THE PRESENCE OF HARMFUL ELEMENTS IN BLAST FURNACE PROCESS AND THE POTENTIAL METHODS OF THEIR REMOVAL

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Abstract

Metallurgical production in blast furnaces is characterized by its high energy intensity and complex nature of production. Pig iron as input raw material also contains various other elements. These elements are contained in pig iron in the form of compounds, and some of them can be described as harmful for metallurgical production. Harmful elements have a negative impact on the production process, the final product of metallurgical production and some of these elements also have a negative impact on the environment. These elements must be removed by means of various methods because of their deteriorative impact on production. This article deals with the analysis of the presence of harmful elements in the blast furnace process and the potential methods of their removal.

Keywords: Harmful elements, blast furnace process, iron

1. INTRODUCTION

Blast furnace process of production of pig iron represents the first step of metallurgical cycle at the end of which we obtain various products from a material based on iron [1, 2]. The pig iron production is characterized by extensive movements of raw materials and products, as well as by enormous energy consumption. The basic input raw materials of the blast furnace include metalliferous materials, slag-making materials and fuel. The charge materials should be balanced, with a low share of fine-grained particles and sufficient mechanical strength. Metalliferrous materials should have optimal lumpiness and good reducibility. Another prerequisite of metalliferous materials is high iron content and low content of undesirable components. The most common metalliferrous materials used in the production of pig iron include iron ore or metal waste materials from industrial production. In an effort to remain competitive, metallurgical enterprises have been trying to reduce their production costs and thus the price of their products. Cutting purchasing costs of raw materials is a possible method of cost reduction at the current period of high prices of raw materials and energies [6, 7, 8]. The efforts focused on buying cheaper inputs, however, often lead to the use of iron ore of inferior quality with a higher content of harmful substances.

Iron ore is one of the key raw materials of metallurgical enterprises [3, 12]. Undesirable elements that are present in iron ores do not behave the same way during the blast furnace process. The main harmful elements include, in particular, sulphur, zinc, lead, copper and cadmium [13]. Sulphide sulphur is relatively easy to remove. Other harmful elements can be removed using added chlorides during the sintering process, or by providing reducing conditions. The difficult removal of undesirable elements during the treatment of ore is caused by their even distribution in the raw materials and by the fact that they not merge into gas phase in cases where chlorinating agent is not used. Some elements do not cause problems in the production of pig iron, but they are considered to be harmful, because they interfere with the steelmaking processes following the production of iron, or as a result of their negative impact on the environment. Harmful effects of the individual elements must be assessed in a complex way, based on the knowledge of iron production [9, 10].

The above mentioned harmful elements must be removed in a suitable way during the production of iron with regards to the costs of production [4, 11]. The aim of this article is to analyze the possibility of removing harmful elements in production of iron. The values of selected harmful elements in the individual iron ores have been obtained on the basis of a research conducted in a monitored metallurgical enterprise.

2. EXPREIMENTAL WORK

The research is focused on the content of selected harmful elements, especially phosphorus, sulphur and zinc in the input raw material - iron ore. The results of the measured values of these undesirable elements are summarized in **Table 1**. The content of each element is expressed in percentage value and is also quantified as a weight per 1000 t of iron ore. The concentrations of the individual elements are expressed in kg·1000 t^{-1} of iron ore, as a result of their lower concentrations.

Table 1 Content of iron and harmful elements per 1000 t of iron ore

Ore	P [%]	P [kg]	S [%]	S [kg]	Zn [%]	Zn [kg]
Zaporozhye sinter ore	0.03	300	0.02	200	0.005	50
Jugok concentrate	0.02	200	0.05	500	0.004	40
Lebedinskiy concentrate	0.02	200	0.04	400	0.004	40
Sevgok concentrate	0.018	180	0.045	450	0.004	40

Fig. 1 shows the percentage share of the individual harmful elements per 1000 t of input raw material. Despite the fact that the individual harmful elements are contained in ores in negligible amounts, they have a negative effect on the production of iron and it is desirable to remove them by means of various methods. According to the measured values, sulphur has the highest proportion among the undesirable elements, with values ranging from 0.02 to 0.05%. The lowest proportion in the examined ores was measured in case of zinc, with content ranging from 0.004% to 0.005%.

