Wasteless Solid-Phase Method for Conversion of Iron Ores Contaminated with Silicon and Phosphorus Compounds

A. V. Panko, E. V. Ablets, I. G. Kovzun, M. A. Ilyashov

***Abstract*—**Based upon generalized analysis of modern know-how in the sphere of processing, concentration and purification of iron-ore raw materials (IORM), in particular, the most widespread ferrioxide-silicate materials (FOSM), containing impurities of phosphorus and other elements compounds, noted special role of nanotechnological initiatives in improvement of such processes. Considered ideas of role of nanoparticles in processes of FOSM carbonization with subsequent direct reduction of ferric oxides contained in them to metal phase, as well as in processes of alkali treatment and separation of powered iron from phosphorus compounds. Using the obtained results the wasteless method of solid-phase processing, concentration and purification of IORM and FOSM from compounds of phosphorus, silicon and other impurities was developed and it excels known methods of direct iron reduction from iron ores and metallurgical slimes.

***Keywords*—**Iron ores, solid-phase reduction, nanoparticles in reduction and purification of iron from silicon and phosphorus, wasteless method of ores processing.

I. Introduction

DESPITE the recent global development of crisis phenomena at metallurgical and metal mining industries, world demand for iron-ore materials and metalized in-process stock are still at sufficiently high level. It is stipulated by constant demand for steel goods for various branches of the world economy both at the past, currently and at the future. Therefore, development and improvement of science intensive methods and technologies for processing, concentration and purification of iron-ore materials, first of all ferrioxide-silicate ores, is a strategically important trend in research, scientific and technical and production activities for the benefit of mining and smelting branches of industry, where tangible flows amount to billions of tons.

Along with classical blast-furnace processing of iron ores and concentrates, more economical solid-phase direct reduced iron methods (DRI – Direct Reduced Iron) [1], [2] are intensively developed of late decades. According to DRI iron is obtained mainly in a form of metalized pellets or hot-pressed bricks with metal phase content up to 85%, and their world production volumes approach to 100 million tons. However, cheat natural gas and high-quality iron concentrates with iron content up to 68-70% is required for the most DRI technologies. Except for high content of iron such concentrates shall have low content of impurities of silicates, nonferrous metals, sulfur, phosphorus and other unwanted elements. Therefore, economic appeal of DRI methods will be decreasing with the lapse of time caused by reduction of high-quality ore reserves and necessity for solving of appeared ecological problems connected with it. That’s why metallurgical slimes and low-grade ferrioxide-silicate ores, including sedimentary biocolloidal origin ores containing impurities of silicates, as well as frequently phosphorus and other elements, have been lately involved for technological process of solid-phase of processing, concentration and purification. World reserves of the latter reach 25% of all iron ores reserves [3], [4]. Besides, new ores processing methods involving nanotechnological initiatives are not only economically beneficial, but also ecologically inviting following involvement of wasteless technologies into the production process [2]-[4]. Availability of such development way is evidenced by the fact that lately many world countries – India, Republic of South Africa, China, Peru – have started application of processes SL/RN, JINAL, DRC, CODIR, SILL, JSIL, TISCO, DAV, Grate-Car and others, where they take attempts to solve the said problems [1]. From 2012 in Ukraine Makeyevka Metallurgical mini-plant has began processing of metallurgical slime and coal slack. Although economic efficiency of such processes is proved their ecological safety still gives rise to doubt due to detrimental emissions and waste products.

In this connection the Institute of Biocolloid Chemistry of the National Academy Sciences of Ukraine along with the Donetsk Metallurgical Plant has proposed essentially new method to solve the aforesaid problems through application of consistent nanoparticles-aided processes of solid-phase reduction of ferrioxide-silicate materials contaminated by impurities of phosphorus and other elements, magnetic concentration of metallized products and its alkali treatment from residuals. The method is patented in Ukraine, Russia, China and other countries. Its main feature besides of nanotechnological elements is the fact that not primary raw material but metalized product is purified, its weight is 3-4 times less of the weight of raw components and it provides for reduction of costs for concentration and purification of final product at the same amount and practically completely use waste products in other branches of industry and agriculture.

However, it is required for achievement of optimal process

A. V. Panko, E. V. Ablets, and I. G. Kovzun are with Institute of biocolloid chemistry named after F.D.Ovcharenko, National Academy of Sciences of Ukraine, Ukraine (e-mail: wiz@list.ru, protsenkoit@ukr.net, protsenkoit@ukr.net).

