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Metallurgy



Research on the possibility of obtaining medium-carbon ferromanganese from the Djezdinskoe deposit

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<p>Received: December 10, 2023 Peer-reviewed: January 3, 2024 Accepted: January 12, 2024</p>	<p>ABSTRACT In this article, the results of laboratory studies on the smelting of medium-carbon ferromanganese using Djezdinskoe ores are presented. Kazakhstan has significant reserves of manganese ores represented by iron-manganese and carbonate-oxide ores. The manganese ores of the Djezdinskoe deposit are characterized by a relatively high manganese content (48%) and low iron content (2-5%). Sieve analysis was used to study the particle size distribution of the ore. Based on the results of the sieve analysis of ore samples obtained after sieving, a high manganese content (53.54%), low iron content (0.47%), and silicon dioxide content (2.25%) were identified. Laboratory experiments were conducted on smelting medium-carbon ferromanganese in the high-temperature Tamman furnace. According to the results of the laboratory experiments, it is recommended to use the size classes of -5.0 + 0.0 mm to obtain high-quality low-phosphorus silicon-manganese alloy and the size class of +5.0 to produce medium-carbon ferromanganese. The average chemical composition of the metal and slag is as follows: % Mn – 86 – 88; Si – 0.04 – 0.35; Fe – 1.78 – 2.0; P – 0.06 – 0.09; C – 1.5 – 2.0; MnO – 19-20; SiO₂ – 13.94-14.5; CaO – 23.35 – 24.85; MgO – 13.25-14.0. Thus, an optimal technological scheme has been developed for the production of a wide range of manganese ferroalloys.</p>
	<p>Keywords: Manganese ore, medium-carbon ferromanganese, low-phosphorus refined silicomanganese, differential thermal analysis, high-temperature furnace, ferroalloy.</p>
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Introduction

Manganese is a crucial strategic metal with widespread industrial applications in various aspects of social economics. Approximately 90-95% of manganese is consumed in steel production, while the remaining portion is utilized in non-ferrous metallurgy, battery manufacturing, and food additives [1].

The applications of manganese stem from its physicochemical properties. It is well-known that adding manganese to steel enhances its mechanical properties such as wear resistance, ductility, and

strength [2]. Consequently, the primary consumer of manganese and its alloys is the metallurgical industry. Around 80% of extracted manganese ores are utilized in the production of manganese ferroalloys. This is because, from an economic perspective, the steelmaking industry generally prefers the use of manganese alloys with iron, such as ferromanganese.

In ferrous metallurgy, manganese alloys are essential for producing various types of steel, including carbon, low-alloy, tool, and corrosion-resistant steels, as well as for refined and cast iron. Manganese is also added to bronzes and brass.

Copper alloys with manganese are used for manufacturing turbine blades, while manganese bronzes are employed in producing propellers and other components requiring a blend of strength and corrosion resistance is required.

According to confirmed reserves of manganese ores, Kazakhstan ranks fourth in the world, and eighth in extraction, with a share of Kazakh ores in global reserves amounting to 8% [3]. The demand for manganese products continues to grow. Kazakhstan's reserves are found in oxide iron-manganese and carbonate-oxide manganese ores. The share of confirmed reserves of manganese ores by industrial categories is approximately 700 million tons, of which around 200 million tons are suitable for open-pit mining and 500 million tons for underground mining [4].

The average manganese content in Kazakhstan's ores is 19.4%, lower than in the ores of most countries worldwide (30–50%). The manganese ores of the Republic stand out for their low phosphorus and sulfur content, virtually lacking harmful impurities like arsenic and antimony, and featuring a significantly oxidized mineral composition. This characteristic advantageously distinguishes them from Ukrainian and Georgian ores. However, a drawback is the considerable iron content (ranging from 2 to 30%), and on certain sites, the presence of lead and zinc (up to 0.01-0.4%).