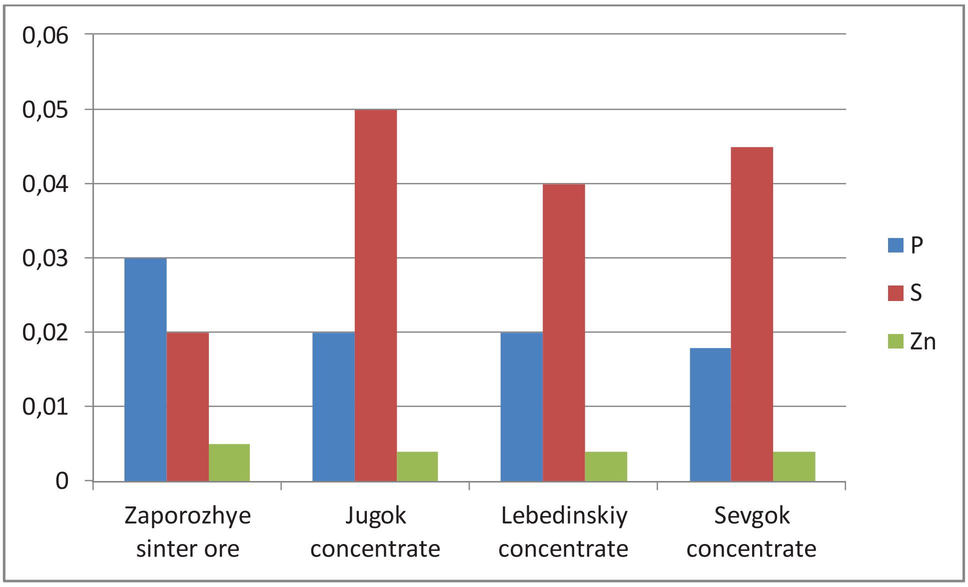

Fig. 1 Proportion of harmful elements in % per 1000 t of ore

2.1. Methods of removal of sulphur

Sulphur is a harmful component especially in steel, because it causes its brittleness [5]. Pig iron should contain as little sulphur as possible, only hundreds of percent. In order to remove it, it must be converted into a compound insoluble in iron, which can be firmly bound in slag. CaS is an example of such a compound. This compound can be produced by adding CaO into the blast furnace. The reaction of sulphur with calcium oxide is the main desulfurization reaction in the blast furnace. The chemical reaction is as follows:

$$FeS + CaO + C\ (coke) = Fe\ (l) + CaS + CO\ (g) \quad (1)$$

The reaction of FeS with CaO produces a solid substance - CaS, which can be absorbed in blast furnace slag.

Another method of removal of sulphur is the utilization of MgO. Desulphurization by means of magnesium oxide follows a reaction producing a solid substance - MgS absorbed in slag:

FeS + MgO + C (coke) = MgS + Fe (l) a CO (g) (2)

A simultaneous application of lime and magnesium is one of the methods of removal of sulphur. In terms of expensiveness, the desulphurization of iron is a cost-intensive process, but it is very important to improve the properties of the final product.

2.2. Reduction of phosphorus

Phosphorus enters the blast furnace process especially in the form of phosphorite $Ca_3P_20_8$ or as vivianite $Fe_3P_20_8 \cdot 8\ H_2O$. Most of it passes into the produced pig iron. In majority of produced steel grades, the presence of phosphorus is very harmful and reduces the value of the pig iron, which is why it is necessary to minimize its content. Its content can be reduced by selecting suitable charge.

At reduction temperatures phosphorus oxide is only in gaseous state, and phosphorus and its oxides are temporarily generated during the reduction by means of hydrogen. The reduction of phosphorus proceeds according to the following reaction:

$2\ P_2O_2\ (g) + 10\ H_2 = P4\ (g) + 10\ H_2O$ (3)

$P_4\ (g) + 6\ H_2 = 4\ PH_3\ (g)$ (4)

Phosphides of iron Fe_2P or Fe_3P emerge during the reduction of vivianite. The reduction by means of hydrogen starts at the temperature of about 400 °C and ends around 1300 °C. Reduction by means of carbon monoxide proceeds in similar fashion. The individual reactions are:

$2\ Fe_3(PO_4)_2 + 16\ C = 3\ Fe_3P + P + 16\ CO$ (5)

$Fe_3(PO_4)_2 + 8\ C = Fe_3P + P + 8\ CO$ (6)

The resulting phosphides can be further reduced by iron oxide, as a reaction of:

$2\ Fe_3P + 5\ FeO = P_2O_5 + 11\ Fe$ (7)

The presented reactions show that phosphorus can be perfectly reduced up to the reduction of iron itself.