M. A. Iljashov is with Private joint-stock company Donetsksteel – metallurgical plant, Ukraine (e-mail: ilyashov@donetsksteel.com).

conduct conditions to specify, at least, the mechanism of solid-phase reduction ferrioxide materials with participation of nanoparticles of reducer, substantiate rational approaches for qualitative purification of metalized product and waste utilization, as well as evaluate engineering-and-economical performance of a new process. Main results of investigations set forth here concerns solution of the said tasks.

II. Experimental

Sedimentary biocolloidal dispersed ore from Kerch deposit similar to specimen used in [2], containing, mass %: 32.88 Fe; 4.78 Mn; 1.38 P; 0.12 As; 0.09 S; 1.13 CaO; 1.88 Al_2O_3; 11.11 SiO_2 was used as the basic specimen for analysis. Also there has been used powder ores with higher content of iron (up to 39.5%), metallurgical slimes, limestone and sodium chloride. Coal slack has been used as regenerator. Reaction mixture was prepared according to recommendations [1] and burnt at 1200°C till obtaining the metalized product. Original substances and reaction products have been studied using roentgen-phase, derivatographic and electron-microscopic methods, as well as chemical analysis. Alkali treatment process of metalized product was studied pursuant to recommendations [3].

III. Results and Discussion

Study of obtained metalized cakes has shown that their composition includes, except for spongy iron particles, fayalite and traces of magnetite. Calcium silicate is formed while using limestone as additive to reaction mixture and fayalite in cake is practically absent. Microphotography of concentrated spongy iron (Fig. 1) shows that it has nonmagnetic impurities of silicates with particles sizes less than 1 micron, and nanoparticles of carbon and ferric carbide (Fig. 2), confirming results obtained in [2].

Study of original reaction mixture subjected to nanochemical milling [3], has shown that there are superdispersed and nanodispersed carbonic structures present, along with macro- and microparticles. Hereinafter salt additive melting takes place on oxides surface at burning of ground reaction mixture. It facilitates efficient delivery of carbonaceous nanoparticles to chemical reaction areas of ferric oxides direct reduction by solid carbon and ferric carbide initiating reaction cycle with intermediate formation of ferric carbide and obtaining of final product in a form of spongy iron:

from reaction mixture; C_{nano}

$$Fe_2O_3 + C_{nano} \rightarrow 2FeO + CO; 2FeO + 2C_{nano} \rightarrow 2Fe + 2CO; 2Fe + 6C \rightarrow 2Fe_3C \quad (1)$$

Fe_{sponge}; Fe_{sponge}; Fe_{sponge}

According to (1) formed labile ferric carbide (cementite) is melted at 1160-1180°C providing formation of eutectic cementite-iron containing solid nanoparticles of carbon, formed following fractionation labile cementite, as well as nanoparticles of cementite. Those particles are participating in metallization process according to (1) and, thus, mechanism of carbide cycle of ferric oxide metallization with participation of fluxes is “launched” at 1180-1200°C. The process is progressing during 10-60 minutes depending on reaction mixture milling degree.

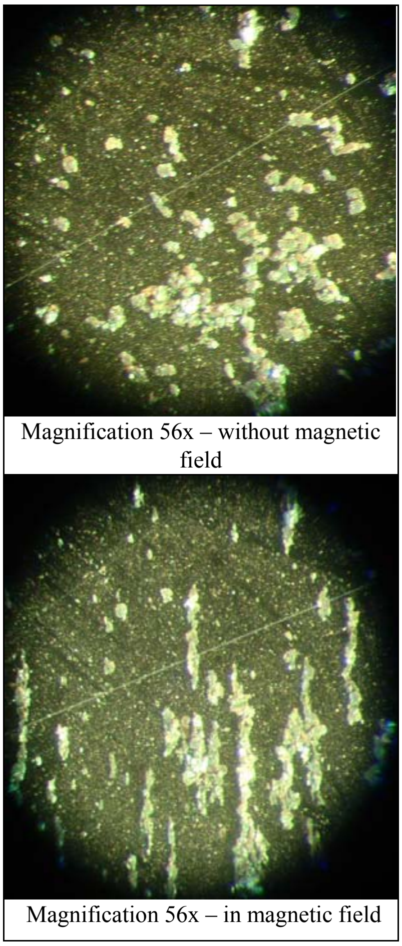

Fig. 1 Microphotographies of metal particles of fraction 0-63 μm with chemisorbed impurities obtained on light microscope

