STUDY OF PROPERTIES OF Mn ORE FINES AND POSSIBILITIES THEIR UTILIZATION IN THE PRODUCTION OF FeSiMn

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Abstract
This article deals with the analysis of the physical and chemical properties of undersize samples of Mn ore from the mine Buzim in Bosnia and Herzegovina, comparing individual samples, followed by the production of Mn sinter and analysis of the Mn sinter. Mn ore fines are formed in different steps of Mn ores processing. These fines can not be directly put into the ferroalloy furnace. The most suitable way of Mn ore fines processing is sintering and the article deals with this method of processing. On each sample of Mn ore from Bosnia and Herzegovina marked Mn ore 1, Mn ore 2 and Mn ore 3 have been performed the analysis of physical and chemical properties. The results showed that the granulometry of the samples affects their chemical composition. On the sample of Mn ore 1 was performed an experimental laboratory sintering, in which succeeded to produce an Mn sinter. The Mn sinter is suitable for further use in the production of FeSiMn, in terms of low phosphorus content and suitable phase composition, but the Mn sinter had also a high content of SiO_2, which adversely affect the granulometry and strenght of the sinter.

Keywords: sintering, Mn ore fines, processing, physical and chemical properties

1 Introduction

Manganese ore is an indispensable raw material for the steel industry, which is used in the production of pig iron, steel, ferroalloys and in the foundry industry [1]. Only manganese ores with suitable physical and chemical characteristics can be used [2]. Manganese ores are mainly used in ferroalloy plants as the main part of the charge in the production of manganese ferroalloys, which are used in steelmaking plants as alloying additions to ensure the required properties of the produced steel grade [3]. With the continuous decrease of resources with good quality manganese ores and increasing prices of manganese ores with Mn_{tot} content of about 50 %, the companies start to use low grade carbonate and hydrate manganese ores with manganese content of about 30 %, ores with a higher content of SiO_2 and undersized fractions of Mn ores [4]. A number of studies, which are focused on processing of the Mn ores by hydrometallurgical or pyrometallurgical methods, currently deals with the study of enrichment and processing of low grade manganese ores [5, 6]. There is a study of enrichment and processing of low grade manganese ores, where iron was removed by magnetic separation. This separated material with adition of binders was further briquetted and used in the EAF [7]. In a study of carbonate Mn ore with high SiO_2 content calcination at 800 °C was found, that the final product had lower

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porosity and a higher content of Mn_{tot} and SiO_2 than the starting ore. The final product was categorized as suitable for the production of FeSiMn regarding its chemical composition [8]. Another method of obtaining of Mn from low grade ore is leaching of Mn ore in sulfuric acid using sawdust as the reducing agent, where by the leaching yield 98 % of Mn is achieved [9]. One of the most perspective secondary materials that are formed at ferroalloy plants and mines are Mn ore fines [10]. These small fractions are not directly used in the production process of ferroalloys because of their adverse effect on technological and economic indicators of production. Therefore these small fractions are sorted out and not used in most plants [11, 12]. However manganese ore fines contain high content of manganese, which regarding high prices of imported ores can not be ignored classifying them as waste [13]. Their further processing into a product with higher added value suitable for further use is the subject of number of studies and research projects [14]. Literary sources indicate a number of ways to process these small particles for their further use [15, 16]. With production of manganese pellets dealt a study where the produced pellets had high content of Mn_{tot}, they were low in impurities and they demonstrated high strength. Bentonite was used as a binder and pellets were fired in a furnace at 1335 ° C [17]. A study in the manufacture of manganese briquettes dealt with the processing possibility of Mn ore fines, where the input materals were flue dust from FeSiMn production, undersize fractions of oxide and carbonate Mn ores and portland cement was used as a binder. The produced briquettes containing 31 % of Mn_{tot}, and 24 % of SiO_2 were added in experimental amounts from 5 to 40 % into the charge for FeSiMn production. The produced briquettes positively influenced the entire production process and the final quality of FeSiMn [18]. One of the most common methods for processing of Mn ore fines is sintering because the produced sinter improves technological and economic indicators of production [19]. A study in Russia dealt with production of manganese sinter from FeSiMn slag and manganese concentrates produced from low grade manganese ores with a particle size of 0-2 mm. The final manganese sinter which contained 32.3 % Mn_{tot} and 28.3 % SiO_2 was added as a part of the charge in the production of FeSiMn [20].

