The modern techniques of involvement of phosphorous-containing sedimentary oolitic ores into industrial metallurgical production

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The world production of steel tends to be growing constantly, which requires increasing volume of production and cleaning of iron ores as well as supply of iron-ore concentrates. The stocks of traditionally used ores without admixture of phosphorus and sulphur from the deposits of magnetite are gradually exhausted, that requires mining of haematite and sedimentary oolitic ores. However the latter often contain increased amount of phosphorus (up to 1%), which restrains their use. Traditional gravitationally magnetic methods of such ore cleaning allow at the best transfer only of the minor part of the phosphorus into the waste of cleaning, and in most cases phosphorus remains mainly in the iron-ore concentrate, which does not allow application of such concentrates in the blast-furnace practice. Owing to the phosphorous behavior in blast-furnace treatment the amount of phosphorus in blast-furnace charge should be not more than 0.2-0.3% [1].

The iron ore deposits with increased phosphorus content are widely distributed throughout the world (France, Canada, Kazakhstan, Ukraine etc.) [2]. In Russia phosphorus-rich iron ores coincide usually with bog iron ore deposits (Bakcharskoe, Kolpashovskoe, Angaro-Ilimskoye, Beryosovskoye, Nikolaevskoe etc.). There are some deposits in China. Iron ore there contains increased amount of phosphorus. The typical representative is the NingXiang-type of ore [3]. As a rule all such deposits contain huge stocks of iron ores (hundreds of millions and billions of tons). In addition most of such iron ores are of sedimentary origin and they are mostly represented by oolite-like shape of small iron-ore particles (less than 0.5-1.0 mm).

The typical representative of such ores is the Lisakovskoe deposit in Kazakhstan which is represented mostly by bog iron ore with size of less than 1 mm. The ore contains 30-
35% of iron and 0.6-0.7% of phosphorus. The main constituent of dead rock is quartz (15-30%). In addition lisakovskaya ore contains increased amount of aluminium oxide (3-6%). In terms of its mineralogical composition lisakovskaya ore is represented mainly by hydrogoethite. Therefore the content of hydrate moisture in the ore is 10-12%. Ore particles are represented by oolites (see Figure 1), in most cases there are particles of quartz in their centre. The ore particles with size less than 1.0 mm are 80-90% of all the mass of the ore.

Figure 1. Oolites of the original lisakovsky concentrate (section)

Mining and Processing Integrated Works where ore cleaning is performed according to the gravity-magnetic scheme has been built on the base of the Lisakovskoe deposit. The concentrate produced contains (%): Fe – (39-40); SiO₂ – 10.8; Al₂O₃ – 4.6, hydrate moisture – (11-12). It also contains 0.8-0.9% of phosphorus. It is supplied to the Integrated Iron-And-Steel Works Arcelor Mittal in Temirtau, where it is used in blast-furnace treatment together with other concentrates with decreased content of phosphorus. It is required to resolve the problem of preliminary phosphorus removal at the stages of concentrate production to increase the consumption of lisakovsky concentrate.

Removal of phosphorus from the cast iron in buckets requires substantial additional expenditures, and the dephosphorization technique is complicated by the necessity of thorough mixing of the great amount of cast iron. To remove phosphorous in steelmaking (converter) treatment double slag skimming is required, which unacceptably raises the prime cost of steel. In such a situation it is advisable to remove phosphorus at the stage of ore preparation to metallurgical treatment.
The problem of iron-ore materials dephosphorization is widely investigated in different countries. Analysis of various dephosphorization techniques allows concluding that it is expedient to use hydrometallurgical leaching of phosphorus. The variant developed in Russia [4] is offered as the most effective one. It includes the preliminary sweet roasting of iron-ore material with subsequent phosphorus leaching from the roasted product with a weak inorganic acid.

To implement the technique Arcelor Mittal Temirtau built an industrial area (Construction Services Company Orken, Lisakovsk, Kazakhstan). The preliminary roasting of the lisakovskoye concentrate is performed in a rotary roaster, its diameter is 4.5 m and its length is 110 m [5]. Phosphorus leaching out of the roasted concentrate is made with weak sulphuric acid [6, 7]. According to the patent mentioned [4] the roasting is performed at a temperature of 800-1000 °C, and the sulphuric acid concentration at the leaching is 1-10 % [7]. The parameters allow obtaining the residual phosphorus in the leached concentrate not more than 0.25 % if the phosphorous content in the original lisakovskoye gravity magnetic concentrate is 0.8-0.9 %. On the industrial plant the optimum mode parameters are worked out. The designed output of the plant is 80 tons per hour of the dephosphorized concentrate.

