

## HEAVY METALS AND THEIR IMPACT IN PRODUCTION OF IRON

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#### Abstract

The production of iron in blast furnaces involves a number of entirely different processes, such as: chemical, mechanical, and physical. The input raw materials often contain many negative elements, such as heavy metals. The typical elements of this category can include lead and zinc. These elements usually enter the blast furnace in the form of oxides and sulphides. Due to the physical and chemical properties of these metals, there is a cycle between the lower parts of blast furnace with high temperatures, leading to reduction and evaporation, and the upper parts of furnace stack with low temperatures, where the vapours condense. Heavy metals can significantly influence the blast furnace process, as well as its costs. Among other things, they can fundamentally affect the life time of the blast furnace lining, which is disrupted by the formation of deposits containing some of the heavy metals. Given these facts, it is important to monitor the content of heavy metals in the input raw materials, but also throughout the entire blast furnace process. The article deals with the analysis of the impact of heavy metals within the scope of the blast furnace process.

Keywords: iron, zinc, lead, costs

### 1. INTRODUCTION

The blast furnace process is a set of a large number of physical and chemical, thermal and mechanical processes, which do not take place separately, but they are mutually connected with each other. These partial phenomena include the reduction of the oxides of iron and the residual elements of pig iron as the basic task of the blast furnace, as well as the fuel burning process in the well, reverse flow of gas, charge and liquid products of the melting process, dissociation processes, and the reactions in the solid and liquid phases [1].

The blast furnace charge consists of fuel, iron ore raw materials and flux materials [2]. All input raw materials must be supplied in such a ratio that ensures the production of a certain amount of pig iron in a given quality [3]. The function of fuel is to supply a sufficient amount of heat and reducing agent into the blast furnace, to carburize iron until it is saturated and to create, in particular in the lower part of the furnace, a solid structure, which facilitates the flow of gases through the charge, even in temperatures at which the ore raw material softens and melts [4]. The functions ensuring the passage of gases from the lower parts of the blast furnace to the higher ones fundamentally influence the entire blast furnace process. Other forms of heat and reducing agents can be supplied into the blast furnace process in the form of earth gas, oil or powder fuels.

The basic harmful elements in the blast furnace process include, in particular: S, P, Cd, Zn, Pb, As, Na<sub>2</sub>O, K<sub>2</sub>O [5]. Sulphur is usually a harmful component of steel, as it causes its brittleness in red heat. It is equally harmful in gray cast iron, in which it also causes the production of castings with blownholes. It enters the blast furnace especially together with coke and heavy oils, in smaller quantities also with other charge materials in the form of FeS, FeS<sub>2</sub>, and CaSO<sub>4</sub>. Pig irons should contain as little sulphur as possible, because its further removal options in the steel processes are limited [6]. The removal of sulphur from pig iron requires it to be converted to a compound that is insoluble in iron, and can be tightly bound in slag. Such a compound is, for example, CaS. To make sure the desulfurization reaction is as complete as possible, the slag must be well liquid; it must have the highest possible temperature and adequate alkalinity. The removal of sulphur using basic additional agents through its allocation in slag is among the most efficient desulphurisation processes. The sulphur controlled to some extent by means of secondary metallurgy. This



(1)

objective of this article is to analyze the content of zinc and its compounds in blast furnace input raw material, as well as its impact in the entire process of production of iron.

## 2. PROBLEM FORMULATION

There are numerous oxides in the blast furnace process, including ZnO, belonging to very stable ones. The blast furnace charge, which goes down during the process, is gradually heated and the zinc compounds are reduced. Zinc melts at a temperature of 450 °C - 920 °C. In the presence of CaO, zinc may react according to the following reaction:

## $ZnS+CaO+C \rightarrow Zn+CaS+CO$

There are simultaneous reactions with carbon and iron taking the form of the following reactions:

$$ZnS+Fe \rightarrow Zn+FeS$$
 (2)

$$ZnO+C\leftrightarrow Zn_{(g)}+CO$$
 (3)

