

УДК 669.168:669.15'74-198

<https://doi.org/10.34185/tpm.2.2020.04>

Мяновська Я.В., Проїдак Ю.С., Камкіна Л.В., Анкудінов Р.В., Бабенко О.В., Киричок В.

Твердофазні реакції між компонентами шихти в зонах горіння твердого палива та особливості формування рідкої фази

Mianovska Ya, Projdak Yu., Kamkina L., Ankudinov R., Babenko O., Kirichok V.

Solid phase reaction between components of the charge in the areas burning solid fuel and features of formation liquid phase

Objective. The influence of solid-phase reactions in the agglomerated charge layer on the quality of manganese agglomerate is considered. Research methodology. Thermodynamic analysis was used to establish the predominance of reactions. The phase (mineral) composition of manganese concentrates and the experimental agglomerate was investigated by X-ray diffraction method on a DRON-2 diffractometer in monochromatic $Cu\alpha$ radiation. The interplanar distances at the corresponding values of the X-ray reflection intensity from the investigated samples of concentrates and agglomerate were determined by comparing the obtained data with the corresponding tabular data given in the reference books on X-ray diffraction analysis of substances. Sintering of the experimental agglomerate was performed on a laboratory agglomeration bowl. Research results. It is established that the dissociation of higher manganese oxides begins at relatively low temperatures and proceeds in stages to the formation of MnO. Since the chemical affinity of manganese for oxygen is significant, reduction to metallic Mn was not observed, as this requires a high content of reducing agent and a reducing atmosphere, which is difficult to achieve in real agglomeration processes. Dissociation of rhodochrosite carbonate concentrate and gradual dissociation of dolomitized limestone leads to an increase in CO₂ content in the atmosphere. Slag bonds are represented by compounds Mn_2SiO_4 , $MnO \cdot Al_2O_3$, Mg_2SiO_4 , $CaO \cdot MgO \cdot SiO_2$, $2CaO \cdot SiO_2$. Thermodynamic calculations show that at moderate temperatures, compounds such as calcium ferrites are not formed, which is likely for the interaction between basic flux oxides and manganese oxides. Scientific novelty. Studies have shown that CaO does not completely convert to a slag bond, and even with a basicity of order 1, there is undigested lime. White spots are formed in the structure of the finished agglomerate. Such an agglomerate during transportation and storage loses strength and a large amount of trifles is formed.

Key words: manganese agglomerate, moderate temperatures, solid-phase reactions, lime, bonds, fine particles

Мета. Розглянуто вплив твердофазних реакцій в шарі агломерованої шихти на якість марганцевого агломерату. Методика досліджень. Застосовано термодинамічний аналіз для встановлення переважаючого здійснення реакцій. Фазовий (мінеральний) склад марганцевих концентратів і дослідного агломерату досліджували рентгеноструктурним методом на дифрактометрі ДРОН-2 в монохроматичному $Cu\alpha$ випромінюванні. Міжплоскіні відстані при відповідних їм значеннях інтенсивності відображення рентгенівських променів від досліджуваних зразків концентратів і агломерату визначали методом порівняння отриманих даних з відповідними табличними даними, наведеними в довідниках по рентгеноструктурному аналізу речовин. Спів'язання дослідного агломерату виконували на лабораторній агломераційній чаші. Результати досліджень. Встановлено, що дисоціація вищих оксидів марганцю починається при відносно низьких температурах, проте до утворення MnO. Оскільки хімічна спорідненість марганцю до кисню значна, відновлення до металевого Mn не спостерігалось, оскільки для цього потрібен високий вміст відновника та відновлювальна атмосфера, чого в реальних процесах агломерації важко досягти. Дисоціація родохрозиту карбонатного концентрату та поетапна дисоціація доломітизованого вапняку призводить до збільшення вмісту CO₂ в атмосфері. Шлакові зв'язки представлені сполуками Mn_2SiO_4 , $MnO \cdot Al_2O_3$, Mg_2SiO_4 , $CaO \cdot MgO \cdot SiO_2$, $2CaO \cdot SiO_2$. Термодинамічні розрахунки показують, що при помірних температурах не утворюються такі сполуки, як ферити кальцію, що ймовірно для взаємодії між основними оксидами флюсу та оксидами марганцю. Наукова новизна. Як показали дослідження, CaO не повністю переходить у шлакову зв'язку і навіть при основності порядку 1 є незасвоєне вапно. У структурі готового агломерату утворюються білі плями. Такий агломерат при транспортуванні та зберіганні втрачає міцність та утворюється велика кількість дрібниці.

Ключові слова: марганцевий агломерат, помірні температури, твердофазні реакції, вапно, зв'язки, дрібні частинки

INTRODUCTION

In market conditions, the growth of production, expansion of the range of metal products and significant improvement of its quality are priority areas of development of the metallurgical industry of Ukraine, which is associated with the modernization of existing facilities and commissioning of new, more efficient production lines. Ensuring the most effective conditions for physical and chemical processes in the recovery and heat treatment by improving the quality of ore and coke is the basis for the productive operation of smelting units. The problem of improving the quality of raw materials for use in the smelting of metals and alloys is becoming increasingly important.

In the development of metallurgy a special place is

occupied by primary and secondary material resources, which are equivalent components of the raw material base of the industry. The balance of growing volumes and scales of production with logistics should be achieved by increasing the share of raw materials and materials in resource consumption and the release of primary resources. [1].