Out of 300 identified manganese deposits and occurrences, the State reserves balance accounts for 19 manganese deposits situated in Central Kazakhstan. In other regions, only isolated occurrences reach the size of small deposits. Many occurrences remain poorly studied, and the scale of manganese mineralization is limited by visual assessments. This limitation is primarily associated with the presence of rich ores at the Djezdinskoe deposit and the largest accumulations of manganese ores in the Atasu district. Consequently, the scope of work to study manganese mineralization in other regions of the Republic has been restricted [[5], [6], [7], [8], [9]]. Despite the impressive reserves of manganese ores in Kazakhstan, the production of medium-carbon ferromanganese has not been established.

The research was conducted to study the processes involved in smelting medium-carbon ferromanganese from manganese ore. The Djezdinskoe deposit was chosen as the subject of the study due to its status as one of the largest manganese ore deposits and its high industrial significance.

Experimental part

The work was carried out at the Zh. Abishev Chemical-Metallurgical Institute. To conduct laboratory experiments, it was necessary to perform a particle size analysis. For determining the particle size distribution of the ore submitted for examination, a set of sieves according to GOST 9758-86 with the following opening sizes in mm was used: 40, 20, 10, 5, 2.5, 0.5, and 0.16 [[10], [11]]. A dry sieving analysis was conducted on the examined ore sample. Following the particle size analysis, thermal analysis of the ore was performed.

One of the widely adopted methods for studying calcination processes is thermal analysis [[12], [13], [14], [15]]. Therefore, this presented work includes calculations to determine the apparent activation energy using the non-isothermal kinetics method for phase transformations occurring in iron-manganese ores during heating. The possibility of determining the activation energy by three parallel paths using the heating curves of DTA (differential thermal analysis), DTG (differential thermogravimetric analysis), and TG (thermogravimetric analysis) derivatives was verified. Sequentially discussed are the physicochemical transformations occurring in iron-manganese ores in both oxidizing and reducing environments.

Differential thermal analysis was conducted in an oxidizing atmosphere of air and an inert argon atmosphere using a Paulik, Paulik, and Erdéy system derivatograph. This equipment allowed for the recording of changes in sample mass (TG), the rate of change of mass (DTG), and the temperature difference (DTA) between the sample and an inert reference during continuous heating at a specified rate. Derivatograms of manganese, iron-manganese, and iron ores (Table 1) revealed several endo- and exothermic effects associated with the dissociation and oxidation of manganese and iron-bearing minerals [[16], [17]]. These thermal effects and the related physicochemical transformations became the subject of investigation in this chapter. Temperature and differential curves were recorded using a platinum-platinum-rhodium thermocouple. The heating rate was set at 10 degrees per minute. The sensitivity of the DTA derivatograph was 1/10. Dissociation studies were conducted in an argon atmosphere. Samples, in powder form, were placed in a corundum crucible with a diameter of 10 mm and a height of 12 mm. The duration of the experiments was 100 minutes.

The interpretation of thermal effects was based on available literature data and the results of X-ray phase studies. In many cases, reference was made not only to individual publications on the thermoanalytical characteristics of minerals but also to summary tables that consolidate this data [[18], [19], [20]].

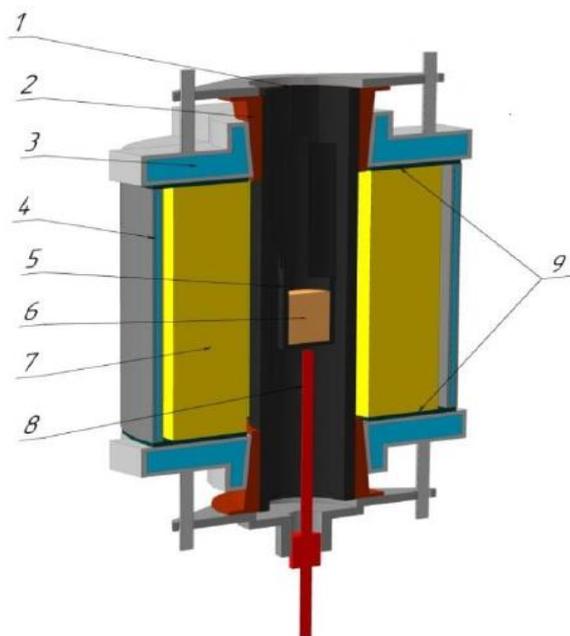


Figure 1 - High-temperature Tamman furnace (in section) 1 - Carbon-graphite tube; 2 - Copper compression ring; 3 - Water-cooled cover; 4 - Water-cooled housing; 5 - Alundum crucible; 6 - Investigated charge; 7 - Protective lining; 8 - Thermocouple; 9 - Lower electrode.

