PHOSPHORUS AND ITS INFLUENCE IN THE BLAST FURNACE PROCESS

Petr BESTA [1], Kamila JANOVSKÁ [1], Tomasz SZCZEPANIK [2], Tomáš MALČIC [1]

[1]VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU, petr.besta@vsb.cz

[2]CUT - Czestochowa University of Technology, Faculty of Management, Czestochowa, Poland, EU
tomasz.szczepanik@wz.pcz.pl

Abstract

The course of the blast furnace process can be significantly affected by many harmful substances. Some elements may affect the technological parameters of the blast furnace process, others may fundamentally disrupt steelmaking processes following the production of crude iron. Alkaline carbonates also have a negative impact on the quality of blast furnace coke. Zinc and lead contribute to the degradation of the blast furnace lining and thus reduce its service life. For all harmful substances, it is necessary to continuously monitor and reduce their content in feedstocks as well as in crude iron. The elements that reduce the value of the produced metal include phosphorus. This element mainly affects the mechanical properties of the steel produced. The presence of phosphorus at higher concentrations is therefore harmful, except for selected machine steels. For these steels, phosphorus may be added as an alloying element. However, in most steel produced, its content is reduced in secondary metallurgy processes. Within the framework of the research, the content of phosphorus in the input raw materials and the output products of the blast furnace process was monitored. On the basis of the measurements made, the continuous cycle of this element in the blast furnace process and its influence on the technical indicators of production was analysed. The article aims to evaluate the conclusions of the research conducted to identify phosphorus reduction potential during the blast furnace process.

Keywords: Iron, costs, reductions, defects

1. INTRODUCTION

Blast furnace production of pig iron is based on the use of physical, chemical, heat and mechanical processes [1]. Primary feedstocks include the ore part, fuel and slag-forming ingredients. The ore part consists of iron ores and concentrates. The often-used ore raw materials include manganese ores [2]. Among the feedstocks containing the metal-bearing part, there are also various types of wastes containing iron. The ore is then used in the blast furnace process as the heat-treated agglomerate or pellets. The agglomerate is used as a dominant metal feedstock in the Czech Republic (70-90%). The agglomerate is produced from ore raw materials which may be anhydrous oxides, hydrated oxides, carbonates or silicates [3]. Waste materials used as a source of metals include steel waste, scrap, sludge, slag.

In addition, negative and harmful elements get into the blast furnace as a part of the feedstocks. Their effects can be seen in several levels: negative impact on the production technology, reduction of quality parameters of the metals produced, adverse effects on the environment, but also a negative impact on the human organism [3, 4]. Therefore, the harmfulness of these elements must be evaluated in a comprehensive way, not only through the selected parameter.

The elements that can be classified as negative include, for example, heavy metals, alkaline carbonates, sulphur compounds, phosphorus, and others. Alkaline carbonates enter the blast furnace in all blast furnace burden components (large quantities as a part of manganese ores but also through metallurgical waste). Coke as a primary fuel also often contains more alkalis [5]. When coking under operating conditions, the amount of alkalis does not change. Virtually all alkalis remain in coke, which brings up to 35% of the total amount to the blast furnace. From heavy metals, blast furnace operations can be mainly influenced by elements such as zinc and lead. Both elements are continuously circulating in the blast furnace process. They affect the production process itself but also negatively affect the life of the blast furnace lining (zinc) [6]. Moreover, phosphorus has a negative impact primarily on the raw metal produced, which fundamentally influences some properties of the steels produced [7, 8]. In the framework of the conducted research, the content of zinc and phosphorus was monitored in the process of the pig iron production. The aim is to minimize the influence of the negative elements on the production technology, but also the negative consequences on the quality of the produced metal. At the same time, it also optimizes the total cost per tonne of pig iron produced.

