

Development of stabilization measures aimed at removing zinc with smelting products and accumulating titanium in the hearth of a blast furnace

Yurii Semenov¹  | Viktor Horupakha¹ | Serhii Vashchenko¹ |
Oleksandr Khudyakov¹ | Ievhen Shumelchuk¹ | Kostiantyn Baiul^{1,2}

¹Department of Technological Equipment and Control Systems, Iron and Steel Institute of Z.I. Nekrasov of the National Academy of Sciences of Ukraine, Dnipro, Ukraine

²Department of Machines and Units of Metallurgical Production, Faculty of Machines Design and Environmental Protection, Institute of Industrial and Business Technologies, Ukrainian State University of Science and Technologies, Dnipro, Ukraine

Correspondence

Yurii Semenov, Department of Technological Equipment and Control Systems, Iron and Steel Institute of Z.I. Nekrasov of the National Academy of Sciences of Ukraine, Dnipro, 49107, Ukraine.
Email: yuriy.semenov.isi@gmail.com

Abstract

This paper presents the results of the development of stabilization measures aimed at the removal of zinc with the products of melting and accumulation of titanium in the hearth of a blast furnace. The relevance of the development and use in practice of such measures is due to the unstable fuel and raw materials conditions for the production of cast iron, when their stabilization is a complex and difficult task, as well as the need to extend the campaign of blast furnaces during the overhaul period. The negative effect of zinc oxides on the condition of the blast furnace shaft lining, accompanied by slab formation, and the overconsumption of specific coke consumption, which occurs when zinc circulates in the volume of the blast furnace, require measures to remove zinc from the smelting products. The article proposes such measures, which consist of flushing according to the proposed schedule during the operation of the blast furnace at planned blowing parameters and with the provision of the necessary thermal reserve. In order to lengthen the campaign of a blast furnace, one of the most common methods for protecting the hearth lining is the periodic introduction of titanium-containing materials into the charge of blast furnaces. The entry of titanium oxides into the furnace, as a rule, is ensured by the use of concentrate or specially prepared ilmenite briquettes with a high titanium content as part of the sinter charge, which can be introduced directly into the composition of the blast furnace charge. The article analyzes the experience of using titanium-containing materials as part of a blast furnace charge and formulates measures to intensify skull formation in the hearth.

KEYWORDS

blast furnace, blast furnace control, hearth washings, pulverized coal, thermal state, titanium content in cast iron, zinc content in the charge

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1 | INTRODUCTION

The main problem of blast furnace (BF) production always remains ensuring maximum energy efficiency at a maximum or given level of production. In the current situation in recent years, this problem requires the development of new and improvement of existing solutions, approaches and methods to achieve this goal. The instability of technological conditions in the production of cast iron in Ukraine has reached a critical level in the last decade.^{1–5} It lies, first of all, in the import dependence of the coal industry, which gives rise to the use of coke of variable quality and pulverized fuel from coal of different grades,^{6–9} the transition from technology using natural gas to technology using pulverized coal when using natural gas in small quantities depending on seasonal prices on it, work without injecting fuel additives in especially crisis periods.^{1–5} The use of iron ore raw materials is also extremely unstable, consisting in a changing content of pellets in the BF charge, as well as high variations in the components of the sintering charge when using both secondary resources and when the ratio of sintering ore and iron ore concentrate changes during the production of sinter. Thus, in the existing unstable fuel and raw material conditions for the production of cast iron in Ukraine, when their stabilization is a complex and difficult task, the urgent task is to improve and develop special stabilization measures. Thus, the purpose of this work is to increase the efficiency of BF smelting and extend the BF campaign under variable technological and fuel and raw material conditions through the development and implementation of stabilization measures aimed at removing zinc with smelting products and accumulating titanium in the blast furnace hearth.

2 | MATERIALS AND METHODS

The following approaches and methods were used in the work: literary analysis of previous experience, methods of statistical processing and analysis of data obtained from control tools for technological processes in blast furnace production, industrial testing of developed technical solutions and recommendations. Industrial tests of improved and developed stabilization measures for the removal of zinc with smelting products and the accumulation of titanium in the hearth of blast furnaces were carried out in the blast furnace production conditions of the PrJSC “Kamet-steel” (Kamianske, Dnipropetrovsk Oblast, Ukraine).^{4,5,10,11}

3 | RESULTS AND DISCUSSION

3.1 | Removal of zinc from smelting products

The quality of iron ore raw materials is determined both by the thermos-physical properties of the charge materials, by the level of iron and slag-forming components, and the presence of components in them that worsen their technological properties. These primarily include zinc oxide and alkali metal oxides.^{12,13} Zinc, entering the BF with the charge, is reduced in the lower part of the shaft and steam, volatilizes, and then, as it moves with the BF gasses to the upper part of the BF, it is deposited in the lining and skull; the other part of the zinc is condensed in the charge (this part is involved in the circulation of zinc in the BF), and part is carried out of the BF by the top gasses and captured in the gas cleaning system (Figure 1).^{14–16}

The circulating mass of zinc in the BF has the following forms: metallic zinc, fine particles of zinc oxide formed in the gas flow during the oxidation of zinc vapor, oxide in the form of shells on the surface of pieces of the charge.¹⁷ The study of the processes occurring in the BF during the melting of zinc-containing materials, and the chemical composition of the skull samples taken during BF shutdowns for repairs, show that the skull along the entire height of the BF from the level of the cast iron tapholes to the upper half of the shaft contains a large amount of zinc oxide, which is present in the form of crystals of different sizes and colors.