Experimental studies on the smelting of medium-carbon ferromanganese were conducted in a high-temperature Tamman furnace, designed for modelling metallurgical processes (Figure 1). Its working zone is constructed with a graphite tube. Temperature regulation is achieved using a thyristor voltage regulator connected to the primary winding of the power transformer. This allows for obtaining a current of up to several thousand amperes on the output buses at voltages ranging from 0.5 to 15 volts. The furnace temperature was measured using a tungsten-rhenium thermocouple WR-5/20 in a corundum casing.

To conduct laboratory research on the process of smelting medium-carbon ferromanganese, we are evaluating the quality of the reducing properties of low-phosphorus refined silicomanganese, manganese ore from the Djezdinskoye deposit and lime.

Results and Discussion

Initially, a dry sieving analysis was conducted on the material of the investigated sample with a size of $-40.0 +0.0$ mm. The results of the analysis, showing the distribution by particle size classes and the content of manganese, iron, and silicon dioxide, are presented in Table 1. Based on the calculated granulometric composition of the ore obtained from dry sieving (Table 1), the weighted average content of manganese, iron, and silicon dioxide in the ore sample was determined to be 48.49%, 1.76%, and 5.59%, respectively. The particle size distribution curve corresponding to the dry sieving is depicted in Figure 2.

Table 1 - Sieve analysis of the initial ore from the Djezdinskoe deposit.

№	Particle size class, mm	Output, %	The chemical composition, %			Extraction, %	
			Mn	Fe	SiO ₂	Mn	Fe
1	-40+20	26.36	53.54	0.47	2.25	29.11	7.02
2	-20+10	32.99	52.09	0.41	1.41	35.44	7.66
3	-10+5	26.88	49.19	2.06	4.64	27.27	31.36
4	-5+2.5	9.85	30.22	7.31	21.23	6.14	40.76
5	-2.5+1	3.74	25.67	5.84	30.65	1.98	12.36
6	-1+0.5	0.08	19.14	8.55	30.51	0.03	0.38
7	-0.5+0.16	0.02	21.53	7.55	25.17	0.01	0.09
8	-0.16+0	0.08	19.46	8.02	21.37	0.03	0.38
Total (ore)		100	48.49	1.76	5.59	100	100

The analysis of the results obtained from the dry sieving (Table 1) demonstrates relatively high outputs for particle size classes ranging from -40 mm to $+5.0$ mm. The highest output corresponds to the particle size class $-20+10$ mm, accounting for 32.99%, gradually decreasing to 13.77% for the particle size class $-5.0+0.0$ mm.

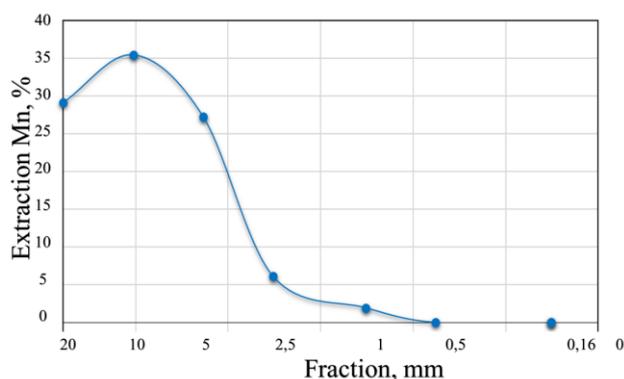


Figure 2 - Sieve analysis of the initial ore (dry sieving)

