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

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Abstract

Growth of steel production is accompanied by increased production of ferroalloys. When beneficating of manganese ore the large amounts of finely dispersed concentrates are produced. The conditions of their sintering by agglomeration were considered. The quality of experimental agglomeration depends on several technical factors. The usage of peat processing product as the binder was proposed.

Keywords: MANGANESE CONCENTRATE, AGGLOMERATE, CHARGE COMPOSITION, SIMULATION, SINTERING

A distinctive feature of Ukrainian ferroalloy industry is the orientation toward production first of all manganese ferroalloys which is associated with the presence in Ukraine of the large reserves of manganese ore raw materials. In Ukraine the balance reserves of manganese ores are about 2 billion tons. About 70% of domestic manganese ores are carbonate and oxide-carbonate species and are rebellious. Extracted from the subsoils raw manganese ore due to the high content of gangue components is beneficated by various technological schemes. There are data [3] that when beneficating manganese ores the amount of produced tailings of wet magnetic separation is up to 6% of the processed ore and the wastes from flotation and desliming are up to 45% of the processed ore.

The direct use of these concentrates in production of ferroalloys is accompanied by certain difficulties of technological nature. The proposed technical solutions on engaging in metallurgical conversion are limited by small quantities of finely dispersed fractions of wastes of manganese ore that does not solve the problem of their complete reclamation.

Agglomeration is the most famous mastered industrial method of domestic manganese ore raw materials sintering, which has received development in the last decade. The use of manganese agglomerate in the charge for electric furnaces has been studied by many authors [4 - 7] and it has economic feasibility. The increase of agglomerate strength is one of its important properties, besides agglomerates should have rational values of basicity, reducibility, softening temperature. This set of its properties defines the behavior of agglomerate in the ferroalloy furnace.

One of the basic requirements for quality of manganese concentrates is the grain fineness; particle size is highly dependent on the applied method of benefication (Table 1).

Table 1. Grain fineness of manganese concentrates of different beneficiation methods

Fraction, mm	Concentrate			
	Foam separation	Flotation of 1 grade	Flotation of 2 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

The selected concentrate sample of 2nd grade from Ordzhonikidze MBP (mining and beneficiation plant) was subjected to grading. The concentrate had a granular crystalline structure with a certain grain size (Table. 2).

Table 2. The result of granulometry of sample of granular concentrate 0-1 mm

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

Thus, most of the investigated 2nd grade concentrate is presented by fine fraction 0-1mm having a low manganese content. The mineralogical composition is characterized by significant quartz content SiO_2, it has a granular nature and does not provide a good enough pelletizing ability of agglocharge. Improving the process of pelletizing is possible via the charge composition by adding binding materials in the charge.

Thermodynamic simulation of the components distribution between the phases when obtaining manganese agglomerate

In order to determine the optimal parameters of the agglomerate obtaining process (temperature, amount of reducing agent, composition of the gas phase) the thermodynamic analysis of the system Mn-P-Si-Fe-

Ca-K-Na-H-C-O-N was performed when using carbon as the reductant. Calculation of the equilibrium composition of above system was carried out in air medium at a pressure of 0.1 MPa in the temperature range of 400 - 1400K. Analysis of obtained results has shown that in the absence of reducing agent in the gas phase only oxygen, nitrogen, and water vapors are presented, and the condensed phase is represented by the manganese-containing compounds: MnO_2, Mn_2O_3 and Mn_3O_4. An additional introducing the carbon reducing agent changes the equilibrium composition of both the gas and condensed phases of the system. Introduction to the charge of insufficient compared with the stoichiometric amount of reducing agent leads to only a partial reduction of manganese dioxide with the formation of Mn_2O_3. Maximum amount of Mn_3O_4 is formed when adding of 9% of 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 the reducing agent in the amount of 12 - 15%.