In conditions of using zinc-containing raw materials for metallurgical enterprises, in order to prevent the formation of deposits in BFs, it was recommended to limit the supply of zinc with charge materials at the level of 0.3 kg/t of cast iron at a top gas temperature of 150–300 °C with a peripheral zone charged with iron-containing materials. In modern conditions, at the BFs of leading metallurgical companies, the supply of zinc with charge materials is limited to the range of 0.15–0.20 kg/t of cast iron. The permissible zinc load accepted at Ukrainian enterprises is no more than 0.50 kg/t. For the raw materials conditions of Ukraine, in whose iron ore deposits zinc is practically absent, it mainly comes with sludge

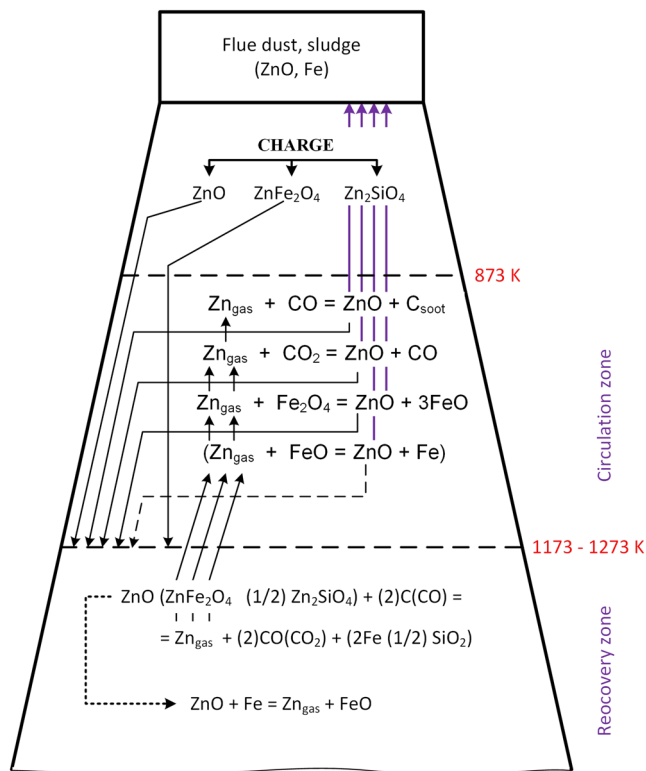


FIGURE 1 Mechanism of recovery and circulation of zinc in a blast furnace.¹⁶

and slag from steelmaking. Despite the low zinc content in the main ore components (background supply), constant monitoring of supply with secondary resources of the sintering charge is necessary.

Based on the foregoing, for the conditions of PrJSC “Kamet-steel” in 2021, the authors of this work recommended constant monitoring of the supply of zinc to the charge of the sintering plant by determining the zinc content in the components of the sinter, which are the main sources of zinc supply (sludge from metallurgical processing, top dust, concentrate of “Central Iron Ore Enrichment Works”) at least once a week. In addition, to control the flow of zinc into the BF charge, it was recommended to monitor the zinc content in the sinter, as the main source of its entry into the blast furnace, at least 2 times a week, with constant: sinter plant charge, consumption of secondary materials and zinc content in them. If deviations are detected (increasingly) and changes in the structure of sinter charge consumption, control of the zinc content in the sinter must be strengthened to daily monitoring of the zinc content. An analysis of the supply of zinc with the charge to the production facility of PrJSC “Kamet-steel” is shown in Figure 2. As follows from the diagram, maximum zinc loads exceeding the permissible (0.5 kg/t) by 2 times or more were noted in June–July 2021, as well as from December 2021. Consequently, removal measures zinc from blast furnaces was an urgent task.

When charge materials containing zinc are used in BF smelting, negative phenomena occur, characterized, as mentioned above, by the deposition of zinc on the lining of the BF shaft, as well as the accumulation of zinc in the charge column.¹⁸ In the working space of the BF, zinc is localized in two circulation circuits: in the dry zone and in the cohesion-hearth zone, while zinc can be in all states of aggregation: vapor, liquid and solid (metal and its oxide).^{19,20} According to data from some plants, it was also found that in case of disturbances in the process of BF, the accumulation of zinc increases by 1.2–1.5 times with a relatively constant supply with the charge.

