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ISSN 0543-5846
METABK 51(3) 325-328 (2012)
UDC – UDK 669.1: 669.2: 658.5 =111

THE EFFECT OF HARMFUL ELEMENTS IN PRODUCTION OF IRON IN RELATION TO INPUT AND OUTPUT MATERIAL BALANCE

Received – Prispjelo: 2011-06-07
Accepted – Prihvaćeno: 2011-12-25
Preliminary Note – Prethodno priopćenje

The main objectives of blast-furnace operators include maximum production of pig iron of required chemical composition at minimal cost. This can be ensured only in case of quality raw material basis and trouble-free operation of blast-furnace. Both parameters are influenced by the concentration of undesirable elements. The negative elements contained in the blast-furnace raw materials cause many technological problems in the sintering as well as in the blast-furnace process. These are mainly heavy metals and alkaline carbonates. The article deals with the analysis of material balance of zinc and selected alkaline carbonates contents in the input raw materials and output products of the blast-furnace.

Key words: iron, harmful elements, input raw materials, alkaline carbonates

Utjecaj štetnih elemenata pri proizvodnji sirovog željeza u odnosu na ulaznu i izlaznu materijalnu bilancu. Glavni cilj visokopećara uključuje maksimalnu proizvodnju sirovog željeza zahtijevanog kemijskog sastava uz minimalne troškove. To se može postići jedino na bazi kvalitetnih sirovina i besprijekornom radu visoke peći. Na obadva parametra utječe koncentracija nepoželjnih elemenata. Negativni elementi sadržani u visokopećnim sirovinama uzrokuju mnoge tehnološke probleme pri sinteriranju kao i u visokopećnom procesu. To su prvenstveno teški metali i alkalni karbonati. U radu je analizirana materijalna bilanca cinka i pojedinih alkalnih karbonata sadržanih u ulaznim sirovinama te izlaznim proizvodima visoke peći.

Ključne riječi: željezo, štetni elementi, ulazne sirovine, alkalni karbonati

INTRODUCTION

Disruption of blast-furnace process is raised by a number of typical causes which most often lead to sudden changes in gas flow speed or decreased charge, and cooling or excessive heating of the furnace heart [1]. The outcomes can be changes in slag or pig iron viscosity and problems connected with their discharge from blast-furnace [2]. Most of these causes occur due to harmful substances such as alkali, zinc, lead and their compounds which can influence the course of blast-furnace process in various ways to such an extent that they can cause emergency situations. That is why it is necessary to pay extra attention to these substances and their compounds so as to prevent various serious malfunctions during the blast-furnace process.

The amount of harmful substances in blast-furnace process can therefore have significant effect on its course and technological and economic parameters [3]. Heavy metals, alkaline carbonates and silicates must be regulated and their contents in input and output raw materials must be continuously monitored.

The objective of this article is to compile the material balance of zinc, Na_2O and K_2O at the input and output of blast-furnace. The results of measurements in the period of one year, which were continuously performed in the monitored blast-furnace, will be used as the data.

NEGATIVE ELEMENTS IN PRODUCTION OF IRON

Zinc belongs to heavy metals and it enters the blast-furnace process together with blast-furnace charge in the form of oxides and sulphides. With regards to its physical and chemical properties, there is a cycle in blast-furnace created between the lower parts with high temperatures which cause reduction and evaporation and the upper parts of the furnace stack with low temperatures where the vapours condensate [4]. Out of all these heavy metals, it is just zinc having the highest content in the raw materials. That is why the cycle of heavy metals can be analysed using zinc as an example. The presence of zinc in blast-furnace has a very negative effect on the lining, as it leads to build up in small pores and gaps. During the transition of zinc from gas phase to solid phase, zinc increases its volume, which may cause the distortion of the furnace lining surfaces. The main causes of blast-furnace lining damage by zinc compounds

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are: higher thermal stress, mechanical stress, oxidation and reaction with alkaline carbonates. Alkaline carbonates are supplied into blast-furnace by means of wide spectrum of components of blast-furnace charge. Great part of these components can be found in fuel.

More than one third of the total volume of alkaline carbonates entering the blast-furnace process in the form of charge can be found just in coke. It can be found mostly in the following compounds: (K)$Na_2O·SiO_2$, (K) $Na_2O·Al_2O_3·xSiO_2$, (K)$Na_2O·Fe_2O_3$, (K)Na_2CO_3 [5].

Alkaline carbonates have negative effect on the sintering process, quality of blast-furnace coke, quality of slag, and the lifetime of the lining. The penetration of alkaline carbonates into the lining significantly reduces the strength of refractory materials and thus the overall lifetime. That is why it is absolutely necessary to monitor the balance of harmful elements in the input raw materials and output products of the blast-furnace.