The reaction with carbon is more frequent, as contact of ZnS with iron is tighter than with solid CaO. The blast furnace process also results in a reduction of zinc by means of carbon monoxide, as well as hydrogen [7]. This process is, however, complicated due to the fact that the boiling point is lower than the temperature of reduction. The reduced zinc is therefore instantaneously vaporized and returned with gas to the upper part of the furnace, where the temperature is lower [8]. Zinc is oxidized by carbon dioxide and condenses on the surface of the larger pieces of charge. These parts gradually go down into the lower parts of the blast furnace again, where the temperature rises and the process is continuously repeated. The amount of zinc within this circulation is not constant of course, because the amount is increasing due to the supply of new charge. Part of zinc also leaves the blast furnace process in the output raw materials. The actual reduction and oxidation, evaporation and condensation of zinc (or another waste material) has negative economic and environmental impact. The reduction of the oxides of zinc and its evaporation are endothermic processes that take away the heat in the middle section of blast furnace [9]. Heat is released again during reverse oxidation and condensation in the upper part, its use is, however, no longer possible, and it only heats up the blast furnace gas coming out of the blast furnace. These processes increase the specific consumption of coke with the corresponding economic and environmental consequences [10]. The conducted research has also monitored the content of zinc in the blast furnace process input raw materials. The measured values are presented in Table 1.

The values defining the content of zinc were recalculated per kilogram of produced iron for all input materials and, at the same time, the total percentage content of zinc was determined in all raw materials.

## 3. EXPERIMENTAL WORK

The results of the research, which was focused on the content of zinc in the input raw materials, are shown in **Table 1**. These values were measured within the scope of one year, when the research focused on the amount of zinc and its influence in the blast furnace process was conducted. The performed research has revealed that the highest content of zinc was concentrated in the sinter mixtures (61.615 % of the total content of zinc entering the blast furnace process).



#### **Table 1** Content of zinc in the input raw materials

|                                | Weight    | Quantity             | Zn    |                        |                        |
|--------------------------------|-----------|----------------------|-------|------------------------|------------------------|
|                                | / t       | / kg∙kg⁻¹            | / %   | / kg∙kg⁻¹              | / %<br>Total<br>amount |
| Sinter - A                     | 492 645   | 0.484                | 0.007 | 3.38·10 <sup>-5</sup>  | 20.155                 |
| Sinter - B                     | 413 314   | 0.406                | 0.006 | 2.43·10 <sup>-5</sup>  | 20.966                 |
| Sinter - C                     | 404 004   | 0.397                | 0.006 | 2.38·10 <sup>-5</sup>  | 20.494                 |
| Slag - granulation product     | 9 991     | 0.009                | 0.021 | 2.06·10 <sup>-6</sup>  | 1.774                  |
| Beneficiated steel slag        | 92 434    | 0.091                | 0.006 | 5.45·10 <sup>-6</sup>  | 4.689                  |
| Aggregate from a spoil heap    | 1 350     | 0.001                | 0.003 | 3.98·10 <sup>-8</sup>  | 0.034                  |
| Separated material from sinter | 12 492    | 0.012                | 0.011 | 1.35·10 <sup>-6</sup>  | 1.162                  |
| Granules A (Sevgok I.)         | 195 500   | 0.192                | 0.004 | 7.68·10 <sup>-6</sup>  | 6.611                  |
| Granules B (Sevgok II.)        | 77 698    | 0.076                | 0.002 | 1.52·10 <sup>-6</sup>  | 1.314                  |
| Lump ore - záporoží            | 104 814   | 0.103                | 0.004 | 4.12·10 <sup>-6</sup>  | 3.545                  |
| Mn concentrate                 | 2 210     | 0.002                | 0.01  | 2.17·10 <sup>-7</sup>  | 0.187                  |
| Limestone A (Varin)            | 21 200    | 0.021                | 0.003 | 6.25·10 <sup>-7</sup>  | 0.538                  |
| Limestone B (Vitosov)          | 16 690    | 0.016                | 0.004 | 6.56·10 <sup>-7</sup>  | 0.564                  |
| Coke                           | 530 400   | 0.521                | 0.002 | 1.04·10 <sup>-5</sup>  | 8.968                  |
| Ground coal                    | 4         | 3.0·10 <sup>-6</sup> | 0.001 | 3.93·10 <sup>-11</sup> | 3.0·10 <sup>-5</sup>   |
| Furnace oil                    | 3 200     | 0.003                | 0     | 0                      | 0                      |
| Regenerated furnace oil        | 520       | 0.0005               | 0     | 0                      | 0                      |
| Raw materials - Total          | 2 378 466 |                      |       |                        |                        |

