



DOI: 10.31643/2020/6445.19

UDC 669.168

IRSTI 53.31.21

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Promising ways to increase raw material base of the chrome industry of the metallurgical industry of the Kazakhstan

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Received: 26 May 2020 / Peer reviewed: 01 June 2020 / Accepted: 09 June 2020

Abstract. Various lumping technologies of finely dispersed chromite concentrates using charge roasting processes have been considered. In this respect, it was noted that the charge formulation used in the production does not provide the required strength of the produced pellets. The authors of the article propose the use of the well-known method for the ferrosilicon calcium fluxes (FSCF) synthesis with the replacement of Callovian clays with a composition based on diatomites and industrial and waste products of the Eurasian group (ERG) enterprises in order to increase the strength of pellets and agglomerate. This method enabled us to produce roasted pellets with high strength, to ensure the optimal ratio of components, to decrease the pellet roasting temperature by 150-200°C and to increase water resistance and congelation resistance. Technological parameters can be also improved by beneficiation of the source chromite raw material, effectively used by Turkish manufacturers of chrome products. One way to increase the chrome industry raw material base of the Republic of Kazakhstan is the involvement of the "12 Geophysical Deposit" into the processing of the industrial ore. However, the produced finely dispersed chromium concentrates require lumping followed by smelting in furnaces for ferrochrome. The high silica and iron content in the host rock of chromium concentrate enables to obtain strong pellets without additional additives.

Keywords: chromium-containing raw materials, material agglomeration, chromium pellets, refined ferrochrome slag, diatomite, ferrosilicon calcite fluxing.

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Introduction

The chrome sector enterprises of the Kazakhstan metallurgical industry affiliated with TNK Kazchrome JSC are one of the largest manufacturers of ferrochrome products in the world. However, at present, production is negatively affected by the deterioration of the quality of the source raw material: the total Cr₂O₃ content is

reduced, the dispersion of the material is increased, the content of harmful to ferroalloys impurities is increased. The increasing of chromium concentrates dispersion during electric-arc melting of raw materials in AC furnaces leads to the decrease in the technical-economic indicators of the processes.

In this regard, TNC Kazchrome JSC enterprises improve processes to solve current production problems. The technologies of finely

dispersed chrome raw materials lumping have been introduced: at first, the simplest briquetting technology was used, but the briquettes strength was low and did not allow its transportation for long distances. Then the technologies of roasting “green” pellets on a flexible ribbon of roasting machines and producing sinter on a sinter machine were implemented. However, technological solutions for the lumping of finely dispersed chromium concentrates were not effective enough due to the improper choice of the charge material composition and frequent process equipment failures due to the high roasting temperature of 1,350°C, resulting in low crushing strength of the produced roasted pellets and agglomerate with a high yield of defective pellets of the agglomerated product. For example, due to breach of roasting technical regime on roast machines with a flexible ribbon, refused material was more than 10% with the planned output of defective pellets up to 3% of the total number.

Effective processing of small and substandard pellets began with the launch of the 4th workshop at Aktobe Ferroalloy Plant JSC. The shives and defective pellets problem was solved due to its remelting in direct-current furnaces. But since the total capacity of direct-current arc furnaces at TNK Kazchrome JSC enterprises is less than 50%, the problem of using small pellets, low strength of the agglomerates and the possibility of its intact transporting them for long distances remains relevant and requires a technologically and economically feasible solution.

The agglomerated material strength problem can be solved by using the advanced pellets and sinter roasting technology, during which the complex compounds – ferro silicon calcium fluxes, so-called FSCF, synthesis is performed.

The theoretical justification for the synthesis of FSCF compounds was proposed in papers [1–3,] for iron-ore pellets producing technologies using Callovian clays as binding components. Important characteristics of natural Callovian clays for the selection of formulation for incoming components included:

- quartz amorphization and sufficiently high content of intracrystalline water;
- increased content and mobility of cations Ca²⁺, Mg²⁺, Na⁺, K⁺;
- the presence of iron oxides contributing to the formation of ferro silicon calcium compounds.

Due to the lack of raw materials with similar characteristics in Kazakhstan, it was proposed to synthesize Callovian clays analogue on the basis of diatomites as available domestic natural raw materials, industrial products and ERG enterprise waste. The use of the produced FSCF will significantly improve the strength of the roasted

pellets, technological, economic and environmental indicators of the processes [4, 5]

Methods of conducting technological experiments

The physicochemical characteristics of the types of raw materials and materials used have been studied, and the mass ratios of the components in each type of raw material were calculated to ensure the most optimal values of the components in the producing of chemical compounds that make up the FSCF formulation.

