RESOURCE SAVING IN MANGANESE FERROALLOY PRODUCTION USING LOW-GRADE MANGANESE ORE CONCENTRATES

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ABSTRACT

To use low-grade (fine grain) of sludge enrichment of manganese ore in the sinter production determined the optimal parameters of the firing process of slimes of manganese ore (temperature, amount of reducing agent, the composition of the gas phase), thermodynamic analysis of Mn-P-Si-Fe-Ca-C-O and experimental test of identified patterns in the laboratory were carried out. To improve balling manganese concentrates of the 2nd grade reagent of peat hydroxide 5% can be used with the increased degree of pelletizing from 1.62 to 3.27. The agglomerate was obtained with a high mechanical strength.

INTRODUCTION

Manganese ore is concentrated using gravitational, magnetic, flotation techniques or their combinations [1]. Reject of wet magnetic separation amount up to 6% of the ore processed. High-powered electric furnaces are required for ferroalloy production. They provide high production performance and labour conditions. For normal operation of closed furnaces lump material is required [1].

Issue elaboration.

Agglomeration [1-3] is a commercial industrial method of sintering domestic manganese crude ore. Reduced agglomerate quality is conditioned by the change of chemical, mineralogical, granulometric composition of manganese concentrates. Increase in the number of small fraction fines (<5 mm) in the charge materials leads to instability of the smelting process, increases specific consumption of raw materials and electricity. The amount of fines in the charge is determined by the strength of agglomerate**.** Industrial experience of manganese agglomerate manufacturing [2-7] shows that known technological offers do not provide an increase in agglomachines performance and required strength properties of fluxed manganese agglomerate.

Sintering techniques of fluxed sinter manganese agglomerate with high mechanical strength and high moisture resistance are known. Dolomite burnt at 1600-1800°C is used in agglomeration charge [4, 6]. The demerit of these activities is a significant complication of agglomeration production line and an increase in energy costs. The agglocharge requires the introduction of high-quality manganese concentrate with silica content less than 10%.

In the process of manganese agglomerate production the processes of dehydration, dissociation of oxides and carbonates, redox reactions, interactions in complex oxidation systems take place. Formation of free manganozite in the agglomerate is complicated by its high strength. MnO_2 and Mn_3O_4, Mn_2O_3 oxides are not strong and recover at low temperatures. The exothermic reactions heat of higher manganese oxides recovery shift the temperature interval of one-type reactions towards higher temperatures (150-120°C) [1]. Silica in the manganese concentrates bounds a part of Mn_3O_4 in tephroite Mn_2SiO_4. Liquid phase appears at 1250° C.

TARGET SETTING

In order to determine optimum parameters of the firing process of manganese ore concentrates thermodynamic analysis of the Mn-P-Si-Fe-Ca-C-O system was carried out. The established regularities were tested experimentally.

RESULTS OF THE RESEARCH AND THEIR ANALYSIS

There is an optimal content of carbon in the agglomeration charge. With increasing of carbon content to more than 8% the melting of top layers of the charge occurs, gas permeability gets worse and lower layers of the charge remain raw. Decreasing carbon content to less than 5% worsens agglomerate strength due to scarcity of liquid phase.

As a result of thermodynamic calculations it was established that in the absence of reducing agent a condensed phase is shown represented by MnO_2, Mn_2O_3 and Mn_3O_4. Insufficient amount of reducing agent leads only to a partial recovery of manganese dioxide with the formation of Mn_2O_3. Further increase in the amount of carbon added leads to the formation of hausmannite (Mn_3O_4) in the condensed phase. The maximum amount of Mn_3O_4 is observed when 9.5% of carbon reducing agent is added. Further increase of the carbon content in the charge leads to the formation of MnO in the condensed phase. The maximum degree of recovery is achieved when 12-15% of reducing agent is added manganese oxide product.

The influence of temperature on the recovery rate of manganese compounds was studied at the optimal concentration of the reducing agent in the charge. Thermodynamic calculations showed that at low temperatures MnO oxide forms along the partially reduced Mn_3O_4. At a temperature of 800-900K in the condensed phase only a small amount of Mn_3O_4 is left. The major amount of manganese compounds is represented by target product - MnO.

Agglomerate must have high strength, lumpiness, porosity and good reducibility at a given chemical composition. The use of manganese sludges in the agglomeration process is limited by their physical, physio-chemical properties and content of detrimental impurities [1]. Increase in sludge percentage in agglomeration charge requires increasing of permissible limit of sludge moisture for utilization in the agglomeration mixture, improving of slugs averaging in the agglomeration charge, ensuring of gas permeability of the sintered layer on the sintering strand and reducing dust ejection. Manganese slags should be agglomerated to improve gas permeability and obtain the pellets of the required shape and size.

