Improvement of a Preparation Process of Chromite Raw Material Used for Ferroalloys and Pigments Manufacture

K.T. Zhantasov*, Zh.U. Myrhalykov, B.B. Turakulov, M.K. Zhantasov, E.N. Kocherov, D.M. Zhantasova

M. Auezov South Kazakhstan State University, Taukekhan av., 5, 160012, Shymkent, Kazakhstan

Abstract

The given article contains the research results of carbon-containing chromite pellets’ production from off-grade raw material with application of internal coal-mining overburden rocks as flux. Besides, for the purpose of improvement of ecological situation in industrial regions and expansion of a raw-material base for ferrochrome and pigments manufacture we suppose to use in a charge composition the dust of aspiration units and electrostatic precipitators, which is formed at the preparation of raw materials and production of chromite pellets. The production technology of chromite pellets with use of a slime formed at the concentration of chrome ores as a binding substance was developed. Testing the suggested technology has been carried out in laboratory and trial conditions. The data of a chemical composition of initial components of a charge and calcined carbon-containing chromite pellets have shown economic and ecological efficiency of the developed technological process. Research results lead to the conclusion that the proposed granulation feedstock mixture pellets with a moisture content of 11–12% are obtained crude granules have a compressive strength of 2.3–3.2 kg/splashed. Increasing the content of Cr$_2$O$_3$ in the pellets to 7.6% occurs due to the increase in the extraction of chromium oxide and due to the charge of chromium oxides contained in the sludge, as well as removal of the batch formulation was heat treated carbonates, and volatile organic substances. It was established that during this mode, the temperature in the lower layers is about 1200 °C, and a reduction in natural gas consumption achieves 50% and the residual carbon content in the pellets is about 1.5%, which leads to improvement of technical and economic indices of production chromite pellets and ferrochrome.

1. Introduction

Environment protection, complex processing mineral raw materials and technogenic wastes, improvement of well-being of the humanity, flora and fauna – are actual problems of the modern Kazakhstan.

Complex processing poor and off-grade chrome ores and concentration tails promotes ecological advancement and ipso facto raises significance of use of nonconventional raw materials at manufacture of chrome-containing products and pigments. Besides, the rational use of sub-standard raw materials and industrial wastes allows releasing and placing in operation considerable areas of agricultural lands.

Kazakhstan chromite deposits are located in Aktyubinsk area in the Kempirsaiksky Mountain mass situated in the southern part of the Urals Mountains – in the Northern Mugodzhary.

Chromic ores of the Donskoye deposit is basically applied for ferrochrome manufacture. Chrome-containing minerals of these ores are chrome spinellides containing up to 62% of Cr$_2$O$_3$ and also FeO, MgO, Al$_2$O$_3$, SiO$_2$. The most important requirements making to chromic ores are:

a) Cr$_2$O$_3$ content ≥ 40%;
b) Cr$_2$O$_3$/FeO ratio ≥ 2.5; such ratio provides production of an alloy containing 60% of chrome;
c) for manufacture of the most generally used carbonaceous ferrochrome of the grade of FC650 (with...
low carbon content) a part of a chromic ore should be lump, hard-reducible and should contain a minimum quantity of fusible dead rock [1].

At the manufacture of ferrochrome a reducer is culled coke breeze in the size of 10–25 mm, which contains no more than 0.5% of sulphur and no more than 0.04% of phosphorus.

In addition the chromic ores contain iron oxides, which provide required amount of iron to an alloy produced.

At the preparation of raw materials, in particular at crushing and sorting conditional ores, ore fines is formed, a part of which is stored in special dumps, and the other part is added to marketable ores.

Off-grade ores containing 15–30% of chrome oxide represents mixtures of dead rock with a poor or rich ore, and they can serve as an additional source of chrome-containing raw material in the case of improvement of the present technology.