EXPERIMENTAL PART

Content analysis of negative elements in the input raw materials and the output products were performed during a one year period in the monitored blast-furnace. Main attention was paid to the contents of Zn, Na_2O and K_2O in input and output materials. In case of alkaline carbonates, the feasibility limit of their quantities is expressed by sum of $Na_2O + K_2O$.

This limit depends on the blast-furnace but also on conditions of its operation, and, generally, it is 2,5-8,5 kg/t of pig iron [6]. When measuring the content of Na_2O and K_2O, both negative substances were evaluated separately. The quantities of the individual negative elements had been determined on the basis of their measured percentage contents which were subsequently converted with regard to the weight of each raw material. Table 1 also shows the used quantities of raw materials per kilogram of produced pig iron.

Their total weight was afterwards determined on the basis of the chemical analysis results which had quantified the contents of the individual negative elements in all input raw materials. The total quantity in the input raw materials entering the blast-furnace process was determined for all the monitored elements. Table 2 shows the total percentage distribution of the content of the individual harmful elements in all input raw materials. Both sintering mixtures were unquestionably the largest sources of zinc in the blast-furnace charge within the scope of the measured values. Sinter - 2 was the source of 43,3 % of the total zinc content and sinter - 1 accounted for 36 %. Both used sintering mixtures thus contained 79,3 % of the total Zn content at the entry into the blast-furnace. The secondary sources may include pellets (6,5 %), coke (4,4 %) and a modified steel slag (3,1 %). Lump ore was the last significant source of zinc in the input raw materials; it contained 2,7 % of this metal. The content of zinc in other input raw materials can be considered as negligible due to its low levels. In case of Na_2O content in the input raw materials, three main sources can be identified: Sinter - 2 (30,8 %), coke (26,8 %), Sinter - 1 (25,8 %).

Table 1 **Material balance - inputs into the blast-furnace process**

	Weight	Quantity	Zn		Na_2O		K_2O	
	/ t	/ kg·kg^{-1}	/ %	/ kg·kg^{-1}	/ %	/ kg·kg^{-1}	/ %	/ kg·kg^{-1}
Sinter - 1	584 159	0,637	0,007	$4{,}46·10^{-5}$	0,07	$4{,}46·10^{-4}$	0,05	$3{,}18·10^{-4}$
Sinter - 2	698 538	0,762	0,007	$5{,}33·10^{-5}$	0,07	$5{,}33·10^{-4}$	0,04	$3{,}01·10^{-4}$
Slag – granulation product	8 914	0,009	0,022	$2{,}13·10^{-6}$	0,07	$6{,}80·10^{-6}$	0,05	$4{,}86·10^{-6}$
Beneficiated steel slag	87 100	0,095	0,004	$3{,}80·10^{-6}$	0,05	$4{,}75·10^{-5}$	0,03	$2{,}85·10^{-5}$
Separated material from sinter	11 869	0,012	0,011	$1{,}42·10^{-6}$	0,14	$1{,}81·10^{-5}$	0,33	$4{,}27·10^{-5}$
Granules	247 301	0,269	0,003	$8{,}09·10^{-6}$	0,06	$1{,}61·10^{-5}$	0,13	$3{,}35·10^{-4}$
Lump ore - Zaporoží	103 900	0,113	0,003	$3{,}40·10^{-6}$	0,04	$4{,}53·10^{-5}$	0,03	$3{,}40·10^{-5}$
Mn concentrate	2 094	0,002	0,013	$2{,}97·10^{-6}$	0,36	$8{,}22·10^{-6}$	0,82	$1{,}87·10^{-5}$
Limestone	35 397	0,038	0,003	$1{,}15·10^{-6}$	0	0	0	0
Coke	504 334	0,550	0,001	$5{,}50·10^{-6}$	0,084	$4{,}62·10^{-4}$	0,171	$9{,}41·10^{-4}$
Oil	8 723	0,009	0	0	0	0	0	0
Raw materials - Total	2 292 329							

Table 2 **Percentage content of harmful elements in input raw materials**

	Zn	Na_2O	K_2O
	/ %	/ %	/ %
Sinter - 1	36,0	25,8	16,5
Sinter - 2	43,3	30,8	14,9
Slag – granulation product	1,7	0,4	0,2
Beneficiated steel slag	3,1	2,7	1,4
Separated material from sinter	1,2	1,0	2,1
Granules	6,5	9,4	17,0
Lump ore - Zaporoží	2,7	2,6	1,7
Mn concentrate	0,2	0,5	0,9
Limestone	0,9	0	0
Coke	4,4	26,8	45,3
Oil	0	0	0

Pellets represent another important source containing 9,4 % of the total volume of Na_2O in charge. Other input raw materials can be considered insignificant in terms of Na_2O content.