2 Experimental materials and methods

Three samples of Mn ore fines from the mine Buzim in Bosnia and Herzegovina, which differ in their granulometry and the time when they were analyzed, were analyzed: Mn ore sample from 2014 (further Mn ore 1), Mn ore sample from 2015 - A (further Mn ore 2) and Mn ore sample from 2015 - B (further Mn ore 3). On each sample of Mn ore were analyzed: moisture content, specific bulk density, granulometric composition and chemical composition. Analysis of phase composition, DTG analysis and thermodynamic analysis of the dissociation of Mn oxides were analyzed only on the sample of Mn ore 1. Granulometric composition of Mn ores was analyzed with the separator KVT-U-2 with a set of screens that have been compiled into a column. The analysis of chemical composition of the samples of Mn ores was realized by combining analytical methods: AAS elemental analysis of the prepared solutions and optical quantification method. Phase composition of the sample of Mn ore 1 was determined by X ray diffraction X-ray analysis on the diffraction spectrometer SEIFERT XRD 3003 / PTS. Thermal analysis on the sample of Mn ore 1 was carried out on Derivatograph C-fy MOM Budapest. Thermodynamic study of the sample of Mn ore 1 was realized using the module Equilibrium Compositions in the version of HSC CHEMISTRY 5.11. During the laboratory sintering of sample Mn ore 1 a

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laboratory sintering pan (LSP) (**Fig. 1**) was used. The produced manganese sinter was analyzed for: chemical and phase composition, granulometric composition and strength of the Mn sinter. Chemical, phase and granulometric analysis of Mn sinter took place analogously to the Mn ore samples. Strength of the sinter was determined with a drum test according to STN ISO 3271 (441570).

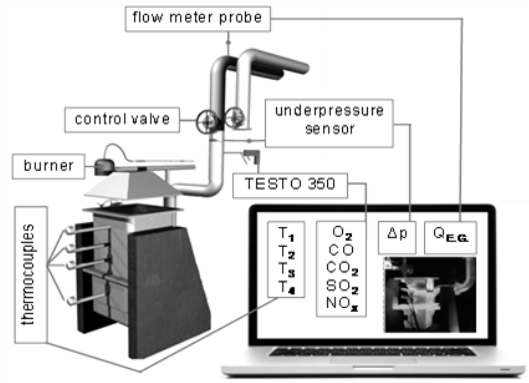

Fig. 1 Schematic description of the laboratory sintering pan (LSP)

3 Results and discussion

The use of the low grade manganese ores and ores with high SiO_2 content becomes a more and more actual topic. Plants producing ferroalloys are increasingly focusing on those ores. One of these ores is also the Mn ore from Bosnia and Herzegovina. The aims of this study is to analyze and compare Mn ore fines from the mine Buzim in Bosnia and Herzegovina, then use these Mn ore fines in the production of Mn sinter, analyze the produced sinter and evaluate prerequisites for processing of samples Mn ore 2 and Mn ore 3. Moisture values of the samples have approximately the same values (**Table 1**).

Table 1 Moisture and specific bulk density of Mn ore samples

Name of the sample	Moisture (%)	Specific bulk density (kg/m^3)	
		Wet sample	Dry sample
Mn ore 1	16.0	1196.1	1356.4
Mn ore 2	16.2	1213.6	1221.7
Mn ore 3	14.4	1326.6	1265.1

The samples were already looking very wet, what was also reflected on the resulting moisture. These values of the moisture are too high for further processing, therefore the ore must be dried before the further processing. Specific bulk density was analyzed on wet and dry samples (**Table 1**). The results show that the specific bulk densities are higher in the samples of Mn ore 1 and Mn ore 2 for dry samples. An opposite effect occured for the sample of Mn ore 3, specific bulk density is higher for wet sample. This may be caused through fixation of water in the sample, the granulometry of the sample and through the very nature of the ore. Granulometric composition was evaluated on samples in the dry state using a sieve analysis, where different particle size

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fractions were generated (**Fig. 2**). The results show that in all analyzed samples the grain size of under 8 mm represented approximately 97 %, which is an advantage because in the sintering process only Mn ores with grain size up to 8 mm can be used.