The exhaustion of resources of the rich ores mined by the open way and rise in price of underground mining predetermine that the further prospect of chrome manufacture is connected with use of poor and off-grade chromite ores and their preliminary dressing up to 46–50% of chrome oxide.

The scientific literature analysis testifies that the companies developed agglomeration technologies of chromite raw material apply known methods and rich production experience of iron-ore raw material agglomeration [2]. Despite long-term searches of optimal parameters of iron-ore concentrates’ agglomeration, this problem is still far from perfection because of constant change of extracted ores’ quality; in addition deficiency of solid carbon-containing and gaseous fuel compels to search for new kinds of fuel, fluxes, etc. [3–25].

Known ways of agglomerates production provide for the application of an ore and carbonaceous materials; a quantity of the ore part in a charge can vary within a wide range and reach to 90%. Carrying out the processes of joint agglomeration of ore and carbonaceous components of a charge with their subsequent heat treatment provides for necessary conditions for extraction of demanded metals at melting [4–7].

Granulation and briquetting methods are the most widespread ones at agglomeration of a preliminary crushed charge. Conditions of the heat treatment depend on a purpose of produced granules and briquettes and a kind of their use at manufacture of ferroalloys or pigments.

Also for the purpose of complex use of low-quality chromite ores acid methods are applied for production of cakes; products of leaching the cakes are a sodium monochromat solution or chrome sulphide.

For the purpose of reduction of fuel and energy consumption at manufacture of chromite pellets and increase of service life of calcining plants’ lining a production way of chrome pellets with use of carbon-containing materials such as schungite, slates, internal coal-mining overburden rock, oil-slime, coke and coal fines is suggested [5, 21–25].

Solving the problem of recycling the off-grade wastes formed at mining, preparation and transportation of chromite ores and the dust formed at manufacture of chromite pellets allows to expand a raw-material base and to improve environmental situation of industrial regions.

A schematic diagram of calcined pellets manufacture used on the Donskoy mining and processing plant is represented in the Fig. 1. In accordance with the scheme a chromic ore of a class of 0–10 mm is given from a crushing shop by means of a conveyor and loaded into an ore bin.

A chromite concentrate from a receiving bin is given in feed bins by a grab crane. Batching the chromite concentrate is performed by means of disk feeders on belt conveyors, and batching the chromic ore – by a belt feeder on a belt conveyor.

Coke fines is also loaded into a corresponding feed bin and fed on a collecting conveyor with the help of a belt feeder.

The collecting belt conveyor transports the chromite ore, throughproduct (middlings), the concentrate and coke on a grinding stage.

Grinding is carried out in a ball mill with central unloading and open operational cycle. For maintenance of necessary grinding energy grinding balls are dosed in a loading funnel of the mill every 30 minutes by means of a shaking feeder.

A discharge hole of the mill is equipped by a drum screen with a spiral for return of underground material in the mill. A pulp in density of 2.2 kg/l passes through a sieve (mesh size is 2×2 mm) of the screen and gets in a funnel, which is located under the screen, and then by means of pumps the pulp is pumped over in a tank for pulp hashing.

The pulp tank is equipped by a mixer whereby the pulp is mixed and averaged.

Then the produced pulp is pumped over on ceramic filters for water removal; humidity of a filter cake is 9–12%.

The filter cake is unloaded by a belt conveyor on a shuttle conveyor, where it is mixed with a calibrated factory dust; a mixture is given in a mixer. Humidity of the mixture is regulated by water fed in the mixer.

According to the suggested technology of carbon-containing chromite pellets production we offer to use a bowl granulator instead of a drum pelletizer because a granulation process in it occurs more effectively.
In accordance with the developed technology the charge, mixed in the mixer, is fed in a bowl granulator by means of a conveyor, where there is a formation of crude pellets in diameter not less than 13 mm; a slime formed at the classification of chromite concentrates is used as a binding agent.

