	0.57	0.55
Mg	—	—	—	—	0.71	1.14

Table 6.
EDX analysis of selected iron ore materials.

Quality sinter grade ores is characterized by a high content of total iron (min. 63%), Al_2O_3 content max. up to 1.3%, SiO_2 up to 6%, P below 0.04% and alkali content max. up to 0.08% [8].

Mineralogical phase	Content of phase (wt%)		
	Sinter grade ore Krivbas	Sinter grade ore Brazil	Concentrate Inguletsky MBC
Hematite	72.50	75.48	—
Magnetite	—	—	89.70
Goethite	15.20	18.73	—
Mayenite	—	1.23	—
Quartz	12.30	4.56	10.30

Table 7.
RTG analysis of selected iron raw materials.

From the mineralogical point of view, it is important to know the ore texture and structure that characterizes the distribution of individual mineralogical components, respectively indicates the shape and size of the mineral components and the nature of their structure. The mineralogical composition of Fe ores is characterized by the majority shape of the grain in terms of their structure, **Table 8** [2].

Some iron bearing materials were evaluated prior to laboratory experiments and the grain shape factor was determined [9]. The grain shape factor specifies calculation a grain periphery, which differs from the circle (for circle is shape factor = 1). The iron ore shown in **Figure 5a** consists the grains with polyhedron shape (shape factor = 0.59) in a size of 5–40 μm. The iron ore shown in **Figure 5b** consists of the grains with polyhedron shape (shape factor = 0.94) with smooth surfaces in a size of 10–50 μm. In this case, the hematite grains are clearly visible. The iron ore shown in **Figure 5c** consists of the grains with partially smoothened edges of polyhedron shape (shape factor = 0.78) in a size of 10–100 μm. The iron ore shown in **Figure 5d** consists of the grains with lamellas shape (shape factor = 0.70) in size of 10–250 μm. The hematite grain can be seen at the top.

In addition to the chemical-mineralogical composition of sinter grade ores and concentrates, it is also necessary to know their granulometry. The grain size

Mineralogical composition	Shape of grain
Magnetite, pyrite, quartz	Spherical, cubic
Magnetite, hematite, goethite, quartz	Cubic, platelet-shaped
Hematite, goethite, quartz, kaolinite	Platelet-shaped, fragmentary
Hematite	Polyhydral, plate-shaped

Table 8.
Major grain shape types of iron ores [2].

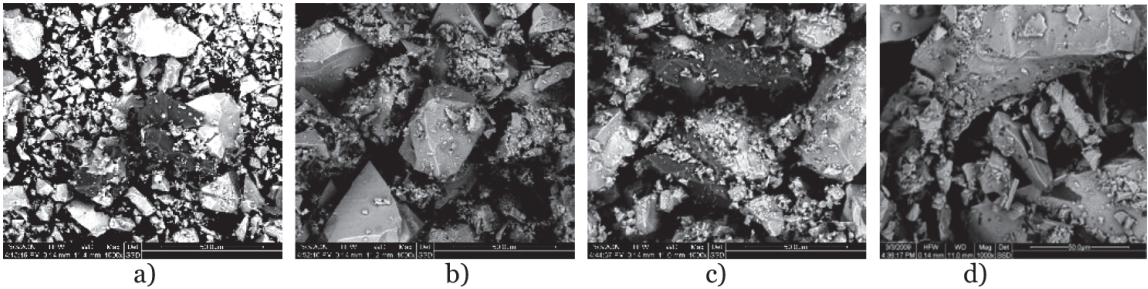


Figure 5.
Microstructures of iron ores with various shape factors [9]. (a) 0.59, (b) 0.94, (c) 0.78, (d) 0.70.

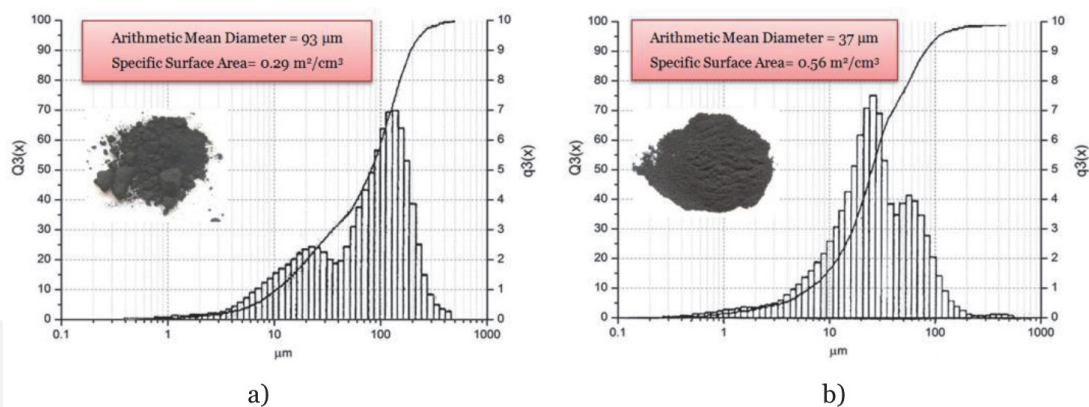


Figure 6.
Distribution of grain in iron concentrates. (a) Concentrate Kovdor MBC, (b) concentrate Lebedinsky MBC.

distribution will be related to the processing and treatment of extracted ore or the production of iron concentrate. Fine-grained concentrates are the product of flotation enrichment of ores and their predominant grain size is about 0.04 mm. The granularity is also directly related to the mineralogical composition and structure of the ore. The concentrates used in the sintering process have an overall wide grain size range. Most Ukrainian and Russian concentrates are very fine-grained in nature, where the extracted magnetite quartzite is crushed and ground below 0.075 mm and enriched by magnetic separation into a concentrate with Fe content up to 68%. Swedish magnetite concentrate, on the other hand, has only about 4% of the fraction below 0.1 mm at a richness of about 70%. Canadian magnetite concentrates have a proportion below 0.1 mm of about 15%, while the upper grain limit does not exceed 1 mm. The results of analysis of the selected concentrates are given in **Figure 6**.

