

Article

Experimental Manufacturing of Ferromanganese Alloy from Man-Made Manganese-Containing Wastes

Aisha Tastanova ^{1,2}, Saniya Temirova ^{2,*}, Bulat Sukurov ², Alla Biryukova ² and Gulnar Abdykirova ²¹ Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty 050000, Kazakhstan; aisha.tastanova@stud.satbayev.university² Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, Almaty 050013, Kazakhstan; b.sukurov@satbayev.university (B.S.); biryuk.silikat@mail.ru (A.B.); abdgul@mail.ru (G.A.)

* Correspondence: s.temirova@satbayev.university; Tel.: +7-778-312-7510

Abstract: The results of experiments on manganese pellets based on beneficiated manganese-containing sludge and the melting of ferromanganese alloy with their use are presented. Via beneficiating manganese-containing sludge (16.32% Mn), a concentrate with a manganese content of 35.2% was obtained. The composition of the charge used to prepare manganese pellets is proposed, and the conditions affecting their strength are determined. It was established that manganese is present in the composition of calcined pellets in the form of jacobsonite $MnFe_2O_4$ and hausmannite Mn_3O_4 . The formation of a phase of ferrobustamite $(Ca_{0.79}Fe_{0.21})SiO_3$, a ferrosilico-calcium binder that helps increase the strength of pellets, was found. Ferromanganese alloy was obtained as a result of the melting of calcined manganese pellets in a high-temperature Tamman-type unit. The Fe-Mn-Si alloy corresponds to the DIN 17 564 as-grade FeMn70Si in terms of manganese (63.76%) and silicon (17.21%) contents. The content of limiting impurity elements—carbon and phosphorus—in ferromanganese alloy is within acceptable limits. The structure of Fe-Mn-Si alloy and slag formed during their smelting process were studied.

Keywords: manganese-containing waste; manganese concentrate; manganese pellets; Fe-Mn-Si alloy

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1. Introduction

The growth in global steel production has been accompanied by an increase in the demand for manganese alloys. Moreover, Fe-Mn-Si alloys, which have a memory effect due to the reversible phase transformation of γ -austenite to ϵ -martensite, have attracted considerable interest in additive manufacturing [1–3].

Substandard mineral and industrial wasted materials can be considered an extra source of raw materials due to the limited resources of high-quality manganese ores for the production of ferromanganese alloys [4–11].

The technology of suspension–reduction roasting and magnetic separation is proposed for the processing of low-grade iron-containing manganese ore with the extraction of iron and manganese [12].

The beneficiation of Indian fine manganese ore with low manganese content was reported [13]. Classification followed by a two-stage process of high-intensity magnetic separation enabled us to produce a FeMn concentrate with a Mn content of 40% with a recovery of 48%.

When beneficiating ore raw materials from the Charagah deposit (Iran) using jigging, a pyrolusite concentrate with a manganese oxide content of 20% was obtained; at the next stage of magnetic separation, it was possible to increase the MnO content to 44% with an extraction of 61% [14].

A method was proposed for the selective reduction in low-grade manganese ore followed by magnetic separation to obtain manganese concentrate [15,16].

Low-manganese content Indonesian manganese ores were beneficiated by gravity separation and reduction-roasting process followed by magnetic separation to improve the Mn/Fe ratio [9].

Thus, the choice of the method intended to beneficiate manganese-containing raw materials depends on the mineralogical and material composition, dispersion, and structure of the material. Magnetic separation is a promising direction in the beneficiation of ferromanganese ores.

About 30% of the raw material is converted into manganese ore fines (–10 mm) with a low manganese content during the extraction, crushing, beneficiation, and transportation of manganese ores [13].

Fine manganese raw materials cannot be directly sent to metallurgical melting since small particles will prevent the uniform passage of gas through the charge and reduce the preliminary reduction degree of the ore [17]. It must be agglomerated into agglomerates, pellets, or briquettes to use fine manganese ore. There are known methods used to produce pellets with various types of equipment.

One of the technologies to produce pellets is granulation—the pelletizing process for moistened, finely ground materials to form globular granules.

The melting and reducing properties of agglomerates and pellets, as well as the effect of adding fluxes, such as dolomite and quartz, were studied [18]. It was established that the increased content of acid oxides increases the rate of reduction processes during the melting process. Based on beneficiated chromium-containing sludge, composite pellets suitable for smelting into ferroalloys were obtained [19].

The consolidation properties of agglomerates of high-iron manganese ores with natural basicity are described [20]. It was established that sintering ore with high Fe and Mn contents requires a high dosage of coke breeze. It was shown via the use of X-ray phase analysis and scanning electron microscopy that the main mineral phases in the agglomerates include Fe-Mn oxides $\text{Fe-Mn}(\text{Fe}_x\text{Mn}_{3-x}\text{O}_4)$, ferrotrophite $((\text{Fe}, \text{Mn})_2\text{SiO}_4)$, Ca-, Al-, Mn-, iron-containing silicate melts, a small amount hausmannite, and free quartz.

The study [21] investigated the oxidative consolidation behavior of manganese ores with different Mn/Fe mass ratios to determine cold compressive strength, phase transformation, evolution of morphology, and distribution of elements in pellets.

A method intended to pelletize fine manganese ore (fraction 0–5 mm) from the Western Kamys deposit (Central Kazakhstan) was proposed, and an effective technology to produce ferrosilicomanganese using manganese pellets in the charge was developed [22]. The formation of intermediate phases was found during the sintering process of the sinter charge in the presence of dolomite: forsterite Mg_2SiO_4 and diopside $\text{CaMg}(\text{Si}_2\text{O}_6)$, which contribute to an increase in the melting temperature of the final slag during the melting of ferrosilicomanganese.