The formation of large masses of waste is typical of most industries. According to the accounting of production and consumption waste at all CIS enterprises, about 5 billion tons of solid waste have accumulated in various sectors of the economy, which are mostly not processed and stored in dumps, dumps, tailings, etc. Rational use of mineral resources of man-made deposits should be considered in the fol-

Мяновська Яна Валеріївна – к.т.н., доц. НМетАУ
Проїдак – Юрій Сергійович – д.т.н., проф. НМетАУ
Камкіна Людмила Володимирівна – д.т.н., проф. НМетАУ
Анкудінов Руслан Валентинович – к.т.н., доц. НМетАУ
Бабенко Олександр Вікторович – к.т.н., доц. НМетАУ
Киричок Владислав – аспірант НМетАУ

Mianovska Ya. - Ph.D., Assoc. Prof. NMetAU
Projdak Yu - Ph.D., prof. NMetAU
Kamkina L. - Ph.D., prof. NMetAU
Ankudinov R. - Ph.D., Assoc. Prof. NMetAU
Babenko O. - Ph.D., Assoc. Prof. NMetAU
Kirichok V. - graduate student

lowing main aspects: resource, economic, technological, environmental and national security [2]. It is very characteristic that this problem is relevant both for countries with rich subsoil and for poor countries in this regard. The development of the mineral resource base is aimed at the fact that mineral reserves can be increased by involving in the practical use of man-made industrial waste. Most often, the only alternative to storing waste in dumps is their utilization in sinter production.

STATEMENT OF THE PROBLEM OF THE RESEARCH

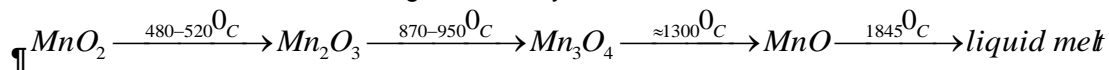
In Ukraine, the balance reserves of manganese ores are about 2 billion tons. More than 70% of domestic manganese ores belong to the carbonate and oxide-carbonate varieties and are difficult to enrich. Manganese ores of domestic deposits contain a relatively low amount of manganese and have a high concentration of phosphorus and silica [3, 4], which does not allow, unlike most foreign ores, to use raw materials without prior enrichment and processing. Due to the limited reserves of high quality manganese ores, the use of poor ores in the production of manganese alloys is becoming increasingly important. The agglomerate must have high strength, lumpiness, porosity and reproducibility at a given chemical composition. However, the use of manganese-containing sludge in the sintering process is limited by their physical, physico-chemical properties and the content of harmful impurities [3, 5–9].

The purpose of the sintering process is to manufacture a product with the appropriate characteristics (thermal, mechanical, physical and chemical) supplied to the melting unit. This process has been widely studied and researched in the metallurgical industry to

know the effective parameters that allow to obtain high quality agglomeration product [10]. It is known that the agglomeration mixture is partially melted and undergoes a series of reactions to form an agglomeration cake, which must be loaded into a melting furnace to obtain an alloy. There is an internal relationship between process parameters and the actual quality of the sinter in the sintering process. However, several studies have been recorded to establish process parameters and actual agglomeration quality for engineering applications. For example, with the help of numerical methods in previous studies, only the parameters of the technological process (flow resistance, thermal state of the sintering layer and the composition of gases) can be obtained [11-14]. Considerable attention is paid to the consideration of the phase composition of liquid phases that occur in the process of increasing the temperature during sintering of raw materials. The reactions between the components of the initial charge at moderate temperatures are insufficiently considered, which was set as the purpose of the work.

EXPERIMENTAL RESEARCH OF SOLID PHASE PROCESSES IN AGGLOMERATION AND THEIR DISCUSSION

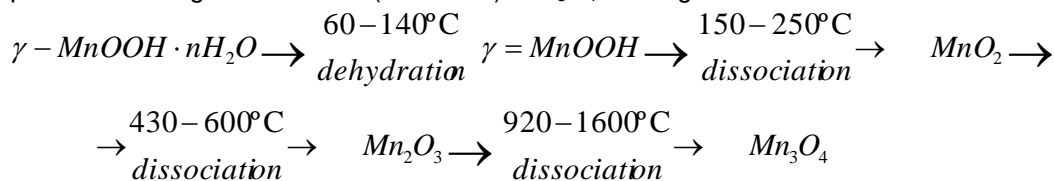
In the MnO system, oxides of MnO₂, Mn₂O₃, Mn₃O₄ and MnO are formed, the composition and properties of which depend on the temperature and oxidative potential of the gas phase [15]. When higher manganese oxides are heated, the cations of which have a valence above two, they thermally dissociate and turn into lower oxides. These transformations, according to various literature sources, occur at the temperatures below:



MnO₂ is a stable compound of manganese at low temperatures. In nature, an analogue of this compound Pyrolusite exists in several modifications. The most common form is β-modification of Pyrolusite. Known rhombic modification γ-MnO₂ (mineral Ramsdellite) and α-, δ-, ε- forms of oxide as solid solutions of various forms of dioxide MnO₂. MnO₂ is a non-stoichiometric compound. There is always a lack of oxygen in its lattice (MnO_{2-x}). Mn₂O₃ oxide exists in two modifications: rhombic - α (mineral Kurnakit) and cubic - β (mineral Bixbiite). Conversion temperature α↔β 670°C. Manganese oxide (II and III) Mn₃O₄

(Mn₂+Mn₂₃+O₄, mineral Gausmanite). Tetragonal modification α-Mn₃O₄ at 1600°S goes into β-Mn₃O₄ cubic lattice.