The assessment of influence of CaO introduction on the content of condensed equilibrium phases is of interest, since introducing the third component changes the ratio of the components activity. The results of thermodynamic simulation have shown the formation of compounds that are stable at high temperatures: MnO, $CaO·SiO_2$, $2MnO·SiO_2$, $3CaO·2SiO_2$, SiO_2, $MnO·SiO_2$, $3CaO·SiO_2$, CaO. For system $MnO-CaO-SiO_2$ the effect of temperature and basicity on phase distribution was investigated. The calculations were performed in the range of 1100-1450ºC when basicity was 0.286 and MnO content was 48% (Fig. 1).
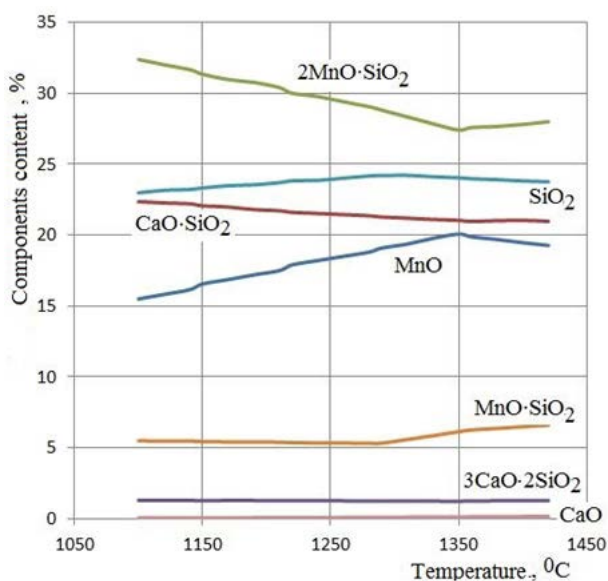
With increasing temperature up to 1350ºC the amount of free MnO oxide increases, since the probability of binding MnO in tephroite decreases. However, due to the melting of $2MnO·SiO_2$ in temperature higher than 1350ºC the amount of free manganese oxide decreases. Further calculations were conducted at a constant temperature (1350ºC) for a more detailed analysis of basicity influence on the equilibrium composition of the phases (Fig. 2).
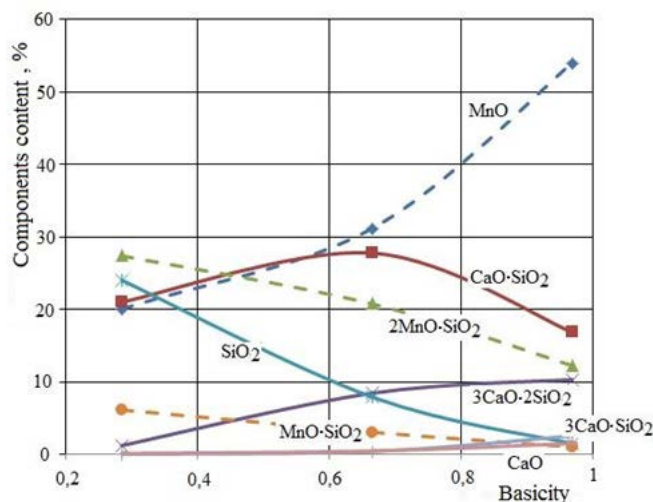
Figure 2. Changing the equilibrium composition of phases in the system $MnO-CaO-SiO_2$ depending on the basicity of slag at a temperature of 1350ºC and MnO content of 48%

Increasing the basicity at a constant amount of manganese oxide in the ternary system $MnO-CaO-SiO_2$ leads to decrease in the amount of MgO-containing compounds, in particular $2MnO·SiO_2$ and $MnO·SiO_2$, and leads to the increase of MnO free oxide, which should facilitate the reduction of manganese. Increase of the basicity results in the exclusion of free oxide SiO_2 reacts to compounds with

CaO, such as $CaO·SiO_2$, $3CaO·2SiO_2$, and when basicity is 0.6 the significant amounts of oxide $3CaO·SiO_2$ appear. On the curve of changing the phase equilibrium composition $CaO·SiO_2$ maximum is observed when basicity is 0.6-0.7, its further increase leads to a decrease in the content of $CaO·SiO_2$, which in turn increases the level of free oxide MnO. Thus, preliminary thermodynamic calculations show that increasing the amount of free manganese oxide in the system is associated with a specific basicity value achievement of which provides preferential binding of silica into the compound $3CaO·2SiO_2$.