It was established that the use of dolomite in the agglomeration of fine manganese raw materials ensures the formation of more refractory slags in the production of ferrosilicomanganese [23,24].

The pellets with the addition of bentonite as a binder were obtained [25]. The pellets were dried, fired at a temperature of 1300 °C and cooled. After sifting out the fines, pellets of the 6.4–19.0 mm class were sent to smelting, whose physical properties met the requirements of ferroalloy production.

The behavior of carbon-containing manganese pellets at temperatures up to 1400 °C has been studied [26]. Iron and manganese oxides are reduced to MnO, Fe, and some FeMn at temperatures up to 1000 °C. The formation of the liquid FeMn phase occurs due to the dissolution of reduced Mn in Fe at temperatures from 1000 to 1250 °C. Manganese continues to be reduced, and the composition of the metal phase is close to industrial FeMn at temperatures from 1250 to 1350 °C.

Thus, a study conducted for the electric smelting of agglomerates and pellets obtained from fine ore and sludge found the efficiency of their use for the production of ferromanganese alloys.

Processing and extraction of valuable components from industrial wasted materials is a real environmental and technological challenge. The review [13] notes that the demand for ferromanganese alloys is very high, and research on the beneficiation and agglomeration of ore fines to obtain a product suitable for metallurgical smelting in terms of manganese content is important.

Declining high-grade manganese raw material reserves and growing demand for manganese in the production of magnetic and energy storage materials have drawn attention to low-grade manganese resources [27]. Currently, work is actively underway to extract manganese from manganese-containing waste. In addition, recycling waste generated in large quantities during the beneficiation of rich manganese ore is beneficial both environmentally and economically.

The purpose of the research was to prove the possibility of melting ferrosilicomanganese using manganese pellets obtained from beneficiated manganese-containing wastes.

2. Materials and Methods

The following analysis methods were used to determine the composition of the initial raw materials and the resulting products: chemical, X-ray diffraction, X-ray fluorescence, and scanning electron microscopy with electron probe microanalysis. Equipment: atomic emission spectrometer Optima 2000 DV; X-ray diffractometer D8 Advance BRUKER (Karlsruhe, Germany), Cu α radiation; X-ray fluorescence spectrometer Venus 200 PANalytical BV; electron probe microanalyzer JXA-8230 (JEOL), (Tokyo, Japan); laboratory 2-chamber diaphragm depositor; laboratory concentration table, laboratory mixing granulator (Eirich), (Moscow, Russia); Roller crusher DG (Mekhanobr-tekhnika, Moscow, Russia); laboratory ball mill MSHL-7 (Mekhanobr-tekhnika, Moscow, Russia); and Tamman furnace (Aktobe Ferroalloy Plant, (Aktobe, Kazakhstan)).

A sample of manganese sludge weighing 200 kg was taken from the Ushkatyn deposit (Central Kazakhstan). The manganese content in an average sample of sludge with a particle size of $-5 + 0$ mm is 16.32%. Diatomite from the Zhalspak deposit (Western Kazakhstan), containing 71.24% SiO₂, was used as a binder in the production of manganese pellets.

The pellets based on beneficiated manganese-containing sludge were obtained by pelletizing in a laboratory mixing Eirich granulator. The mixing granulator consists of a 1-L steel drum and a turboprop swirler equipped with a blade scraper. The swirl speed can be varied from 100 to 6000 rpm. The drum has two rotation modes: clockwise and counterclockwise, at a speed of 85 and 170 rpm. The tilt angle of the drum is adjustable in the range of 0–30°.

The manganese concentrate was crushed in a ball mill to a fraction of less than 0.5 mm to obtain pellets. The crushed manganese concentrate was fractionated on a vibration table. Part of the concentrate (30%) was finely ground in a vibrating mill to a powdery state with a particle size of not more than 0.063. The charge used to produce pellets had the following fractional composition: 0.5–0.16 mm—40.3%; 0.16–0.063 mm—30.2%; less than 0.063 mm—29.5%.

Diatomite from the Zhalspak deposit, the main mineral phase of which is quartz, was used as a binding component of the charge to obtain manganese-containing pellets (Table 1).

Lime was used as a component that promotes the formation of slag with a diopside-anorthite composition.

The use of fine special coke in the charge in an amount of up to 5% promotes uniform heating of the pellets and preliminary reduction in iron and manganese. When smelting ferromanganese alloys, special coke of JSC Sary-Arka was used, which is characterized by a porous structure, mechanical strength and significant reactivity. The ash content of the coke used is 9.3%, with a porosity of 24%.

Diatomite and special coke were crushed in a roller crusher, followed by fine grinding in a vibrating mill to a powder state with a particle size of not more than 0.063 mm. A batch of 10 kg for granulation was prepared (Table 2).

Table 1. Phase composition of diatomite sample.

Pattern #	Compound Name	Formula	S-Q, %
PDF 01-085-0865	Quartz	SiO ₂	69.4
PDF 00-029-0713	Goethite	Fe ⁺³ O(OH)	7.0
PDF 00-039-0264	Barium Manganese Silicate	Ba ₂ MnSi ₂ O ₇	6.7
PDF 01-075-6047	Magnesium Silicate	Mg(SiO ₃)	4.2
PDF 00-052-1344	Calcium Aluminum Silicate	Ca _{0.88} 0.12Al _{1.77} Si _{2.23} O ₈	3.7
PDF 00-045-1489	Calcium Aluminum Silicate Hydrate	Ca ₈ Al ₁₆ Si ₂₄ O ₈₀ ·16H ₂ O	3.6
PDF 01-074-3123	Bigcreekite	Ba(Si ₂ O ₅)(H ₂ O) ₄	3.2
PDF 01-071-2108	Srebrodolskite	Ca ₂ Fe ₂ O ₅	2.2

Table 2. Components of the charge for manganese pellets.