2. PROBLEM FORMULATION

Phosphorus as an element primarily influences the mechanical properties of the steels produced in iron production. It usually enters the blast furnace process in the form of compounds such as $Fe_3P_2O_8.8H_2O$ or $Ca_3P_2O_8.CaF_2$. Phosphorus is reduced in the blast furnace at a temperature range of 900-1200°C, mainly by means of carbon coke or hydrogen [3, 9]. In the case of carbon reduction, we can write everything using the following Equations 1 and 2

$$2\,(Fe_3P_2O_8) + 16\,C = 3Fe_2P + P + 16\,CO \qquad (1)$$

$$Ca_3P_2O_8 + 5C = 3(CaO) + 2P + 5CO \qquad (2)$$

Elemental phosphorus is reduced at high temperatures. With hydrogen reduction, transient or final products are formed in addition to phosphorus, its lower oxides, acids and water vapour [3, 9]. The reduction of phosphorus by hydrogen can be simply written in the form of Equations 3 and 4.

$$2\,P_2O_5 + 10\,H_2 = P_4 + 10\,H_2O \qquad (3)$$

$$P_4 + 6\,H_2 = 4\,PH_3 \qquad (4)$$

Reduction of phosphorus from the P_2O_5 compound by carbon can be written in the form of Equation 5. Carbon monoxide reduction can only take place in areas with low carbon dioxide concentrations.

$$P_2O_5 + 5\,C = \tfrac{1}{2}\,P_4 + 5\,CO \qquad (5)$$

Zinc enters the blast furnace in the form of a series of compounds that are contained in iron ores. The typical compounds include ZnS, FeS, ZnO, $ZnCO_3$. Zinc reduction generally occurs in the lower parts of the blast furnace [3, 10]. Permanent oxides include ZnO. Zinc can react with both CaO, C, Fe. The reactions can be written in the form of Equations 6, 7, 8.

$$ZnS + CaO + C = Zn + CaS + CO \qquad (6)$$

$$ZnS + Fe = Zn + FeS \qquad (7)$$

$$ZnO + C = Zn + CO \qquad (8)$$

The negative impact of zinc can be seen mainly in its effect on blast furnace lining, deterioration of parameters in the production of the agglomerate, but also its impact on the human organism [11, 12]. Zinc vapours, which rise to the higher parts of the blast furnace, settle in the pores of the lining. When passing from the gaseous to solid state, zinc increases its volume by several percent. This effect contributes to the degradation of blast furnace lining. Zinc also affects some parameters in the production of the agglomerate. In the case of higher concentrations of zinc, there is a reduction in the specific power, but also a decrease in the sintering speed. Zinc can also, along with other elements, influence the consumption of coke in the agglomeration process. Finally, it is necessary to mention the negative impact of zinc on the human organism. Vapours of zinc or very fine dust, containing high concentrations of zinc cause nausea and irritation cough.

3. EXPERIMENTAL WORK

In the framework of the conducted research, the content of zinc and phosphorus was monitored within the individual blast furnace components. Measurements were carried out within one year in the monitored metallurgical plant. Within the input raw materials, the content of the elements was monitored in the individual components. **Table 1** shows the zinc content in the selected feedstocks. For each feedstock, its concentration was monitored. Subsequently, the quantity found was converted to one tonne of the pig iron produced. According to this value, the total amount of zinc in all feedstocks was determined. As shown in **Table 1**, where some of the selected components are listed, the largest proportion entering the blast furnace process is brought by both agglomeration mixtures. Both used agglomerates contain a total of 68.253% of zinc entering the agglomeration process. This is the dominant source of this element in the blast furnace process.

Table 1 The amount of zinc in the selected feedstocks of the blast furnace process

	Weight (t)	Converted amount ($kg \cdot kg^{-1}$)	Zinc		
			(%)	($kg \cdot kg^{-1}$)	(%)
Agglomerate (01-06)	860 059	0.9384	0.008	$7.50 \cdot 10^{-5}$	31.566
Agglomerate (07-011)	617 638	0.6371	0.007	$4.71 \cdot 10^{-5}$	36.687
Granulate - slag	19 147	0.0207	0.016	$4.48 \cdot 10^{-6}$	1.701
Pellets	201 009	0.2190	0.005	$1.09 \cdot 10^{-5}$	5.395
Ore (lump)	63 917	0.0697	0.006	$2.09 \cdot 10^{-6}$	2.560
Limestone	52 147	0.0561	0.004	$2.27 \cdot 10^{-6}$	0.819
Coke in total	493 110	0.5380	0.003	$5.38 \cdot 10^{-6}$	4.078

Besides monitoring the content of negative elements in feedstocks directly entering the blast furnace, the concentrations of the selected pollutants in the materials prior to their processing in the agglomeration process were monitored. This also concerned raw materials that are used directly in the blast furnace process before being treated. The values for phosphorus and zinc were subsequently recalculated in terms of the total volume of specific raw materials. **Table 2** shows the average values over a one-year period.