The proposed charge materials composition for “green” pellets producing includes:

- finely dispersed chrome concentrate (50% Cr₂O₃) produced by Donskoy GOK (Donskoy Mining and Processing Plant) JSC (DGOK JSC) – 88%;
- the mineral part of the refined ferrochrome slag (RFC slags) as a source of calcium and silicon oxides (1-2%) and of chromium oxide in a small amount of 2.5 - 3.0%;
- ferriferrous varieties of diatomite from the Zhalpak deposit (Aktobe region) as a source of hydrated amorphous silicon oxide – 4.5-5.0%;
- dusty screening of special coke of Sary-Arka JSC for uniform temperature heating in the body volume of pellets – 2.0-2.5% in the charge materials;
- liquid glass as a reagent that promotes the pelletizing and formation of “green” granules – up to 1.5%.

The ratio of rich chromium-containing components in the charge materials may vary insignificantly depending on the current stocks of rich chromite raw materials in warehouses, but on average, the components ratio in the “green” pellets charge will be preserved. A positive quality of the FSCF producing technology is a small dependence of the produced pellets strength on the qualitative composition of the chrome raw materials. The chemical composition of the mineral part of the RFC slag, which serves as a source of silicon and calcium oxides, is shown in table 1.

Table 1 – the chemical composition of the mineral part of the RFC slags

Components	Content, weight %
Cr ₂ O ₃	2.00
SiO ₂	18.40
Fe ₂ O ₃	0.26
MgO	7.70
Al ₂ O ₃	6.20
CaO	38.76
Other	26.68

The use of natural diatomites as components in the preparation of glandular pigments and porous foam glass is described in [6, 7].

The average chemical composition of the ferriferrous diatomite of the Zhalpak deposit is shown in Table 2.

Table 2 – Average chemical composition of ferriferrous diatomite from Zhalpak deposit

Components	MgO	Al ₂ O ₃	SiO ₂	SO ₃ ⁻²	K ₂ O	CaO	Cr ₂ O ₃	Fe ₂ O ₃	Cl ⁻	Oth.
Content, weight %	0.96	8.04	67.0	0.58	0.80	0.36	0.02	10.4	0.40	11.44

The technological characteristics of the special coke of Sary-Arka JSC are presented in table 3.

Table 3 – Technological characteristics of the special coke of Sary-Arka JSC

Characteristics	Value
Size, %	5.0-40.0
Sulphur content, %	≤1.0
Ash content, %	6.0-10.0
Volatile content, %	4.0-7.0
Specific surface area, m ² /g	3.0
Porosity, %	22.0...25.0

Results and discussion

The components composition was selected taking into account the current storage of rich chromium raw materials stocks in the TNK Kazchrome JSC warehouses. The components composition of the charge materials for the pellets producing was compiled taking into account the minimum dilution by Cr₂O₃ and the ferro silicon calcium synthesis and conforming by the chemical composition to charge materials for melting on high-carbon ferrochrome in variable furnaces current at JSC TNK Kazchrome. The feed of special coke, additional iron scrap and/or iron ore and cobbled quartz ore into industrial furnaces was taken into account when forming the charge materials composition to optimize the smelting process.

Table 4 - The results of x-ray phase analysis of roasted pellets produced at 1,200°C and a coke content in the charge materials of 2.5 wt. %

Mineral	Formula	Content, weight %
Chrome magnesite	Mg(Cr ₂ O ₄)	35.5
Chromite	(FeO _{0.632} Mg _{0.358} Mn _{0.01})(Al _{0.45} Fe _{0.283} Mg _{0.022} Cr _{1.201} Ni _{0.004} Ti _{0.03})	28.5
Magnesian hedenbergite	Ca(Fe,Mg)Si ₂ O ₆	7.8
Paragonite - 2M1	NaAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	8

The solid components of the charge were ground in a laboratory grinder and sieved on a laboratory sieve with -0.25 mm size mesh. Finely dispersed chrome concentrate and the mineral part of RFC slags were not grinded, since its fineness is less than -0.25 mm and its additional grinding is not required. Pellets were produced on a laboratory granulator.