1.1.2 The influence of the properties of iron ores and concentrates on the final quality of the sinter and on the production of pig iron

The operation of the blast furnace and the results of its work are most often evaluated according to the output and consumption of coke. Changes in the chemical composition and particle size distribution of the iron-bearing materials significantly affect their technological properties and thus the balance of components and the course of the blast furnace process. The development of iron metallurgy is conditioned by the quantity and quality of iron ores. The raw material base for iron production is characterized:

- lack of high-quality natural ores - only 10–12% of the world's iron ore reserves meet the current requirements of blast furnace practice,
- uneven distribution of world stocks in individual countries,
- low content of metal-bearing substance in mined ore,
- use of high-performance equipment in ore mining and enrichment.

To meet the requirements of the metallurgical industry, mined ores are increasingly treated and processed before being used in blast furnaces, and the treatment of ores must ensure:

- an increase in the iron content and removal of harmful and unwanted impurities,

- improving the physical and mechanical properties of ores,
- improving the reducibility of individual types of ores,
- averaging and stability of chemical composition and lumpiness of iron ore raw materials.

The implementation of the above requirements will achieve good permeability of the burden column, reduction of the amount of slag-forming additives in the burden, reduction of specific coke consumption, increase of blast furnace output, improvement of pig iron quality, more even operation of the furnace without more serious failures and fluctuations, reduction of iron production costs. In the blast furnace process, zinc and lead from iron raw materials belong among the so-called harmful elements with a significant influence on the formation and growth of sediments [5–7]. Potassium and sodium are undesirable in the blast furnace charge due to the disruption of the integrity of the carbon and graphite linings [5, 7].

The requirements for the quality of sinter are constantly increasing. The chemical and mineralogical composition of sintered materials affects the wettability of their surfaces and also influences considerably the strength of the binding of the material grains in the green pellets, and in this way also influences the conditions of sintering. The sintering rate depends on the initial properties of the iron ores and concentrates and the heating conditions of the sintered materials, i.e. it depends on the geometric parameters of ores and concentrates (grain size composition, the size of specific surface, grain morphology, microgeometry of the surface, porosity) and on the structural activity of the material.

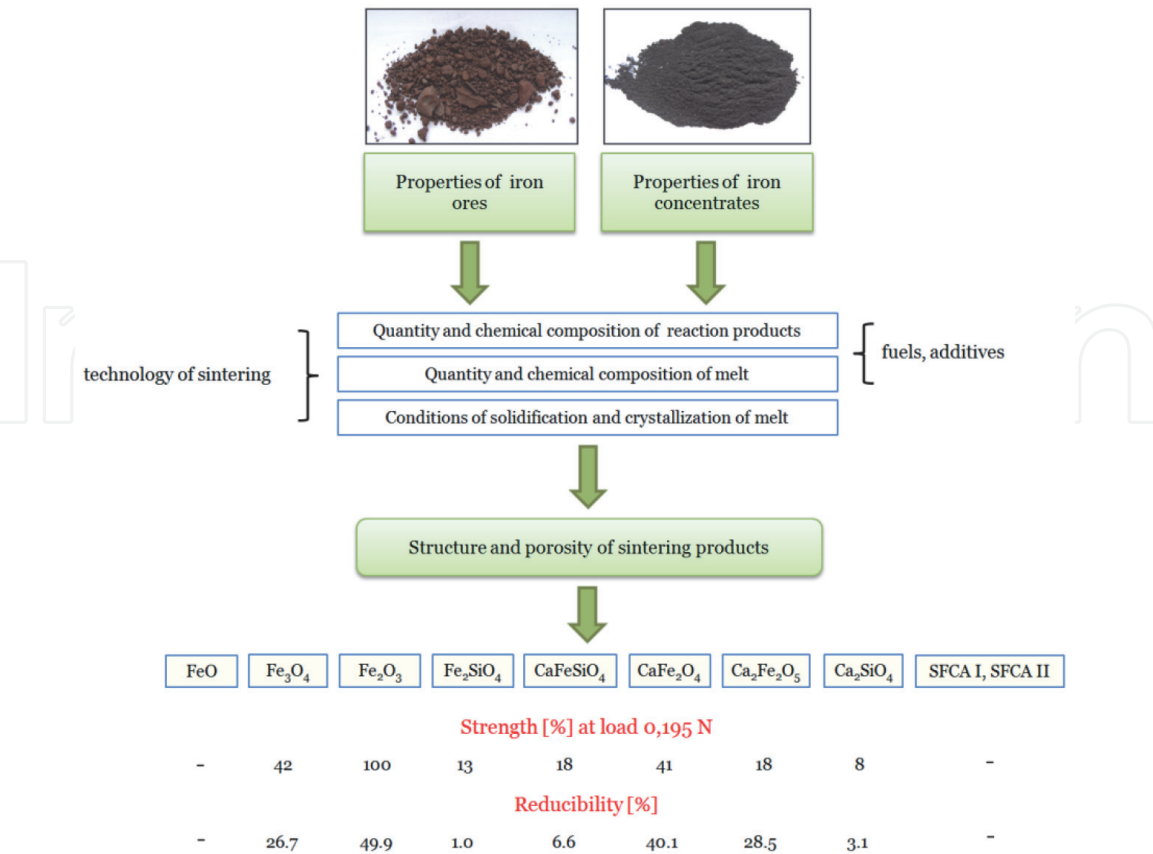


Figure 7. The influence of various factors on the Fe sinter (modified by authors according [2]). SFCA = silicoferrites of calcium and aluminum, strength and reducibility were realized on pure mineral compounds.

A good quality sinter is characterized by a suitable iron content, high reducibility, good strength and low fine grain shares content prior to charging into blast furnace and high strength after reduction in the blast furnace shaft. The influence of the properties of iron ores and concentrates on the final quality of the sinter is specified on **Figure 7**. **Figure 7** shows very good mechanical (strength) and metallurgical (reducibility) properties of major oxides (hematite and magnetite) and calcium ferrites. On the other hand, silicates have unfavorable properties.