Depending on the type of manganese ore, it may to a greater or lesser extent contain manganese hydroxide minerals - Manganite (γ-MnOOH), Psilomelan (MnO· MnO₂·H₂O). Under conditions of high temperatures, manganese hydroxides dehydrate, and the decomposition products of hydroxides - oxides are subjected to thermal dissociation [16]. The following is a diagram of the probable sequence of conversion of Manganite when heated:



Psilomelan MnO·MnO₂·H₂O turns into Gausmanite due to the stage of loss of H₂O with the formation MnOOH, and then Mn₃O₄. Decomposition reaction products Mn(OH)₂ is manganese oxide and H₂O.

Thermal dissociation of carbonate minerals in the composition of manganese carbonate ores occurs from manganese carbonate MnCO₃. In the natural mineral Rhodochrosite MnCO₃ the manganese atom may be replaced by elements Fe, Mg, Ca and others

[17]. By analogy with the dissociation of calcium carbonate $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$, the dissociation reaction of manganese carbonate can be imagined

$\text{MnCO}_3 \leftrightarrow \text{MnO} + \text{CO}_2$, activation energy of manganese carbonate dissociation $E_{act}(\text{MnCO}_3) = 205 \text{ kJ/mol}$.

Table 1 - Chemical composition of raw materials

Material	Content components, wt%.									
	Mn	SiO ₂	Fe ₂ O ₃	CaO	MgO	Al ₂ O ₃	P	C	CaF ₂	LOI (loss on ignition)
Manganese concentrate 2nd grade	34,6	21,4	2,7	6,7	1,2	2,1	0,224	-	-	15,8
Manganese carbonate concentrate	28,6	16,0	2,5	12,0	1,4	2,5	0,15	-	-	26,0
Sludge from the sinter plant	31,1	13,4	41	7,0	2,2	5,0	0,23	7,7	-	10,4

Evaporation of hygroscopic moisture of the charge during agglomeration occurs in the zone of drying and heating of the charge up to 30 mm thick with a speed 30-35 g/(m²·s). It is established that at almost any vertical sintering rate the drying of the charge will have time to end under the combustion zone of solid fuel. Portlandite Ca(OH)_2 begins to dissociate from a temperature of 450° C. This process is accompanied by a loss of strength of ore lumps in the area of heating and drying and deterioration of gas permeability of the sintered layer.

In the agglomeration of Siderite (FeCO_3) and Rhodochrosite (MnCO_3) ores, the dissociation reactions of iron and manganese carbonates are also largely completed in the zone of maximum temperatures (the main solid products of dissociation in this case, respectively, are Fe_3O_4 and Mn_3O_4). When agglomerating, for example, Bulgarian Rhodochrosite ores, up to 60% of the total MnCO_3 charge enters the solid fuel combustion zone, where a large amount of heat is expended on the dissociation of carbonates. Introduction of CaCO_3 limestone and dolomitized limestone $\text{CaCO}_3 \cdot \text{MgCO}_3$ in the sintering charge allows to obtain fluxed agglomerate [18, 19].

Dissociation of limestone occurs in the upper part of the heating zone of the charge, but mainly in the combustion zone of solid fuel. On average, as calculations show, the duration of this process during agglomeration does not exceed two minutes, which forces strict requirements for the size of limestone. While there is a lack of oxygen around the burning fuel particles, high temperatures and a reducing atmosphere prevail, and there is a direct contact of the fuel with the ore particles, in the adjacent volumes, where there is no fuel, there is an oxidizing atmosphere. In this regard, the gases of sintering plants contain 3-5% O₂. The ratio of the numbers of volumes of the first and second kind in the combustion zone depends on the consumption of coke fines for the sintering process. At low fuel consumption, the combustion zone is dominated by volumes through which heated air seeps. If the Gaussmanite charge is sintered, then in these volumes there is an intensive ox-

idation of Gaussmanite Mn_3O_4 to Braunite Mn_2O_3 and the process as a whole is oxidative. In the heat balance of the agglomeration in this case it is necessary to take into account the heat released during the oxidation of Gaussmanite, which is a kind of additional fuel. The opposite picture is observed with an increase in the consumption of coke trifle to normal and high.

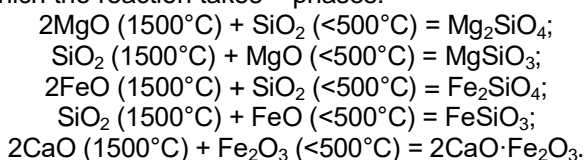
At the same time, the volumes of the charge, which do not contain solid fuel, play a smaller role until they disappear completely. Around the burning particles of coke trifle is an intensive recovery of Pyrolusite MnO_2 , Braunite Mn_2O_3 and Gaussmanite Mn_3O_4 in the charge. The finished product contains more MnO than the original charge. With a sufficiently high fuel consumption, the reduction can provide not only gausmanite, but also manganosite agglomerate. When the consumption of coke fines over 10% in the structure of the agglomerate there are traces of metallic manganese, with increasing solids content in the charge the degree of metallization of manganese agglomerate (100 Mnmet : Mnov) is increased.

Let us now consider the course of reactions between the components of the charge, which occur at the points of contact of the particles when heated in the zones of combustion of solid fuel and heating of the charge [20]. The yield of reaction products in the solid phase is determined mainly by the number of contacts of the reacting particles. The chemical affinity of the reactants in this case plays a secondary role. Thus, if the chemical affinity of substance A to substance B is much higher than to substance C, then in the presence of contacts A-C and the absence of direct contacts A-B the reaction product will be only ABC. The nature of the solid reaction product is also important for reactions in the solid phase. Being in contact with the reactants, the reaction product can significantly inhibit the reaction, creating additional difficulties for the diffusion of reagents.