During the development of the Nikopol manganese ore deposit the slurry pit of Ordzhonikidze Ore-dressing and Processing Plant was filled with the sludge of the manganese content of 10-12%. The second-quality concentrates of manganese ores benefication in Ordzhonikidze Ore-dressing and Processing Plant shows are characterized by granular sand structure. This complicates coking ability of agglocharge and does not allow obtaining required grain-size composition and strength properties during granulation. This further leads to a decrease in performance of agglomachine. The difficulties of using second-quality benefication consist in bad viscidity during pelletizing and briquetting.

The essence of pelletizing process is in the physico-chemical interaction of solid particles of the charge and liquid. Molecular forces appear at the input of liquid or colloidal substances. Capillary pelletizing mechanism is explained by the action of surface tension of liquid. Glutinous, or cementing, pelletizing mechanism is explained by the influence of molecular forces at the input of colloidal substances, glues. The main factor of the charge pelletizing is surface tension of moistening liquid, moistening angle of the material and dimensions of the capillary.

It is technologically difficult to use the influence of surface tension. Process water only with approximately the same value σ is currently used as a moistening liquid. Charge materials are wetted with water in different ways. Limestone and limonite are more wettable than hematite, magnetite and their concentrates. Coke is not practically wettable. To improve the process of pelletizing it is necessary to use materials which are well wettable by water; introduce fine-grained materials into the charge; create optimal humidity in a pelletizing device; introduce colloidal additives into the charge or use ores with clayey waste rock. Changes of physico-chemical properties of wetting fluid can improve pelletizing of charge. A decrease in limiting wetting angle does not always lead to improved process of charge pelletizing.

The pelletizing degree of second-quality manganese concentrates following the conventional technique with additional wetting is 1.62, and the strength of granules is less than 1 kg per sample. Such material is almost not sintered, that limits their use in the charge for agglomeration. We found that the input of 5% peat reactant increased the pelletizing degree from 1.62 to 3.27. During the pelletizing on plate granulator with a plate diameter of 3 m with speed of 12 RPM the performance of 1.0-1.2 t/h was achieved; solid pellets were produced. The granules were being dried in normal conditions for 12 hours to increase their strength when transshipped.

In laboratory conditions of NMetAU peat reactant is tested when obtaining agglomerate from the charge which contains the second-quality concentrate – 73.53%; coke breeze – 7.35%; peat reactant – 4.41%; recycled material – 14.71%. The following conditions were provided for sintering: the height of the charge layer - 300 mm; pressure - 1000 mm of mercury; ignition time – 1.5 min; ignition temperature - 1220^0C; time of sintering – 14.5 min; maximum temperature of sintering - 1360^0C; shrinkage - 80 mm. The quality of agglomerate obtained: the quality agglomerate output – 81.3%; impact strength – 3.0%; abrasion strength – 1.5%; chemical composition of finished agglomerate: Mn_{total} – 28.72%, S – 0.211, C – 0.91%. When other binding materials are used (sulfite liquor, solution of flour, bentonite, etc.) high mechanical strength and increase in Mn_{total} content is not observed.

Morphological analysis of sintered mixture and input components was carried out by using raster electronic microscope NeoScope II (by Jeol, Japan) in high vacuum mode with acceleration voltage of 15 kV. Surveillance mode - secondary electron image. Characteristic shape of sintering structures prior to and after sintering is shown in Fig. 1 and 2.