Another important source was coke (8.968 %) and pellets which, when counted together, accounted for 7.925 %. The last important source was beneficiated steel slag (4.689 %). In the case of sinter mixture, it is primarily necessary to monitor the quality of the input ore raw materials and to monitor the content of the negative elements. The quality of ore raw material is currently often in conflict with the effort to reduce costs, which can mean buying materials of lower quality.



Fig. 1 Relative content of zinc in input raw materials



The problem of the reduction of zinc is its repeated entry into the blast furnace process. Zinc is gradually reduced as the charge goes down. Zinc in gaseous form is carried into the upper parts of the blast furnace, where it settles on larger parts and returns into the process again. It can be assumed that the actual reduction and oxidation, evaporation and condensation have a negative effect on costs. This is due to the nature of the reduction processes of zinc oxide, which are endothermic. These processes consume large amount of heat during their course, which affects the thermal conditions, particularly in the central part of the blast furnace. During reverse oxidation and condensation of zinc at the top of the blast furnace, the heat is released again, but it can no longer be effectively used. This is due to the fact that it only heats furnace gas going out of the blast furnace. This fact certainly significantly affects the consumption of fuel, particularly that of coke. Higher consumption naturally has a negative impact on the overall price of the produced metal. Very small part of zinc is carried out of the blast furnace area, when zinc is caught on micro-particles of charge. Generally, the amount of condensed zinc is directly proportional to the material surface. As far as the output products are concerned, the largest amount is concentrated in blast furnace sludge, which has also been demonstrated by the conducted research. The negative characteristic of zinc is based on the fact that it often settles in the colder parts of blast furnaces and enters the lining. The action of this element leads to a gradual deterioration and degradation of the lining, resulting in shorter intervals between the furnace repairs.

## CONCLUSIONS

The effect of zinc in the blast furnace process can be seen at several levels. The most serious consequence of the cycle of zinc in the blast furnace process is its penetration into the lining pores, where it later oxidizes. This causes an increase in volume, which causes the damage to the lining integrity. The removal of zinc from the blast furnace process can be performed especially by its allocation in the blast furnace sludge (fine and coarse), but also by means of blast furnace gas. The higher the temperature of the blast furnace gas, the higher the volume of zinc it contains. Given this fact, a permeable charge column is often created as a result. It is oriented in the axial part of the blast furnace which consists of coke. The conditions of high temperatures and the reduction atmosphere lead to the leakage of the largest quantity of zinc vapours. The entire process is also favourably influenced by the high velocity of flowing gas. The reduction of the content of zinc in the blast furnace lining is very difficult due to the circulation of zinc in the blast furnace areas. The key factor is to monitor and to reduce the content of zinc and other harmful elements in the input raw materials. In the production of sinter mixture, the amount of zinc can be reduced by using larger volume of fuel. The increasing amount of fuel in the sinter mixtures leads to the creation of reducing conditions in the sintered layer, which are suitable for the removal of zinc, but unsuitable for the removal of sulphur. The increased amount of fuel simultaneously negatively affects the costs of the entire process. The amount of negative elements entering the blast furnace process can be primarily reduced by purchasing high-quality ore raw materials. Ore raw materials from Brazil and Australia are very rich in terms of the content of iron and, at the same time, they also contain lower amounts of harmful elements. These ore raw materials are, however, significantly more expensive than, for example, resources from Ukraine or Russia. In addition, the logistics costs associated with the transportation of ore raw materials to their destination will play important role here as well. The manufacturing companies will constantly have to deal with the technological and cost problems, both today and in the future.

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