Charge Components	Quantity, kg
Manganese concentrate	8.0
Diatomite	1.0
Lime	0.5
Special coke	0.5

The chemical composition of the starting materials of the charge to produce the manganese pellets is shown in Table 3.

Table 3. Chemical composition of materials for the manganese pellets.

Material	Oxides Content, wt. %										
	Mn	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	C	Other	Loss of Ignition
Ore fines (sludge)	15.93	28.08	3.61	6.88	9.6	1.53	0.66	0.53	-	18.20	6.91
Fine-grained manganese concentrate	35.2	10.31	1.83	9.57	6.85	1.31	0.17	0.09	-	15.38	3.94
Diatomite	-	71.24	8.06	10.21	4.95	3.42	-	-	-	2.12	-
Lime	-	0.23	0.05	0.09	76.32	1.80	-	-	-	0.54	20.97
Coke	-	-	-	-	-	-	-	-	89.3	10.7	-

The manganese pellets were obtained by pelletizing in an automated laboratory mixer-granulator made by Eirich. The granulation process took place in the following mode: steel drum rotation speed, 170 rpm; swirler rotation, 2000 rpm; drum inclination angle, 30°; drum rotation, counterclockwise.

One kg of charge was poured into the mixer-granulator in one operation to obtain the pellets. The mass was mixed for 30 s at a maximum rotation speed of the swirler of 2000 rpm. Then, a binder component was introduced—a 1.5% aqueous solution of carboxymethylcellulose (CMC) in an amount of 20% of the total amount of the mixture. The granulated material was dried under natural conditions for 24 h, and then at a temperature of 110–200 °C for 40–60 min to a residual moisture content of not more than 3.0%. Standard pellets were fired at 1170 °C with a holding time of 1 h. The size of the calcined pellets was about 6–8 mm (Figure 1).

A total of 8.81 kg of pellets were obtained, 0.61 kg of which were scrap. During roasting, coke is consumed for redox reactions between the components of the charge, remove the organic binder (CMC), and remove moisture from the raw materials. The total weight loss of the product during firing was 4.19 kg.

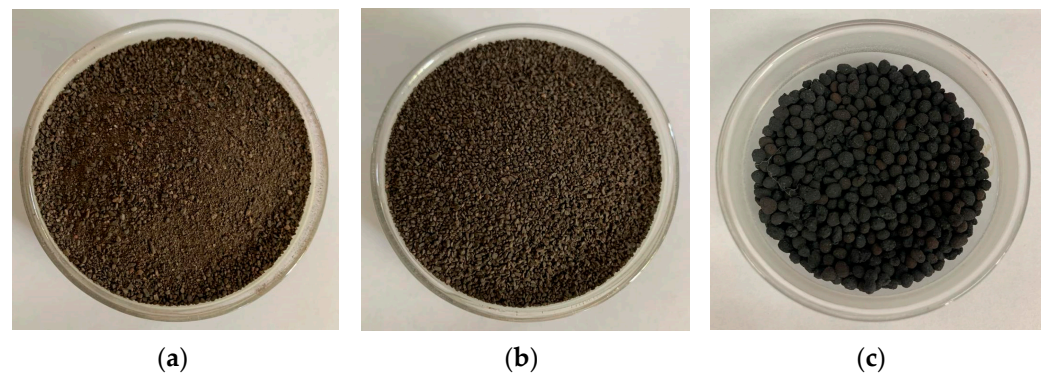


Figure 1. Manganese-containing sludge (a), beneficiated sludge (b), and manganese pellets (c).

Experimental smelting of manganese pellets was carried out in a Tamman apparatus. The temperature was measured with a tungsten–rhenium thermocouple VR-5 20.

A charge of a given composition was loaded into graphite crucibles with a volume of 300 cm³. The crucibles were placed in an oven at room temperature and heated at a rate of 10 degrees per minute up to a temperature of 1600 °C for melting ferrosilicomanganese for 30 min. The Tamman furnace was turned off at the end of the melting, and the crucibles were unloaded at 700 °C. The crucibles were broken, and the slag and metal parts were separated after cooling the crucibles to room temperature, which were weighed to calculate the material balance (Figure 2).



Figure 2. Ferrosilicomanganese melting products: (a) alloy; (b) slag.

3. Results and Discussion

A sample of manganese-containing sludge weighing 50.0 kg was sieved on sieves with particle sizes of 2.5, 1.25, and 0.071 mm. The manganese and iron distribution by sludge size classes is shown in Table 4.

Table 4. Distribution of manganese and iron by size class of manganese-containing sludge.

Class of Size, mm	Yield, %	Element Content, %		Distribution of Elements, %	
		Mn	Fe	Mn	Fe
- 2.5 + 1.25	44.39	16.36	6.40	48.27	47.1
- 1.25 + 0.071	47.62	15.03	5.81	47.56	45.77
- 0.071 + 0	8.01	7.82	5.37	4.16	7.13
Total	100.0	15.04	6.03	100.0	100.0

The optimal conditions were determined for beneficiation of size classes—2.5 + 1.25 and—1.25 + 0.071 mm on a jigging machine—bed size (manganese grains)—10–8 mm, bed height 30–40 mm, pulsation frequency—350 oscillations /min, vibration amplitude—8 mm. The particle size class—0.071 + 0 mm was beneficiated on a SKL-0.5 laboratory concentration table with the following optimal parameters: table stroke—14 mm, number of deck swings per minute—240, deck inclination—35 degrees.

The resulting manganese concentrate was subject to magnetic separation, which made it possible to increase the manganese content in the concentrate from 28.6% to 35.2%. The beneficiation results of manganese-containing sludge with the gravitational-magnetic scheme are shown in Table 5.