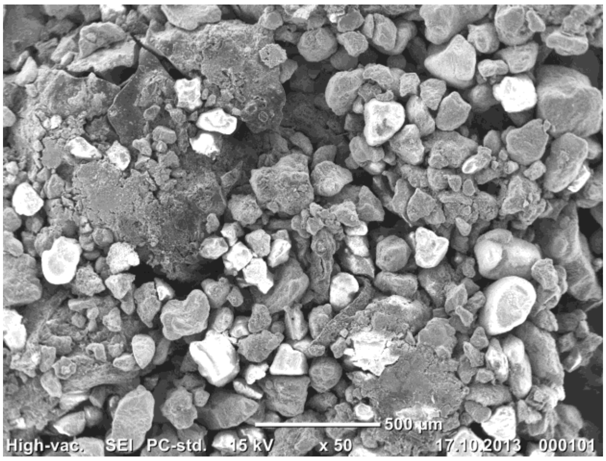
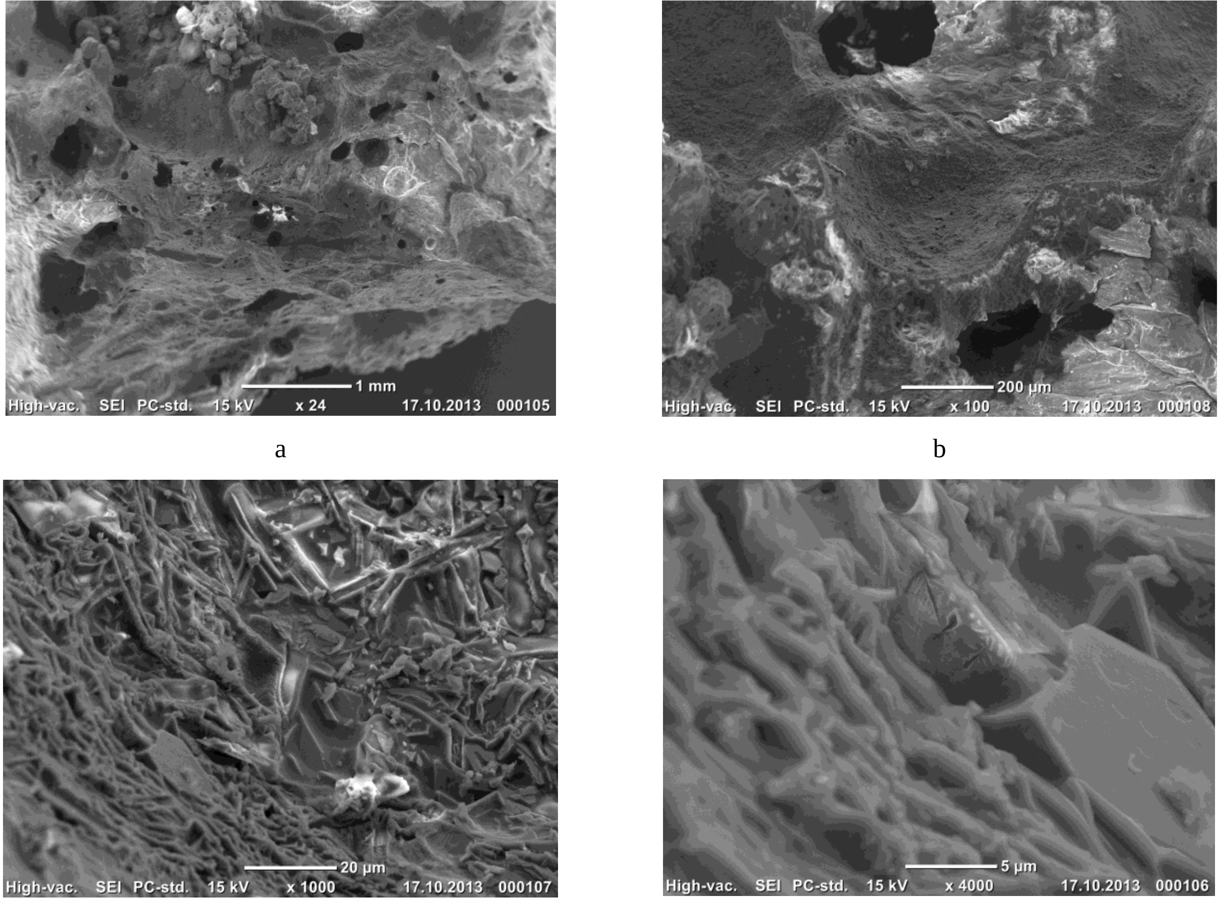


Figure 1: The structure of charge mixture for agglomeration prior to sintering (×24)

As can be seen from Figure 1, peat is quite evenly distributed between the grains of the initial charge mixture and creates conditions for the pelletizing of fine-grain fractions of the second-quality concentrate.



a b

c d

Figure 2: The structure of sintered mixture: a – ×24; b – ×100; c – ×1000; d – ×4000

During fractographic analysis fine structure of fracture of the sintered sample was found. Surface structure of destruction is characterized by pit microstructures. Characteristic relief is formed by the combination of individual facets. Such a structure occurs when the limit state is reached in local volumes, when obstacles to continuous deformation arise, where microvoids form. As stresses increase, microvoids grow, merge, and destruction takes place. Recesses in the form of pits on the fracture are formed which are interconnected by bridges. Different size of holes evidences different size of structure’s grains. This is related to different dispersion of initial materials in the mixture.