The sintering product should have the proper physical features to bear transporting and should not produce dust while in the blast furnace. The sinter should be of good chemical, mineralogical and metallurgical properties and should contain as few detrimental admixtures as possible. In **Table 9**, some important properties of industrially produced sinters are listed, while the critical requirement for all sinter properties is stability [10].

Property of Fe sinter	SI unit	Min	Max
Content of Fe _{TOT}	[%]	48.20	57.00
Content of FeO	[%]	8.70	19.80
Content of CaO	[%]	7.30	14.40
Content of SiO ₂	[%]	5.40	9.60
Content of P	[%]	0.02	0.04
Content of S	[%]	0.03	0.05
Content of Na ₂ O + K ₂ O	[%]	0.05	0.08
Basicity	[–]	1.15	2.10
Granulometry	[mm]	5.00	50.00
Porosity	[%]	27.00	38.00
Real density	[g.cm ^{–3}]	4.13	4.44
Reducibility (ISO 7992)	[%]	60.00	85.00
Reducibility (ISO 4695)	[%/min]	0.80	1.40
Drum strength +6.3 mm	[%]	65.00	78.00
Abrasion index –0.5 mm	[%]	4.20	9.80

Table 9.
Properties of Fe sinters [10].

1.2 Modeling and simulation of sinter production under laboratory conditions

1.2.1 Material-heat balance and thermodynamic study of sinter production

The course of processes in the sintered material can be evaluated on the basis of changes in the physical and metallurgical properties of the sintering product. The transformation of the components of a material is related to the decrease in Gibbs free energy. It is possible to calculate the maximum work of reactions, i.e. oxidation reactions, reaction in solid state, reactions during formation of a melt and also reactions taking place during the recrystallization and cooling down of sintering products.

Thermodynamic calculations are thus essential when determining the characteristics of a technological process and they enable one to clarify the formation of

the major sintering products. By changing the basic condition of the thermodynamic system, it is feasible to find the optimum operating conditions of the sintering process and minimize the consumption of raw materials and energy [11].

For mathematical modeling the basic chemical reactions with standard Gibbs energy and mass and thermal balance were calculated. Thermodynamic data was obtained from the software HSC Chemistry. HSC Chemistry offers powerful calculation methods for studying the effects of different variables on the chemical system at equilibrium. The aim is to get the simplest approach (using this software to calculate equilibrium) which allows one to predict the output parameters (amounts, chemistry, mineralogical composition, and total heat) based on the initial composition analysis [11].

The mathematical model used by the authors in modeling the sintering process allows the calculation of Gibbs equilibrium diagrams, which characterize the change in the equilibrium composition of reactants and reaction products with changes in temperature. Using Kellogs diagrams of stability areas in the considered systems based on the combustion of carbonaceous fuel in the sintering charge, it is also possible to determine the stability of individual phases at different partial pressures of gaseous components. The modeled systems and the results of thermodynamic calculations can specify the influence of the amount and type of fuel used on oxidation–reduction processes. The said model allows the control of the overall thermal effect of the sintering process during individual instances of experimental laboratory sintering while it employed the prediction of sinter phase composition at the sintering temperatures in the calculations. Since the phase composition of the sinter is determined on samples of sinter after cooling, the computational model should bring a new perspective of the processes taking place during sintering [11].

Figure 8 shows the global method with modeling the mass and thermal balance of the sintering process. Pursuant to the modeling of the sintering process in the

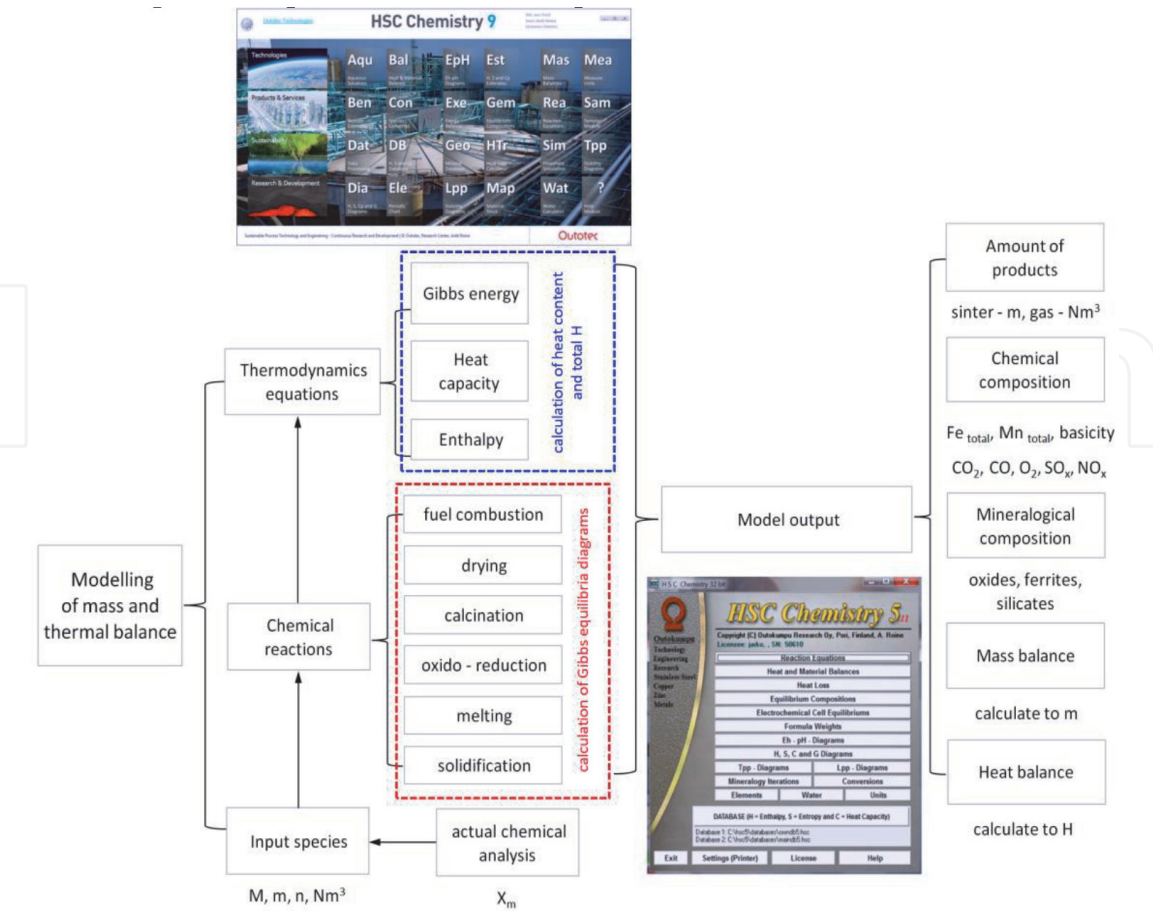


Figure 8. Scheme presenting the global method with modeling the mass and thermal balance (modified by authors according [11]).

