Material Science of Sintered Iron Ore Materials.
Part 1 . The Composition and Properties of Sinter.

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Abstract. The article systematizes the definition of sintering products and describes the classification of products produced and standardization of iron ore sinter according to the characteristics of chemical composition. The laws of the fragmentation of sinter cakes are described and characteristics of these processes are suggested with taking into account the kinetic nature of the observed phenomena.

Agglomeration as a method of sintering ores and concentrates occurred as a result of creative reflection and practical application of the previously repeatedly observed phenomenon of the formation of a strong sintered mass after roasting of sulfide ores, which were similar to ash left over after solid fuel burning [1].

The latter is a close analogy, which further has allowed calling sintering as an process of fuel burning containing 95% ash.

Ensuring autothermal effect of sinter process is a very important factor indeed, but the essence of the sintering process (turning dust into lumps) lies not in the fuel combustion. Moreover, the lumps are not ordinary, but having a whole set of properties that significantly distinguish them from natural ores, and which make them desirable material for the subsequent metallurgical processing. Therefore, since we have already mentioned the properties, whether we want it or not, we are first forced to pay close attention to the composition and structure of the material occurred after burning of fuel, which determine both the individual characteristics of its quality and the metallurgical value in general.

The essence of the agglomeration process by the sintering method consists in the formation of such a material structure, which when specified composition provides it with the required set of quality characteristics for further efficient metallurgical treatment.

Years of experience of blast furnaces operation with application of the iron ore sinter allowed formulating the definition of high-quality sinter. First of all, this is a durable material of a certain size containing small amount of fines, not breaking during transportation, transferring and reduction, combining all these properties with high reducibility and onset softening temperature, as well as a short interval of the latter.

Such non-existent material is a collective image combining the best individual quality characteristics possessed by some separate sinter samples. In fact, currently produced sinter includes a variety of metallurgical properties of different blast-furnace sinter materials. Moreover, when it comes to assessing its quality, sometimes it causes serious difficulties not only in terms of its general definition, but also in evaluation of specific values of its size, mechanical, physicochemical and other properties.

In addition to the above, it is necessary to remember that sinter like any other type of raw material is used in blast furnace smelting primarily because it contains such an amount of iron and useful minerals that ensures the economic feasibility of smelting pig iron from them and among quality characteristics, its chemical composition takes the leading place. And if a few decades ago, it was enough to indicate the content of Fe_{total}, FeO and basicity, then today the requirements for the content of magnesia and alumina in the sinter mix are becoming increasingly common and strictly regulated.

Thus, nowadays, the composition of the sinter is characterized by its content of six basic oxides: FeO, Fe_2O_3, CaO, SiO_2, MgO, Al_2O_3 and harmful impurities (Zn, S, P_2O_5, Na_2O, K_2O) and in some cases requires taking into account amounts of titanium and vanadium oxides. This article is limited to the description of content of the six main oxides.

1. Chemical composition. We have proceeded from the fact that sinter is a synthetic iron ore material, which differs from all types of natural materials not only by the values of individual characteristics of chemical composition, but also by their more successful combination for further blast furnace treatment [2].

Characteristics of the chemical composition of the “average” sinter are given in Table 1.

Table 1. Statistics of the distribution of characteristics of sinter chemical composition

Statistics of distribution	CaO	MgO	Fe_{tot}	FeO	Fe_2O_3	Al_2O_3	SiO_2
Average	11.71	1.87	53.20	14.09	60.30	2.06	9.96
Standard deviation	3.42	1.40	3.39	3.14	5.80	1.06	2.07
Min	0.44	0.1	43.07	6.01	44.67	0.71	4.37
Max	19.01	8.65	60.68	22.75	77.11	6.38	16.86
Asymmetry	-9.14	24.56	-6.29	5.52	-8.48	13.54	5.74
Flat-toppedness	7.12	34.5	1.78	1.56	2.56	6.97	2.91

The asymmetry and flat-toppedness of the distribution curves unambiguously indicated that the observed characteristics did not follow the normal distribution law, but, most likely, were a combination of several distributions artificially combined into one.

Nowadays the following types of sinter are produced: fluxed and non-fluxed, high- and low-oxidized, high-grade and low-grade, alumina-containing, magnesia-containing, etc. In other words, we are dealing with a certain sinter sets, which we have to divide into certain groups.

