ALKALINE CARBONATES IN BLAST FURNACE PROCESS

The production of iron in blast furnaces is a complex of physical, chemical and mechanical processes. The input raw materials contain not only metallic components, but also a number of negative elements. The most important negative elements include alkaline carbonates. They can significantly affect the course of the blast furnace process and thus the overall performance of the furnace. As a result of that, it is essential to accurately monitor the alkali content in the blast furnace raw materials. The article analyzes the alkali content in input and output raw materials and their impact on the blast furnace process.

Key words: blast furnace, alkalis, negative elements, cost

INTRODUCTION

One of the main objectives of blast furnace operators is the maximum production of pig iron with the desired chemical composition at minimal costs [1]. This requires a high quality raw material base and a regular, smooth operation of the blast furnace. The quality of ore charge can be characterized by its: grain size, chemical and mineralogical composition, strength, reducibility, the extent of decomposition during reduction, and thermoplastic properties [2]. Great attention is currently also paid to the content of negative elements in the input charge and in the entire blast furnace process. These pollutants, such as alkalis and heavy metals, cause a number of technological problems in the sintering and blast furnace processes. At the same time, they significantly affect the costs of the entire blast furnace process.

Alkalis cause higher reactivity of coke, premature softening of ore charge, decomposition of sinter, swelling of pellets, they are involved in the formation of deposits on the refractory lining of blast furnaces and they accelerate their wear [3]. Heavy metals have similar effect. These problems lead to a higher consumption of coke, irregular operation of blast furnace and they also shorten its life.

The objective of this article is to assess the effect of alkaline carbonates in the blast furnace process and their content in the input and output raw materials. The used data are based on an annual research monitoring the impact and alkali content in a selected blast furnace.

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ALKALINE CARBONATES IN THE BLAST FURNACE PROCESS

Alkalis enter blast furnaces in all parts of the blast furnace charge, but mainly in manganese ore and in metallurgical waste materials. A large part of alkalis is brought by coke. In operating conditions, the amount of alkalis does not change during the coking process. Virtually all of the alkalis remain in coke that carries up to 35 % of the total amount into the blast furnace. These elements come in the form of $(K)Na_2O.SiO_2$, $(K)Na_2O.Al_2O_3.xSiO_2$, $(K)Na_2O.Fe_2O_3$, and in small amount also as $(K)Na_2CO_3$ or $(K)NaCl$. The content of Na_2O in the sintering mixture varies to 0,1 %, and to 1,2 % in pellets [4]. The content of K_2O in the sintering mixture reaches the value of up to 0,08 %, and up to 1,5 % in pellets. The content of alkalis exceeding 0,2 % has a negative impact on the metallurgical properties of sinter.

Exceeding the permissible alkali content in the blast furnace charge per ton of pig iron causes failures of the technological process and reduces the performance of blast furnaces. It is not possible to clearly determine the permissible content of alkali share in charge.

From practical experience with blast furnaces, the acceptable limit of the amount of alkalis, which is expressed as the sum of $Na_2O + K_2O$, is, depending on the blast furnace and the conditions of its operation, within a broad range of 2,5 to 8,5 kg/t of pig iron [5]. Exact recommended maximum values are, however, always determined according to the specific features of each blast furnace facility [6]. The quality of the input ore raw materials, which affect the amount of negative elements entering the primary metallurgical processes, plays an important role here. Using ore raw materials with low alkaline carbonate content is one of the options how to reduce the negative impacts.

Table 1 **Measured alkali contents in input raw materials**

	Weight	Quantity	Na$_2$O		K$_2$O	
	/ t	/ kg·kg^{-1}	/ %	/ kg·kg^{-1}	/ %	/ kg·kg^{-1}
Sinter – A	692 645	0,549	0,06	3,29·10^{-4}	0,08	4,39·10^{-4}
Sinter – B	813 314	0,644	0,08	5,15·10^{-4}	0,08	5,15·10^{-4}
Sinter – C	105 004	0,083	0,08	6,66·10^{-4}	0,09	7,49·10^{-4}
Slag – granulation product	19 901	0,015	0,04	6,31·10^{-6}	0,05	7,89·10^{-6}
Beneficiated steel slag	145 634	0,115	0,06	6,98·10^{-6}	0,06	6,93·10^{-5}
Aggregate from a spoil heap	3 400	0,002	0,04	1,08·10^{-7}	0,04	1,08·10^{-6}
Separated material from sinter	18 601	0,014	0,24	3,54·10^{-5}	0,36	5,31·10^{-5}
Granules A (Sevgok I.)	205 500	0,162	0,05	8,14·10^{-5}	0,05	8,14·10^{-5}
Granules B (Sevgok II.)	99 698	0,079	0,05	3,95·10^{-5}	0,06	4,74·10^{-5}
Lump ore – záporoží	150 900	0,119	0,09	1,07·10^{-4}	0,07	8,37·10^{-5}
Mn concentrate	4 000	0,003	0,22	6,98·10^{-6}	0,52	1,65·10^{-5}
Limestone A (Varin)	29 899	0,023	0	0	0	0
Limestone B (Vitosov)	26 002	0,021	0	0	0	0
Coke	690 678	0,543	0,062	3,39·10^{-4}	0,098	5,36·10^{-4}
Ground coal	8	6,34·10^{-6}	0,059	3,47·10^{-7}	0,178	1,13·10^{-6}
Furnace oil	4 200	0,003	0	0	0	0
Regenerated furnace oil	1 520	0,001	0	0	0	0
Raw materials – Total	3 010 904					