In compliance with the existing technology the produced crude pellets are given on a roller screen for screening. The throughproduct in diameter < 8 mm and a coarse fraction of the product in diameter > 13 mm pass through a roller crusher and are given on a wide belt conveyor, located under the screen, and then with the help of a conveyor system a mixture is fed in a bowl granulator.

Conditioned pellets (with diameter > 13 mm) are stacked on a fire grate of a calcining kiln on a bed from calcined pellets. Thickness of the bed is 100–150 mm, thickness of the crude granules’ layer is 250–300 mm. The pellets are subjected to drying by circulating gases with temperature of 350–450 °C, heating, calcination and cooling (the existing technology).

This technology of phosphorite pellets manufacture was introduced in 1990–1992 on the former pellet factory of the joint-stock company “Sary-Tas” with use of a unique roasting machine OK-520/536 Φ, which at the present time does not operate owing to a variety of objective reasons.

The heating of pellets is carried out in a heating chamber. The heating purpose is the arrangement of favorable conditions of pellets’ calcination and carbon ignition in a layer of dried chromite pellets located over the bed from calcined pellets. For this purpose a gas heated in the second zone of cooling that is fed in a heating zone. The necessary temperature of heating gases is 1100–1200 °C; it is regulated by means of the gases formed at burning a small amount of a natural gas in a burner.

If it is necessary the temperature of heating gases in the calcination chamber is increased to the calcination temperature, which makes 1400 °C.

Cooling the roasted pellets is carried out in three cooling chambers by means of blowing a fresh air. The air is given to funnels by fans. The air feed
control is made in accordance with the change of pressure in the chamber over the pellets’ layer. Then the cooling gas is transported in chambers of the calcining kiln’s head.

The cooled granules are unloaded on a steel pocket conveyor, and then poured on a belt conveyor, which moves the pellets on a vibrocrible located over the bunkers of marketable pellets and through-product.

The marketable pellets from the bunkers (cones) are given on a conveyor with the help of a shaking feeder and unloaded on a finished-products storage area with the subsequent shipping to consumers in open-top wagons.

In accordance with the suggested technology of processing off-grade chromite ores and technogenic wastes for economy of material and fuel-energy resources we recommend the following innovations:

– at the granulation to use 2–2.5% of coke fines and up to 10% of internal coal-mining overburden rocks in a mixture with a chrome-containing material consisting from an off-grade chromite ore, concentration tails formed after water classification of slimes and aspiration dust;

– to use a bowl (plate) granulator instead of a drum pelletizer;

– to apply a water suspension of the slime formed after classification as a humidifier and a binding substance instead of water;

– application of a preliminary wetted charge before the granulation [6].

Further the produced crude pellets are subjected to drying and calcination in compliance with the existing technological scheme.

It is necessary to notice, that the process of carbon-containing roasted chromite pellets’ manufacture is a thermal process based on melting surfaces of the granules. It consists of the following stages: batching and hashing of components of a charge, joint crushing, pelleting, drying and high-temperature calcination, cooling and sorting of an end-product.

For solving the above-stated actual problems connected with production of carbon-containing chromite pellets the experimental researches and trial tests have been carried out [26].

1.1. Technique of carrying out the research

The researches connected with production of calcined carbon-containing chromite granules from internal overburden rocks and the technogenic wastes formed at the manufacture of chromite pellets were performed in laboratory and trial conditions on a pilot installation represented in the Fig. 2. This installation consists of a plate granulator in diameter of 1 m and 1.3 m and a calcining bowl intended for drying and heat treatment of pellets with units of control and regulation of temperature on height of a pellets’ layer in each 100 mm represented in the Fig. 3.

The crude pellets in diameter of 10–20 mm and with humidity of 11–12% were dried and calcined on the installation “calcining bowl”. This installation works on natural gas at passing a gas-heat-carrier from top to down.