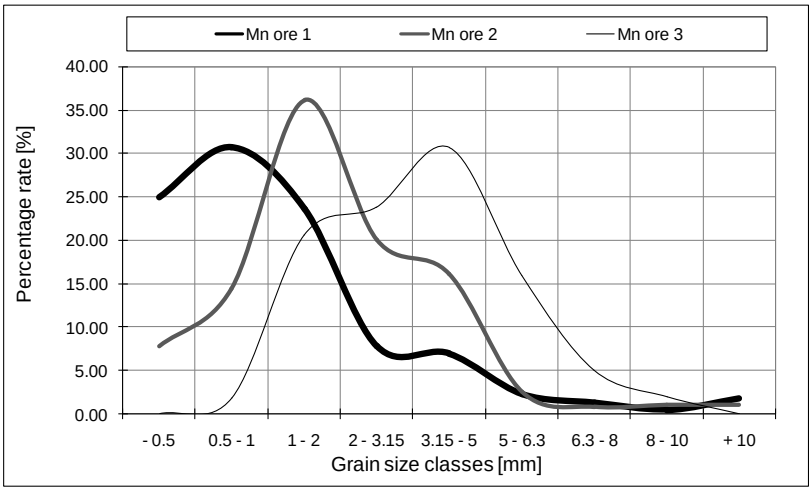

Fig. 2 Granulometric composition of Mn ore samples

Ores with a larger grain size must be adjusted before the further use. Too rough grain makes the charge highly permeable in the process of sintering, the air takes away an excessive amount of heat, the reactions do not run until the very end, the melt occurs only at the surface, the sinter has bad quality. The highest presence of dust is in the sample of Mn ore 1, where is the highest granulometric proportion of classes from 0 to 2 mm. Sample Mn ore 2 has the highest granulometric proportion of classes from 0 to 5 mm and the sample Mn ore 3 has the highest granulometric proportion of classes from 1 to 8 mm, which is also reflected in the average grain size. Chemical composition of Mn ore samples was analyzed for each sample of Mn ore Bosnia and Herzegovina (**Table 2**).

Table 2 Chemical composition of Mn ore samples

Name of the sample	**Chemical composition (%)**									
	Fe_{tot}	**Mn_{tot}**	**SiO_2**	**Al_2O_3**	**CaO**	**MgO**	**S**	**P**	**C**	**K_2O**
Mn ore 1	7.79	23.28	31.33	8.12	3.35	1.65	0.18	0.19	0.54	-
Mn ore 2	6.13	26.33	30.72	6.69	1.01	1.63	0.01	0.10	-	1.62
Mn ore 3	4.98	32.04	23.96	5.97	0.99	1.40	0.01	0.08	-	1.53

The comparison of the analyzed results show that the particle size of the samples has a significant effect on the chemical composition. The highest content of manganese is in the sample of Mn ore 3, which is characterized by higher grain size distribution with separate dust particles. The analysis shows that the manganese compounds are concentrated in larger grains. The different particle size of the samples was also reflected in the content of other elements in the samples. The sample of Mn ore 3 has a lower content of SiO_2, Al_2O_3, CaO, MgO and P. We can say that with increasing grain size the content of Mn_{tot} increases and content of other analyzed components decreases. This is also clear from the dependence of Mn_{tot}, Fe_{tot}, SiO_2 and P on the average grain size of the samples (**Fig. 3**).

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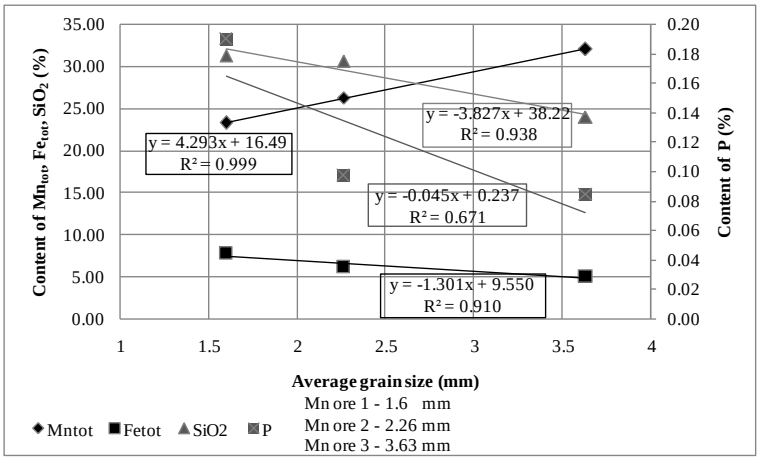

Fig. 3 Dependence of Mn_{celk}, Fe_{celk}, SiO_2 a P on the average grain size

The phase composition of samples Mn ore 2 and Mn ore 3 has not yet been analyzed but it will be the point of further examination. In the table is only the phase composition of Mn ore 1 (**Table 3**). The sample has high content of SiO_2 and Mn as in the form of MnO_2, $Mn^{II}Mn^{III}{}_6SiO_{12}$, $Fe_{1.25}Mn_{0.75}O_3$ and $Fe_3Mn_3O_8$.