If phosphorus is present in ore in the form of phosphorite, it is reduced by carbon and the reduction takes place at the temperature of 1100 °C:

$Ca_3P_20_8 + 8\ C = Ca_3P_2 + 8\ CO$ (8)

Most of the phosphorus contained in the ores is reduced to a liquid phase, when the concentration of P_2O_5 in slag gradually decreases and, after certain time, the process stops. The reduction of phosphorus in the blast furnace process is therefore almost perfect. The concentration of phosphorus in pig iron can be influenced only by the choice of suitable input raw materials.

2.3. Reduction of zinc

Zinc in iron ores is found in the form of different compounds. Its negative impact is primarily felt on the blast furnace lining. It becomes gaseous in the form of ZnO and it is depositing on various parts of blast furnace during the blast furnace process. Zinc can be removed from the blast furnace by maintaining the temperature at around 400 °C in the centre of the furnace, and zinc is removed together with the blast furnace gas in the form of fine ZnO particles, which are completely captured during the treatment of the blast furnace gas. If calcium oxide is present as well, it can react together with zinc according to the following reaction:

$$ZnS + CaO + C = Zn + CaS + CO \quad (9)$$

At the same time, there will be a reaction with carbon and iron:

$$ZnS + Fe = Zn + FeS \quad (10)$$

$$ZnO + C = Zn\ (g) + CO \quad (11)$$

Zinc gets into the blast furnace in ore and coke. The resulting vapours containing zinc go upwards during the blast furnace process, and they form a closed cycle of the circulation of Zn and increase its content in the blast furnace shaft. One part is deposited in the pores and cracks in the lining, while the volume of zinc increases during the transition from solid to gaseous state, which can cause cracking of the lining. Zn cycle in the blast furnace is shown in **Fig. 2**.

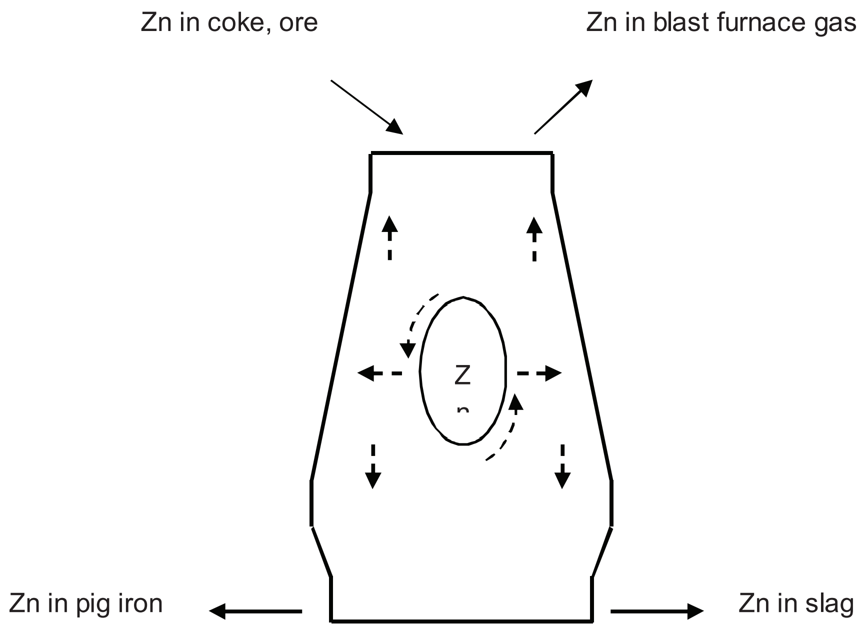

Fig. 2 Zn cycle in production of pig iron [1]

3. CONCLUSION

The conducted research has shown the amount of selected harmful elements contained in the analyzed four types of iron ores. The research was focused on sulphur, phosphorus and zinc. In terms of the blast furnace processes and the product quality as well, it is necessary to reduce these elements in pig iron in a suitable way. Especially the removal of sulphur is a costly process, because it is necessary to add CaO or MgO into the blast furnace process, which increases the production costs. Adding CaO, however, has a positive impact on the reduction of not only sulphur during the production of iron, but also on the reduction of Zn.

At present time, when the prices of raw materials are high, metallurgical companies have been trying to save costs spent on the purchase of iron ore and coal. However, the purchase of low-quality ore is also associated with higher levels of undesirable elements that may ultimately lead to an increase in production costs. Costs will go up primarily as a result of removing harmful elements in order to achieve an optimal production process and the desired quality of the final product. Metallurgical enterprises should focus on monitoring the quality of input raw materials and the content of the individual harmful elements.

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