Because of the primary classification, the products produced by the sinter plants are divided into **types**. Firstly, these are raw materials of mass production (more than 90% in the total output), and, secondly, these are special types of sinter, the production of which either has developed historically and needs rethinking or from time to time occurs to solve problematic technological situations in blast-furnace production, for example, blast furnaces cleaning.

It is necessary to pay special attention to the fact that these are objectively different types of sinter with qualitatively different properties and features of the technologies for their production and application.

The classification of mass production products has shown that a large variety of sinter has been produced and is being produced to date, which can be reduced to eight grades without any damage to consumers*.

Assessing the composition of the different grades of sinter with respect to the efficiency of their melting in blast furnaces [3,4], the first place was rightfully given to $1{,}6F6M_{0{,}5}{}^{1}A_{1}{}^{1{,}5}S6$ grade, which is promising for metallurgical enterprises of Ukraine. Second place has been given to $1{,}2F15M_{1{,}5}{}^{2}A_{1{,}5}{}^{2}S7$ grade, which is the most suitable for blast furnaces in Russia, but in case of sinter mix of Ukrainian enterprises which contains a limestone, it requires additional fluxing. Third place went to $1{,}5F7M^{0{,}5}A_{1}{}^{1{,}5}S9$ grade, which can be considered as the most suitable for nowadays domestic metal production.

Grades $1{,}4F11M_{1}{}^{1{,}5}A_{1}{}^{1{,}5}S10$ and $1{,}25F14M_{1}{}^{1{,}5}A_{1{,}5}{}^{2}S9$ sharing the fourth and fifth place are almost indistinguishable from the standpoint of the efficiency of their smelting in a blast furnace. Then, in descending order of metallurgical value, the following grades were placed: $1{,}25F15M_{1{,}5}{}^{2}A_{1{,}5}{}^{2}S11{,}5$; $1{,}25F11M_{2{,}5}A_{1{,}5}{}^{2}S14$ and $1{,}2F18M_{1{,}5}{}^{2}A_{3{,}5}S12{,}7$ respectively.

The calculations and analysis of the results obtained have showed that it is time to abandon the abstract sinter and understand the feasibility of adopting a limited set of specific grades of sinter.

* *In sinter grades description:*

– first figure is a simple basicity, ***F*** *– FeO;* ***M*** *– MgO;* ***A*** *- Al_2O_3;* ***S*** *– SiO_2;*

– subscript is the lower limit of the component content;

– superscript is the upper limit of the component content in the grade.

This in turn will provide conditions for the optimization and standardization of both the production technology of sinter mix and the smelting of pig iron from it significantly reducing the variety of emerging technological situations and the risks of making erroneous technological and managerial decisions. It should only be admitted that a qualitatively different sinter with its well-known metallurgical value and previously known, worked out technological parameters of production and technical and economic indicators of blast furnace smelting is beyond the permissible boundaries of variation of a certain grade composition.

1.1. Stability of chemical composition characteristics. It is believed that in order to ensure the stable operation of blast furnaces, the values of characteristics of the composition of iron ore raw materials should fall within the following ranges:

Fe_t	……………...	+/- 0.5 %
Basicity	……………...	+/- 0.05 unit.
FeO	……………...	+/- 1.0 %

In this case, it is not only the dependence of the permissible deviations on the absolute value of the chemical composition index that is overlooked, but also the fact that these requirements shall be met together. This means that if one of the characteristics of the sinter composition is beyond specified limits, then the product does not meet the technical specifications. The calculations showed that the simultaneous meeting the requirements for the sinter chemical composition is rather improbable situation and this significantly affects the quantity, chemical composition and properties of blast furnace slags.

Table 1. Characteristics of the chemical composition of promising sinter grades.