Table 5. Summary of beneficiation technological indicators for the manganese-containing sludge under the gravitational-magnetic scheme.

Product	Yield, %	Content, %		Recovery, %	
		Mn	Fe	Mn	Fe
Fine-grained manganese concentrate—2.5 + 0 mm	27.6	35.2	6.7	60.96	38.39
Concentration tailings	72.4	8.6	4.1	39.04	61.61
Total	100.0	15.9	4.8	100.0	100.0

Thus, a fine-grained manganese concentrate was obtained containing 35.2 manganese and 6.7% iron, with a recovery of 60.96 and 38.39%, respectively, according to the gravitational-magnetic beneficiation scheme.

X-ray diffraction analysis of the concentrated sample obtained via beneficiation of the manganese-containing sludge demonstrated that manganese is present mainly in the form of braunite and a smaller amount of hausmannite. Impurities are represented by hematite and riversiderite, ackermanite, and clinocllore (Figure 3).

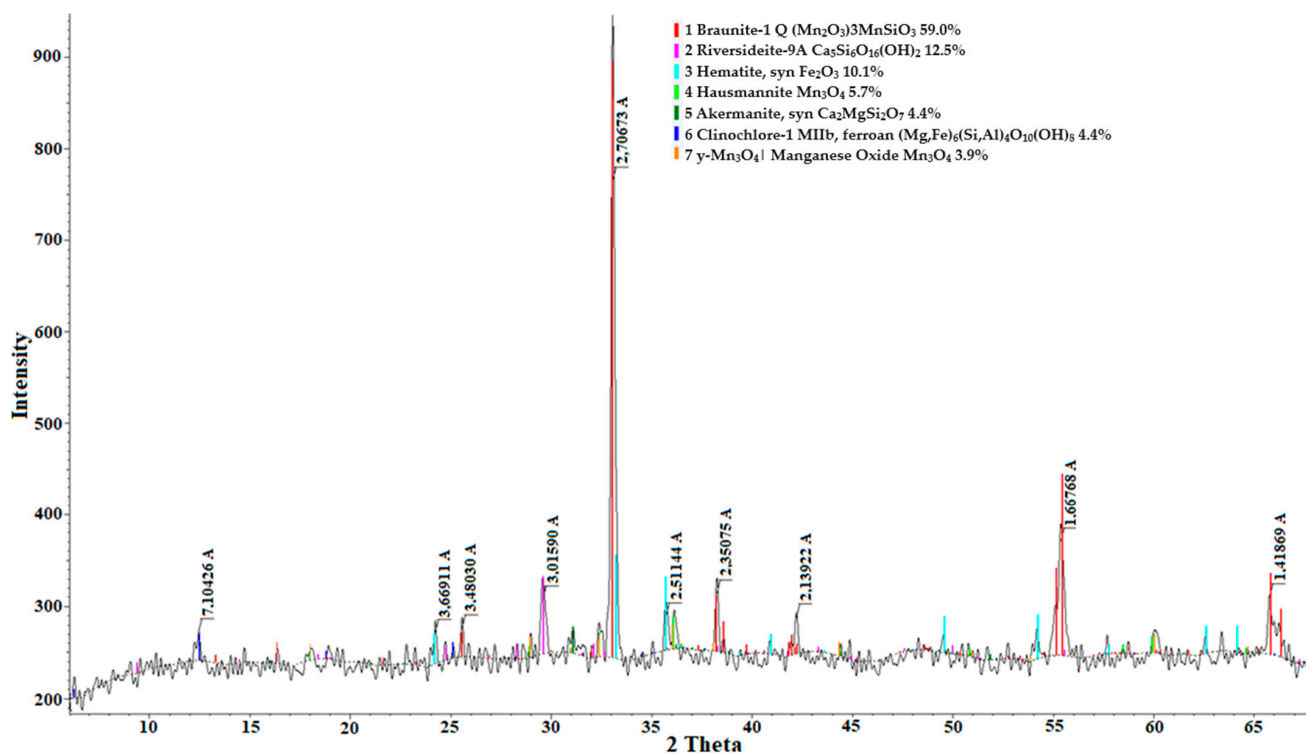


Figure 3. X-ray diffraction pattern of a manganese concentrate sample.

The results of testing samples of the manganese pellets obtained from beneficiated manganese-containing sludge showed that the fractional composition of the charge and the firing temperature affect their strength characteristics.

The properties of manganese pellets fired at 1170 °C were studied depending on the material and fractional composition of the charge. The compressive strength of pellets obtained with a fractional composition of charge 1 was as follows: 0.5–0.16 mm—61.2%; 0.16–0.063 mm—34.1%; and less than 0.063 mm—4.7% amounted to 22.1–24.6 kg/pellet. For pellets obtained from a charge with fractional composition 2, it was as follows: 0.5–0.16 mm—40.3%; 0.16–0.063 mm—30.2%; and less than 0.063 mm—29.5% of the strength value—33.7–35.3 kg/pellet (Table 6).

Table 6. Properties of the manganese pellets fired at 1170 °C depending on the material and fractional composition of the charge.

Material Composition of the Charge	Fractional Composition of the Charge	Properties of Pellets		
		Porosity _{found} , %	Apparent Density, g/cm ³	Compressive Strength kg/Pellet
Mn concentrate—85, diatomite—10, CaO—5 wt.%	No. 1	30.2	1.87	24.6
Mn concentrate—80, diatomite—10, CaO—5, coke—5 wt.%		37.5	1.39	22.1
Mn concentrate—85, diatomite—10, CaO—5 wt.%	No. 2	27.3	1.91	35.3
Mn concentrate—80, diatomite—10, CaO—5, coke—5 wt.%		34.5	1.45	33.7

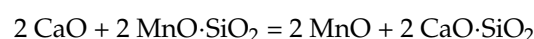
Lower values of the strength of fired pellets obtained based on composition 1 indicate that there was not enough finely dispersed fraction less than 0.063 mm in the charge. In other words, it is necessary to take into account the correct ratio of fractions in the charge during granulation.

