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## Management of the process of obtaining manganese agglomerate by varying the components ratio in initial charge

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### Abstract

Growth of steel production is accompanied by increased production of ferroalloys. When concentrating manganese ore large amounts of finely dispersed concentrates are produced. The conditions of their pelletizing by agglomeration are considered. The quality of test agglomerate depends on several technical factors. It is proposed to use as the binder a peat processing product.

Key words: MANGANESE CONCENTRATE, AGGLOMERATE, CHARGE COMPOSITION, MODELING, SINTERING

## Introduction

A distinctive feature of Ukrainian ferroalloy industry is the orientation on the production first of all manganese ferroalloys, due to the presence in Ukraine of large reserves of manganese ore raw materials. In Ukraine, the balance reserves of manganese ores are about 2 billion tones. About 70% of domestic manganese ores belong to carbonate and oxide-carbonate species and they are complex ores. Extracted from the subsurface resources raw manganese ore due to the high content of gangue components is beneficiated by different technological schemes. There is an information [3] that when concentrating the manganese ores volume of generated tailings of wet magnetic separation is up to 6% of the ore processed and flotation and desliming tailings are up to 45% of the ore processed.

The direct use of these concentrates in the production of ferroalloys is accompanied by certain difficulties of technological character. Proposed solutions on involving in metallurgical treatment are limited to small quantities of fine fractions of manganese ore discard portion of the raw materials that does not solve the problem of their complete recycling.

The most well-known mastered industrial method of pelletizing of the domestic manganese ore raw materials which gain traction during the last decade is the agglomeration. The use of manganese agglomerate in the electric charge has been studied by many authors [4 - 7] and is economically feasible. Increasing the strength of the agglomerate is one of its important properties, besides agglomerate should have rational values of basicity, reducibility, softening temperature. This set of its properties determines the behavior of the agglomerate in the ferroalloy furnace.

One of the basic requirements for quality of the manganese concentrates is grain fineness. The grain size is highly dependent of the applied method of concentration (Table 1).

**Table 1.** Grain fineness of manganese concentrates of different concentration methods

Fraction, mm	Concentrate			
	Foam separation	Flotation 1st grade	Flotation 2nd grade	Reverse flotation
1-0.5	17.86	-	-	-
0.5-0.6	61.45	-	-	-
0.2-0.074	19.53	51.15	50.0	69.76
-0.074	1.11	48.85	50.0	30.84

A selected sample of the 2nd grade concentrate from Ordzhonikidze MBP was subjected to sizing. The concentrate had a granular-crystalline structure with a certain grain size (Table. 2).

**Table 2.** The result of the size analysis of a sample of granular concentrate of 0-1 mm

Grain size class, mm	-0.063	+0.063	+0.4	+1
Fraction content, %	1.9	67.1	26.7	3.9

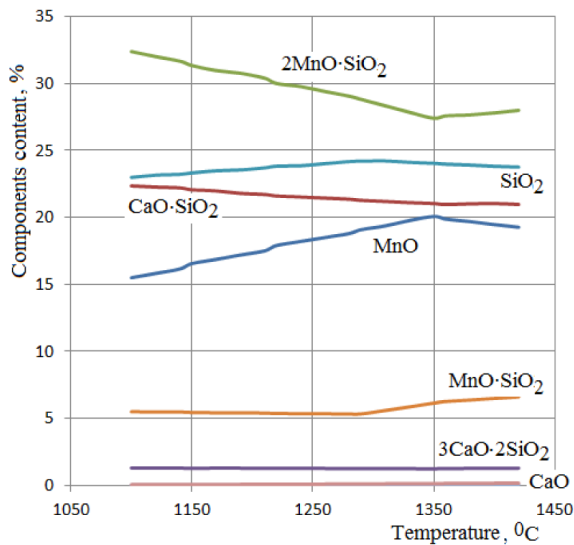
Thus, the main part of the investigated concentrate of the 2nd grade is represented by fine fraction 0-1mm having low manganese content. The mineralogical composition is characterized by large quartz content  $\text{SiO}_2$ , it has a granular nature and does not provide a reasonably good pelletizing ability of agglomerate. Improving of the pelletizing process is possible to perform through the composition of the charge, by addition in it binding materials.