The size of the green pellets is 6-10 mm and corresponds to the size of the granules produced on the drum granulators of the factory for the production of chromium pellets at the Donskoy GOK. The green pellets were kept at room temperature for 24 hours. The strength of the aged green pellets was 125.0 N/pellet. The batches of produced pellets were roasted in a laboratory muffle furnace at temperatures of 1,050; 1,100; 1,150 and 1,200°C for 1 h at a heating rate of 15 deg./min.

The produced roasted pellets (7 pieces in each batch) were tested for breaking using the MIP-25R laboratory press and the strength arithmetic mean values were determined. The average strength at the roasting temperature was, N/pellet: 2,862 at 1,050°C; 3,994.6 at 1,100°C; 4,570.1 at 1,150°C; 5,440 at 1,200°C. The chemical composition of the produced pellets was, weight %: 44.0 Cr₂O₃; 6.00 Al₂O₃; 18.80; SiO₂; 12.50 FeO; 1.62 CaO; 10.02 MgO; 7.28 the rest.

X-ray phase analysis data showed the presence of complex ferro silicon calcium compounds (magnesian hedenbergite (Ca (Fe, Mg) Si₂O₆) and chloritoid-A (FeAl₂SiO₅(OH)₂) (Table 4).

Norstrandit	$\text{Al}(\text{OH})_3$	7
Periclase	MgO	4
Chloritoid-A	$\text{FeAl}_2\text{SiO}_5(\text{OH})_2$	4

In terms of composition, the roasted pellets are close to the average composition of the charge materials of workshop No. 3 of Aktobe Ferroalloy Plant JSC. Previously, the possibility of pre-reduction of chromium oxide with producing of metallic beads was revealed at the processing of finely dispersed chromium concentrates with the production of roasted pellets using the FSCF producing technology. Partial pre-recovery with metallic chromium producing was noted. Using point electron microscopy method (Jeol microscope), metallic beads were detected in roasted pellet in the amount up to 10 wt.% [4-5]. The studies showed that the amount of reduced metal remained virtually unchanged and amounted to 9.5 wt.% at 1,200°C, which is, apparently, associated with the thermodynamic and kinetic features of the pre-reduction of chromium oxide compounds in the producing reducing medium in the pellet body.

Therefore, pre-reduction is possible within these limits, and increasing of the pellet roasting temperature above the specified temperature leads to its partial melting due to the melting of the binding base of FSCF (minerals: magnesian hedenbergite ($\text{Ca}(\text{Fe},\text{Mg})\text{Si}_2\text{O}_6$) and chloroid-A ($\text{FeAl}_2\text{SiO}_5(\text{OH})_2$). Therefore, the increase of the amount of special coke in pellets (up to 20-25 wt.%) does not lead to the significant increase in the amount of pre-reduced metal and is declared inefficient in producing of open type roasted pellets (open belt roasting machines, sinter machines of Aktobe Ferroalloy Plant JSC) [3].

The completed studies showed that, FSCF technology enables to produce durable roasted chrome pellets from a mixture consisting of the initial finely dispersed concentrates and recycled materials (pellet shives and agglomeration dust). Moreover, the achievable crushing strength is higher than 5,440 N/pellet at 1,200°C in roasting machines with a flexible moving metal tape (Donskoy GOK), the optimal coke content in the charge materials is 3%. The charge materials composition with 2.5 wt.% coke allows to reduce the pellet roasting temperature from 1,350°C to 1,200°C. Now, the pellet shives are partially processed in the furnaces of the new workshop No. 4 of Aktobe Ferroalloy Plant JSC [8].

The process of shives recycling can be performed using FSCF technology. The roasting temperature conditions can be achieved by using cheap apparatuses of a simple design — tunnel or muffle furnaces with a floating floor (for example, used to produce granulated foam glass) instead of

expensive pelletizers with a movable flexible metal tape [6]. Other technological equipment (mills, screens, dish granulators) used in the technology is standard and has numerous industrial analogues [9-13].

The technology for producing complex durable chromium pellets with FSCF synthesis can be widely used in industry in the pelletizing of finely dispersed chromium raw materials. But its manufacturing process management requires production of the finely dispersed pellets in significant quantities first. Outdated chromite sludge beneficiation technologies at Donskoy GOK do not enable Cr_2O_3 extracting higher than 10 wt.%, while this indicator amounts to 27-30 wt.% in Turkish chrome plants and this for less enriched raw materials than Kazakhstan raw materials. When implementing such effective technologies technical and economic indicators of the enrichment process will increase.