Alkaline carbonates get into blast furnace especially from sinter and pellets, but also from raw materials that are fed directly into the blast furnace, i.e. lump ore, limestone or dolomite [7]. Carbonates of sodium and potassium, which melt at temperatures of 850 °C and 901 °C, do not decompose or reduce in solid state [8]. The reduction of carbonate takes place at temperatures higher than 1200 °C, according to the reactions:

$$K_2CO_3 + CO \rightarrow 2K_{(g)} + 2CO_{2(g)} \quad (1)$$

$$Na_2CO_3 + CO \rightarrow 2Na_{(g)} + 2CO_{2(g)} \quad (2)$$
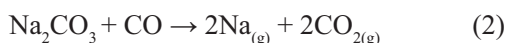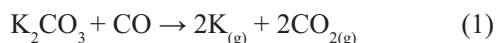
The resulting gaseous potassium and sodium are brought upward with the gases in the area of lower temperatures, where they deposit on the cooler charge pieces going down into the lower part of stack. Carbonates may form again in temperature below 900 °C, that go down together with the charge into areas of higher temperatures, where they are reduced again [9]. This leads to the creation of alkaline compounds that enter the cycle again.

EXPERIMENTAL PART

The contents of alkaline carbonates were measured in the monitored blast furnace plant within the scope of the selected blast furnace over the period of 365 days. The research project, monitoring the alkali content values, was focused on Na$_2$O, K$_2$O, as significant compounds of this category. Table 1 shows the measured values of the contents of Na$_2$O, K$_2$O in the used input blast furnace raw material. The amount of Na$_2$O, K$_2$O is determined both in their relative share and in the converted amount per kilogram of pig iron for each raw material. The total alkali content was determined for all input raw materials, and the relative share was determined on its basis.

Table 2 **Measured contents of alkalis in input raw materials**

	Weight	Quan-tity	Na$_2$O		K$_2$O	
	t	kg·kg^{-1}	%	kg·kg^{-1}	%	kg·kg^{-1}
Pig iron	1 260 987	1	0	0	0	0
Slag	498 233	0,395	0,41	1,62·10^{-3}	0,49	1,19·10^{-3}
BF sludge fine	8 333	0,006	0,11	7,32·10^{-6}	0,12	7,91·10^{-6}
BF sludge rough	11 900	0,008	0,06	5,76·10^{-6}	0,12	1,13·10^{-5}
Discharge	27 256	0,021	0,14	3,03·10^{-5}	0,21	4,54·10^{-5}

If we compare the results of the individual raw materials, we can see that there are three dominant raw materials in terms of the content of Na$_2$O: sintered B 32,26 %, coke 21,23 %, sinter A 20,60 %. In the case of K$_2$O compound, the raw materials with the highest content are: coke 27,85 %, sinter B 26,77 %, sinter A 22,80 %. In terms of the contents of the monitored alkalis, these input raw materials are among the most important.

The research also closely monitored the alkali content in the output raw materials. The contents of Na$_2$O, K$_2$O in key raw materials are shown in Table 2. If we use the converted values to determine the total alkali content for the individual output raw materials, we will come to this order of Na$_2$O: slag 97,40 %, discharge 1,82 %, BF sludge fine 0,44 %, BF sludge rough 0,34 %. In the case of K$_2$O content, the order of input raw materials is the following: slag 96,77 %, discharge 2,27 %, BF sludge rough 0,57 %, BF sludge fine 0,40 %.

The highest alkali content is found in slag. This can be seen as a very positive outcome, because one of the tasks of blast furnace slag is removing harmful elements. The total alkali content in the output raw materials is naturally reduced due to settling of these elements in the blast furnace lining. It takes place mainly in the upper parts of blast furnace, where the hot gases are cooling.