laboratory conditions, it was feasible to specify the created model by the following parameters [11]:

- calculation of the quantity and chemical composition of sinter,
- prediction of the mineralogical composition of sinter at the sintering temperatures,
- calculation of the mass and thermal balance on the basis of the input and output enthalpies of individual components.

The authors of this chapter have already carried out a large number of laboratory experiments [9–11], the results of which can be compared with the calculated thermodynamic models. It is apparent that the model calculations of added fuel in charge are highly correlated with the experimentally determined values, **Figure 9a**. A higher correlation was found for the yield of produced sinter (calculation for 100 kg of charge), **Figure 9b**.

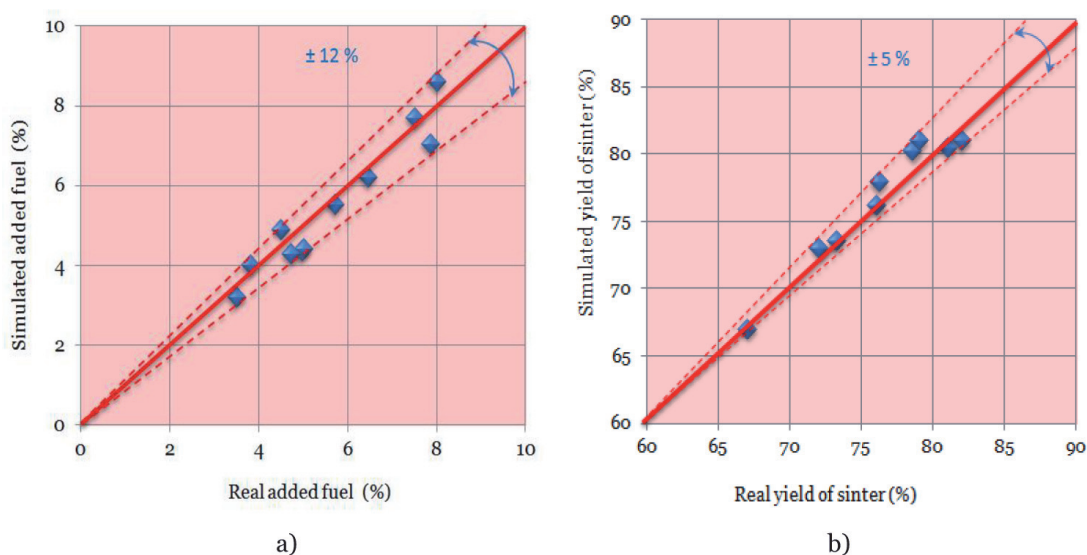


Figure 9. Comparison between the real and simulated added fuel for sintering (a) and real and simulated amount of the sinter (b).

1.2.2 Specification of the model of laboratory sintering pot and monitoring of the sintering process

The sintering process is thermal process used to transform fine particles of iron ore and concentrate into porous product known as sinter. In the sintering process fuel is in the form of coke breeze (or in the form various types of carbon fuels) used for production of iron-ore sinter [10]. In this sintering process are basic materials mixed, granulated, ignited and fired at a temperatures 1200–1380°C. Sintering of materials can take place under the temperature conditions, which allow binding the particles by reaction in solid state, or under the temperature conditions, which allow the origin of the melt acting as a binding phase after its cooling. In the case of sintering with the presence of the melt, its quantity and chemical compositions is important.

The process of laboratory sinter production is divided into two stages – cold section and hot section, **Figure 10**. In the cold section, the supply of raw materials, adjustment of grain size to the required piece size, averaging of the chemical composition of materials and granulation of the final sintering burden is ensured. The hot section ensures ignition of the sintering charge, sintering of the sintering charge, removal of hot flue gases (subsequent cleaning) and cooling of the sinter.