The developed industrial reserves of Kazakhstan raw materials of large deposits (the “Ten Years of Kazakhstan Independence”, “Molodezhnaya”, “Voskhod-Chrom” mines) require the lean approach to their extraction and processing. The medium-sized “12 Geophysical” deposit (65 million tons reserves of chromite ore) which was explored in the second half of the last century is situated at the Donskoy GOK industrial site. The VNIItsvetmet Institute (Ust-Kamenogorsk) performed studies which showed that the host rocks of the chromite metallization of this deposit are altered serpentinites developed according to magmatic rocks of ultrabasic composition.

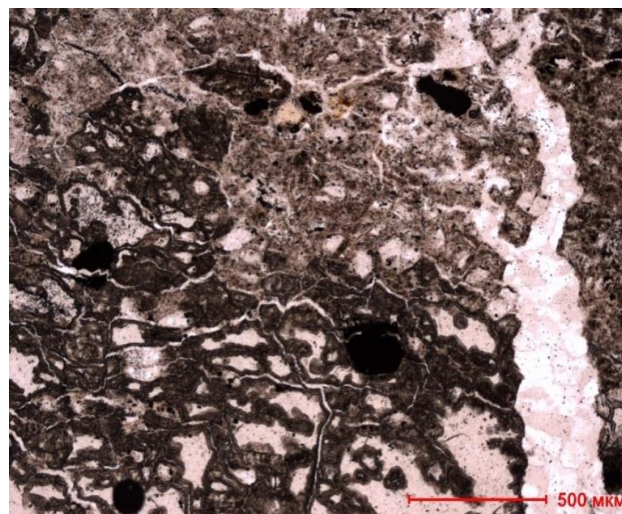


Figure 1 - Rare chromite impregnation of not more than 10% of the area, the light bar to the right is quartz vein

Thus, the “12 Geophysical” deposit is characterized by the fact that the host rock consists mainly of silica and iron-containing minerals. The Cr₂O₃: FeO ratio in the collected samples does not exceed 2.5, which indicates that chromite is represented by ferruginous forms. The presence of cleavage in chromite crystals, commonly found in only in glandular variations, also constitutes confirmation. The presence of a sufficient amount of Al₂O₃ in the samples allows to assign these chromites (chromespinelides) to aluminochromites (Fe, Mg) (Cr, Al)₂O₄ with a rather low Cr₂O₃ content. The chemical composition of the ore from “12 Geophysical” deposit indicates a low content of chromium oxide and a high content of silicon oxide (table 5).

Studies on gravity methods of ore beneficiation showed that the best performance can be achieved using the methods of depositing and centrifugal separation, while the yield of total concentrate was 35.1%, the total content of Cr₂O₃ was 44.6%, the extraction of Cr₂O₃ was 87.6%, the residual Cr₂O₃ content in the tails was 12.5%.

Table 5 - The chemical composition of the ore from “12 Geophysical” deposit

Components name	Content, wt. %
Cr ₂ O ₃	17.87
Fe	6.48
CaO	0.5
MgO	8.81
Al ₂ O ₃	3.72
K ₂ O	0.12
SiO ₂	57.1
S _{total}	0.18
Cu	0.01
Zn	0.02
Ni	0.1

The difficulty in unique ores beneficiation of this deposit is associated with the silicate composition of the host rocks and the finely dispersed structure of chromite mineral crystals. The produced concentrates cannot be remelted in electric arc furnaces without preliminary pelletizing. At the same time, silicate minerals contained in concentrates are a valuable component for the production of FSCF. This enables significant increasing of the chromium oxide content without main component diluting, producing hard roasted pellets and increasing the technical-economic indicators of the smelting process in ferrochrome electric-arc furnaces.

Conclusions

The use of FSCF synthesis technology in the rich chrome raw materials pelletizing process allows to get roasted pellets with high strength (3-4 times higher than production indicators); to ensure the optimal ratio of components, eliminating the need of the additional fluxing reagents during the melting of scrap iron waste and lumpy quartzite ore, to reduce the pellet roasting temperature by 150-200°C to increase the water resistance and resistance to materials congelation in the winter during transportation due to the formation of a glass-like structure. The technology can be used to pelletize prospective types of chromite-containing raw materials, for example, concentrates from ores of the “12 Geophysical” deposit.