In the BF, a significant part of the zinc is removed with the BF top gas, while the main part settles in dust collectors and turns into BF top dust, thus forming a closed loop in the metallurgical cycle of the blast furnace – sinter plant. The smallest part of zinc is removed with the products of BF smelting – up to 10% with cast iron and about 5% with slag. The main removal with smelting products occurs when the deposits break, accompanied by cold snaps in the BF.

The latter indicates the connection obtained in September–October 2021 at BF-1 M and BF 12 of PrJSC “Kamet-steel”, the temperature of cast iron and the zinc content in it (Figure 3). Those. The cooling of the furnaces is a consequence of the arrival of unheated materials into the BF that have come off the BF walls and contain zinc deposits, including

Dynamics of the supply of Zn with the blast furnace charge, the consumption of secondary iron ore at the sinter plant and Fe in the entire charge for the period 2020 (on average) - January 2022

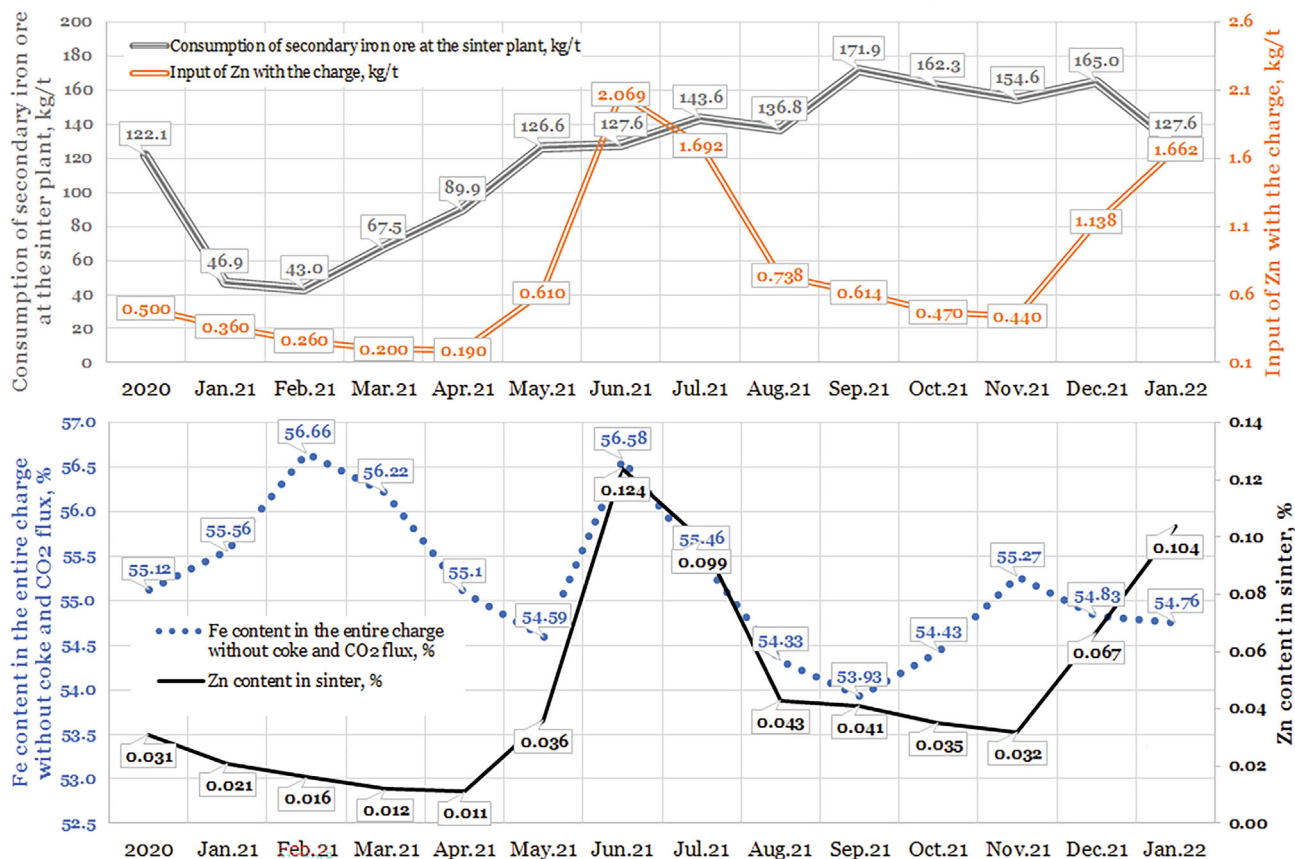


FIGURE 2 Dynamics of changes in the arrival of zinc from the BF charge, consumption of secondary iron ore, zinc content in the sinter of PrJSC "Kamet-steel" in 2020, on average, and in 2021 - beginning of 2022 on a monthly basis.

metallic zinc condensate, which is carried out with the smelting products during sharp local cold snaps in the BF. In addition, as a result of the analysis of changes in the zinc content in cast iron, its increase was noted with reductions in blast consumption (Figure 4).