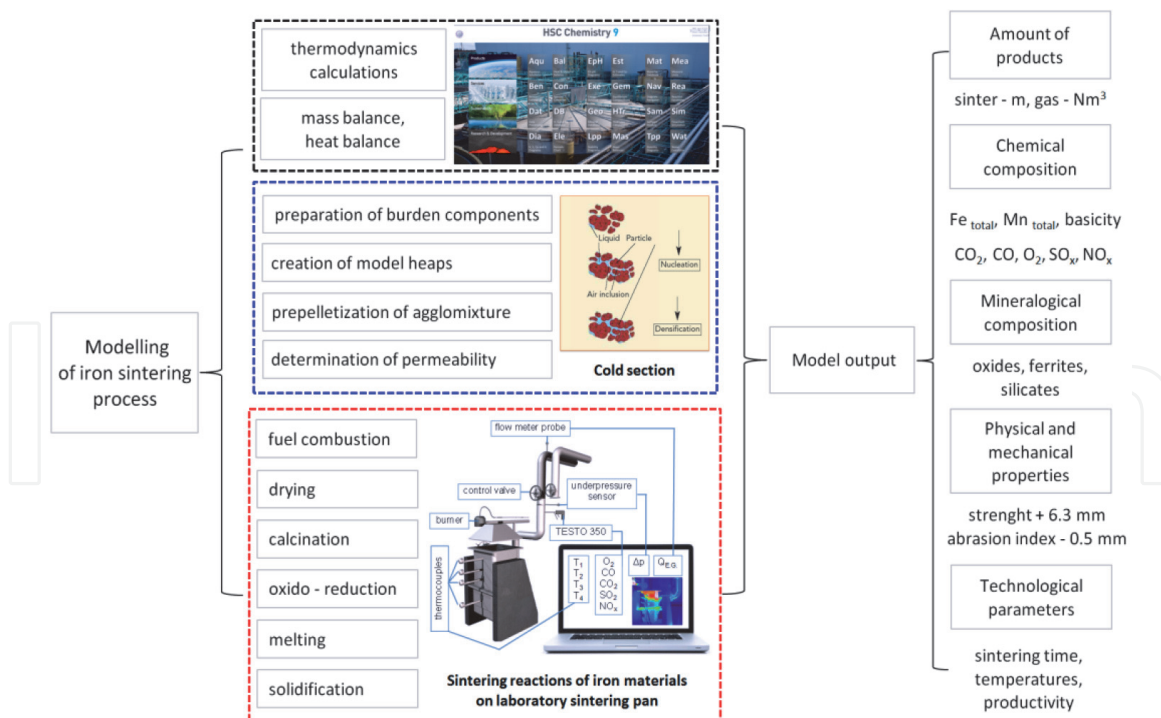


Figure 10.

Scheme presenting the global method with modeling of the iron sintering process in laboratory conditions in Slovakia.

Many physico-chemical processes take place during sintering – fuel combustion, drying of components, calcination of carbonates, oxido-reduction processes, melting of grains and solidification.

The authors of this chapter carried out many laboratory experiments [9–13], the results of which can be generalized and used to expand the information database on the use of carbonaceous fuels in the production of sinter. These experiments were carried out in a laboratory sintering pot (LSP), which is located at the Institute of Metallurgy, Faculty of Materials, Metallurgy and Recycling, Technical University of Košice in Slovakia, **Figure 10**.

In order to simulate the production of sinter close monitoring of the sintering process is necessary. Laboratory sintering pot is fully equipped with measuring devices and analyzers. The temperature was measured by thermocouples. For the high temperature range in the sintered layer, three thermocouples of the PtRh10-Pt type were used. The flue gas temperature was read at two levels by NiCr-Ni type thermocouple. Chemical composition and temperature of the flue gas were analyzed by TESTO 350 device. The differential pressure was measured by Annubar type probe, which served for calculating the amount of sucked air (or flue gas). All quantities were read at 15-second intervals and collected in a logger. After each experiment, the collected data were transformed into a form usable on a personal computer.

Implementation of an experimental sintering model is also possible using the monitoring of the temperature field of the sintering pot by a thermal imaging camera. With the help of the sensed thermal imaging profile of the sintering pot (**Figure 11**), it is possible to monitor the displacement of the fuel combustion zone in the sintering layer. By sensing the surface of the layer after ignition of the burden, (**Figure 12**), it is possible to monitor the inhomogeneity of the temperature field of the sintered layer. The thermal profile of thermal imaging monitoring indicates different conditions of fuel combustion in the volume of the layer, which may be caused by heterogeneity of fuel distribution. The model of LSP has been innovated by a transparent high-temperature wall that allows visual monitoring of

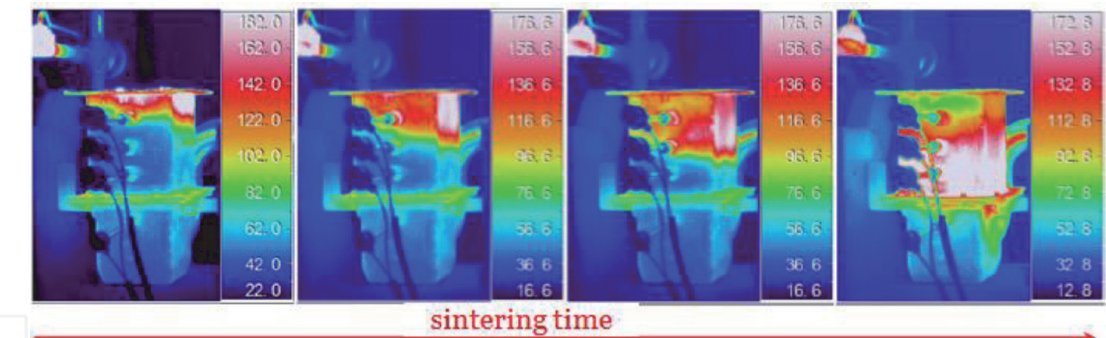


Figure 11.
Thermal imaging of a laboratory sintering pot.

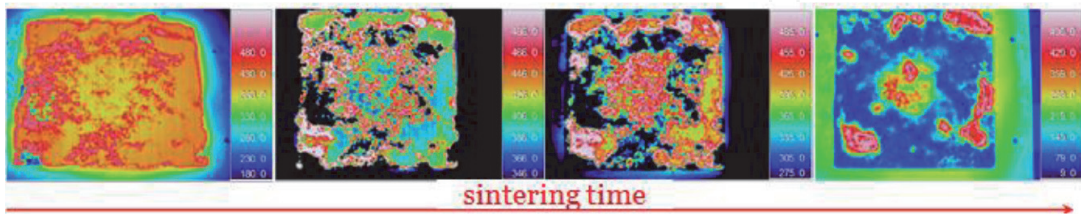


Figure 12.
Thermal imaging of the surface of the burden after ignition.