Acknowledgments

This work was financially supported by the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan (No. AP05131028).

Cite this article as: Kuldeev E.I., Bondarenko I.V., Temirova S.S. Promising ways to increase raw material base of the chrome industry of the metallurgical industry of the Kazakhstan. // *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. / Complex Use of Mineral Resources / Mineraldik Shikisattardy Keshendi Paidalanu.* - 2020. - №2 (313). - p. 64-70. <https://doi.org/10.31643/2020/6445.19>

Қазақстанның металлургия өнеркәсібі хром саласының шикізат базасын ұлғайтудың перспективалық жолдары

Келдеев Е.И., Бондаренко И.В., Темирова С.С.

Түйіндеме. Шихтаны күйдіру процесін қолданумен ұсақ дисперсті хромитті концентраттарды кесектеудің әртүрлі технологиялары қарастырылған. Бұл ретте өндірісте қолданылатын шихта рецептурасы алынатын шекемтастардың талап етілетін беріктігін қамтамасыз етпейтіні айтылған. Шекемтастар мен агломераттың беріктігін арттыру үшін мақала авторлары келловей балшықтарын диатомиттер, өнеркәсіптік өнімдер мен

Еуразиялық Топ кәсіпорындарының (ERG) қалдықтары негізіндегі композицияға ауыстыра отырып, ферросиликокальцит қождамаларын (флюстерін) (ФФС) синтездеудің белгілі тәсілін қолдануды ұсынады. Бұл жоғары беріктігі бар күйдірілген шекемтастарды алуға, компоненттердің оңтайлы арақатынасын қамтамасыз етуге, шекемтастарды күйдіру температурасын 150-200°C төмендетуге, суға төзімділікті арттыруға және қатқылдыққа төзімділігін арттыруға мүмкіндік берді. Технологиялық көрсеткіштер сондай-ақ бастапқы хромит шикізатын байыту кезінде жақсартылуы мүмкін, ол түрік кәсіпорындарында хром өнімдерін өндіру бойынша нәтижелі қолданылады. ҚР хром саласының шикізат базасын ұлғайту жолдарының бірі «12 Геофизикалық» кен орнының кендерін өнеркәсіптік өндеуге тарту болып табылады. Алайда алынған ұсақ дисперсті хром концентраттары кейіннен феррохромдағы пештерде балқыта отырып, кесектеуді талап етеді. Хром концентратының сыйымды жынысындағы кремнезем мен темірдің жоғары мөлшері қосымша қоспаларды енгізбестен берік шекемтастарды алу мүмкіндігін қамтамасыз етеді.

Түйінді сөздер: хромы бар шикізат, материалды кесектеу, хром шекемтастар, тазартылған феррохром кожи, диатомит, ферросиликальцитті қождамалаушы (флюстеуші).

Перспективные пути увеличения сырьевой базы хромовой отрасли металлургической промышленности Казахстана

Кульдеев Е.И., Бондаренко И.В., Темирова С.С.

Аннотация. Рассмотрены различные технологии окускования мелкодисперсных хромитовых концентратов с применением процессов обжига шихты. При этом отмечено, что используемая в производстве рецептура шихты не обеспечивает требуемой прочности получаемых окатышей. Для повышения прочности окатышей и агломерата авторами статьи предлагается применение известного способа синтеза ферросиликокальцитовых флюсов (ФФС) с заменой келловейских глин на композицию на основе диатомитов, промпродуктов и отходов предприятий Евразийской группы (ERG). Это позволило получить обожженные окатыши с высокой прочностью, обеспечить оптимальное соотношение компонентов, снизить температуру обжига окатышей на 150-200°C, увеличить водостойкость и устойчивость к смержаемости. Технологические показатели могут быть также улучшены при обогащении исходного хромитового сырья, которое эффективно применяется на турецких предприятиях по производству хромовой продукции. Одним из путей увеличения сырьевой базы хромовой отрасли РК является вовлечение в промышленную переработку руд месторождения «12 Геофизическое». Однако полученные мелкодисперсные хромовые концентраты требуют окускования с последующей плавкой в печах на феррохром. Высокое содержание кремнезема и железа во вмещающей породе хромового концентрата обеспечивает возможность получения прочных окатышей без введения дополнительных добавок.

Ключевые слова: хромсодержащее сырье, окускование материала, хромовые окатыши, шлак рафинированного феррохрома, диатомит, ферросиликальцитовое флюсующее.

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