Thus, it was recommended to periodically use methods for removing zinc from smelting products (steam-blast washing) in blast furnace smelting technology. In August 2021, regulations for these events were developed by the authors of the article and applied as recommendations at the PrJSC "Kamet-steel". It should be noted that the zinc content in cast iron decreases significantly (4–5 times) as the cast iron in the ditch moves away from the cast iron tap hole. This occurs due to the oxidation of zinc metal and the evaporation of its oxide from the lower circulation circuit. Therefore, it is important to take this into account when sampling cast iron for analysis.

When implementing measures to remove zinc (for example, 3 times a month at each BF with zinc consumption exceeding the permissible limit) with smelting products from the BF, it is necessary to monitor the zinc content in cast iron and slag at 3 outlets preceding the activities, during washing time and at the first release after the events. The developed and approved zinc removal program is presented below. In addition, control of the zinc content in BF melting products must be carried out in the event of disturbances in the BF process, sliding of the skull and cold snaps.

Steam-blast flushing is an additional effective way to flush the hearth without the use of special flushing materials. They consist in increasing the amount of oxygen spent on the secondary oxidation of cast iron elements during its passage through the oxidation zone. All blast oxygen is consumed in the BF for the oxidation of coke carbon, hydrocarbon-containing additives and secondary oxidation of cast iron elements. With a decrease in the amount of oxygen spent on the oxidation of additives, its amount for the secondary oxidation of cast iron elements will increase, the concentration of iron oxide and manganese in the slag will increase, which will lead to gasification of carbon from coke waste.

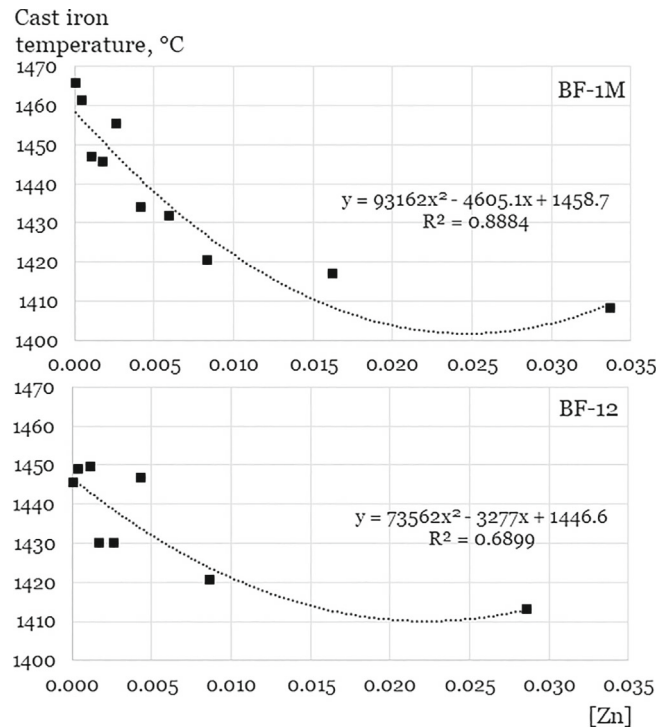


FIGURE 3 Dependence of cast iron temperature on zinc content in cast iron at BF-1 M and BF-12 (each point: 14 releases of smelting products for BF-1 M and 19 releases for BF-12, on average).

The use of steam-blast washings was widely used earlier when using natural gas (NG) in smelting technology.^{21–23} In 2021, their use was aimed at removing zinc from BFs when used on an ongoing basis in high-flow pulverized coal (PC) fuel technology. The use of steam-blowing washings is aimed at removing zinc with the smelting products when it is high in the feed materials and when the permissible load per ton of cast iron is exceeded – 0.5 kg/t of cast iron.

The developed regulations for steam-blast washing provide for:

1. Carrying out washings during the operation of the BF at the planned blast parameters and ensuring a thermal reserve: $[Si] + 0.44 [Mn] \geq 0.7$, where 0.44 is a coefficient that takes into account the amount of heat required to restore two difficult-to-recover elements (the [Si] content must be at least 0.6% and the temperature of the cast iron must be at least 1440 °C).
2. 30 min before the start of production of smelting products, reduce the supply of pulverized coal to 6 t/h, replacing it with an appropriate amount of water vapor to maintain the operating value of the raceway adiabatic flame temperature (RAFT) (Table 1).
3. After the start of production of smelting products, gradually increase the flow rate of pulverized coal with a gradual decrease in the flow rate of water vapor while maintaining the RAFT until the operating flow rate of pulverized coal is restored. The increase in pulverized coal is carried out as follows: at the first stage from 6 to 10 t/h, then every 15 min – increase by 2 t/h until the working consumption of pulverized coal is restored.
4. Monitor the effectiveness of washing by changing the content of alkalis and zinc in cast iron and slag.