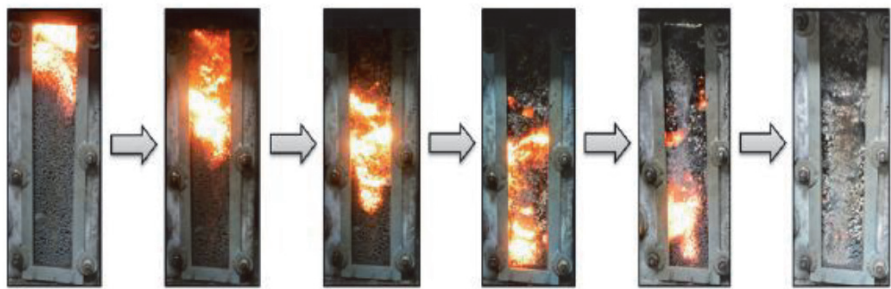


Figure 13.
Course of sintering and moving of sintering zone.

the combustion zone in the sintered layer during the production of iron ore sinter, **Figure 13.**

1.2.3 Technological and ecological aspects of the production of sinters from poor and rich iron-bearing materials

As part of the implementation of laboratory experiments on a laboratory sintering pot, the following iron-bearing raw materials were used for sintering, **Table 10.**

In the sintering process, standard coke breeze was used as fuel. These raw materials were incorporated in the prepared sintering mixtures, which had a basicity in the range of 1.7–2.8. The next relation was used to calculate the basicity: $B = (\text{wt.\%CaO} + \text{wt.\%MgO}) / (\text{wt.\%SiO}_2 + \text{wt.\%Al}_2\text{O}_3)$. It was therefore the production of highly basic sinters. The produced sinters had content of iron in the range of about 46–52%.

In the experiments, the ratio of ferriferous raw materials (Krivbas and Michajlov) – 100% sinter grade ore and 100% concentrate was changed. Concentrate Nižná Slaná was used in mixtures of sinter grade ore/concentrate. In this chapter, primarily the experiments with separate ferriferous raw materials are specified due to the more significant impact of fuel consumption on sinter quality.

Iron ore material	Fe	FeO	Fe ₂ O ₃	Mn	SiO ₂	Al ₂ O ₃	CaO	MgO	P	S	Na ₂ O	K ₂ O
	(wt.%)											
Sinter grade ore Krivbas	60.70	0.14	86.26	0.02	9.61	1.35	0.07	0.06	0.05	0.02	0.29	0.08
Concentrate Michajlov	64.52	23.57	66.44	0.01	8.60	0.06	0.19	0.09	0.01	0.01	0.08	0.20
Concentrate Nižná Slaná	51.76	20.02	45.19	1.97	5.30	1.83	3.82	6.58	0.08	0.12	0.07	0.42

Table 10.
Chemical analysis of iron materials for sintering.

Table 11 shows a thermal profile and sinter made by sintering using 100% sinter grade ore, while coke breeze was used for sintering. Due to lack of fuel (3% of coke in mixture), there were low temperatures of 600–900°C in the sintered layer. The sinter had unacceptable properties – only some microgranules were connected. The

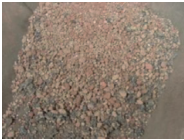
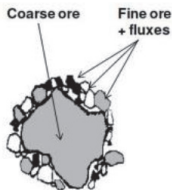
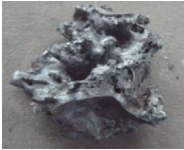

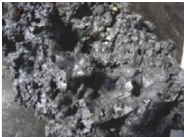
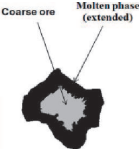

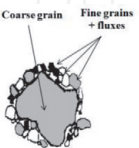

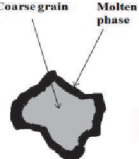
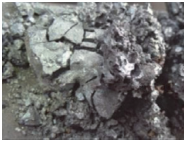
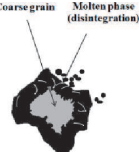
Iron burden	Coke breeze (%)	Photo	Mechanism	Temperatures (°C)
Iron ore (100%)	3			600–900
Iron ore (100%)	5			1150–1320
Iron ore (100%)	7			1180–1420
Iron concentrate (100%)	4			530–1020
Iron concentrate (100%)	6			1130–1350
Iron concentrate (100%)	8			1210–1440

Table 11.
Production of sinters in laboratory conditions.

essence of the sintering process – i.e. producing the sinter with the required production, qualitative and quantitative parameters, was not accomplished in this case. The theoretical minimal quantity of fuel is always required for sinter production, which depends on the physical–chemical properties of input iron bearing raw materials and basicity of the produced sinter. In the presence of 5% of coke in sintering mix, standard temperatures of 1150–1320°C were achieved in the sintered layer with 100% of sinter grade ore, resulting in sinter with the required properties. On the surface of individual grains, the melt was formed, and due to the low viscosity of the liquid phase, multiple grains were bound together producing a sinter. At 7% of coke in mixture, high temperatures (up to about 1420°C) were reached in the sintered layer, resulting in sinter with the extended melting phase. Similar connections were found in the sintering of iron concentrates, with the fact that at higher fuel content (8% of coke) the sinter was disintegrated. A high FeO content was determined in this sinter (14.23%), which was a significant increase compared to FeO content in the charge (5.2%). Since the added fuel was probably not uniformly distributed into the individual grains (some were already partially sintered), there might have been microvolumes with a higher proportion of fuel. In these volumes, reducing conditions were created with high temperatures (up to about 1440°C), under which higher Fe₂O₃ and Fe₃O₄ oxides were reduced to FeO. In some samples of the sinter, break-up of sinter was observed. The disintegration of the sinter is sometimes associated with the formation of dicalcium silicate, sometimes with higher content of fuel. When using poor iron concentrate Nižná Slaná in the mixtures, higher amounts of fuel had to be used and the properties of the sinter were not adequate for the blast furnace process.

The achieved results from laboratory experiments can be summarized in the following points:

- Theory and balance calculations of the sintering process defined fuel (coke breeze) were the main source of gaseous emissions of CO and CO₂ in the flue gases.
- Due to the production of a highly basic sinter, a certain amount of CO₂ passes into the flue gas also through the dissociation of carbonates present in the burden (approx. 3–7% depending on the basicity).
- By reducing the underpressure, the temperature level in the sintered layer increases, the yield of the produced sinter is increased and the required quality parameters of the produced sinter are achieved.
- It has been found that increasing the fuel in the sintering charge increases the FeO content in the sinter. This fact is also confirmed by the effect of increasing FeO in the sinter with an increase in temperatures in the sintered layer.
- By increasing the ratio of concentrate/ore in the sintering burden (from 1.2 to 1.8) there was a decrease in the yield of the produced sinter.
- Technological recommendations were proposed in terms of achieving the required qualitative and quantitative parameters of the sintering process with emphasis on reducing CO and CO₂ emissions. Among the most important can be mentioned regular control of the permeability of the sintering charge, control and regulation of the vertical sintering rate in operating conditions, optimization of the underpressure, etc.) [10].