Table 3 Phase composition of sample Mn ore 1 [21]

Identified phase composition		**Content (wt %)**
Chemical formula	**Mineralogical name**	
MnO_2	Pyrolusite	5.7
$Mn^{II}Mn^{III}{}_6SiO_{12}$	Braunite	1.8
$Fe_{1.25}Mn_{0.75}O_3$	Bixbyite	1.3
$Fe_3Mn_3O_8$	-	4.4
SiO_2	Quartz	65.9
Fe_2O_3	Hematite	5.2
FeO(OH)	Lepidocrocite	15.7
Amorphous content	-	81.2

The sample is high in amorphous content. On the basis of the chemical composition and the fact that the samples Mn ore 2 and Mn ore 3 are from the same mine we assume that the phase composition will be analogous. Based on the phase analysis the behavior of the sample Mn ore 1 during the thermal analysis can be assumed. **Fig. 4** shows a record of derivatogram of sample Mn ore 1. The decrease of the total weight was approximately 10 wt. %. In analysed sample the input moisture was 5.5 %, and a small proportion of bound water. The input humidity 16 % was reduced to 5.5 % as a result of the ore storage in the hall for 6 weeks.

The release of water occurs in the temperature range 50 - 350 °C. Further decrease in mass of the sample, which is evident from the TG curve and another less pronounced coherence peak of the DTG curve is attributed to the decomposition of manganese oxides. On the basis of the

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thermodynamic analysis, it is assumed that there occurs a decomposition of MnO_2 to Mn_2O_3, and Mn_2O_3 to Mn_3O_4. The decomposition of Mn_3O_4 to MnO occurs at higher temperatures (**Fig. 5)** [21].

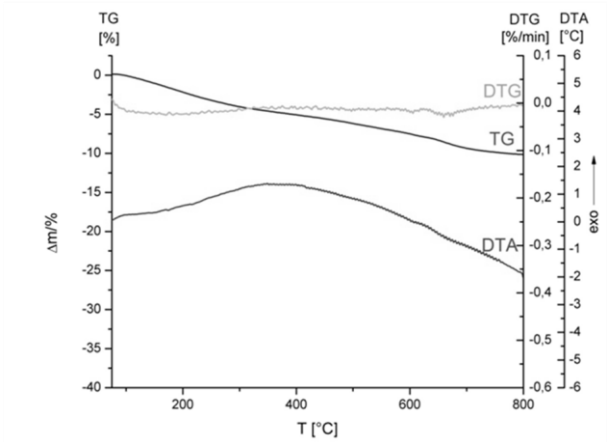

Fig. **4** Thermic analysis of Mn ore 1 sample [21]

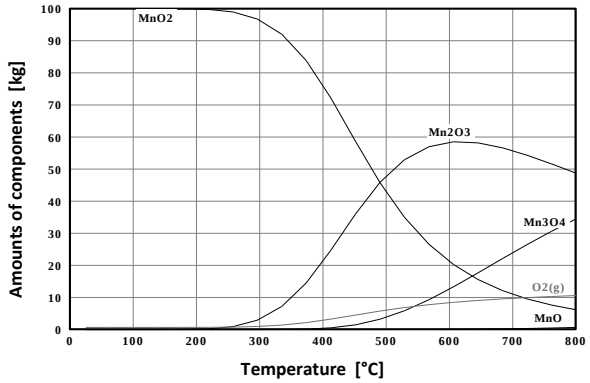

Fig. **5** Thermal decomposition of MnO_2 in the temperature range 25 - 800 ° C

Mn sinter have so far been made only from the sample Mn ore 1. Production of sinters of from samples Mn ore 2 and Mn ore 3 and their analysis will be the point of further examination. Mn sinter from Mn ore 1 was produced in laboratory conditions from sinter mixture. Based on the determination of the specific bulk density of Mn ore 1, the sintering charge was weighed. Sinter mixture consisted of 47.16 kg of Mn ore 1 and 3.3 kg of coke breeze. The highest temperature in this sintering was reached at 2nd thermocouple (about 20 cm from the grid) and is represented by the value of 1083 °C (**Fig. 6**). Although the temperature at 1st and 3rd thermocouple was lower (about 750 - 900 ° C), in the sintered layer can be found micro-volumes, where the temperature have reached significantly higher value than the temperature measured by thermocouples at each level of the LSP. Lower temperatures in this sintering do not automatically relate to a deficiency of fuel in the sinter mixture, but may also relate to the conditions of heat conduction and porosity of the sintered charge. In a lighter and more porous