Values in the **Table 1** represent data on the amount of selected input raw materials. There are listed the total quantity per year and the quantity converted per kilogram of the produced metal for each raw material. In the case of zinc, it is indicated its concentration, the total amount per kilogram of metal and the relative proportion in each raw material.

Table 2 The percentage of monitored elements in the feedstocks

	Phosphorus (%)	Zinc (%)
Ore Russia I.	5.92	6.69
Ore Russia II.	11.61	5.51
Ore Ukraine I	18.93	12.01
Ore Ukraine II	12.63	9.63
Ore concentrate - Russia	10.35	32.65
Limestone	0.93	0.001
Blast furnace discharge	3.97	12.2
Slag	42.12	21.6
Fine slag	31.69	11.1
Coke	4.19	1.9

In the case of phosphorus, ore raw materials represent one of the major sources (Russia, Ukraine). The primary sources of zinc are heads (Russia) and one type of iron ore from Ukraine. For both elements, slag is also a significant source.

Table 3 The percentage of monitored elements in the output raw materials

	Phosphorus (%)	**Zinc (%)**
Pig iron	98.9	31.8
Slag	0.009	11.2
Discharge	0.114	5.7
BF sludge fine	0.209	21.6
BF sludge rough	0.768	29.7

In the case of the raw materials (**Table 3**), most phosphorus is contained in the raw iron. Only a small part is contained in the slag and blast furnace sludge. About a third of the total amount of zinc is contained in pig iron. The remaining two-thirds are part of blast furnace sludge.

4. RESULTS AND DISCUSSION

Phosphorus converts mostly into pig iron. If we want to reduce its amount in the metal produced, we need to reduce its quantity at the entry into the blast furnace process. Significant amounts of phosphorus are contained in ore minerals (subsequently agglomerate), slag, but also coke. Reducing the quantity in the blast furnace can be supported by the appropriate composition of the agglomeration mixture. The key is the use of high-quality ores, which contain lower concentrations of pollutants, but at the same time have an adequate metal content. In the case of coke, it is also appropriate to choose a quality raw material that contains a minimum amount of ash. Slag as another significant source of phosphorus is used because of the content of the metal part. In this case, we can talk about the repeated entry of phosphorus into the blast furnace process through slag (blast furnace, steel). In general, phosphorus reduction in the blast furnace is exceptionally high. The basicity of the slag does not affect its course. An important aspect will be the use of quality raw materials and the reduction of phosphorus content entering the blast furnace process. Zinc can be partially removed through waste products. Approximately one-third of its content goes to raw iron. The negative impact of its effect in the blast furnace can be seen in its influence on blast furnace lining. In particular, the higher parts of the blast furnace exhibit higher concentrations of this element in the lining. This is due to its circulation in the blast furnace space. In the lower parts of the blast furnace, some zinc passes into the gaseous form and goes along with other products of combustion to cooler parts. Zinc is deposited on the blast furnace burden, as well as on the lining pores. Zinc, which remains part of the burden, goes down again to the lower parts of the blast furnace, where it is partially reduced. Zinc, which remains in the pores of the lining, increases its volume due to the change of state and contributes to the violation of the integrity of the lining of the blast furnace.

5. CONCLUSIONS

The technology of iron production in a blast furnace can be negatively affected by harmful elements. Their influence may also have a secondary impact on the cost of the whole process and hence the price of the metal produced. Removal of harmful elements is possible primarily in the preparation of feedstocks, but also during the iron production in the blast furnace. Many pollutants can be removed in the form of slag, whether in the production of iron or steel. It is through the slag that the harmful elements may enter the blast furnace process repeatedly. The amount of slag and other waste produced is considerable due to the nature of the blast furnace process. Therefore, although slag contains only a small amount of metal, its reuse in the iron production process is interesting in view of its volume. This results in the re-entry of harmful substances into the blast furnace process. In the case of the monitored elements, it has also been shown that natural raw materials are a significant source. It is therefore essential to monitor the quality of the used ore raw materials and to make the best use of high-quality ores. This is especially important in eliminating the elements that cannot effectively be eliminated in the blast furnace process from the iron production process. The use of high-quality ore raw materials is associated with a higher purchase price and therefore affects the cost of the metal production. Iron producers must, therefore, quantify both technological and cost criteria.

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