RESULTS AND DISCUSSIONS

The highest contents of alkaline carbonates from the input raw materials are found mainly in sinter mixture and coke. Their elimination in the sinter production process is difficult, particularly in terms of the production costs. As far as the ore raw materials are concerned, alkalis enter the sintering process (thereinafter blast furnace process) especially from manganese ores. The amount of alkalis in sinter is closely related to its basicity. Increasing the basicity of sinter goes hand in hand with decreasing the alkali content in it. The conditions of removal of alkalis from the sintering charge are affected by the content of FeS, the ratio of K / Na in the raw materials and the presence of chlorides in the sinter mixture. Sulphides inhibit the transfer of alkalis into the gas phase. The increasing ratio of K / Na in the raw materials and the addition of chlorides positively support the removal of alkali components of the sinter mixture.

The problem of removal of alkali carbonates from the blast furnace process is complicated due to their repeated entry into the blast furnace process. The gaseous products of reduction reactions are carried to the upper parts of blast furnace, where they settle on cool pieces of charge and they go down into the lower parts of the blast furnace again. This circulation, among other things, affects the total costs of the production of iron. The cycle of carbonates results especially in increased consumption of coke, which is consumed during their reduction in the lower part of the blast furnace, which has a highly endothermic character. Although heat is released again during the oxidation in the upper part of the furnace, but it is not used anymore, it only increases the temperature of blast furnace gas. In the liquid phase, carbonates may cause the aggregation of dust charge particles and the reduction of the charge column permeability, or the creation of deposit nucleus on the walls of blast furnaces. This may again significantly affect the costs of the whole process. The research has verified that the penetration of alkalis in the blast furnace lining may significantly reduce its lifetime. There is clear evidence that the degree of reduced strength of refractory materials is proportional to the amount of harmful elements and their combination, causing the cracking and the destruction of the microstructure.

Alkali carbonates act primarily on the part of lining that is above the level of molten iron in the well. Alkali metals in liquid or gaseous state have significant impact. They cause the destruction of both carbon and graphite lining, and they also cause a network of cracks of different sizes already at low temperatures. The effect of potassium is much larger than the effect of sodium. In liquid or gaseous state, they react with carbon material, causing the formation carbon-alkali intercrystalline connections. This connection causes the enlargement of intercrystalline spaces in the graphite network, which results in the creation of local tensions. The size and speed of tension is closely linked to the resistance of the material to mechanical stress.

CONCLUSIONS

The removal of pollutants in blast furnaces can be performed either by minimizing their amount in charge raw materials, or by using the technological means removing pollutants. When reducing the amount of alkalis entering the blast furnace, it is important to choose materials containing the minimal quantity of pollutants. A critical content of pollutants is determined for each blast furnace separately, taking into account the volume of the furnace, its conditions, thermal, technological and charge conditions. As a rule, at least 70 - 80 % of the supplied amount of alkalis should be removed by slag. Because the presence of harmful substances, in particularly alkalis, but also zinc in blast furnace leads mainly to the creation of deposits and the follow-up technological disruptions, these problems can be reduced by recycling waste materials through another unit than the blast furnace. Recycling part of sludge, e.g., through an oxygen converter, can reduce the entry of zinc in blast furnaces.

The removal of alkalis using slag is strongly linked to effective technological process control. In this form, it is possible to remove up to 95 % of alkali carbonates. About 3 % are removed by blast furnace gas, and the rest circulates in the blast furnace. The amount of removed alkalis is associated with the basicity and the amount of slag. With steady amount of slag, the increase in the content of alkali in slag requires a reduction of its basicity. Heavy metals, such as zinc, are removed by being discharged together with blast furnace gas. They represent about 80 % of the pollutants. The higher the temperature of blast furnace gas, the more zinc it contains. This is the reason why a permeable charge column is sometimes formed in the axial part of the furnace, consisting mainly of coke. High temperature, reduction atmosphere, and high gas velocity ensure the removal of large quantities of zinc vapour from the blast furnace. In order to avoid the negative effects of harmful materials (alkalis and heavy metals) to normal blast furnace process during the blast furnace operation time, it is necessary to monitor their material balance. Removing harmful elements from the blast furnace process is not only a matter of technology, but it is also increasingly often an issue of sustainable costs. Ultimately, it is necessary to find a solution that will take into account all the relevant criteria, and that will ensure a trouble-free flow of the blast furnace process and the production of competitively priced metal.

Acknowledgement

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