An interesting feature of the reactions in the solid phase is the fact that regardless of the mass of the substances entering the reaction, when heating the reagent mixture, the first reaction product in all cases

is a substance with the simplest crystal lattice or lattice, which are easily combined with crystal lattices of reagents [21, 22]. Formation reactions Ca_2SiO_4 and Mg_2SiO_4 (the first reaction product between MgO and SiO_2) actively go at 680-690°C. As established at the Moscow Institute of Steel and Alloys in 1981, the nature of the first product of solid-phase reactions is decisively influenced by the temperature of the reagents. Thus, the product of the interaction of heated to 1500°C silica with cold lime is CaSiO_3 , while cold SiO_2 when interacting with heated CaO to 1500°C forms Ca_2SiO_4 .

Scheme of interaction of the equimolecular mixture of silica-calcium oxide at temperature 1200°C according to the data Lander-Hoffman [23, 24] based on the diffusion theory, according to which the reaction takes



The discovery of this effect made it possible for the first time to control the nature of the first product of solid-phase reactions. Usually during the agglomeration the temperature of the reagents in the charge in the combustion zone of solid fuel and below it are the same, but when introducing a highly heated return to

place on the contact surface of the phases. It is assumed that first a layer of dicalcium silicate is formed, then an additional layer of tricalcium silicate is formed. The authors believe that lime diffuses much faster than SiO_2 , and the formed tricalcium silicate is unstable at temperatures below 1250°C and it disappears and begins to grow rapidly an additional layer of calcium metasilicate. Thermodynamic analysis of systems CaO-SiO_2 and $\text{CaCO}_3\text{-SiO}_2$ shows that the system CaO-SiO_2 similar to the system $\text{CaCO}_3\text{-SiO}_2$ [25]. The obtained values of the Gibbs energy change are negative and the thermodynamic possibility of the reaction of calcium metasilicate formation is greater than that of dicalcium silicate [3].

Similarly, other reactions occur between solid phases:

the cold charge should take into account the effect of differences in the temperature of the reagents.

When sintering the manganese charge in the solid phase, it is preferable to develop the process of formation of Tephroite $2\text{MnO}\cdot\text{SiO}_2$, when adding dolomitized limestone - silica from waste rock interacts with basic oxides.

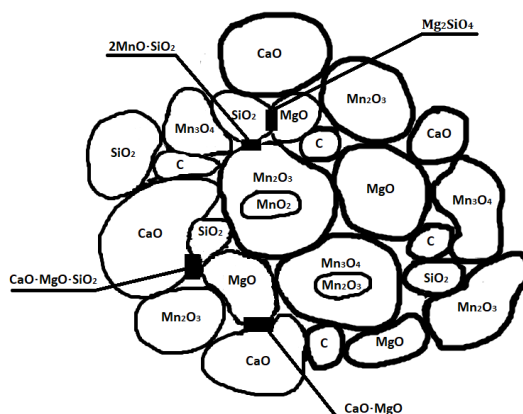
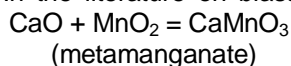


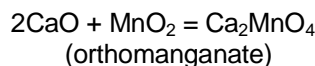
Figure 1. Hypothetical representation of the interaction of the components of the sinter charge in the solid phase [26]

The formation of a tephroite bond during the sintering of manganese agglomerate does not cause problems. One of the tasks of this work is to find the connection of manganese oxides with the main oxides of dolomitized limestone. Thus, in the sintering of iron ore agglomerate of great importance is the formation in the solid phases of calcium ferrites with high metallurgical properties [27]. In the literature on blast fur-



For thermodynamic modeling of the equilibrium of phase components in the structure of manganese agglomerate, calculations were performed using the module «Equilib» Program «FACTSage 6.0» and databases «FTOXID» and «FACT». The program database contains information on 390 connections and up

nace and agglomeration production, data on such compounds in the agglomeration of manganese-containing materials were not found. However, it is known [28] that when fused without access to oxygen with metal oxides and alkalis, manganese forms salts of hypothetical ortho- and meta-manganese acids. (H_4MnO_4 , H_2MnO_3)



to 48 different solutions. As determined by the results of the preliminary analysis in the work took into account the phases that are most thermodynamically stable (their own activity is 1), as well as their content exceeds 10-23%. The results of calculating the thermodynamic equilibrium of mineral compounds in the

oxide-silicate system, which characterizes the composition of manganese agglomerate, when changing the temperature of computer simulation of thermodynamic equilibrium of phases can be the basis for determining the rational composition of agglomerate and temperature-kinetic parameters of the agglomerate..

As initial data investigated the composition of the phases, the formation of which is possible based on the chemical composition of the charge to obtain the experimental agglomerate, the number of components of which are shown in the table 2.

Table 2 - Chemical composition of manganese concentrates for the production of experimental agglomerate AMHB-2Г when using fine-grained concentrates of size classes 10 - 1 mm and 1 - 00 mm

№	Manganese-containing material	The chemical composition of the components sinter charge, %								The content of components in the charge, % wt.
		Mn	SiO ₂	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	LOI	Wp	
1	Concentrate of 1 grade	45,3	13,1	2,2	1,4	2,0	3,0	12,2	15,2	16,18
2	Concentrate of 2 grades	38,0	15,1	4,7	2,4	2,2	2,7	16,2	10,0	20,51
3	Concentrate of 2 grades, 10-1 mm	37,4	24,5	2,2	1,4	1,9	2,4	10,6	13,2	18,6
4	Concentrate of 2 grades, 1-00 mm	35,2	21,0	2,4	2,1	2,4	4,3	11,5	15,3	32,71
5	Carbonate concentrate	29,4	9,5	12,2	1,9	2,1	2,3	30	9,8	12
Chemical composition of experimental agglomerates using conventional technology (AM-2) and using fine concentrates (AMHB-2Г)										
1	Agglomerate AM-2	41,6	23,1	5,7	2,3	3,0	2,9			
2	Agglomerate AMHB-2Г	39.0	26.5	5.9	2.2	2.3	3.5			
		38.3	29,4	4,2	2,1	2,1	3,8	-	-	-
		39.6	27,4	4,6	2,6	1,9	3,4			
		41,2	24,1	7,0	2,0	1,9	2,5			