The strength of the samples increases, however, at 1200 °C; signs of melting are observed with an increase in firing temperature. The optimal firing temperature is 1170 °C; when intensive sintering is observed, the structure of the samples is compacted and strengthened.

The properties of pellets based on a charge with a high content of fine fraction (less than 0.063 mm) are better: the open porosity of the pellets is lower, and the apparent density and compressive strength are higher compared to pellets based on charge 1.

The X-ray phase analysis for pellet samples fired at 1170 °C showed that manganese is present in them in the form of jacobsonite and hausmannite. The ferrobustamite phase formation (Ca_{0.79}Fe_{0.21})SiO₃, a ferrosilicon–calcium binder that helps increase the strength of the pellets, was noted (Figure 4).

It is known that the addition of quartz reduces the melting point due to the formation of low-melting manganese silicates [17]. Besides manganese ore and a reducing agent, lime was also added to the mixture. Calcium oxide displaces manganese oxide from silicate:



The charge for melting ferrosilicomanganese is composed, taking into account the production of slag of diopside-anorthite composition with a ratio of CaO + MgO/SiO₂ = 0.6.

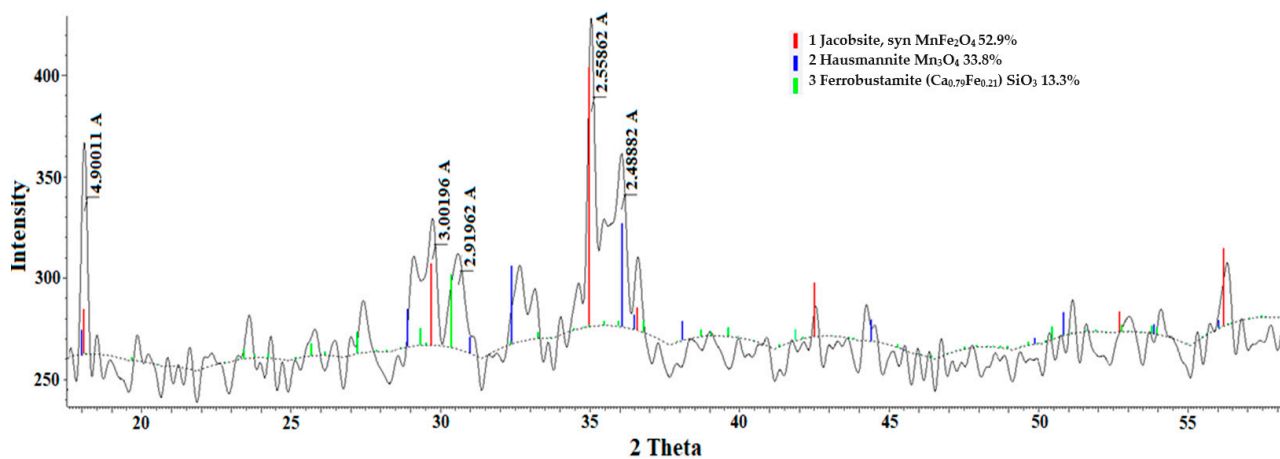


Figure 4. X-ray diffraction pattern of sintered manganese pellets.

The chemical composition of the charge materials is specified in Table 7.

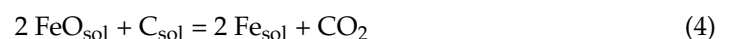
Table 7. Chemical composition of charge materials for melting ferromanganese alloys.

Material	Oxides Content, %									Loss of Ignition
	Mn _{total}	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Other	
Pellets	31.98	19.10	5.43	17.11	11.37	1.39	0.18	0.34	3.83	-
Lime	-	0.23	0.05	0.09	76.32	1.80	-	-	0.54	20.97
MgO	-	-	-	-	-	98.0	-	-	2.0	-
Quartz	-	98.61	0.50	0.26	0.12	0.21	-	-	-	0.30
Coke ash	-	51.40	27.90	10.04	4.00	2.50	-	-	4.16	-

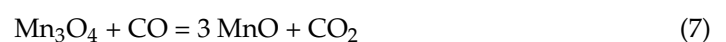
A number of physical and chemical processes occur during the melting process of a charge containing manganese concentrate [17]. When the temperature reaches 800–1000 °C, iron oxides begin to be reduced in manganese concentrates, mainly due to their interaction with carbon monoxide according to the following reactions:



“Direct” reduction in iron with carbon can also occur at local points of contact between ore oxides and reducing agent carbon:



The same is true for the higher manganese oxides to MnO by reactions



When the temperature reaches 1200–1300 °C, the ore and non-ore components of the charge melt to form an alloy and slag. When the temperature rises to 1400 °C, the amount of metal alloy and the resulting slag increases due to the interaction of the components in ore raw materials and flux components. When the concentrate completely melts (1600 °C), a metal melt and liquid slag containing manganese are formed.

Manganese silicates formed during the pre-treatment of manganese ores are the main compounds for the production of SiMn [28]. It is assumed that manganese and silicon in silicates are reduced by carbon to Mn_7C_3 and SiC, respectively, and then the carbides react to form an alloy. It was shown that $MnSiO_3$ was first reduced to manganese and SiO_2 carbides, and then SiO_2 was reduced by carbides to form the Si-Mn alloy. The intermediate product Mn_7C_3 plays a decisive role since SiO_2 is more easily reduced by molten Mn_7C_3 than by carbon.