The amounts of the monitored negative elements that passed into the output raw materials undoubtedly represent a fundamental aspect here. Air losses were neglected as part of the research. The zinc oxides arising during the blast-furnace process, thanks to which there

Table 3 **Material balance – outputs from the blast-furnace process**

	Weight	Quantity	Zn		Na_2O		K_2O	
	/ t	/ kg·kg^{-1}	/ %	/ kg·kg^{-1}	/ %	/ kg·kg^{-1}	/ %	/ kg·kg^{-1}
Pig iron	986 508	1	0,0031	$3,10 \cdot 10^{-5}$	0	0	0	0
Slag	395 692	0,401	0,0019	$7,62 \cdot 10^{-6}$	0,38	$1,52 \cdot 10^{-3}$	0,43	$1,73 \cdot 10^{-3}$
BF sludge fine	6 714	0,007	0,53	$3,61 \cdot 10^{-5}$	0,08	$5,44 \cdot 10^{-6}$	0,15	$1,02 \cdot 10^{-5}$
BF sludge rough	9 270	0,009	0,31	$2,91 \cdot 10^{-5}$	0,09	$8,46 \cdot 10^{-6}$	0,13	$1,22 \cdot 10^{-5}$
Discharge	21 970	0,022	0,034	$7,57 \cdot 10^{-6}$	0,12	$2,67 \cdot 10^{-5}$	0,15	$3,34 \cdot 10^{-5}$

is a closed cycle of this element in the blast-furnace, are the principle important elements from the group of monitored negative elements when judged from this point of view.

During the measured period of one year, the monitored blast-furnace produced 986 508 tons of pig iron. Table 3 also shows the volumes of all other relevant products. Chemical analysis again determined the contents of Zn, Na_2O, K_2O. Percentage contents of harmful elements were determined per kilogram of produced pig iron.

Based on the determined total weight of negative elements in the output raw materials, their relative contents in each component specified in percentage value were set again. The results are shown in Table 4. According to the performed research, the highest amount of zinc on the output side of the blast-furnace process is found in fine blast-furnace sludge (32,4 %), followed by: pig iron (27,8 %), rough blast-furnace sludge (26,2 %), blast-furnace dust (6,8 %), slag (6,8 %). In case of content of Na_2O in the output raw materials, the order was: slag (97,4 %), blast-furnace dust (1,8 %), rough blast-furnace sludge (0,5 %) and fine blast-furnace sludge (0,3 %).

In case of K_2O, the largest part goes into slag (96,8 %); the share of other contents in the output raw materials is as follows: blast-furnace dust (1,9 %), rough blast-furnace sludge (0,7 %), blast-furnace sludge (0,6 %).

Table 4 **Percentage content of harmful elements in output raw materials**

	Zn	Na_2O	K_2O
	/ %	/ %	/ %
Pig iron	27,8	0	0
Slag	6,8	97,4	96,8
BF sludge fine	32,4	0,3	0,6
BF sludge rough	26,2	0,5	0,7
Discharge	6,8	1,8	1,9

The concentrations of all monitored harmful elements in furnace lining were determined as well. That is why samples of lining were taken along its entire height in the course of blast-furnace overhaul. Figure 1 shows the evolution of the contents of the individual monitored negative compounds according to the height of the blast-furnace. The data of concentrations were converted to percentage expression compared to the total content of harmful elements in the lining.

The highest zinc content in the blast-furnace lining was measured at a distance of 9-10 m from the top of the blast-furnace. High levels of this element were also measured at a distance of 21-25 m from the top of the blast-furnace. With regard to the compounds of Na_2O and K_2O, the highest values in the lining were measured at a height of 16-18 meters from the top of the blast-furnace.