Sinter grade	Composition characteristics								
	Fe_t			Basicity			FeO		
	Sinter group			**Sinter class**			**Sinter category**		
	1	2	3	а	б	в	1	2	3
$1{,}6F6M_{0{,}5}{}^{1}A_{1}{}^{1{,}5}S6$	**57.5-58.4**	**58.5-59.5**	**59.6-60.5**	**1.45-1.54**	**1.55-1.65**	**1.66-1.75**	**4.0-4.9**	**5.0-7.0**	**7.1-9.0**
$1{,}5F7M^{0{,}5}A_{1}{}^{1{,}5}S9$	**52.0-52.9**	**53.0-54.0**	**54.1-55.0**	**1.35-1.44**	**1.45-1.55**	**1.56-1.65**	**4.0-5.9**	**6.0-8.0**	**8.1-10.0**
$1{,}2F15M_{1{,}5}{}^{2}A_{1{,}5}{}^{2}S7$	**48.0-49.9**	**49.0-50.0**	**50.1-51.0**	**1.05-1.14**	**1.15-1.25**	**1.26-1.35**	**12.0-13.9**	**14.0-16.0**	**16.1-18.0**

This gives grounds to assume that in the considered cases of multicomponent oxide systems, which include both sinter and slag, the very formulation of the problem of stable production of material with a given grade composition is incorrect.

It is necessary to assume several probable solutions to the problem, namely, to introduce the concepts of iron content group, basicity class and FeO content category (see Table 1).

As it follows from the table, the sinter types of grade composition are significantly different in their iron content, but can be connected and interrelated by areas of possible variations of basicity and oxidation.

1. Grain size distribution. With some reservations, most experts agree that the sinter is a lumpy material with a lump size from 5 to 40 mm. Anything less than 5 mm and more than 40 mm is not considered as sinter.

Upper size limit	Size of lumps, mm	Lower size limit
00	70 and more	
000	65	
000	60	
00000	55	
00000000	50	
0000	45	
00000000000000	40	
00	35	
	30	
	25	000
	20	0
	15	0000
	10	00000000
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Figure 1. Requirements for the sinter size according to the results of a survey of participants of the scientific and technical conference "Theory and technology of modern blast-furnace production" (Dnepropetrovsk, 1982) and a coordination meeting "Sintering of ores and concentrates" (Yekaterinburg, 1983)

The last statement is very important for further consideration and most importantly for understanding the absolute need for crushing the cake to lumps of the specified size and separation of non-standard products after crushing (Table 2).

Table 2. The system of concepts describing the products of sinter production.

Sinter (the most general definition)			
Sinter cake	Sinter		
	Oversized and undersized material (F_{40})	Yeild (F_5^{40})	Non-standard product (F_0^5)

Based on experience and realizing that such strict requirements for the grain size composition of the sinter are unachievable, in practice, a certain amount of non-standard F_0^5 as well as oversized and undersized material F_{40} is allowed. However, the fact that their price is the same as the price of the standard and suitable products is strange.

In the proposed system of concepts, particle size distribution of sinter involves the description of the distribution of its particles by size in the range of 5–40 mm. This knowledge today is insignificant against the background of an unjustifiably high content of oversize/undersized and non-standard materials in the dispatched products.

Repeatedly performed screen sizing and statistical processing of the experimental data found that the grain size distribution of fragmented sinter (including non-standard and oversized/undersized materials) was described by the logarithmically standard distribution of lumps by size and characterized by its parameters i.e. the average logarithmic size of lumps and the logarithm of standard deviation [5]. And this is instead of the usual contents of the size classes F_0^5; F_5^{10}; F_{10}^{25}; F_{25}^{40} and F_{40}.

The result was uncommon. The obtained values of the average and coinciding with it modal diameter of sinter lumps ranged from 7 to 9 mm. In addition, the range of lumps sizes was far from perfect.

The idea of the phenomenon became clear if the facts of various defects fixing in the structure of the cake, oversize material and sinter were taken into account. Defects that have fragmented both the cake itself and the lumps that are made from it. In this case, it could be assumed that the most probable distance between structural defects determining the size of the destruction product was 7-9 mm as indicated above.

Taking into account a wide range of lump size, the existence of a short-range order in the location of these defects but not a strict periodicity of their location in the bulk of the material was admitted.

2.1. The kinetic nature of the grain size distribution. It has been repeatedly observed and based on this, it can be reasonably stated that the destruction of sinter starts right on the belt, continues when it is cooled in air and in coolers, during transportation and storage [6]. Moreover, according to some estimates, the material is subjected to the greatest destruction in sinter coolers.

The general pattern that is observed when cakes are destroyed under the action of internal stresses, as well as under thermal and mechanical shocks, is that the interval of lump size in the destruction process decreases in proportion to the decrease in their average diameter at a constant, logarithmically normal law of grain size distribution.