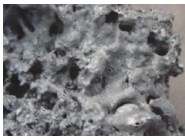

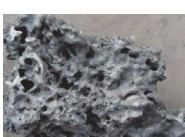



1.3 The use of traditional and alternative carbonaceous fuels in the production of sinters

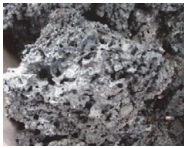



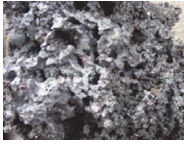



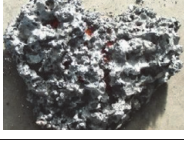





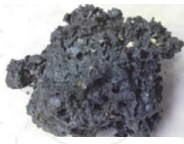

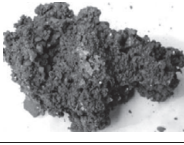



1.3.1 Replacement of coke breeze with biomass

The ways of using biomass for energy purposes are predominantly predetermined by its physical and chemical properties. The biomass is characterized by the relatively high and frequently variable water content, which significantly affects the energy properties of biomass fuel. The various types of biomass (primarily of wood and plant origin) have much higher content of volatile matter than coke breeze. Analyses of the various types of biomass that have been used in the production of iron-bearing sinter in Slovakia shown in **Table 12** [10–13].

Carbonaceous materials	Moisture [%]	Ash [%]	Volatile matter [%]	Fixed carbon [%]	Sulfur [%]	Calorific value [MJ/kg]
Coke breeze	1.5	14.5	3.5	82.0	0.59	28.16
Charcoal	4.9	3.5	8.2	88.3	0.05	30.46
Walnut shells	9.6	0.7	81.3	18.0	0.05	16.90
Oak sawdust	7.1	1.5	83.4	15.1	0.05	16.56
Pine sawdust	13.6	0.9	85.6	13.5	0.05	15.94
Lignin	8.6	3.4	67.90	20.1	0.17	23.14


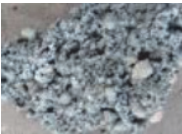

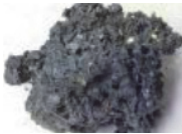

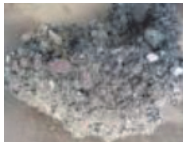
Table 12.
Analysis of selected carbonaceous materials which have been used in sintering in the Slovakia [10–13].

Type of fuel	CS [%]	Photograph of sinter	Sintering zone	Sinter characteristic	Ecological aspects
Coke breeze	0			Standard qualitative parameters	Standard parameters
Charcoal	20			Standard qualitative parameters	Lower emissions of CO _x , NO _x
Charcoal	44			Higher volume of melt, excellent strength	Lower emissions of CO _x , NO _x , SO ₂
Charcoal	50			Higher inhomogeneity, standard qualitative parameters	Lower emissions of CO _x , NO _x , SO ₂
Charcoal	86			Low volume of melt, worse qualitative parameters	Lower emissions of CO _x , NO _x

Type of fuel	CS [%]	Photograph of sinter	Sintering zone	Sinter characteristic	Ecological aspects
Oak sawdust	20			Standard qualitative parameters	Lower emissions of CO _x , SO ₂
Oak sawdust	44			Low volume of melt, unacceptable qualitative parameters	Lower emissions of SO ₂
Pine sawdust	8			Standard qualitative parameters	Lower emissions of CO _x , SO ₂
Pine sawdust	20			Low volume of melt, unacceptable qualitative parameters	Lower emissions of CO _x , SO ₂
Nut shells	8			Standard qualitative parameters	Lower emissions of NO _x , SO ₂
Nut shells	20			Standard qualitative parameters	Lower emissions of NO _x , SO ₂
Nut shells	50			Higher inhomogeneity, standard qualitative parameters	Lower emissions of CO _x , NO _x , SO ₂
Lignin	20			Standard qualitative parameters	Lower emissions of NO _x , SO ₂
Lignin	50			Low volume of melt, worse qualitative parameters	lower emissions of CO _x , NO _x , SO ₂
Lignin	86			Low volume of melt, unacceptable qualitative parameters	Lower emissions of CO _x , SO ₂

CS = coke substitution.

Table 13.
Characteristic of sintering of iron materials with biomass.

Sinter							
		Coke powder (100%)	Charcoal (86%)	Nut shells (20%)	Lignin (20%)	Oak sawdust (20%)	Pine sawdust (20%)
Analysis (wt.%)	Fe	50.94	51.05	50.85	53.43	49.53	50.94
	FeO	8.35	5.32	6.76	7.55	6.33	5.08
	Fe ₂ O ₃	66.71	63.22	61.07	67.54	63.79	67.24
	Mn	0.07	0.05	0.08	0.06	0.07	0.06
	SiO ₂	9.88	10.64	11.65	7.13	10.27	11.04
	Al ₂ O ₃	0.77	0.72	0.79	1.05	0.68	0.69
	CaO	10.29	10.64	12.51	12.54	11.83	12.41
	MgO	2.04	2.75	2.16	1.85	2.66	2.54
	P	0.021	0.026	0.020	0.061	0.024	0.042
	S	0.024	0.028	0.021	0.022	0.011	0.020
	K ₂ O	0.048	0.064	0.050	0.045	0.032	0.043
	C	0.14	0.23	0.21	0.22	0.14	0.18
Grain (mm)	> 25	40.17	44.01	42.36	47.42	24.38	25.17
	25–10	22.88	15.45	25.55	19.43	22.60	16.49
	10–5	14.63	14.28	14.27	11.70	20.38	18.53
	< 5	22.32	26.26	17.82	21.45	32.64	39.80
	d _A	16.71	16.53	17.64	17.85	13.00	12.19
Tumbler index (%)	+ 6.3 mm	62	62	58	65	54	50
Abrasion index (%)	- 0.5 mm	7	10	9	8	10	11