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charge with a higher moisture content in the input micropellets may occur due the condensation of water vapor in the sintered layer and higher rates of cooling of the sinter to record of lower temperatures. Given temperatures indicate that there is still a reserve for fuel increase (coke breeze) in the sintering of this sample of Mn ore.

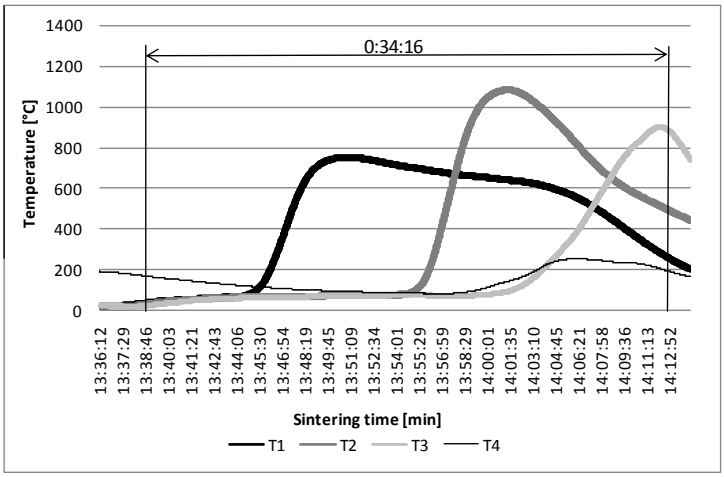
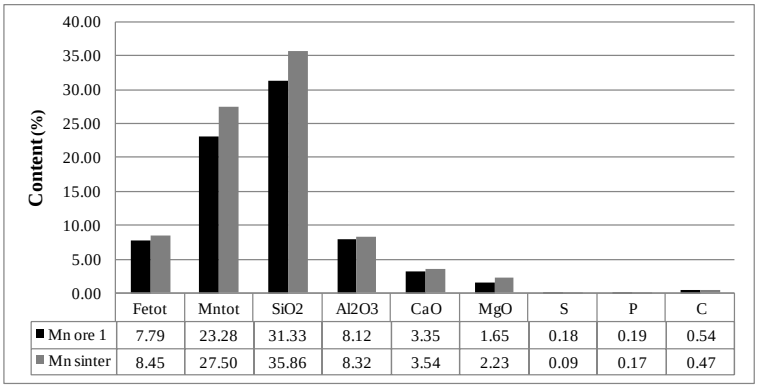


Fig. **6** Temperatures in sintering of sample Mn ore 1

During this laboratory sintering an Mn sinter was produced. For the Mn sinter were analyzed: chemical, physical and mechanical properties. The quality of the Mn sinter was evaluated based on these properties.



	Fetot	Mntot	SiO2	Al2O3	CaO	MgO	S	P	C
Mn ore 1	7.79	23.28	31.33	8.12	3.35	1.65	0.18	0.19	0.54
Mn sinter	8.45	27.50	35.86	8.32	3.54	2.23	0.09	0.17	0.47

Fig. **7** Chemical composition of Mn ore 1 and Mn sinter [21]

The results of the chemical analysis (**Fig. 7**) show that the Mn sinter has a high proportion of SiO_{2t}, because the input ore had already a high proportion of gangue constituents. Mn_{tot} represents 27.5 %. This Mn sinter has low content of P, which means that it is suitable for the production of FeSiMn. For samples Mn ore 2 and Mn ore 3 there is a possibility to produce Mn sinters with a higher content of Mn_{tot} and lower content of other elements like SiO_2 and Fe_{tot}. The percentage increase of Mn_{tot} in the sinter represented 18.1 %. The analysis of the phase composition shows that Mn in the Mn sinter is predominantly in the form of higher Mn oxides

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or in the form of complex Mn oxides, with a smaller proportion of manganese silicates, which is very advantageous for the reducibility in the manufacture of FeSiMn. (**Table 4**).