The developed regulations were included in the technological instructions for BF production of PrJSC “Kamet-steel” for operating conditions of BF with a high supply of zinc with charge materials.

3.2 | Accumulation of titanium in a blast furnace hearth

To form a protective skull in the lower part of the blast furnace (metal receiver-shoulders), it is necessary to create conditions for the crystallization of melts in places of increased heat transfer with the formation of a “metal lattice” of a

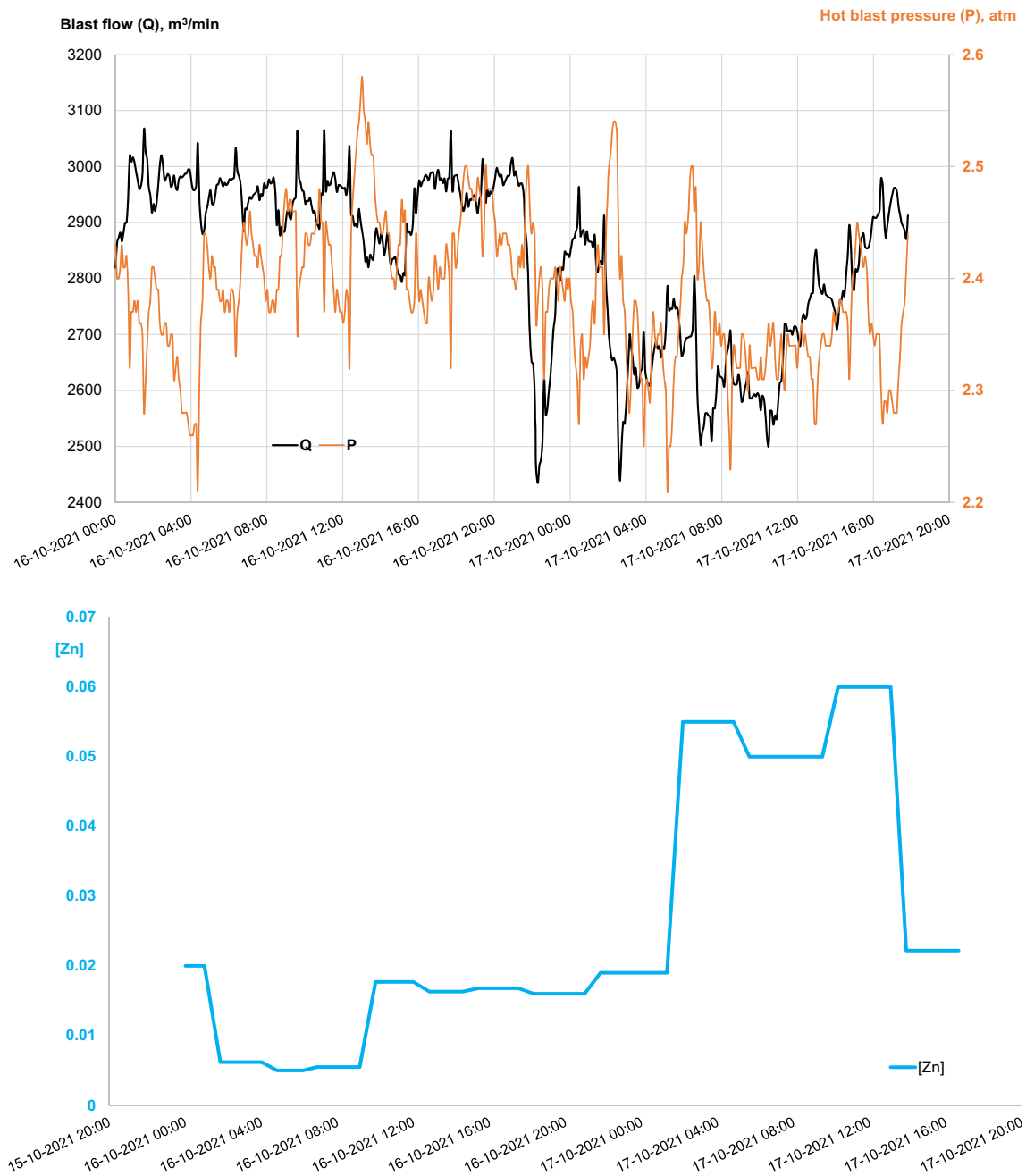


FIGURE 4 Changes in flow rate, blast pressure and zinc content in cast iron at BF-1 M PrJSC “Kamet-steel”.

dendritic structure that has high thermal conductivity, refractoriness and resistance to dissolution in the melt, that is. To create these conditions, it is necessary to have refractory centers of crystal nucleation in the cast iron and coagulation of the cast iron around them, followed by solidification.

One of the most common materials for protecting the furnace lining during its partial combustion is the periodic introduction of titanium-containing materials into the blast furnace charge. The supply of titanium oxides to the furnace is usually ensured by using ilmenite concentrate or specially prepared ilmenite briquettes with a high titanium content in the sinter charge, which can be added directly to the BF charge.^{24–26} It is known from the literature that to protect the hearth lining, it is necessary to introduce 4.5–10 kg/t of TiO_2 cast iron into the BF (to ensure the [Ti] content in cast iron is 0.08%–0.25%).