Experimental studies were performed in the laboratory National Metallurgical Academy of Ukraine in order to obtain an agglomerate from the charge containing sludges of manganese ore beneficiation of different fractional composition and use as a binder in the agglomeration of small fractions of treated peat. The amount of fine coke was 10% to the concentrate (ash content 21%). The quality of the obtained agglomerate: the yield of suitable - 81.3%; impact strength - 3.0%; abrasion resistance - 1.5%; chemical composition of the finished agglomerate: Mn_{total} – 38-41%.

In thermodynamic calculations, the charge mixture was calculated on the total amount of oxides, taking into account that all volatiles, moisture, sulfur and dis-

sociation of carbonates are removed until high temperatures, and this composition, which includes only oxides and carbon, led to equilibrium. In the gas phase was taken into account only CO and CO₂, which can be formed from the charge, without air and gas supply, because their exact supply and composition in the area are not known. For the purpose of admissible simplification the content of only basic components in initial concentrate and agglomerate was considered (Mn, SiO₂, CaO, MgO, Al₂O₃, FeO, P). In the system with these components and the corresponding chemical composition was carried out the calculation of the equilibrium phases at 900-1300°C.

Figures 2 show some compounds whose formation is possible in the system Mn-Mg-Ca-Si-O-C.

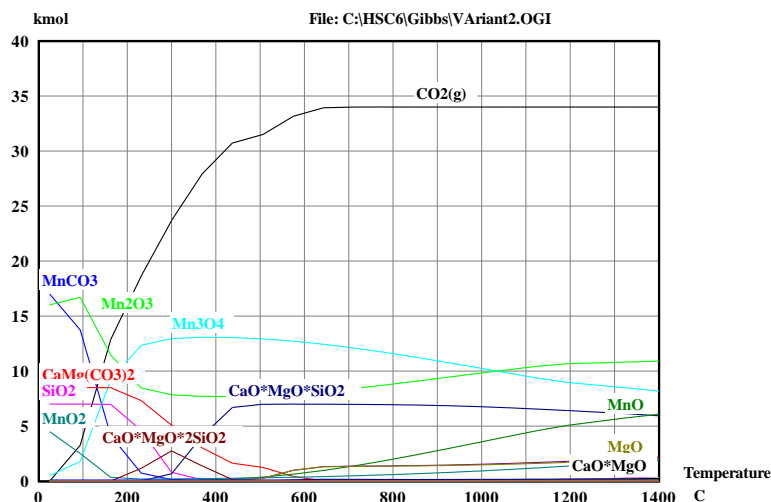


Figure 2. Distribution of substances in the system Mn-Mg-Ca-Si-O-C in the agglomeration of oxidized and carbonate ores

Thermal dissociation and reduction of MnO_2 and Mn_2O_3 oxides begins at relatively low temperatures. This is evidenced by a sharp decrease in the content of these compounds. Thermal dissociation of carbonates is also observed at low temperatures. Decomposition of $MnCO_3$ and $CaMg(CO_3)_2$ leads to a sharp increase in the CO_2 content in the atmosphere. The increase in the content of gausmanite Mn_3O_4 is caused by the processes of dissociation and reduction of Pyrolusite, Brownite and Rhodochrosite. The increase in Mn_2O_3 Brownite content observed at the beginning of the process is associated with thermal dissociation of Pyrolusite MnO_2 .

When using carbonate ores, thermal dissociation of carbonates at low temperatures is also observed. The bond is represented by tephroite Mn_2SiO_4 and complex compounds such as glass $CaO \cdot MgO \cdot SiO_2$. The decrease in $MnCO_3$ content begins at temperature 160-170°C, however, an increase in the MnO ox-

ide content is observed only from the second "fracture" of the $MnCO_3$ content at 230°C. The first "fracture" coincides with a decrease in the content of silica hollow rock SiO_2 , which is involved in the formation of Tephroite Mn_2SiO_4 . This primary bond can later be transformed into a stronger (in terms of thermodynamics) connection Montichelite $CaO \cdot MgO \cdot SiO_2$, the formation of which coincides in time with the beginning of the dissociation of dolomitized limestone. In the conditions of agglomeration process complete disappearance of Tephroite is not observed. It should be noted that in the system, in contrast to the first case, there is the formation of CO gas, the atmosphere is less oxidized. In the conditions of agglomeration process dissociation of Rhodochrosite goes only to Gausmanite Mn_3O_4 .

Interesting information was obtained when determining the phase composition of the system without reducing agent (Fig. 3).