Table 4 Phase composition of Mn sinter [21]

Identified phase composition		**Content (wt%)**
Chemical formula	**Mineralogical name**	
$FeMn_2O_4$	-	44.3
$Fe_{1.25}Mn_{0.75}O_3$	Bixbyite	6.2
Mn_3O_4	Hausmannite	8.7
SiO_2	Quartz	12.9
$CaMn(SiO_3)_2$	Johannsenite	16.2
$Ca_2Fe_2O_5$	Brownmillerite	4.7
$Ca_{1.01}Fe_{0.54}Mg_{0.45}(CO_3)_2$	Ankerite	2.6
$CaMg(CO_{3)2}$	Dolomite	4.4
Amorphous content	-	56.3

The granulometry composition of the produced Mn sinter must be known, because in the FeSiMn charge production can not be used sinters with a particle size less than 8 mm. In this Mn sinter the undersize content reaches up to 42.74%. The increased content of undersize fraction may be due the increased content of SiO_2 in the starting Mn ore and due the deficiency of fuel in the mixture. For the samples Mn ore 2 and Mn ore 3 there is a possibility of lower content of undersize fraction because the samples have lower content of SiO_2. The granulometry comparison of Mn ores and produced Mn sinter shows that Mn sinter has higher grain size distribution than the Mn ore (**Fig. 8**).

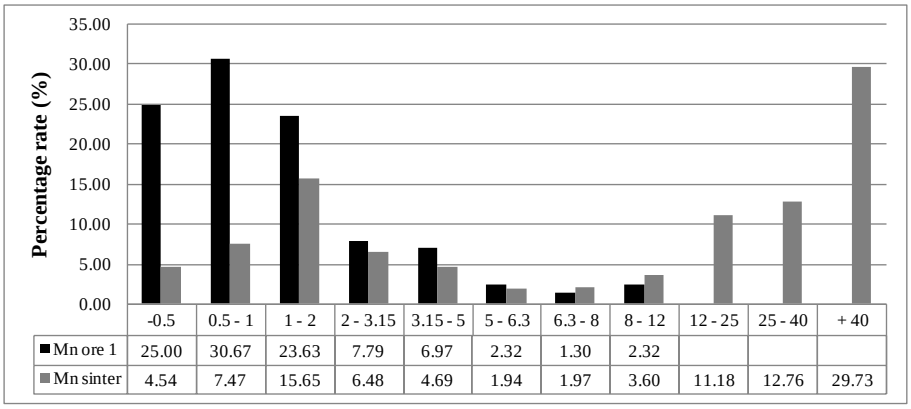

Fig. **8** Granulometric composition of Mn sinter and Mn ore

The quality of Mn sinter is also evaluated by a strength test. STN ISO 3271 (441570) evaluates the strenght of the sinter by determining the strenght index (+ 6.3 mm), and abrasion index (- 0.5 mm). Strength index (+ 6.3 mm) represents in this Mn sinter the value of 48.74 % and the abrasion index (- 0.5 mm) represents the value of 10.52 %. The strength of Mn sinters should

have this values: strength index > 60% and abrasion index < 5%. From the results of this test it is clear that the Mn sinter does not meet the requirements for standard mechanical properties. Low strength index and high abrasion index of this Mn sinter can be caused by the already mentioned negative impact of SiO_2 on the granulometry, which also affects the mechanical properties and through the deficiency of fuel in the mixture. With increasing amount of fuel in the mixture the temperature of sintered layer should increase too, consequently that would create more melt and improve the physical and mechanical properties of the Mn sinter.

4 Conclusions

From the analyses of individual samples of Mn ores it was found that granulometry of the sample has a significant effect on chemical composition. The highest content of Mn_{tot} had the sample Mn ore 3, which had the highest grain size distribution with separate dust particles. Samples Mn ore 2 and Mn ore 3 therefore have good preconditions for further processing and production of high quality Mn sinters. From sample of Mn ore 1 was made a Mn sinter with suitable chemical and phase composition, but inconvenient physical and mechanical properties. The Mn sinter had a high content of undersize fractions and unsatisfactory mechanical properties. With increasing amount of fuel in the mixture its impact on the physical and mechanical properties on sintering of Mn ore 1 needs to be dealt with. For the samples of Mn ore 2 and 3 Mn ore is a possibility to produce Mn sinters with higher Mn_{tot} content, better physical and mechanical properties because they have lower content of SiO_2, which causes the worsening of the above mentioned physical and mechanical properties. The negative impact of SiO_2 on the overall quality of Mn sinter needs to be further explored.

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