Experimental melting of ferrosilicomanganese was performed using the flux method. The results of the experimental heats are shown in Table 8.

Table 8. Results of testing melting of ferrosilicomanganese.

Indicators	Values of Indicators	DIN 17 564, FeMn70Si (Germany)	FeMn60Si 14 (China)
1. Material consumption, g:			
Manganese pellets	200		
Coke	51.42		
Quartz	31.48		
2. Alloy obtained, g	94.78		
3. Average chemical composition of the alloy, %			
Mn	63.76	65.0–75.0	60.0–70.0
Si	17.21	15.0–25.0	14.0–17.0
Fe	16.38		
C	1.51	0.5–2.0	≤2.5
P	0.34	≤0.20	≤0.30
S	0.02		≤0.04
4. Slag received, g	77.28		
5. Average chemical composition of slag, %			
MnO	12.53		
FeO	0.54		
SiO_2	45.58		
MgO	9.71		
Al_2O_3	13.93		
CaO	17.52		
6. Base strength $(CaO + MgO)/(SiO_2)$	0.6		
7. Slag ratio	0.8		
8. Average manganese extraction, %	73		

The average manganese content in the alloy is 63.76%, and silicon is 17.21%, according to the results of chemical and X-ray fluorescence analyses. Limiting impurity elements (carbon and phosphorus) are present within acceptable values. The resulting ferrosilicomanganese alloy is close in composition to the DIN 17 564 grade, FeMn70Si (Germany) [29], and corresponds to the FeMn60Si 14 grade (China) [30].

Alloy and slag samples obtained during experimental melting were examined using X-ray phase analysis and scanning electron microscopy equipped with energy dispersion X-ray spectroscopy.

The results of X-ray phase analysis of the melting products of pellets to produce ferrosilicomanganese showed that the alloy composition contains several phases containing manganese, the main of which are compounds of manganese with iron and silicon: $\text{Fe}_4\text{Mn}_{77}\text{Si}_{19}$ and Mn_4FeSi_3 . The alloy also contains compounds of manganese with iron: $\text{Fe}_{0.5}\text{Mn}_{0.5}$ and Fe_3Mn_7 , ($\text{Fe}_{0.95}\text{Mn}_{0.05}$), and metallic manganese Mn and iron with silicon (Fe_{19}Si)_{0.1} (ferrosilicon) (Figure 5). The slag includes complex silicates of calcium, magnesium, and iron, including diopside (Table 9).

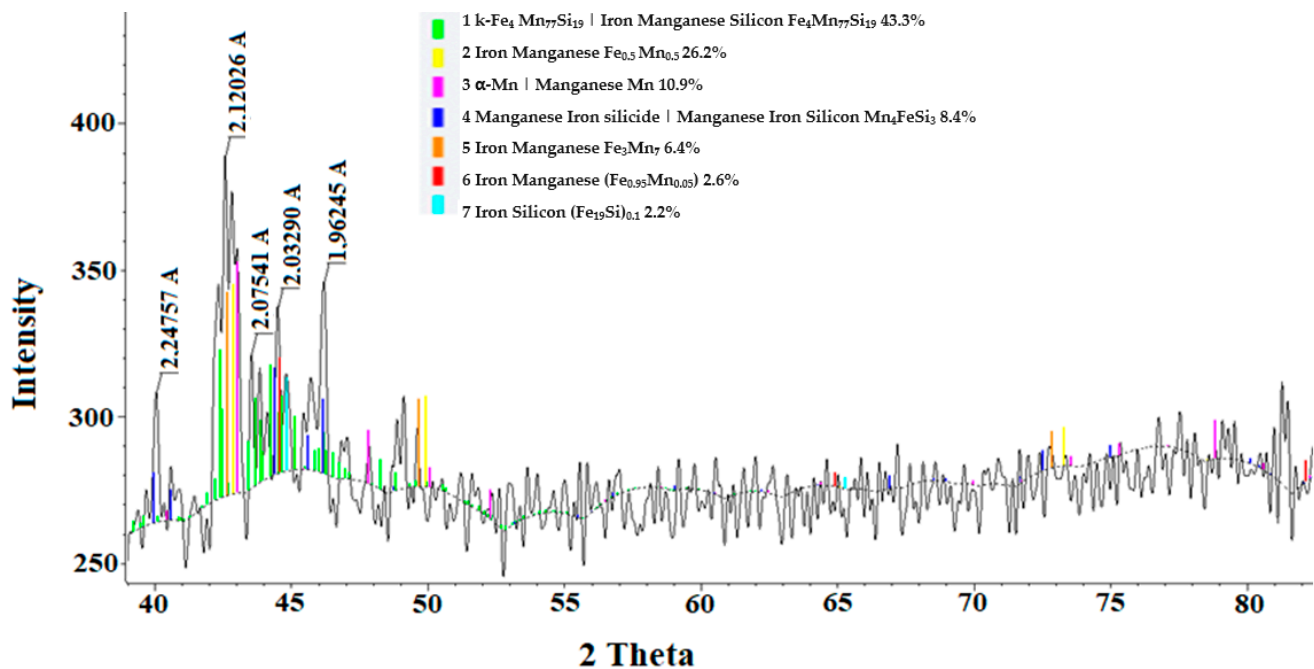


Figure 5. X-ray diffraction pattern of the Fe-Mn-Si alloy obtained by melting.

Table 9. Composition of a slag sample obtained from melting for Fe-Mn-Si alloy.