The established dependence of the logarithm of the standard deviation from the average logarithmic diameter of the lumps is due to the selective destruction of the largest of the available lumps accompanied by the generation of significant quantities of small fractions. Apparently, this is a “scale effect”, according to which in a larger body, there is a greater probability of the occurrence of a dangerous defect leading to the destruction of the material.

This was confirmed by the results of research on the “spontaneous” destruction of sinter cakes. So, when cooled in air and stored, up to 78% of the fraction pieces with a lump size of less than 25 mm were directly formed from the F_{75} and only 9/2% through the intermediate member F_{25}^{75}. Moreover, fines content F_0^5 after 5 hours since the moment of sinter cake preparation reached 42 - 43 % [7].

The conducted studies gave reason to believe that the destruction of the sinter cake due to the special conditions of its obtaining and the characteristics of the material is a natural phenomenon happening in time.

The same can be said about the destruction of the sinter during the tests in the drum modeling the conditions of its “life” until it enters the blast furnace.

In the context of the above arguments, the replacement of the existing characteristics of the sinter strength evaluated by the yield of the fraction F_5 with a logarithmic half-life period calculated from the kinetic curve of the sinter fracture in a standard drum with a justified approximation to the logarithmic-standard distribution of “lifetime” of the test pieces will be clear.

In this connection, the evaluation of the destruction process by the logarithm of the half-life (t_{50}) and the logarithm of the standard deviation from it (s_t) was completely justified..

Obtained information was enough to divide sinter produced nowadays into several groups.

In the first sinter group, the growth of the logarithmic half-life period was due to an increase in the proportion of pieces fragmented to lumps size of more than 5 mm. In the second group, the sinter lumps were more homogeneous in $t_{50,}$ than in the first one and the increase in the logarithm of their half-life period was due to an increase in the retention of all lumps in the drum. The third group showed intermediate results.

A strict dependence between the specified distribution parameters on the studied data array was not established. Perhaps this will be done in future. The main thing is to understand and accept that the sinter grain size distribution, however, like its other properties should be assessed taking into account the temperature of the material and its “age” i.e. the time from the moment of its obtaining to the moment of their determination. In other words, it is necessary to understand the peculiarities of the grain size distribution of chilled or hot, freshly produced or stale, fractionated or not sinter cake.

Second, it is necessary to agree that the destruction of sinter cake, oversized/undersized material and sinter is a process happening in time, which should be evaluated not by static, but by kinetic characteristics, for example, logarithmic half-life period.

2.2. The change in the grain size distribution of sinter during reduction. Unfortunately, the determination of the characteristics of the sinter destruction process in time during reduction according to the current standard methods was not possible due to the serious influence of heat cycles on its grain size distribution.

The following standard stipulated characteristics were determined instrumentally: impact strength (L_{10}), crushability (L_{05}^5) and abrasion (L^{05}), and according to the accepted concepts given in Table 1, the change in the size of the lumps to a particle size less than 5 mm was understood as sinter breaking.

In general, the grain size distribution was estimated by the median particle diameter LD50, namely, the screen mesh size, through which 50% of the material passed. According to this characteristic, it has been clear that the produced types of sinter do not form a homogeneous group of materials subjected to any distribution law, but are two qualitatively different materials. 73% of them have LD50 size close to 12 mm and the remaining 27% are more than 2.3 times bigger than the above. Attention was drawn to the fact that most of lumps are close in size to initial sinter lumps, thus confirming the assumption that the distance between structural defects is fixed in the probabilistic sense.

The process of the sinter reduction was controlled by the surface of the lumps, and therefore, the degree of reduction depended on the lumps size and their quantity, and, consequently, the apparent density of the lumps, and in such a way that the highly porous material with a low apparent density was more fully reduced and more destructed. However, it was and is still produced without causing serious complaints from the subsequent blast furnace treatment.

In all likelihood, this indicates that when ranking individual characteristics of the quality of the sinter types studied [8], their reducibility and strength during reduction are far from being in the first place and certainly are not decisive.

Conclusion

1. The currently produced abstract sinter is a lumpy material with a lump size from 5 to 40 mm, which consists of a various in composition and metallurgical properties range of blast-furnace sinter.