The preliminary drying of pellets is carried out at temperature of 300–400 °C within 15 min, and then the temperature is increased to 1200 °C and the pellets are kept at temperature of 900–1200 °C within 20–25 min. After reaching the temperature of 1200 °C in a layer of granules between 100 and 200 mm the natural gas flow in a burner is reduced.

It was determined, that at this mode the temperature in the bottom layers makes 1200 °C; in this case the natural gas consumption decreases on 50%.

The research results are represented in the Table 1. For comparison we have used physicochemical and mechanical parameters of the pellets obtained from sub-standard chromite material which does not contain internal overburden rocks and coal fines.
Temperature change on height of a layer at heat treatment of the pellets containing carbon of internal overburden rocks and coal fines on a bed from calcined pellets containing carbon (a) and without a bed (b) are represented in the Fig. 4.

At the analysis of Fig. 4a and 4b it is shown, that at the calcination of granules without a bed from calcined pellets and with the bed the time necessary for drying and calcination is reduced almost in 1.5 times. It can be explained that temperature change in the pellets’ layers at the expense of burning the carbon containing in the granules and also feeding a warm fresh air in a mixture with waste smoke gases from the drying and roasting zones. Feeding the warm gas allows to increase efficiency of the burner and to prevent abrupt temperature fall on the surface of calcined granules. Besides duration of the heat treatment in a temperature equalizing zone in a pellets’ layer increases; it leads to increase in durability of the calcined granules.

As a result of the theoretical and experimental researches it was established that the optimum quantity of solid fuel necessary for normal conducting the heat treatment of the pellets containing internal overburden in an oxidizing medium makes from 3.5 to 4.5%; it is reached by the addition about 2% of coke fines in the charge composition.

Also it was established, that a high quality of the product and efficiency of the process are provided if carbon burnup degree from the pellets makes 40–60%. It is reached by limitation of oxygen amount in the gaseous heat-carrier feed for the heating and burnup of carbon from the pellets’ surface.

A ratio of excess oxygen amount in the gaseous heat-carrier to carbon content in the pellets should make 1.9–4.6 m³/kg that provides obtaining high-quality pellets: compression strength – up to 2470 N/pellet, abrasion resistance of the granules increase on 4% judging by the output of a class less than 0.5 mm.

At the mentioned conditions it can possible to increase temperature in a layer of the material on 200–250 °C at the expense of carbon combustion heat (solid fuel). It allows to raise the quality and yield of carbon-containing pellets in comparison with purely chromite ones and also to lower the natural gas consumption.

| A charge composition, % mass | Temperature, °C | Duration, min | Durability, kg/pellet |
|-----------------------------|-----------------|---------------|-----------------------|
|                             | drying | calcination | drying | calcination |                |
| Initial                     | -  400–500 | 1250 | 15  | 25  | Max 102.3 |
| 78                          | 7  400–500 | 1250 | 15  | 25  | 126      |
| 77                          | 8  300–400 | 900  | 15  | 25  | 135      |
| 73.5                        | 7  300–400 | 1000 | 15  | 25  | 269 Partial melting |
| 72                          | 8  300–400 | 1100 | 15  | 25  | 230 Partial melting |
At visual inspection of breaks of the calcined chromite pellets it was defined, that the granules consists of two zones: a periphery (superficial) zone (light) and an internal zone (dark) (Fig. 5).

The results of chemical analysis show, that the carbon residual in the superficial layer making about 40–45% from the pellet volume makes 0.1%, and in the inner layer making 50–60% of the pellet volume the carbon residual is equal its initial value (Fig. 5).

The average carbon content in the pellets after the heat treatment makes about 1–1.5%, and in the bed from calcined pellets containing 1.5% of carbon after the heat treatment the carbon content is slightly reduced or does not change.

Decrease of carbon content in the pellets, selected from the bed for the analysis, can be also explained partial burnup of carbon from the granules at the repeated heat treatment.