Pattern #	Compound Name	Formula	S-Q, %
PDF 01-086-1607	Dalnegorskite	$\text{Ca}_{0.81}\text{Mn}_{0.19}\text{SiO}_3$	42.6
PDF 01-077-7954	Iron Manganese Silicon	FeMn_5Si_3	26.5
PDF 01-077-5198	Diopside	$(\text{Ca}_{0.87}\text{Fe}_{0.13})\text{Mg}_{0.79}\text{Fe}_{0.007}(\text{Si}_2\text{O}_6)$	21.1
PDF 01-080-4478	Aluminum Manganese	Mn_3Al	9.8

The microstructure of the Fe-Mn-Si sample is characterized as non-uniform grains containing the developed net of cracks (Figure 6). The average composition of elements of this selected area obtained via energy dispersion X-ray spectroscopy (EDS) can be presented using the following composition: $\text{Fe}_{0.18}\text{Mn}_{0.54}\text{Si}_{0.28}$.

Using the method of EDS mapping of elements, patterns of the component composition of the Fe-Mn-Si alloy were revealed, which can be described by the terms “co-phasing” and “counter-phasing” (Figure 6b–d).

Thus, Si and Mn demonstrate the so-called “counter-phasing” manner of concentration distributions, whereas Fe reaches its concentration maxima in areas playing the role of “glue” for grains having the maximal concentrations of Si.

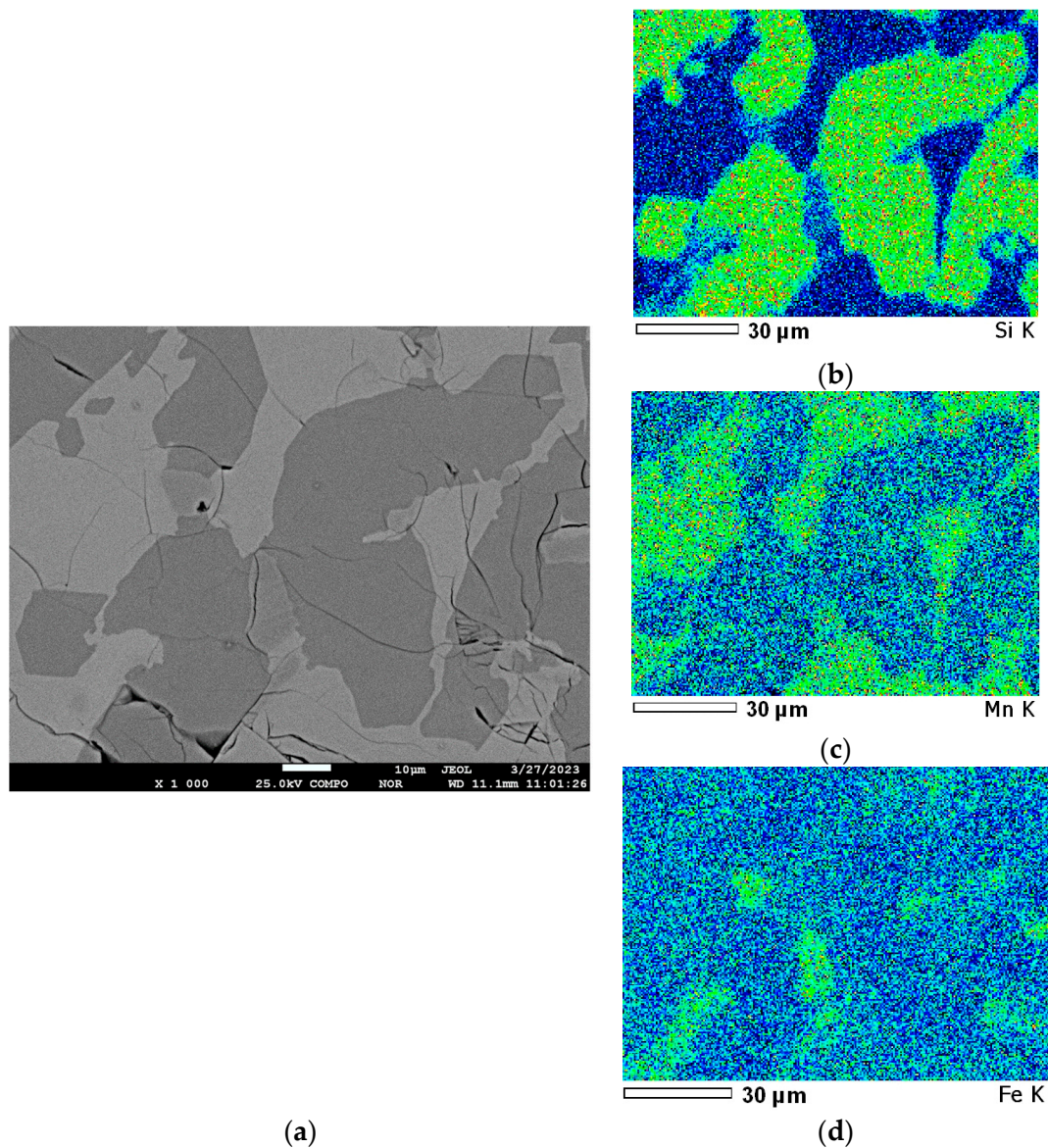


Figure 6. Microstructure of Fe-Mn-Si alloy (a) and its element EDS-mapping; ((b) Si, (c) Mn, and (d) Fe).

This manner of alloy component behavior correlates with the contrast of the micrograph obtained as a backscattered electron image (Figure 6a). The larger the average atomic number of areas, the brighter its contrast.

The local concentrations of alloy components obtained via EDS point microanalyses (Figure 7) can be shown as follows: for areas with higher content of Fe— $\text{Fe}_{0.27}\text{Mn}_{0.50}\text{Si}_{0.23}$; for larger concentrations of Si— $\text{Fe}_{0.16}\text{Mn}_{0.48}\text{Si}_{0.36}$; and for area with higher concentration of Mn— $\text{Fe}_{0.19}\text{Mn}_{0.64}\text{Si}_{0.17}$. Thus, the observed local variations in the element composition can reach the following values: for Si, from 17 to 36%; for Fe, from 16 to 27%; and for Mn, from 48 to 65%.