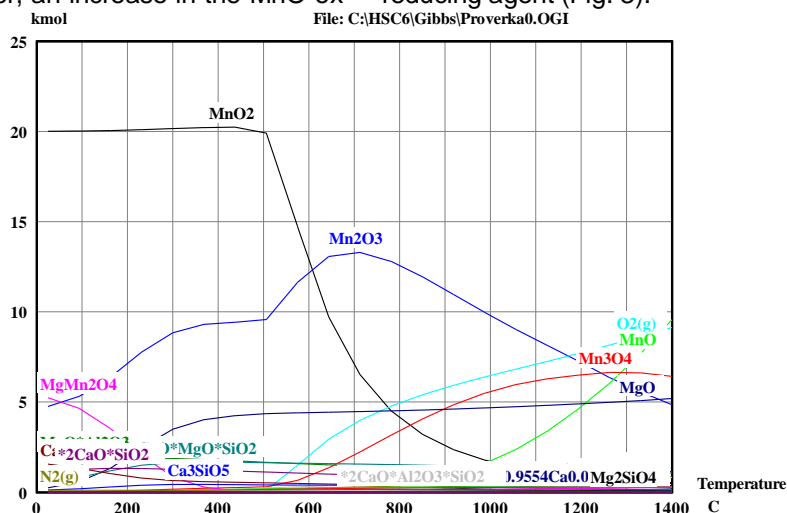
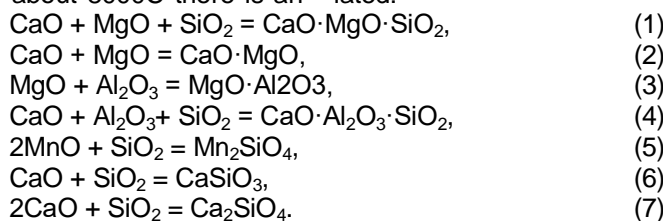


Figure 3. Phase composition of the Mn-Mg-Ca-Si-O system without the use of a reducing agent

Thermal dissociation of MnO_2 Pyrolusite begins at low temperatures, as evidenced by the increase in Mn_2O_3 content. However, the amount of Spinelide ($MgMn_2O_4$) MnO_2 formed during the dissociation completely overlaps this process and the content of Pyrolusite to a temperature of 500°C increases slightly. In the temperature range 350-500°C there is an achievement of equilibrium in the dissociation reaction of MnO_2 , hitherto spinel ($MgMn_2O_4$) has completely dissociated. At a temperature of 500°C the equilibrium is shifted towards dissociation. The process of dissociation of Brownite Mn_2O_3 begins, which is confirmed by the increase in the content of Gausmanite Mn_3O_4 . At a temperature of about 800°C there is an

increase in the content of MnO, the intensity of growth of the content of Gausmanite decreases. The slag bonds in this case will be represented by compounds such as $MgO \cdot Al_2O_3$, $CaO \cdot MgO \cdot SiO_2$, and compounds of lime with silica ($3CaO \cdot 2SiO_2$, $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$). A compound such as calcium orthosilicate is quite strong, in terms of thermodynamics, the compound and its content in the slag bond varies slightly. $3CaO \cdot 2SiO_2$ and spinelide $MgMn_2O_4$ dissociate. The products of their decomposition form a new complex compound $CaO \cdot MgO \cdot SiO_2$. The changes in the Gibbs energy of the reactions of formation of some compounds observed in this system were calculated:



The results of the calculations are presented in Fig. 4.

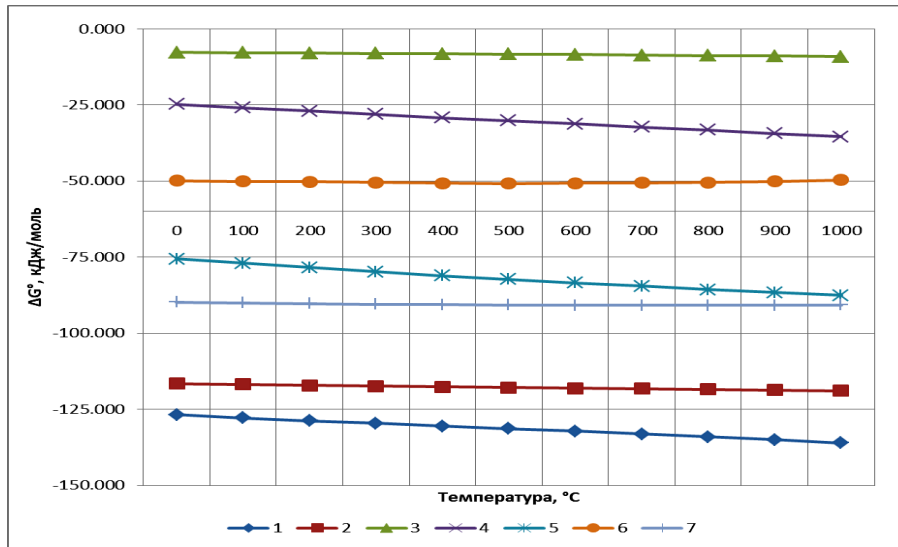


Figure 4. Dependence of Gibbs energy change on temperature

Detailed studies of mineral phases of samples of oxide and carbonate manganese concentrates were carried out by M.I. Gasik [2]. Differences in the amount and types of phases in manganese concentrates of various types were established. We used a mixture of oxide and carbonate concentrates to obtain

manganese agglomerate. The predominant phases of the oxide concentrate, which were established by X-ray phase analysis (Fig. 5), are SiO_2 and MnO_2 in various modifications. The carbonate concentrate is characterized by the presence of manifestations of MnCO_3 , MnO_2