The derivative thermograms of manganese ores from the Djezdinskoe deposit (Figures 3 and 4) are nearly identical. All derivative thermograms display two characteristic (similar) endothermic effects, differing only in their proportions. According to the derivative thermograms, the uniform removal of hygroscopic moisture smoothly progresses up to 250°C and abruptly transitions to the first endothermic effect within the temperature range of 285-400°C, corresponding to the loss of hydrated (structural) moisture associated with vernadite. At this temperature, presumably, the monohydrate dissociates, forming α - β -Mn₂O₃. The total moisture loss (hydrated and hygroscopic) amounts to 20 mg. The second endothermic effect at 500-570°C corresponds to the formation and decomposition of the α -cryptomelane solid solution. At 660-675°C, there is an endothermic pyrolusite effect, indicating the formation of β -Mn₂O₃ from β -pyrolusite (β -MnO₂). At 810-825°C, a permanganate effect is observed (decomposition of psilomelane). Finally, at 970-980°C, a cryptomelane effect is identified, signifying the formation of β -hausmannite from β -Mn₂O₃ (β -cryptomelane).

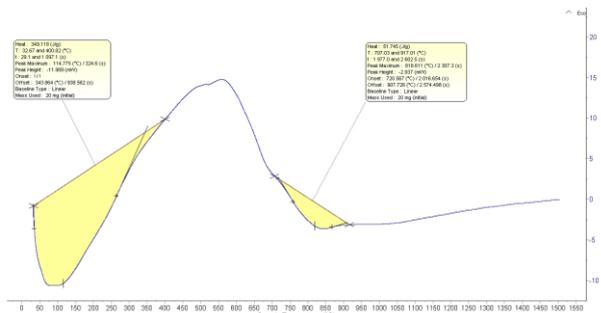


Figure 3 - Derivative thermogram of manganese ore (fraction +5 mm)

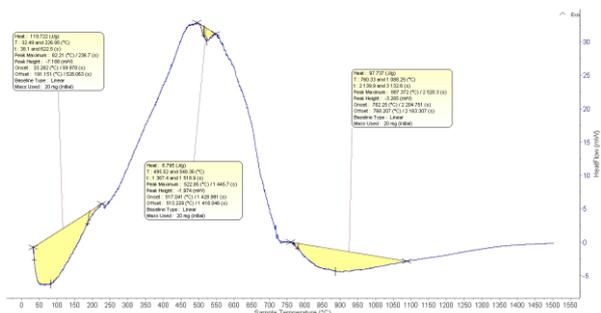


Figure 4 - Derivative thermogram of manganese ore (fraction -5 mm)

Phase composition of the primary manganese ore, as shown in Figure 5-9 for the fraction up to -40 mm, was determined using X-ray phase analysis. The results revealed that the main phases include pyrolusite (MnO₂), hydrated manganese oxide

(MnO₂(H₂O)_{0.15}), quartz (SiO₂), magnesian calcite (Mg_{0.03}Ca_{0.97})(CO₃), lamontite (CaAl₂Si₄O₁₂(H₂O)₂), gibbsite (Al(OH)₃), potassium aluminium silicate (KAlSi₃O₈), calcium and manganese oxide (Ca₂Mn₈O₁₆), iron oxide (Fe₂O₃), barium monoferrite (BaFe₂O₄), manganese-barium hollandite (BaMn₈O₁₆), and aluminium calcium (Al₂Ca).

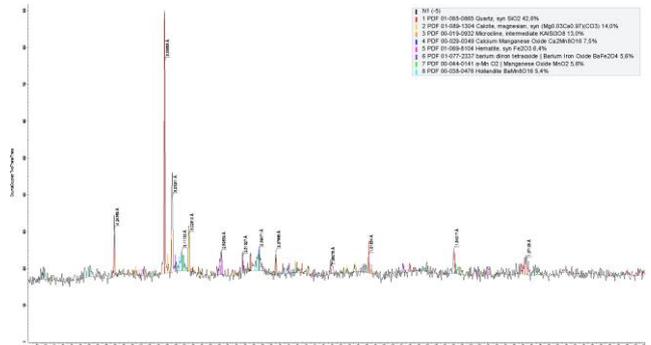


Figure 5 - X-ray diffraction pattern of manganese ores (fraction -5+2,5 mm)