The addition of the binder leads to improvement of pelletizing ability, hardening of the granules in the wet and dried state. It should be noted that the use of inorganic binders (bentonite, lime, etc.) along with a positive effect on the listed parameters of pelletizing process have a negative effect on agglomerate quali-

Figure 1. The influence of temperature on the equilibrium composition of the phases

ty, especially when introducing the binders content of useful components in the agglomerate is reduced, i. e. the dilution process is inevitable.

We suggested using peat hydroxide as reagent in terms of its multifunctionality. The introduction of this material, which is characterized by a minimum content of harmful impurities, as a component of agglocharge allows us to replace part of coke breeze when using the energetic potential of peat (carbon and combustible gases) and improve metallurgical value of the agglomerate.

In the laboratory of NMetAU sinterings were conducted with using of fine manganese concentrate. On the disc laboratory granulator pelletizing of initial agglocharge was conducted with following composition: concentrate (-1mm) - 1400 g; return undersized sinter (5 - 10 mm) - 400 g; manganese ore (0-10 mm) - 350 g; fuel (coke breeze + anthracite) - 250 g. When using selected binders their amount introduced over than 100% of charge without taking into account water was about 8%. When carrying out a number of experimental sinterings peat hydroxide was used instead of coke breeze. Before pelletizing of premixed agglocharge 100g of water was introduced over than 100% of the charge. In preparing the agglo-charches of experimental compositions the binders were introduced alternately. The fraction (8 mm) was used to improve the rolling conditions of initial components and their more uniform distribution in the pellets (coke breeze, peat, finely dispersed concentrate and binder). It was found that the pellet strength parameter depending on the type of binder decreased in the following sequence: peat - 84%, solube glass - 82%, bentonite - 56%, kaolin - 11%. The minimum strength of pellets corresponded to the charge with starch (about 7%).

For the variant with using peat hydroxide the formation of two sintering zones was established. Accelerated development (promotion) of the first sintering zone is obviously due to the higher reactivity of pyrocarbon formed during thermal degradation of peat activated at a given ratio of fuels and their fractional composition. The similar effect was first discovered by the authors of [8], which, in their opinion was due to increased carbon flow led to faster transition of high temperatures zone and its separation from the fuel combustion zone when a total reduction of the vertical sintering speed. We have found that the second sintering zone formed by combustion of coke carbon simultaneously with the first zone lags behind of it in its speed development. This leads to a change in the mechanism of physical and chemical reactions significantly different from the processes typical for

sintering when introducing to agglocharge only one fuel - coke breeze.

It has been established that each elementaly charge layer when sintering undergoes sequential heat treatment first in a low temperature zone heating it to its softening temperature and subsequently in a high temperature zone. In view of 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 long time of its existence fully wraps pieces of unmelted charge. Subsequently, after intensive cooling by swept air flow, this will increase the sintered strength. The increase of the agglomerate porosity by 5 ÷ 7% has been established, which is obviously due to the release of pyrogases formed during thermal degradation of peat burning of which is accelerated because of the presence in the peat composition of their own oxygen.

It can be assumed that by changing the ratio of peat-coke breeze the length of the buffer zone can be regulated by increasing or decreasing the advance of the first zone, where the softening of the charge takes place. In particular minimal proportion of peat the imposition of the two zones can be expected. In this case, the sintering will take place in a common thermal zone. This effect can probably be achieved when reducing the fractional composition of coke breeze (up to the limits do not reducing the strength of the green pellets and the delivery of oxygen to the "pelletized" carbon) resulting in a leveling of the reactivity of both fuels. Thus, the positive role of the buffer zone, where high enough temperatures are created, is reduced to expanding the temporal interval of the charge heat treatment that ultimately leads to increase of agglomerate strength.

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