2. Admitting the fact that beyond the permissible boundaries of variation of the composition of a certain sinter grade is a qualitatively different product with its well-known metallurgical value and previously known, tested technological parameters of its production and smelting in the blast furnace will allow us significantly reduce the variety of emerging technological situations and the risks of making erroneous technological and management decisions.

3. The destruction of sinter cake, oversized/undersized material and sinter is a natural phenomenon passing over time, which should be described by its kinetic characteristics and the particle size distribution and other properties of fragmented sinter cake and sinter evaluated with taking into account the temperature of the material and its “age”(life-time).

4. The reducibility of the sinter and its strength during reduction in some cases affect the characteristics of the blast furnace smelting, but are not decisive in a number of characteristics such as iron content, lump size and fine content.

So far, the planning and design of metal production technology has been associated with an ore base specific for each enterprise and its peculiarities. Hence, a variety of sintered materials with specific chemical composition and metallurgical properties occurred due to the above.

Among this diversity, the advantages and disadvantages of certain types of sinter of certain groups (grades) became apparent. Thus, it is quite natural that the time has come to solve the inverse problem, namely, planning the raw material base of an enterprise based on the conditions of sinter production with the required chemical composition and specified metallurgical properties.

The range of produced sinter shall be limited to several promising grades with guaranteed properties and the necessary raw materials for their production shall be selected with taking into account the fact that the standardization of the products produced by its significance is the same achievement of mankind as the division of labor, which certainly allows us to achieve positive results, in the near future. Without capital expenditures, this will allow real increasing of the efficiency of the agglomeration and blast-furnace production.

Ensuring the requirements for the grain size distribution of the sinter is inevitably associated with capital costs connected with the installation or improvement of equipment for cooling, crushing and screening of sinter cake and non-standard material. According to the practice for sure, these capital costs will be paid off by reducing the consumption of coke and increasing the efficiency of blast furnaces.

References.

1. Lyuiken V., Kreber L. (1934) Issledovaniya po aglomeratsii zheleznyih rud [Research on the iron ores sintering.]. *V sb.: aglomeratsiya zheleznyih rud pod red. Parfenova P. P.* [In the collection of studies: Iron ores sintering edited by Parfenov P.P.]. Leningrad. Moscow. Novosibirsk. State scientific and technical mining, geological and oil publishing house, p.p. 3-36.
2. Smirnov S.V. (2010) Klassifikatsiya i unifikatsiya zhelezorudnyih aglomeratov [Classification and standardization of iron-ore sinter]. *Novyny Nauky Prydniorovya* [Science News of Prydniprovia], p.p. 139-143.
3. Iron Ore Quality Rating (2002), Metal Expert, Metal Courier Agency, Analytical Bulletin. Issue 72, p. p.3-4.
4. Analysis of the market of sintered iron ore raw materials in Ukraine (2003), Metal Expert, Analytical Bulletin of the Metal Courier Agency, Issue 87, p.4-9.
5. Andreev S.E., Tovarov V.V., Perov V.A. (1959) *Zakonomernosti izmelcheniya i ischislenie harakteristik granulometricheskogo sostava* [Regularities of crushing and calculating the characteristics of the grain size distribution]. Moscow. State Scientific and Technical Publishing House for Ferrous and Nonferrous Metallurgy, 437 p.
6. Efimenko G.G., Knyazhansky M.M., Smirnov S.V. (1981) Kineticheskaya priroda granulometricheskogo sostava aglomerata [The kinetic nature of the grain size distribution of the sinter], *Izvestia Vuzov Chernaya Metallurgia* [News of Universities “Ferrous metallurgy”]. No 1, p.p. 17-20.
7. Efimenko G.G., Knyazhansky M.M., Smirnov S.V., Ignatov N.V. (1978) Analiz granulometricheskogo sostava aglomerata [Analysis of the grain size distribution of the sinter]. *Metallurgiya i koksohimiya* [Metallurgy and Coke chemistry]. No. 59. Kyiv. Publishing House Tekhnika, p.p. 16-21.
8. Gelgorn A.V., Gurkin M. L., Nevraev V. P., Nesterov A. S. and others. *Sposob opredeleniya metallurgicheskoy tsennosti domennogo zhelezorudnogo syirya* [Method for determining the metallurgical value of blast-furnace iron ore materials]. Patent RU 2283877.

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