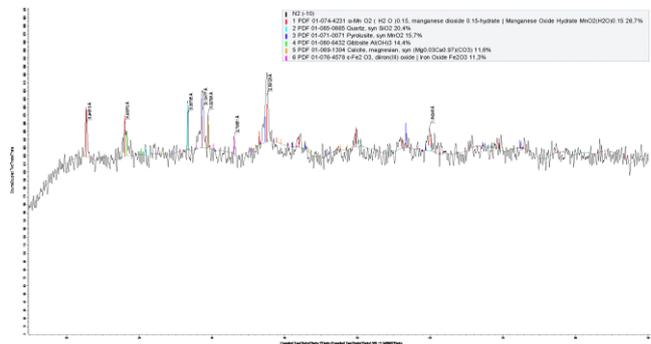


Figure 6 - X-ray diffraction pattern of manganese ores (fraction -10+5 mm)

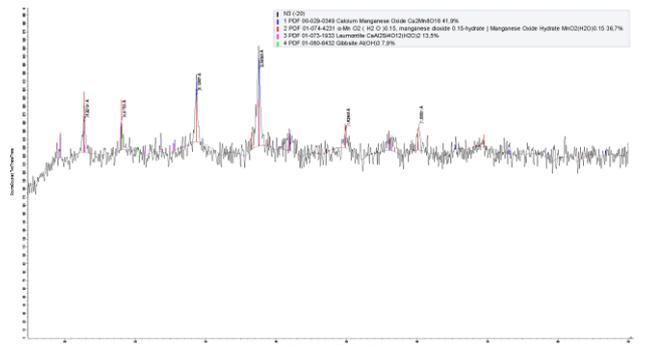


Figure 7 - X-ray diffraction pattern of manganese ores (fraction -20+10 mm)

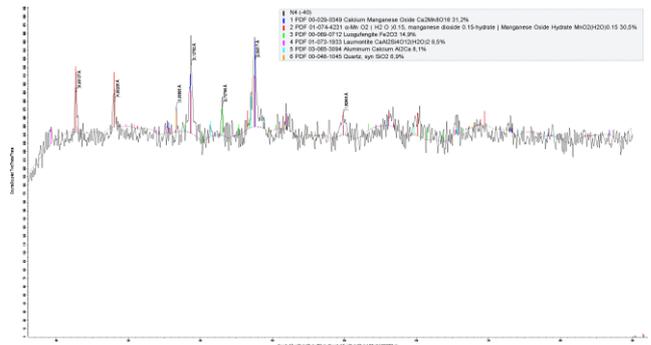


Figure 8 - X-ray diffraction pattern of manganese ores (fraction -40+20 mm)

During the laboratory smelting process in the Tamman furnace, charge materials (ore, low-phosphorus silicomanganese, and limestone) were loaded into a corundum crucible. Upon reaching a temperature of 930°C, the gas release was observed in all experimental melts, characterized by a white deposit on the walls of the carbon tube lid. At 1330°C, the beginning of the charge melting was observed. Around 1450°C, a liquid melt appeared, indicated by the presence of an alloy adhered to the molybdenum wire. At a temperature of 1500°C, gases were formed and released in the crucible, resembling bubbles as if boiling water. At this temperature, the melt was maintained for 60 minutes and then allowed to cool in the furnace. As the temperature decreased to approximately ~200°C, the crucible was removed, and after cooling it to room temperature, the melt underwent sorting to separate the metal from the slag. Figure 9 shows a cross-section of a crucible (metal and slag).

The obtained alloy in terms of its chemical composition complied with the requirements of the GOST 4755-91 standard. The results of the smelting are presented in Table 2. As evident from the table, the compositions of the slags varied in terms of their basicity. The quantity of the reducing agent was adjusted to find the optimal value. During the laboratory experiments, it was noted that the reduction process in the crucible occurred very intensively, resulting in the complete melting of the entire charge and a clear separation between the metal and slag.