2. Results and Discussion

Morphology of the internal overburden rocks and off-grade chromite ores is represented in Figs. 6 and 7.

The Figs. 6 and 7 show, that a size of disperse particles of the internal overburden rock varies within 20–120 microns, and a size of particles of the off-grade chromite ores changes from 0.5 to 180 microns. It indicates that it is necessary to perform the preliminary crushing initial charge materials to a class less than 0.1 mm.

Microphotographs of the chromite pellets calcined at temperature of 1200 °C and containing 10 % of the internal overburden rocks and coal fines are represented in the Fig. 8, and an elemental composition of the internal overburden rocks and calcined carbon-containing chromite pellets is shown in Figs. 9–11 accordingly.
Fig. 8. Microphotographs of the chromite pellets.

| An element | Mg  | Al  | Si  | S   | K   | Fe  |
|------------|-----|-----|-----|-----|-----|-----|
| Mass %     | 0.11| 1.13| 45.04| 0.23| 0.20| 0.39|

| An element | C   | Al  | Si  | K   | Fe  | S   |
|------------|-----|-----|-----|-----|-----|-----|
| Mass %     | 62.72| 0.81| 11.30| 0.10| 0.52| 0.71|

| An element | Cr  | Al  | Si  | Mg  | K   | Fe  |
|------------|-----|-----|-----|-----|-----|-----|
| Mass %     | 34.60| 6.43| 5.93| 7.99| 0.39| 8.46|
In accordance to the spectra the average mass fractions of elements are: C – 62%; Cr – 34.6%; Al – 0.81-3.12%; K – 0.1-0.26%; Si – 6-45%; Fe – 0.3-60%; S – 0.23-1.81%.

At the research of the off-grade chromite ores’ microstructure the mass fractions of elements in the chosen spectra fluctuates as follows: Al – 2.49-5.01%, Si – 2.12-17.64%, Fe – 5.91-8.95% and Cr – 38.3-60.88%. The results of element analysis performed by means of a scanning microscope are represented in the Figs. 10 and 11 [26].

3. Conclusions

The possibility of use of off-grade ore wastes, coal-mining wastes and concentration tails of chromite ores has been substantiated.

The research results allow to draw a conclusion that at the granulation of the suggested charge mixture with humidity of 11-12% it is possible to produce the crude granules with compression strength of 2.3–3.2 kg/pellet.

Burning time of the carbon-containing pellets in
comparison with the same indicator for carbon-free chromite pellets decreases almost in 1.5 times that can be explained the burnup of carbon containing in the pellets.

Natural gas consumption for the calcination of chromite carbon-containing pellets decreases on 50% in comparison with the roasting purely chromite pellets; it is explained the burnup of 50% of carbon, which is a component of the pellets.

As a result of the experiments the chromite pellets with compression strength of 130–330 kg/pellet and containing 48–49% of chrome oxide and 1.5–1.7% of carbon have been obtained.

Increase of Cr₂O₃ content in the pellets to 6–7% occurs probably at the expense of extraction in the charge of additional amount of chrome oxide from the slime and also at the expense of removal of carbonates, volatile and organic substances from the charge at the heat treatment.

Calculations of the chromite pellets containing 84–86% of chromite, 2–3.5% of carbon of the internal overburden rock and 2% of metallurgical coke fines at different temperatures and duration have been carried out.

It was established, that at this mode the temperature in the bottom layers makes approximately 1200 ºC, decrease of the natural gas consumption is about 50% and the carbon residual content in the pellets makes about 1.5% that leads to the improvement of technical and economic indicators of chromite pellets and ferrochrome manufacture.

The given work has been performed on the basis of a grant of the joint-stock company “National agency on technological development” of the Republic of Kazakhstan in accordance with the budgetary program 026 “Assignment of innovative grants within the scope of a direction “Productivity – 2020”; the grant provider is Ministry of industry and new technologies of the Republic of Kazakhstan.

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