On the “walls” of the cup and cone fracture strongly prolate holes are observed (Fig. 2, d). They are the result of material destruction along the surface of localized intense shift. Light structural component of the mixture (peat) is located at the grain boundaries (holes) and performs a connecting function between the largest dark grey structural components. In fracture surface structure macro- and micro proposity is found, which is also located at the grains (holes) boundaries. Based on the results of quantitative metallography, the minimum pore size is 20 microns. The pores of this size make up 57% of all pores. Peat (light structural component) links both coarse grain (pits) sized 300...450 micron (Fig. 2, b), and small grains (holes) sized 2.4...3.2 micron (Fig. 2, b). Thickness of peat bridges increases by 10 times if the grain size is increased by 100 times.

The organic substance of peat consists of plant residues of varying degrees of decomposition. The origin of peat is related to the accumulation of dead vegetation residues. The above-ground parts of plants are subject to humification and mineralized in the surface aerified layer of the bog by invertebrates, bacteria and fungi. Underground parts of the plants in an anaerobic environment are preserved in it and form a structural (fibrous) part of the peat. Elemental composition of peat: 50-60% of carbon, 5.0-6.5% of hydrogen, 30-40% of oxygen, 1-3% of nitrogen and 1.5-0.1% of sulfur in a hot mass. In the composition of peat organic mass the content of soluble substances is 1-5%, 2-10% of bitumens, 20-40% of easy-hydrolyzed compounds, 4-10% of cellulose, 15-20% of humic acid, 5-20% of lignin.

In recent years, there has been a rapid growth in the number of studies in the field of chemistry of humic acids. This is due to their exceptional role in many geochemical, biological and biochemical processes. They are highly reactive and active ion exchange substances. They form strong bonds with many ions and molecules of substances, elements in the solutions, and also those included in the crystal structure of minerals [8-9]. These substances come into reaction with metal cations forming various types of bonds. These interactions are based on ion exchange processes. Humic acids stabilize soluble forms of silica. Critical time of gelation of silica decreases due to joint coagulation of silica sol and humic acids. Coagulation occurs due to increasing of the content of humic acids in solution and increasing of silica concentration in it. As a result, only slightly soluble products of mutual polycondensation are formed. In the process of joint coagulation of humic acids and soluble forms of silica slightly soluble organic units are formed. They perform structure-forming and water-retaining function [10]. This property of reactant peat is used in preparation for sintering of the second-quality concentrates on manganese ore benefication. When the concentrate and peat are both found in the mixture, this provides high lump-forming capacity.

CONCLUSIONS

The change in the few recent years of chemical, mineralogical and grain-size composition of manganese concentrates has led to reduced agglomerate quality and its production performance indicators. Experience of manganese ferroalloys production in powerful closed or hermetic electric furnaces testifies to the facts of instability of smelting modes, increased unit costs of raw materials and electricity with the increase in the number of small fraction fines (<5 mm) in the charge materials. Known technological suggestions do not provide the growth of agglomachines perforamce and required strength properties of fluxed manganese agglomerate.

Carbon-thermal reduction of oxide components of manganese concentrate depends on the input carbon and temperature. At a temperature of 800-900K in the condensed phase only a small amount of Mn_3O_4 is left, the major part of manganese compounds is represented by target product - MnO.

At a given chemical composition agglomerate must have high strength, lumpiness, porosity and good reducibility. The use of low-grade manganese concentrates in the agglomeration process is limited by their physical, physico-chemical properties and content of detrimental impurities. The second-quality concentrate of Ordzhonikidze Ore-dressing and Processing Plant has granular sand structure, does not provide a good enough lump-forming capacity of agglomeration mixture and does not allow obtaining during granulation of required grain-size composition and strength properties.

In laboratory conditions of NMetAU the agglomerate was obtained from the second-quality concentrate and experimental bound. The quality agglomerate output amounted to 81.3%; impact strength – 3.0%; abrasion strength – 1.5%; chemical composition of finished agglomerate: Mn_{total} – 28.72%, C – 0.91%.

In the fractographical analysis of sintered samples the fine fracture structure is found. Destruction surface structure is characterized by pit microstructure. Microivodes form in the local volumes. As the voltages increase, the microivodes extend, merge and decay. Peat bounds both coarse grains (pits) sized 300…450 microns and fine grains (holes) sized 2.4…3.2 microns that leads to the increased strength of the agglomerate obtained.

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