The similar SEM/EPMA survey of slag samples shows that there was an insignificant portion of metal thrown into the slag in the form of globular particles sized under 10 µm.

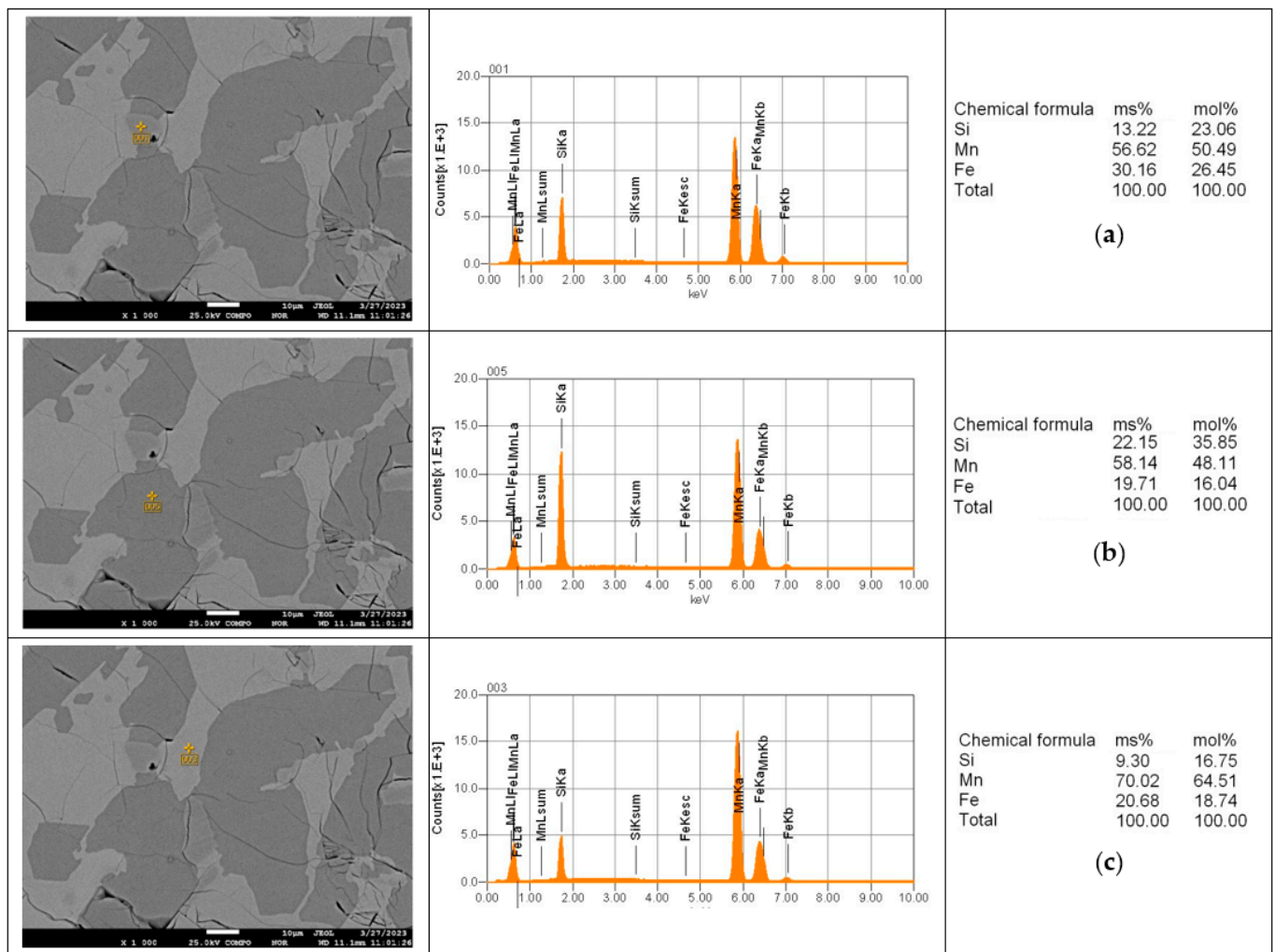


Figure 7. Point element EDS microanalyses of areas benefited by Fe (a), Si (b), and Mn (c).

4. Conclusions

The experiments were carried out on the gravitational-magnetic beneficiation of manganese-containing sludge to obtain a fine manganese concentrate containing 35.2 manganese and 8.1% iron with a recovery of 60.96 and 38.39%, respectively.

The technological parameters for pellet manufacturing based on a charge consisting of manganese concentrate, small fractions of coke, ferrous forms of diatomite, and lime were determined. It has been shown that the fractional composition of the charge and the firing temperature influence the strength characteristics of fired manganese pellets. The optimal temperature for firing pellets is 1170 °C. It has been established that manganese is present in the structure of fired pellets in the form of jacobsonite and hausmannite. The compressive strength of the fired pellets was 33.7 kg/pellet, which is sufficient for their further use in the smelting process.

As a result of the melting of the calcined manganese pellets at a temperature of 1600 °C, a ferrosilicomanganese alloy was obtained. In terms of manganese (63.76%) and silicon (17.21%) content, the ferrosilicomanganese alloy corresponds to the grade FeMn60Si 14 (China).

Using the method of EDS mapping of elements, patterns of the component composition of the Fe-Mn-Si alloy were revealed, which can be described by the terms “co-phasing” and “counter-phasing”.

In this case, Si and Mn demonstrate the so-called “counter-phasing” nature, whereas Fe reaches the maximal concentration in areas that play the role of “glue” (binder) for grains with maximum Si concentrations.

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