That is, part of the titanium oxides is not reduced and remains in the final slag in the form of TiO_2 and does not participate in the formation of the skull, since it has low density and thermal conductivity. Another part of the titanium

TABLE 1 Technological parameters of melting at the basic operating mode of the BF and during the period of steam-blast washing.

BF operating parameters	BF operating mode	Steam-blast washing
PCI consumption, t/h	15	6
Natural air humidity, t/m ³	12	12
Steam consumption, t/h	0.00	4.45
Hot blast temperature, °C	1050	1050
Oxygen content in cold blast, %	23	23
Blast consumption, m ³ /min	2960	2960
PCI indicators		
Volatile substances	21	21
Carbon	0.84	0.84
Blast humidity, g/m ³	12	37
BF capacity, t/day	2700	2700
Specific PCI consumption, kg/t	133	53
RAFT, °C	2103	2103
Duration of work period (depending on the effectiveness of the method), hours	22 (20)	2 (4)

Note: The differing parameters of the two modes are shown in gray.

oxides, with sufficient heat, is reduced to TiO, which has a significantly higher density and precipitates from the slag onto the cast iron. Further, under the influence of temperature and time in the reducing environment of carbon-saturated coke, titanium carbides are formed, which have a melting temperature of more than 3000 °C, accumulate in the BF, and are protruding centers for the formation of metal crystals.

To achieve an increase in the transition of titanium into cast iron from slag, the following basic requirements must be met: the presence of high temperatures and free carbon in the reducing environment, reduced slag yield and the absence of difficult-to-reduce oxides in the BF.

The limitation of titanium content in cast iron at a level not exceeding 0.25% is due to the production experience of technologists operating BFs, which require preventive support for the hearth and flank, since the viscosity of liquid metal with a high titanium content (over 0.25%) increases significantly and complicates the process of processing smelting products, especially during the period of shutdowns of BFs for preventive repairs, despite the fact that BF slags, having a TiO₂ content of 0.25%–2.75%, have a viscosity characteristic of stable BFs slags (0.20–0.50 Pa·s) (Figure 5). Increasing the TiO₂ content in the slag to 2.75% reduces the melting onset temperature of the melt by 100 °C, although the viscosity increases from 0.23 to 0.35 Pa·s. At the same time, as shown in Figure 5, the increase in viscosity occurs at the initial stage of using titanium-containing materials and has a greater increase (up to 0.35 Pa·s) when using pulverized coal fuel (PC ≈ 75 kg/t) than when injecting natural gas (NG ≈ 70 m³/t) – up to 0.33 Pa·s.

The [Ti] content in cast iron at the level of 0.08% can rather be considered a preventive use of titanium additives. According to this, the most rational level of titanium content in cast iron to maintain effective “freezing” of the protective skull on the damaged lining of the hearth and the bottom of a BF is considered to be 0.15%–0.25%.

The high cost of raw materials containing titanium obliges metallurgists to approach the selection of this type of raw material with economical use and look for ways to increase the efficiency of its use. Therefore, one of the ways to reduce the amount of materials containing titanium is to organize BF smelting, which ensures maximum conversion of titanium into cast iron.

Analysis of the smelting products of BFs that melt iron ore materials with various types of titanium compounds in the sintering and BF charge shows that the titanium content in cast iron mainly depends on both the total supply of titanium with the charge and on the distribution of titanium between the cast iron and slag in depending on the silicon content in cast iron. The typical distribution for various plants is shown in Figure 6, from which it can be seen that the [Ti] content is directly proportional to the total supply of titanium with the BF charge (naturally alloyed charge) and the silicon content in the cast iron. Moreover, it should be noted that the ratio (TiO₂)/[Ti] decreases with a higher silicon content in cast iron (the transition of titanium to cast iron is more efficient). The operation of BFs with a silicon content of more than 1.0%