### Thermodynamic modeling of the components distribution between the phases when obtaining the manganese agglomerate

In order to determine optimum parameters of the agglomerate obtaining process (temperature, amount of reducing agent, the gas phase composition) thermodynamic analysis of the system Mn-P-Si-Fe-Ca-K-Na-H-C-O-N was performed when using carbon as a reductant. Calculation of the equilibrium composition of specified system was carried out in air environment at a pressure of 0.1 MPa in the temperature range of 400 - 1400K. Analysis of the results obtained showed that in the absence of a reducing agent in the gas phase only oxygen, nitrogen, and water vapor were contained, and the condensed phase was represented by manganese-containing compounds:  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ . Additional introducing of carbon reducing agent changes the equilibrium composition of both the gas and condensed phases of the system. Introduction to charge of the insufficient compared with the stoichiometric amount of reducing agent results in a partial reduction/deoxidation of the manganese dioxide with the formation of  $\text{Mn}_2\text{O}_3$ . Maximum amount of  $\text{Mn}_3\text{O}_4$  is formed when adding 9% reducing agent. Further increase of carbon content in the charge leads to the formation of MnO in the condensed phase. The maximum degree of reduction is achieved by adding to the manganese oxide product of reducing agent in an amount of 12 - 15%.

The estimation of influence of CaO introduction on condensed equilibrium phases composition is of interest because entering of the third component changes the ratio of the ingredients activity. Results of the thermodynamic modeling showed the formation of compounds which were stable at high temperatures:  $\text{MnO}$ ,  $\text{CaO}\cdot\text{SiO}_2$ ,  $2\text{MnO}\cdot\text{SiO}_2$ ,  $3\text{CaO}\cdot 2\text{SiO}_2$ ,  $\text{SiO}_2$ ,  $\text{MnO}\cdot\text{SiO}_2$ ,  $3\text{CaO}\cdot\text{SiO}_2$ ,  $\text{CaO}$ . For the system  $\text{MnO}\text{-CaO}\text{-SiO}_2$  the influence of temperature and ba-

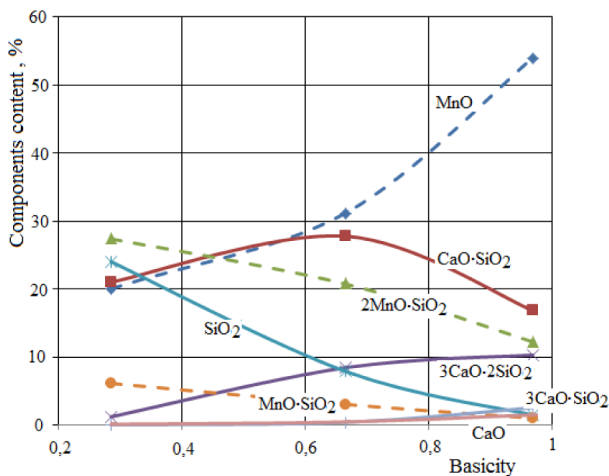
sicity on the distribution phases was studied. The calculations are performed within the range of 1100-1450°C when basicity is 0,286 and the MnO content is 48% (Fig. 1).



**Figure 1.** The effect of temperature on the phases equilibrium composition

As the temperature raises up to 1350°C the amount of free oxide MnO increases, because the probability of binding MnO to tephroite decreases. However, due to melting of 2MnO·SiO<sub>2</sub> is higher than temperature of 1350°C the amount of free manganese oxide is reduced. The calculations below were conducted at a constant temperature (1350°C) for a more detailed analysis of the basicity influence on the equilibrium composition of phases (Fig. 2).

Increase of the basicity when constant amount of manganese oxide in the ternary system MnO-CaO-SiO<sub>2</sub> leads to the decrease of the amount of compounds containing MnO, in particular 2MnO·SiO<sub>2</sub>



**Figure 2.** Changes in the equilibrium composition of phases in the system MnO-CaO-SiO<sub>2</sub> depending on the basicity of slag at the temperature of 1350°C and MnO content of 48%

and MnO·SiO<sub>2</sub>, and results in increase of free oxide MnO, which should simplify the reduction of manganese. Increase in the basicity leads to the exclusion of free oxide SiO<sub>2</sub>, which enters in the compounds with CaO such as CaO·SiO<sub>2</sub>, 3CaO·2SiO<sub>2</sub>, and when the basicity is 0,6 significant amounts of oxide 3CaO·SiO<sub>2</sub> are occurred. On the curve of change of the phase equilibrium composition of CaO·SiO<sub>2</sub> maximum is observed at the basicity of 0.6-0.7, further basicity increase results in a reduction of CaO·SiO<sub>2</sub> content, which in turn increases the content of free oxide MnO. Thus, the preliminary thermodynamic calculations show that increasing the amount of free manganese oxide in the system considered is associated with a specific value of the basicity which achievement provides predominant binding of silica to the compound 3CaO·2SiO<sub>2</sub>.