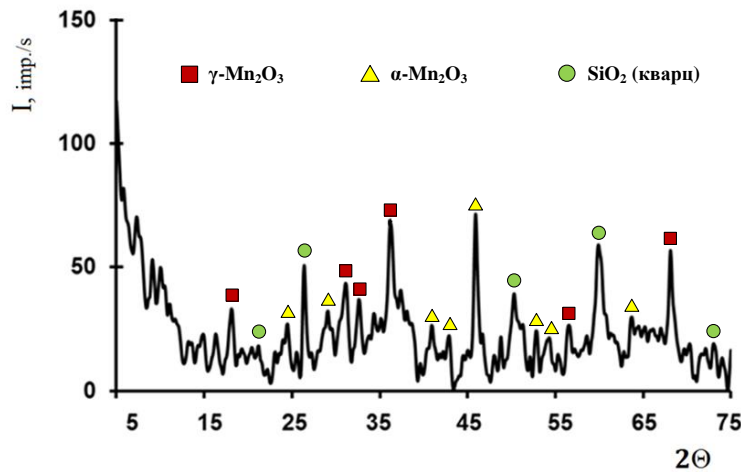


Figure 5. X-ray diffraction pattern of manganese agglomerate AMNB-2Г Cu-K α emitting

The mineral composition of the experimental manganese agglomerate grade AMNV-2G was determined by X-ray diffraction method on a DRON-2 diffractometer in monochromatic Cu - emitting. The interplanar distances at the corresponding values of the X-ray reflection intensity from the studied agglomerate samples were determined by comparing the obtained data with the corresponding tabular data given in the reference books on X-ray diffraction analysis of substances (Fig.5). The manganese minerals that form

the agglomerate are represented mainly by various modifications of manganese oxide and quartz. As the results of modeling the effect of sintering on the distribution of phases during sintering of the agglomerate (Fig. 2-4) show, the identification of phases by X-ray diffraction analysis practically coincides. The macrostructure of the agglomerate (Fig. 6) is represented by the phases of hausmanite, tephroite, there is precipitation of glass and solid solutions based on calcium.

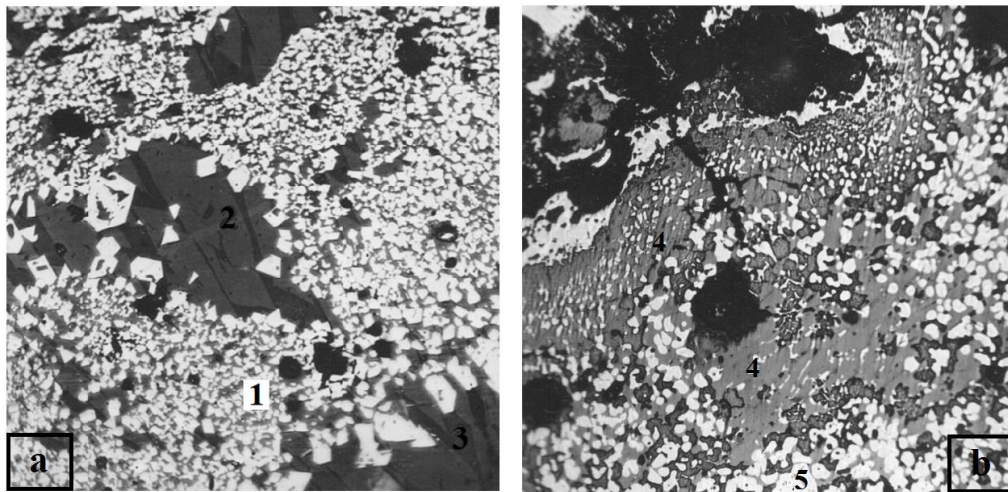


Figure 6. Microstructure of the experimental agglomerate: 1 - Gausmanite, 2 - Tephroite, 3 - glass, 4 - dicalcium silicate, 5 - solid solutions of systems CaO-MgO-MnO

The formation of the microstructure of agglomerates with the involvement of different types of manganese-containing materials depends on the characteristics of the initial composition and changes in mineral components during heat treatment. Most of the samples of raw materials of the Nikopol field have a mixed nature. In oxidative calcination at temperatures of 900 - 1000 °C, the bulk of the products is represented by a solid solution of oxides of manganese, silicon and calcium. As the raw material has an uneven chemical composition, silicate phases are formed in places enriched with silica. The mixed carbonate-oxide nature of the raw material determines the corresponding microstructure of the agglomerates. In the presence of an increased number of oxide components, manganosite and tephroite are formed. At direct contact of oxide and carbonate phases, where there is an increased amount of calcium oxides, the interaction of components with the formation of solid solutions of CaO-MnOx (CaO-Mn₂O₃), tephroite, dicalcium silicates. Places with a predominant content of the origi-

nal carbonate components are represented by solid solutions of CaO-MnOx, silicate solid solution and dicalcium silicates with inclusions of manganese oxides. The small content of silica in the raw material causes the formation of a small amount of silicates. When using Nikopol oxide concentrates and in the case of waste ferronickel production, which have a high content of magnesium oxide, led to the formation in the agglomerate of significant areas of stabilized dicalcium silicate and a solid solution of CaO-MnOx type (Fig. 6).

When using Nikopol carbonate concentrates, which have significant chemical inhomogeneity, the structure of agglomerates differs in the presence of calcium-manganese-containing oxide and silicate solutions of variable composition (Fig. 7). The formation of phases that are resistant to moisture is almost complete, but there are also zones of dicalcium silicates and solid solutions of CaO-MnO, which can reduce the strength of the agglomerate.