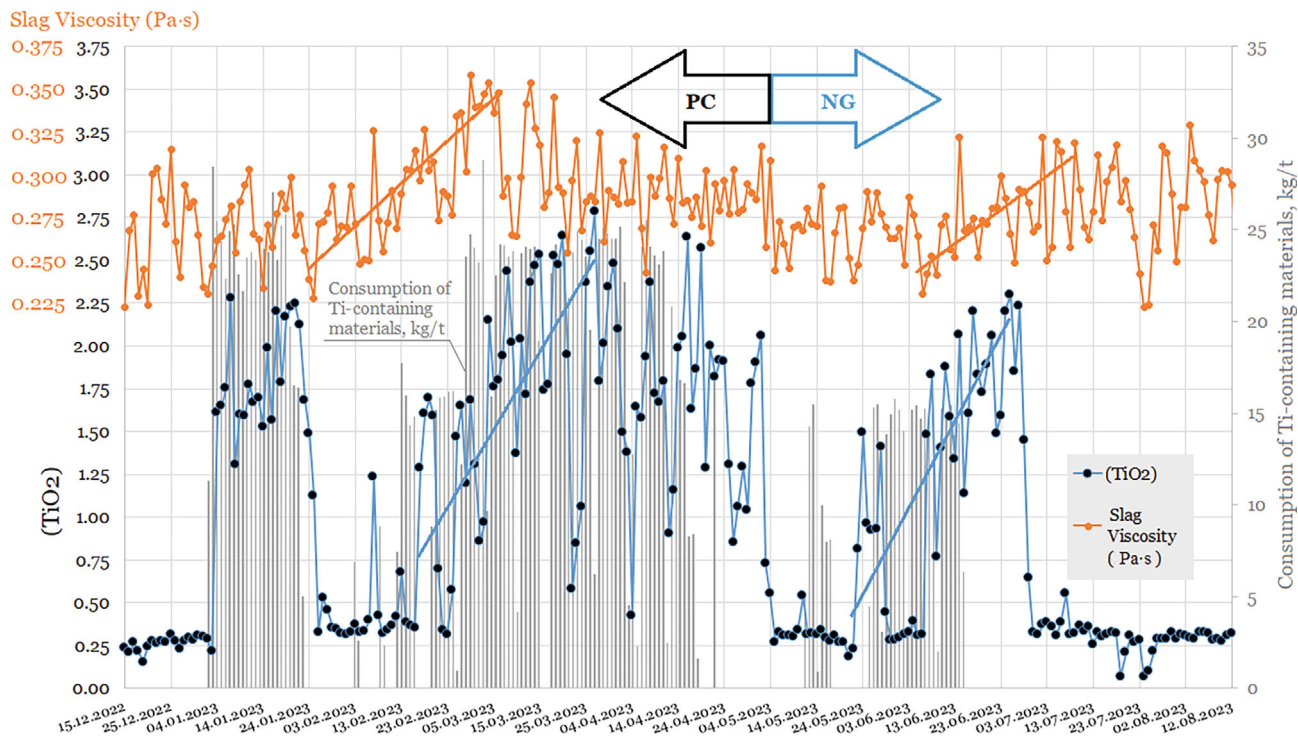


FIGURE 5 Changes in the viscosity of the slag melt, the content of TiO_2 in it and the specific consumption of titanium-containing materials using the example of the operation of BF-1 M of PrJSC “Kamet-steel” in 2023 when injecting separately PC and NG.

is irrational, and a sufficient level of transition of titanium into cast iron and the formation of carbides occurs when the silicon content in cast iron is 0.7%–0.9%.

Selective monitoring of titanium content in cast iron and slag at Ukrainian enterprises (Figure 7) shows that, regardless of the source of titanium, its distribution between cast iron and slag $(\text{TiO}_2)/[\text{Ti}]$ correlates with the patterns of distribution of LTi at enterprises that constantly monitor and melt iron ore materials containing naturally alloyed titanium oxides (Figure 6).

From the above it follows that bringing the titanium content in cast iron to an acceptable level, without irrational waste of titanium-containing materials in the charge, can be achieved by redistributing titanium between cast iron and slag by increasing heating during the period of use of titanium-containing materials in the charge.

Analysis of smelting products from BF of Ukraine, melting iron ore materials with traces of titanium in the BF charge, as well as foreign enterprises melting iron ore raw materials naturally alloyed with titanium oxides, ensuring a content in the charge of 0.24%–0.32% TiO_2 (4.2–8.0 kg/t of cast iron or 0.08%–0.25% [Ti] in cast iron), shows that regardless of the source of titanium supply, the [Ti] content is directly proportional to the silicon content in cast iron, regardless of the level of its supply. A high level of supply of titanium oxides with charge materials is a necessary, but not sufficient condition for the formation of a protective skull in the BF hearth. Therefore, it can be assumed that without the use of special techniques, the efficiency of forming a protective titanium skull in a BF, even with a titanium content in cast iron of 0.15%–0.20%, is not high enough.

Based on practical and experimental data, we can conclude that in order to form a protective titanium skull in the BF hearth, it is advisable to use a mixture of iron ore materials (base 0.85–1.15 units) and agglomerated material containing titanium (preferably with a high titanium content), which ensures the supply of titanium at a level of at least 4.5 kg per ton of cast iron.

At the same time, the conditions that enhance the process of skull formation in the BF hearth include the temperature regime of BF smelting and the nature of the formation of the iron ore portion. The greatest efficiency in reducing the temperature of the BF flange (due to the formation of a protective titanium skull), according to Iron and Steel Institute of Z.I. Nekrasov studies and literary sources, is achieved during a technological shutdown of the BF for a third-class overhaul.