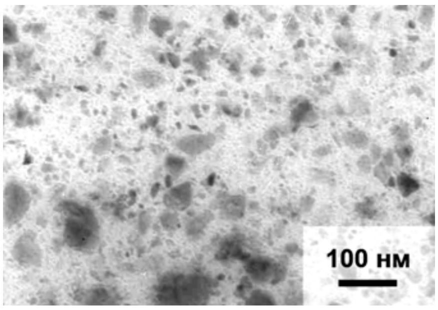

Fig. 2 Electron-microscopic picture of nanocarbon and ferric carbide particles, isolated from spongy iron structure

Introduction of calcium carbonate in a form of limestone, chalk, shell limestone, marl etc. also provides for effective complete metallization process behavior. The process is progressed in compliance with solid-phase reactions:

$$Fe_2O_3 + C \rightarrow 2FeO + CO;\ 2FeO + SiO_2 \rightarrow Fe_2SiO_4;$$
$$CaCO_3 + C \rightarrow CaO + 2CO;\ Fe_2SiO_4 + CaO \rightarrow \quad (2)$$
$$\rightarrow 2FeO + CaSiO_3;\ 2FeO + 2CO \rightarrow 2Fe + 2CO_2$$

Implementation of the aforesaid process mechanism will allow for effective metallization not only high-grade, but also low-grade iron ores, as well as metallurgical slimes at temperatures about 1200°C instead of 1500-1550°C according to known Australian Hismelt process.

So, metallization of hard-to-process metallurgical slime, containing, mass.%: 42.15 Fe; 23.02 SiO_2; 0.10 TiO_2; 2.26 CaO; 0.42 MgO; 1.06 Mn; 0.06 P; 0.46 S and subsequent alkali treatment of cake with iron content 61.42% according to recommendations [3], allowed obtaining of powered iron at iron extraction rate of 89-90% of the following chemical composition, mass.%: 89,33 Fe; 0.49 CaO; 4.92 SiO_2; 1.03 Mn; 0.05 P; 0.05 S.

Kerch ore cake metallization, concentration and purification has allowed obtaining the powered iron of the following chemical composition, mass. %: 95.71 Fe; 0.09 P; 0.01 As; 0.002 S; 0.23 CaO; 0.32 Al_2O_3; 1.73 SiO_2; 1.84 C.

Analysis of obtained results may provide for conclusion that suggested method of nanoparticles-aided solid-phase processing, concentration and alkali treatment of metalized iron-bearing materials can be used for obtaining of spongy iron practically from any iron-ore raw materials, beginning from metallurgical slimes and ending with highly-enriched concentrates. Method application for processing of sedimentary ferrioxide-silicate ores, usually containing 35-40% of iron with manganese admixture, as well as higher content of such impurities as phosphates, arsenates and silicates is the most efficient. Processing of such ores, stocks of which can be found not only in Ukraine but in many world countries, using known methods is unprofitable because of insufficient elimination of phosphorus, silicates and other impurities. During processing of phosphorous-containing iron ores necessity for application of capital-intensive and energy intensive technologies of phosphorus elimination from iron flux, i.e. converter process, is felt away because obtained product can be processed in electric steel furnaces. This method allows obtaining of plants growing accelerators containing macro-, microelements (Mg, Mn, Sr etc.), phosphorus and phosphomanganese fertilizers, pozzolanic admixtures to cement as by-products. Technical and economic assessment has shown that application of by-products will increase method profitability at 40-60% providing obtain of high-clean oxidation-resistant spongy iron as the basic material.

Comparative study of the suggested method for obtaining of directly reduced iron to RN method and SL/RN [1] method has shown that RN method can't be competitive under present-day conditions. At the same time, expected cost price of the concentrate according to suggested method (method IBCC-DMP), which allows obtaining the concentrate with 90-95% Fe-content from low-grade ores and sludges, is 180-220 $/ton lower than cost price of iron concentrate containing 87% of iron, obtained following method SL/RN from high-grade (67-69% Fe) concentrates.

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