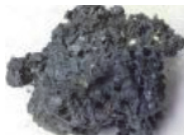


Sinter							
		Coke powder (100%)	Charcoal (86%)	Nut shells (20%)	Lignin (20%)	Oak sawdust (20%)	Pine sawdust (20%)
Production yield (%)	P	78	76	80	79	70	60
Reducibility (%/min)	dR/dt	1.15	1.19	0.94	1.05	1.16	1.15
Mineralogy * (%)	XRD	Fe ox = 60	Fe ox = 51	Fe ox = 54	Fe ox = 57	Fe ox = 57	Fe ox = 57
		Si = 14	Si = 14	Si = 20	Si = 16	Si = 16	Si = 16
		CaFe = 13	CaFe = 24	CaFe = 21	CaFe = 19	CaFe = 19	CaFe = 19
		NA = 5	NA = 9	NA = 6	NA = 7	NA = 7	NA = 7
<i>*Fe ox – iron oxides, Si – silicates, CaFe – calcium ferrites, NA – non-assimilated phases.</i>							

Table 14.
Properties of sinters with coke substitution.

1.3.2 *The influence of carbonaceous fuels on the quality of the sinter and on the economic and ecological parameters of the sintering of iron ores and concentrates*

Starting from an analysis of the considered biofuels (**Table 12**) and proposed methodology for the performance of experiments, coke breeze was partly replaced with a defined quantity of individual biomass types. The materials whose composition is given in the **Tables 5, 10** were used for the experiments. **Tables 13, 14** give characteristics of sinters produced with biomass substitution of coke breeze. It can be seen in some experiments with biomass standard quality parameters on several sinters and lower emissions of CO_x , NO_x and SO_2 are achieved. It is possible to substitute about 10–20% of coke breeze by individual types of biomass in the sintering process. Combustion of plant biomass mainly depends on the carbon structure of the cellulose, hemicellulose and lignin, which differ from the amorphous carbon in coke (coke breeze). The maximum temperatures in the sintering process are lower with biomass than with actual coke breeze [11]. Biomass fuels can burn more quickly than coke breeze due to their high porosity and large interface area, while there is a significant increase in the vertical speed of sintering. The combustion of biomass decreases the maximum temperature and abbreviates the holding time at the high temperature. Lower temperatures in the sintered layer observed with the addition of biomass can also be attributed to the condensation of volatile organic compounds [11]. These compounds can eventually be converted into a phase similar to ash and reduce the heat transfer in the direction of burning.

The content of Fe_{TOT} in laboratory prepared sinters with biomass does not change considerably compared to the standard (reference – with 100% coke breeze) sinter and is within the interval of about 51–53%. The phase composition (mineralogy) of selected sinters is qualitatively comparable, while the differences are observable in the quantity of individual phases, as shown in **Table 14**. A sinter without biomass contains a higher proportion of iron oxides and sinters with biomass have more silicates and calcium ferrites. Compared to standard sinter, the increase in the share of calcium ferrites can be noticed in selected sinters with biomass. The microstructure of the standard sinter mainly consists of primary magnetite and hematite. Forms of silico-ferrites of calcium and aluminum – SFCA are also visible in the microstructure to a small extent. In the microstructure of the sinter with biomass, there is also a visible area of the unsintered surface, which has been identified as lime. Forms of calcium silicates are also visible in the microstructure. The sinter with the substitution of coke breeze by charcoal reached the highest value of reducibility estimated using dR/dt ratio, as seen from **Table 14**. The sinter with the substitution of coke breeze by nutshells has the lowest value of reducibility. Sintners with coke breeze substituted by charcoal and sawdust have a similar reducibility to the reference sinter without any fuel substitution. Higher reducibility relates to sample properties such as its low content of FeO and its high porosity [14], which is related with sintners with the substitution of coke breeze by charcoal and sawdust.

2. Conclusions

In this chapter the properties of iron ores and concentrates were specified. These properties are very important for their efficient processing in the process of sinter and pig iron production. It is important to comprehensively evaluate these raw materials. The evaluation of the properties of iron ores shows that the best ores for blast furnace process have a suitable particle size distribution (10–40 mm), good chemical and mineralogical composition (especially hematite and magnetite,

minimum of carbonate and silicate phases), they are well reducible (R_{i60} below 100 min.) and stable after temperature tests (+6.3 mm above 70%). Sinter grade ores and concentrates are characterized as iron ore raw materials with the required granulometry and chemical and mineralogical composition. In general, the richness of concentrates is in the range of 65–70%, while sinter grade ores have this interval wider and shifted slightly lower (55–67%). The larger grains of sinter grade ore are practically free of impurities and have a relatively homogeneous structure. In addition to iron oxides, the smaller sinter grade ore grains also contain impurities in the form of silicon and aluminum oxides. Undesirable impurities are mainly sulfur, phosphorus, zinc, lead, arsenic, copper, sodium, potassium, which are chemically bound in the minerals of the iron ores.

A new direction in the sintering process is showing the replacement of coke with biomass. It is a more environmentally friendly way of production and practice will show that it will also be more economical in the future. It can be seen in some experiments with biomass standard quality parameters on several sinters and lower emissions of CO_x , NO_x and SO_2 are achieved. It is possible to substitute about 10–20% of coke breeze by individual types of biomass in the sintering process. Properties of input iron bearing and basic raw materials are indeed crucial factors that affect the final quality of sinter, but no less important are the properties and the amount of carbonaceous fuel and high-temperature sintering technology. Progress in the production of pig iron in blast furnaces can be achieved by improving the quality of burden, especially iron ores and sinters. A significant improvement in the performance of blast furnaces is currently achieved by using a burden with a modified chemical and particle size distribution, which allows a more complete use of the chemical and thermal energy of the reducing gas.

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Conflict of interest


The authors declare no conflict of interest.

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