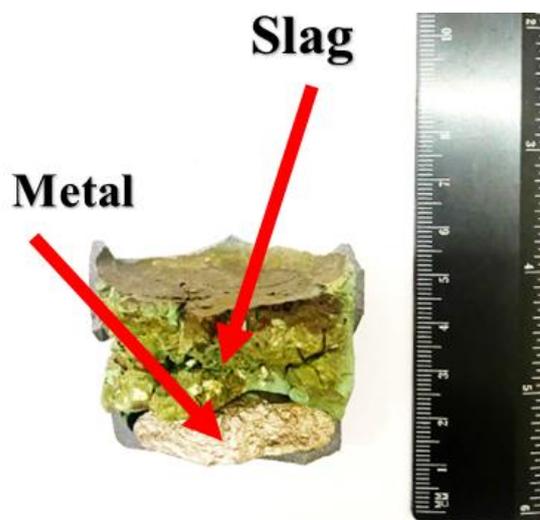


Figure 9 - Cross section of a crucible (metal and slag)

As known, a range of technological indicators depends on the chemical composition of slag, especially its basicity (CaO/SiO₂). As shown in Table 2, the basicity values range from 1.6 to 1.8. The choice of basicity largely determines the technological properties of the slag. In our case, the main goal was to improve the technical and economic indicators of the process, such as the degree of extraction of the leading element into the alloy, the technological efficiency, and the frequency of slag. The degree of manganese extraction from the ore into the alloy was ≥61%. Technological efficiency was characterized by fewer metal droplets entangled in the slag and clear separation of metal and slag when disassembling the solidified melt. A secondary task was to achieve slag stability at the given basicity. Slags from laboratory test melts were obtained in a stony state without signs of disintegration. The above information on optimal data corresponds to basicity values of 1.6-1.8. The recommended technological scheme for the metallurgical preparation of the Jezdinsky deposit is shown in Figure 10.

Table 2 - Chemical composition of metal and slag, %

№	Metal, %				
	Mn	Fe	Si	C	P
1	86.38	10.30	0.21	2.0	0.06
2	86.45	10.25	0.35	2.0	0.07
3	86.51	10.18	0.34	2.0	0.08
4	88.14	9.97	0.03	1.5	0.07
5	88.44	10.00	0.04	1.88	0.08
6	88.35	9.98	0.04	1.78	0.09
№	Slag, %				
	MnO	SiO ₂	CaO	MgO	P
1	19.89	13.94	23.35	13.25	0.001
2	21.05	13.80	25.50	13.31	0.001
3	20.50	13.85	24.51	13.21	0.001
4	20.06	14.00	23.85	13.35	0.001
5	20.05	14.10	24.56	13.45	0.001
6	20.10	14.5	24.75	14.05	0.001

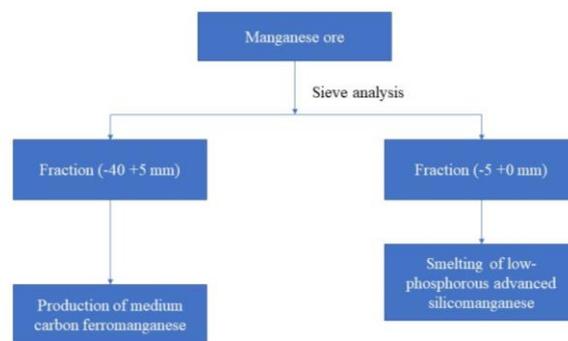


Figure 10 - Recommended technological scheme for metallurgical preparation of the Dzhezdzinskaya deposit

Conclusions

Based on the obtained research results, the following main conclusions can be drawn:

- It has been determined that in the dry sieving of crushed ore down to -80.0 mm, a significant amount of manganese is concentrated in the particle size class up to +5.0 mm, while the minimum amount of iron is concentrated in the particle size class down to -5.0 mm, suitable for low-phosphorus silicomanganese quality of charge materials.

- The phase transformations of charge materials in oxidizing and inert atmospheres were studied by differential thermal analysis (DTA). The experimental data obtained are consistent with the literature.

- The temperature range of the Tamman furnace operation is approximately from 1598 to 1698 K. The

entire smelting process was completed successfully, and the achieved temperature conditions at 1698 K allowed for the complete formation of metal and slag in the melting chamber.

This allows the establishment of optimal parameters for the technological mode to effectively smelt medium-carbon ferromanganese in the refined furnace. The obtained data from thermodynamic and laboratory studies provide a basis for conducting both laboratory and large-scale tests.