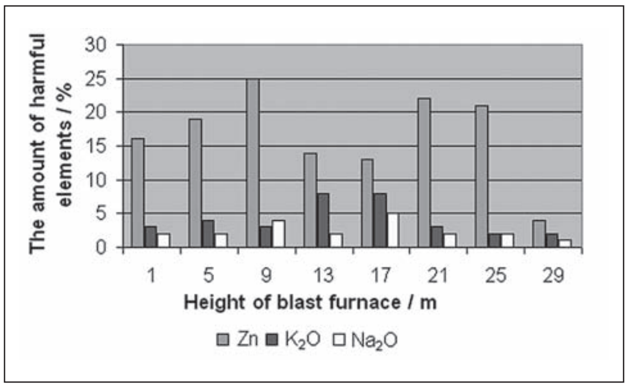

Figure 1 Content of zinc and alkaline carbonates in the lining

RESULTS AND DISCUSSIONS

From the monitored negative elements, particularly high contents of zinc can be found in the blast-furnace lining. Samples of lining collected during repairs of the blast-furnace have shown that zinc is mainly monitored in its metallic form. Zinc was very often found in compounds with lead. The resulting crystals containing zinc were very fragile. Zinc in the form of vapour inhales into the higher parts of the blast-furnace, which leads to formation of its deposits. These newly formed crystalline formations break off and fall back into the lower parts of the blast-furnace due to their instability. This is how a continuous cycle of zinc in the blast-furnace process runs. The most efficient method of removing zinc is during the sintering process. This is important in the face of the results of the research, as the largest proportion of zinc in the input raw materials was discovered in the sintering mixtures. The disposal of zinc within the frame of the sintering procedure requires high content of fuel, which greatly deteriorates not only the economic indicators of sintering production. If we increase the amount of fuel in the sintering mixture it leads to the formation of reducing conditions in the sintered layer and they are suitable for disposal of zinc. At the same time, however, you must be aware that the formation of reducing conditions in the sintered layer is counterproductive with regard to reduction of the amount of sulphur compounds. Zinc and alkaline carbonates can be effectively removed by adding chlorides. Creating reducing conditions represents another option. If chloride agents are used, there is an immediate change into gas chlorides which freely leave the process.

As demonstrated by the performed research, the main sources of alkaline carbonates are especially ores, from which they pass into the sintering mixtures. It is necessary to accurately monitor the alkalinity of sintering mixture, because the amount of alkaline carbonate is in direct relation. With increasing alkalinity of the sintering mixture there is a simultaneous increase of content of alkaline carbonates. Coke is another important source. However, during the process of coal coking, there is no fundamental change in the amount of alkaline carbonates. Most of the alkaline carbonates then merge into the blast-furnace process. The content of K_2O in coke was 45,3 %. The content of this compound is naturally given by the quality blast-furnace coke. The highest contents of alkaline carbonate in the blast-furnace lining were detected in its central part, where they are melting. Alkaline carbonates entering the blast-furnace process, especially as part of ores and coke concentrate and accumulate in temperature range of 950 °C – 1 150 °C. Their presence in the blast-furnace lining can mean increased risk of destruction. The negative effect of alkaline carbonates can already be observed at low temperature zones.

CONCLUSIONS

In order to regulate the negative effects of harmful elements on the blast-furnace process, it is necessary to continuously monitor the material balance. Variability of conditions in the blast-furnace, especially the thermal ones, can significantly contribute to elimination of harmful elements from the blast-furnace. However, it is also important to minimize the harmful elements supplied to blast-furnaces in raw materials of the charge. It is necessary to select such materials that contain minimum amount of harmful elements, despite the economic pressures. In case of removing harmful elements from the blast-furnace, it is necessary to regulate thermal and technological conditions in such a way to make it possible to remove the highest possible amount of alkaline carbonates through slag.

A large number of alkaline compounds entering the blast-furnace process are included in coke. This is unfortunately caused by the economic conditions. In recent years, there has been a significant increase in world prices of all fuels. Blast-furnace coke has become a significantly more expensive raw material and metallurgical companies are forced to buy even raw materials of lower quality. These aspects then naturally affect the amount of harmful elements entering the blast-furnace. In case of purchase of high-quality ore raw materials with low content of harmful elements, a significant reduction of harmful substances entering the blast-furnace process can be achieved. This is particularly important for the regulation of alkaline carbonates which can be reduced during the sintering process but to a very limited extent. Alkaline carbonates in blast-furnace process significantly affect mainly the viscosity of slag, which worsens the technological parameters of the process. Many studies have also proved the negative effect of alkaline carbonates and heavy metals on the properties of lining. Higher amount of harmful elements penetrating into the lining reduces the strength of refractory materials, which must naturally be prevented.

In case of zinc entry into the blast-furnace process, it is also necessary to mention its high content measured in the form of blast-furnace sludge. The utilization of these secondary raw materials obviously means economic effect which, however, brings along negative aspects as well. Using small metallurgical wastes produced during iron ore sintering causes ecological problems, in addition to technological ones. Increased proportion of dust particles in the mixture deteriorates the pelletizing ability of the sintered mixture and reduces the speed of sintering. The sintering process can significantly reduce the content of zinc entering the process in the form of sludge, which, on the other hand, means high amount of harmful elements leaking into the atmosphere. It is important at this point to use a quality system for separation of dust particles and purification of the leaking gases.

Monitoring the individual harmful elements in the manufacturing aggregates and optimizing the composition of the charge in such a way to prevent exceeding certain limit values set on the basis of operational experience remain the main measures of blast-furnace plants in terms of negative effects of harmful substances.

ACKNOWLEDGEMENT

The work was supported by the specific university research of Ministry of Education, Youth and Sports of the Czech Republic No. SP2011/85.

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Note: The responsible translator for English language is Petr Jaroš (English Language Tutor at the College of Tourism and Foreign Trade, Goodwill - VOŠ, Frýdek-Místek, the Czech Republic). Revised by John Vlcek (Literacy Tutor at West Suffolk College, Bury St Edmunds, England).