The addition of the binder leads to improved pelletizing ability and hardening of the granules in the wet and dry state. It should be noted that the use of nonorganic binders (bentonite, lime, etc.), along with a positive influence on the listed indicators of the pelletizing process have a negative impact on the quality of the agglomerate. First of all when introducing the binder materials the content of useful components in the agglomerate is reduced, i. e. the process of dilution is inevitable.

We suggested using the reagent - peat hydroxide, in terms of its multifunctionality. The introduction of this material, which is characterized by the minimum content of harmful impurities, as one of the agglomerate components can replace the part of the breeze coke, when using the energy potential of peat (carbon and combustible gases) and improve the value of metallurgical agglomerate.

Under laboratory conditions of NMetAU sinterings were performed using the fine manganese concentrate. On the laboratory disk pelletizer the pelletizing of initial agglomerate of the following composition was carried out: concentrate (-1mm) - 1400 g; sinter fines (5-10 mm) - 400 g; manganese ore (0-10 mm) - 350 g; fuel (breeze coke + anthracite) - 250 g. When using selected binders, their amount introduced over 100% of the charge without taking into account water is about 8%. When carrying out a number of test sinterings peat hydroxide was used instead of the breeze coke. Before pelletizing preliminary mixed agglomerate of over than 100% of the charge 100g of water were introduced. In preparing the agglomerates of test compositions the binders were introduced alternately. The fraction (8 mm) was used to improve the conditions of the initial components rolling and their more uniform distribution in the pellets (breeze

coke, peat, fine concentrate and binder). It was established that the strength index of pellets according to the type of binder were decreased in the following order: peat - 84%, water glass - 82%, bentonite - 56%, kaolin - 11%. The lowest strength of pellets corresponded to the charge with starch (about 7%).

For the option of using peat hydroxide the formation of two sintering zones were established. Priority development (promotion) of the first sintering zone was obviously due to the higher reactive power of pyrolytic carbon formed during thermal destruction of peat activated at a given ratio of fuels and their fractional composition. A similar effect was discovered first by the authors of [8], which they believe was induced by increased carbon consumption resulting in a total reduction of the vertical sintering speed to faster transition of high temperatures zone and its separation from the fuel combustion zone. We have found that a second sintering zone formed by combustion of coke carbon together with the first zone is behind it in its speed development. This leads to a change in the mechanism of physical and chemical transformations that is significantly different from typical sintering processes when only one fuel (breeze coke) is introduced in the agglomerate.

It is established that each elemental charge layer when sintering is subjected to sequential heat treatment first at a low temperature zone heating it to the softening temperature, and subsequently in a high temperature zone. Taking into account the expansion of the total sintering zone of the oxide material which is characterized by relatively high softening temperature (~ 1200°C), a sufficient amount of liquid oxide phase is formed, which for a longer period of its existence fully wraps around the pieces of non-melted charge. Subsequently, after intensive cooling by air-sweeping flow this will increase the strength of the sinter. Established increasing of agglomerate porosity by 5 ÷ 7% is obviously due to the release of pyrogases formed during thermal degradation of peat. They burn faster because of the presence in the peat of its own oxygen.

One can assume that the change in the ratio of peat / breeze coke can control the length of the buffer zone by increasing or decreasing the advance of the first zone, where softening of the charge is taken place. When determining the minimum share of peat the overlaying of two zones should be expected. In this case, the sintering will occur in a common ther-

mal zone. This effect can probably be reached when decreasing the fractional composition of breeze coke (up to the limits that do not reduce durability of raw pellets and delivery of oxygen to "balled up" carbon) that will result in a leveling of the reactive capability of both fuels. Thus, the positive role of the buffer zone where high enough temperatures are created is reduced to expanding the time interval of heat treatment of the charge, which eventually leads to an increase in strength of the agglomerate.

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