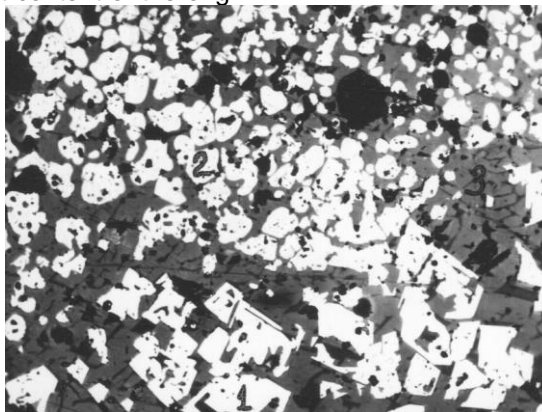


Fig. 7 The microstructure of the agglomerate with the involvement of carbonate concentrate: 1 - Gausmanite, 2 - Tephroite, 3 - glass, 4 - dicalcium silicate, 5 - solid solutions of systems CaO-MgO-MnO

The use of manganese-containing raw materials of different composition, which have a difference in the composition of the waste rock, ie the presence of a significant amount of oxides of calcium and magnesium, with a high content of silica leads to the formation

of agglomerate microstructure of another nature. In this case, a significant role is played by the interaction of oxides of manganese and silicon with the formation of manganese silicates. Taking into account the formation of calcium silicates, which have thermodynam-

ic advantages over the formation of manganese silicates, the formation of compounds of manganese and silicon oxides slows down, including agglomeration. Indeed, the temperature range of the liquid phase, which determines the formation of the agglomerate, and the speed of the sintering process can be adjusted in a wide range, easily controlled by technological parameters: size of materials and their chemical properties, including the presence of fluxing additives controlling silicate synthesis. Thus, the usual industrial

agglomerate AMNV-2 in microstructure (Fig. 8a, b) is characterized by the presence of inhomogeneous areas of tephroite, gausmanite and manganese glass. Gausmanite forms mainly dense clusters of small crystals, rarely large crystals of irregular shape. Tephroite is represented by large prismatic crystals, the optical parameters of which are close to pure variety. Glass of complex composition plays a cementing role in the microstructure of the agglomerate.

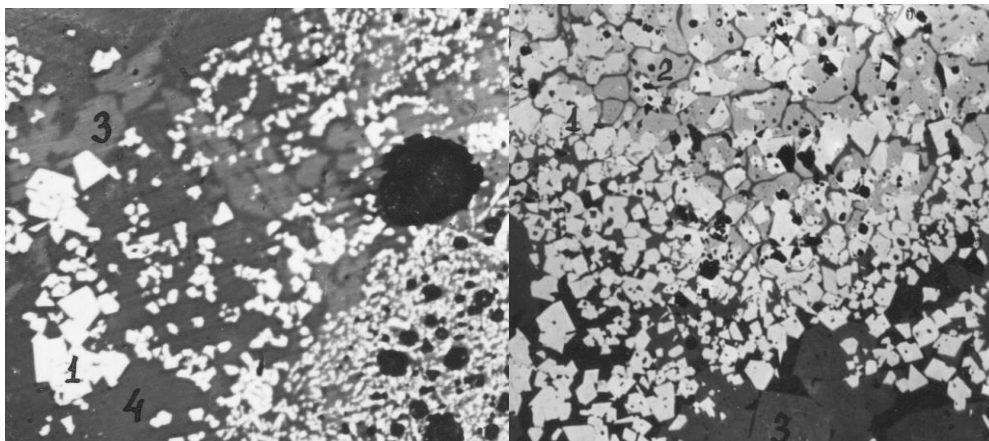


Fig. 8 Microstructure of agglomerate obtained by conventional technology and involving fine carbonate concentrate. 1 - Gausmanite, 2 - Tephroite, 3 - glass, 4 - dicalcium silicate, 5 - solid solutions of systems CaO-MgO-MnO

CONCLUSIONS

From the point of view of thermodynamics the most probable is the formation of $\text{CaO}\cdot\text{MgO}\cdot\text{SiO}_2$, $\text{CaO}\cdot\text{SiO}_2$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, but from the point of view of agglomeration and percentage of compounds in the charge formation of compounds with aluminum ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $\text{MgO}\cdot\text{Al}_2\text{O}_3$) is unlikely, as the number of contacts between them is less than between the main oxides and SiO_2 . However, in this case, the formation of a compound such as $\text{MgO}\cdot\text{Al}_2\text{O}_3$ is of interest.

Thus, the general situation with solid-phase reactions in the layer of the agglomerated charge in the production of manganese agglomerate is as follows. Dissociation of higher manganese oxides begins at relatively low temperatures, proceeds stepwise to the formation of MnO. Since the chemical affinity of manganese for oxygen is significant, reduction to metallic Mn is unlikely, because it requires a high content of reducing agent and reducing atmosphere, which in

real agglomeration processes are difficult to achieve. Dissociation of Rhodochrosite and step dissociation of dolomitized limestone leads to an increase in CO_2 content in the atmosphere. Slag bonds are represented by compounds Mn_2SiO_4 , $\text{MnO}\cdot\text{Al}_2\text{O}_3$, Mg_2SiO_4 , $\text{CaO}\cdot\text{MgO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$. Thermodynamic calculations show that at moderate temperatures no compounds like calcium ferrites are formed, ie compounds that can be formed between basic flux oxides and manganese oxides. Thermodynamic calculations show that at moderate temperatures no compounds like calcium ferrites are formed, to wit compounds that can be formed between basic flux oxides and manganese oxides, CaO will not be fully absorbed in the slag bond and already at the basicity of range of one there is undigested lime, which causes the formation of white spots in the structure of the finished agglomerate. Such an agglomerate must be used immediately in production, as transportation and storage will lead to a violation of the integrity of the agglomerate pieces and the formation of a large number of trifles.

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Стаття поступила 17.12.2019