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Conflict of interest. The corresponding author declares that there is no conflict of interest.

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Жезді кен орнынан орташа көміртекті ферромарганец алу мүмкіндігін зерттеу

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<p>Мақала келді: 10 желтоқсан 2023 Сараптамадан өтті: 3 қаңтар 2024 Қабылданды: 12 қаңтар 2024</p>	<p>ТҮЙІНДЕМЕ Бұл мақалада Жезді кендерін қолдана отырып, орташа көміртекті ферромарганецті балқыту бойынша зертханалық жұмыстардың нәтижелері келтірілген. Қазақстанда марганец кендерінің едәуір қоры бар, олар темір-марганец және карбонат-оксид кендері түрінде болады. Жезді кен орнының марганец кендерінде салыстырмалы түрде марганец жоғары мөлшерде (48 %) және темір аз мөлшерде (2-5%) болады. Кеннің гранулометриялық құрамын зерттеу үшін елек талдауы қолданылды. Електен бөлінгеннен кейін алынған кен үлгілерін гранулометриялық талдау нәтижелері бойынша марганецтің жоғары мөлшері (53,54 %), темірдің мөлшері (0,47 %) және кремний оксидінің аз мөлшері (2.25%) анықталды. Жоғары температуралы Тамман пешінде орта көміртекті ферромарганецті балқыту бойынша зертханалық жұмыстар жүргізілді. Зертханалық жұмыстардың нәтижелері бойынша жоғары сапалы төмен фосфорды өңдейтін силикомарганецті алу үшін -5+0,0 мм кластарды, орташа көміртекті ферромарганецті алу үшін өлшемі +5 класты қолдану ұсынылады. Металл мен қождың орташа өлшенген химиялық құрамы: %: Mn – 86 – 88; Si – 0,04 – 0,35; Fe – 1,78 – 2,0; R – 0,06 – 0,09; C – 1,5 – 2,0; MnO – 19-20; SiO₂-13,94 – 14,5; CaO – 23,35 – 24,85; MgO-13,25-14.0. Осылайша, марганец ферроқорытпаларының кең спектрін өндірудің оңтайлы технологиялық схемасы жасалды.</p>
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Исследование возможности получение среднеуглеродистого ферромарганца из Джездинского месторождения

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<p>Поступила: 10 декабря 2023 Рецензирование: 3 января 2024 Принята в печать: 12 января 2024</p>	<p>АННОТАЦИЯ</p> <p>В данной статье приведены результаты лабораторных работ по выплавке среднеуглеродистого ферромарганца с использованием Джездинских руд. В Казахстане имеются значительные запасы марганцевых руд, которые представлены железомарганцевыми и карбонатно-окисными рудами. Марганцевые руды Джездинского месторождения характеризуются сравнительно высоким содержанием марганца (48 %) и низким содержанием железа (2-5 %). Для исследования гранулометрического состава руды был использован ситовый анализ. По результатам гранулометрического анализа образцов руды, полученных после ситового разделения, было выявлено высокое содержание марганца (53,54 %), низкое содержание железа (0,47 %) и кремнезема (2,25 %). Были проведены лабораторные работы по выплавке среднеуглеродистого ферромарганца в высокотемпературной печи Таммана. По результатам лабораторных работ рекомендуется использовать классы -5 + 0,0 мм для получения качественного низкофосфористого передельного силикомарганца, класс крупности +5 для получения среднеуглеродистого ферромарганца. Средневзвешенные химический состав металла и шлака: %: Mn – 86 – 88; Si – 0,04 – 0,35; Fe – 1,78 – 2,0; P – 0,06 – 0,09; C – 1,5 – 2,0; MnO – 19-20; SiO₂ – 13,94-14,5; CaO – 23,35 – 24,85; MgO – 13,25-14,0. Таким образом была разработана оптимальная технологическая схема для производства широкого спектра марганцевых ферросплавов.</p>
	<p>Ключевые слова: марганцевая руда, среднеуглеродистый ферромарганец, низкофосфористый передельный силикомарганец, дифференциального термический анализ, высокотемпературная печь, ферросплав.</p>
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