In OJSC «VNIIMT» the work package has been performed on investigation of peculiarities of roasting and subsequent leaching of phosphorus from lisakovskoye concentrate with weak sulphuric acid. Phosphorus is not leached from unroasted concentrate because it is bounded. It is determined that the phosphorus from lisakovskoye concentrate is in the form of hydrated phosphorus-containing component (presumably – augelite) which is decomposed when being roasted and free phosphorus oxide is formed. The latter transfers easily into sulphuric solution with phosphorous acids forming. The content of hydrate moisture in lisakovskoye concentrate is 12 %. About 10 % of it (abs.) is bounded in iron hydrates which decompose at 300-350 °C. About 2 % of hydrate moisture is bounded in hydrated phosphorus-containing component which decomposes at higher temperature (more than 730 °C). It is found that when temperature raises phasic decomposition of phosphorus-containing component takes place (see Figure 2). At the same time the degree of phosphorus-containing component decomposition determines unambiguously the completeness of the dephosphorization process which can be evaluated by the amount of residual hydrated moisture in the roasted concentrate: the less the residual hydrated moisture the deeper concentrate dephosphorization and the less phosphorus content in the leached product. The degree of phosphorus-containing component decomposition during the roasting process depends on the temperature and length of roasting. The kinetics of the phosphorus-containing
component decomposition process had been found. The activation energy of the process is 143.7 kJ/mole.

Figure 2. The results of thermal analysis of the lisakovsky concentrate

Notation: 1 – change of mass, 2 – temperature, 3 – thermal effect curve

The efficiency of phosphorus leaching from the roasted concentrate depends on several conditions: sulphuric acid concentration, solid/liquid ratio, pulp temperature and the speed of pulp mixing.

Because the dependency of the result of the phosphorus removing from the concentrate on the efficiency of the two technological processes (roasting and leaching), interdependent optimization of the parameters of these two phases between themselves is necessary, which greatly depend on the nature of the original concentrate. So, when removing water vapour produced during the process of the hydrated phosphorus-containing component decomposition, cracking (see Figure 3) and even destruction of the concentrate particles takes place, which provides the subsequent phosphorus leaching. As a result the described technique allows obtaining of the content of residual phosphorus in the leached lisakovsky concentrate at the level of 0.15-0.18 %.
A great amount of work has been done by OJSC «VNIIMT» in the field of magnetizing roasting of different iron ores (lisakovskaya, kerchenskaya, serovskaya, krivorozhskaya). Magnetizing roasting means reduction of hematite to magnetite possessing higher magnetic properties, which allows effective magnetic separation of the material roasted. One-zone fluidized-bed roaster has been developed for magnetizing roasting of lisakovskaya ore [9]. When performing roasting magnetizing cleaning of lisakovskaya ore the concentrate containing 60-61 % of iron was produced. In the late XX century in USSR at the Central Mining and-Processing Integrated Works (Krivoy Rog, Ukraine) 30 rotating roasters for magnetizing roasting of ferruginous quartzite operated. The subsequent magnetic separation gave concentrate containing 61- 62% of iron.

In OJSC «VNIIMT» extensive research and development have been made in the field of metallization of various iron-ore materials (pellets and fine grained concentrates) using solid-phase reduction with solid reducing agent in a rotary roaster. On the basis of the developments a rotary roaster was built at the Northern Mining-and-Processing Integrated Works (Krivoy Rog, Ukraine) with the diameter of 7.0 m and length of 92 m. The roaster output is up to 100 tons per hour of metallized pellets with the degree of metallization equal to 91-93 %.
In addition investigations and developments have been made on metallization with solid reducing agent of fine grained concentrates in the falling and mixing layer of a rotary roaster. It was found that rich fine grained concentrates are sintered in the process of metallization at a temperature as little as 600-700 °C. It does not allow implementing their industrial metallization. However fine grained iron concentrates containing admixtures of titanium, aluminium, magnesium appeared to be metalized successfully in the rotary roaster without sintering signs [9]. For example, lisakovsky concentrate is metallized in a rotary roaster to 90 % of metallization. The metallization of fine grained concentrate without preliminary pelletizing makes it possible to reduce significantly investments and the cost price of the product.

Two variants of iron-ore raw material metallization have been developed. The first one provides reducing metallization to 50-60 % with subsequent briquetting of the metallized concentrate. It is expedient to use such metallized product in a blast furnace. This allows to decrease the specific consumption of coke and to increase the blast furnace output. The second variant represents deep reduction to 92-93 % of metallization. The product should be used straight in steel treatment. The variant allows producing of high-quality steel without harmful admixtures.

Thus nowadays three above mentioned techniques of treatment of oxidized oolitic iron-ore materials have been developed and tested, namely:
- cleaning of concentrates or ores from phosphorus with roasting and subsequent phosphorus leaching with weak sulphuric acid;
- roasting magnetic ore cleaning;
- solid-phase metallization of iron-ore material with solid reduction agent.

The use of these techniques in different combinations allows involvement of oxidized oolitic and other types of iron ores, the found deposits of which being enormous, into large-scale industrial production.

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