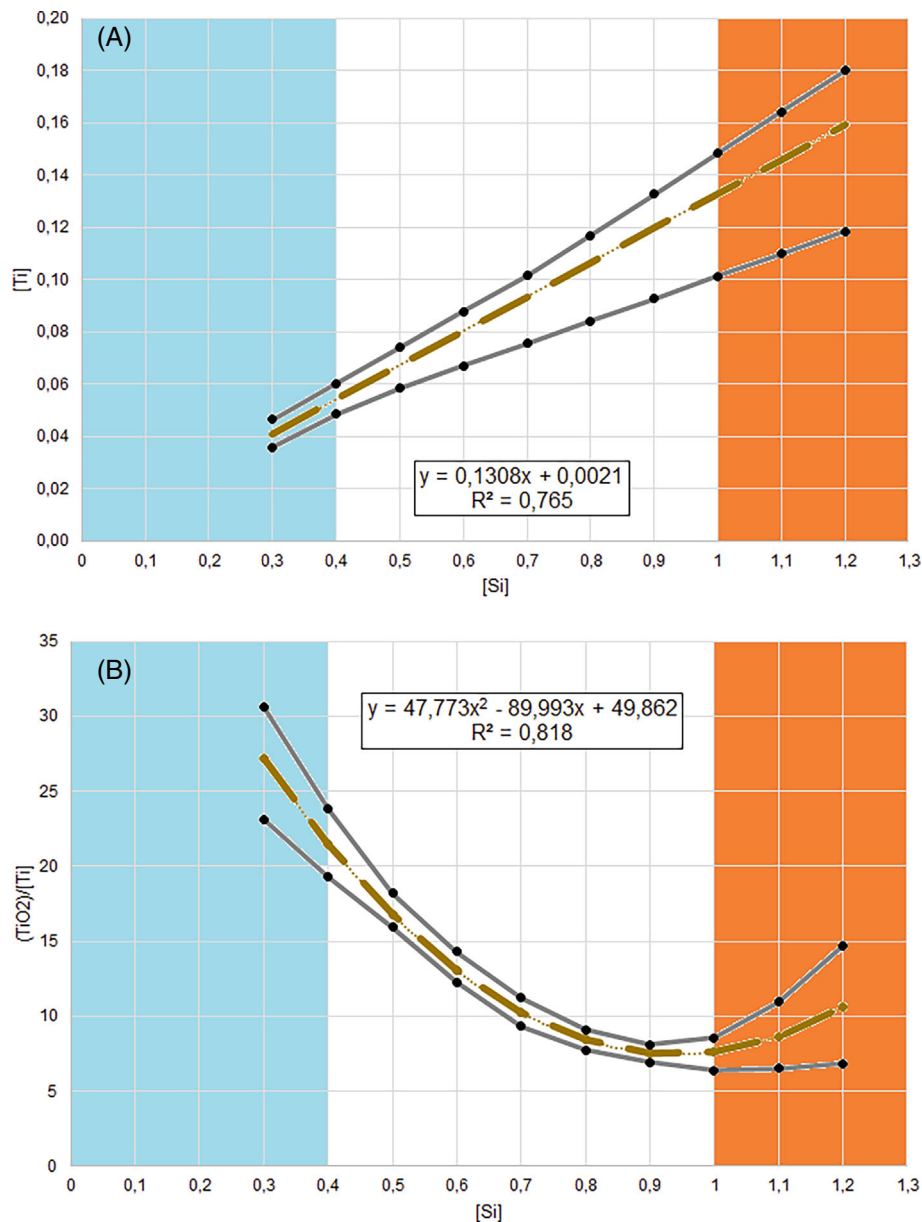


FIGURE 6 Generalized dependence of the titanium content in cast iron [Ti] on the silicon content [Si] in it (A) and the distribution of titanium between cast iron and slag $(TiO_2)/[Ti]$ depending on the silicon content [Si] in cast iron (B) at melting of natural titanium-alloyed charge for a long time.

Three days before the shutdown, a mixture of iron ore materials with a basicity of 0.9–1.2 units and additives containing titanium is charged into the peripheral zone of the BF, ensuring a total supply of titanium at the level of 4.5–6.5 kg/t of cast iron. During this period, it is advisable to maintain the silicon content in cast iron at the level of 0.85%–0.95%. Immediately six to 8 h before stopping the BF, it is advisable to remove the material containing titanium and providing the required level of titanium in the charge from the composition of the charge materials. In accordance with the coke consumption standards adopted at Ukrainian enterprises, an increase in silicon content for every 0.1% corresponds to an increase in specific coke consumption by 1.2%.^{27,28} The use of titanium-containing materials with a corresponding increase in the silicon content in cast iron from the base (most commonly used) value of 0.5%–0.6% will lead to excess consumption of coke by 4.2% (during periods of use of titanium-containing materials), however, taking into account the reduction of unscheduled downtime, extension of the BF campaign, increase the duration of the overhaul periods of the BF and the production volumes of cast iron, this measure is quite justified.

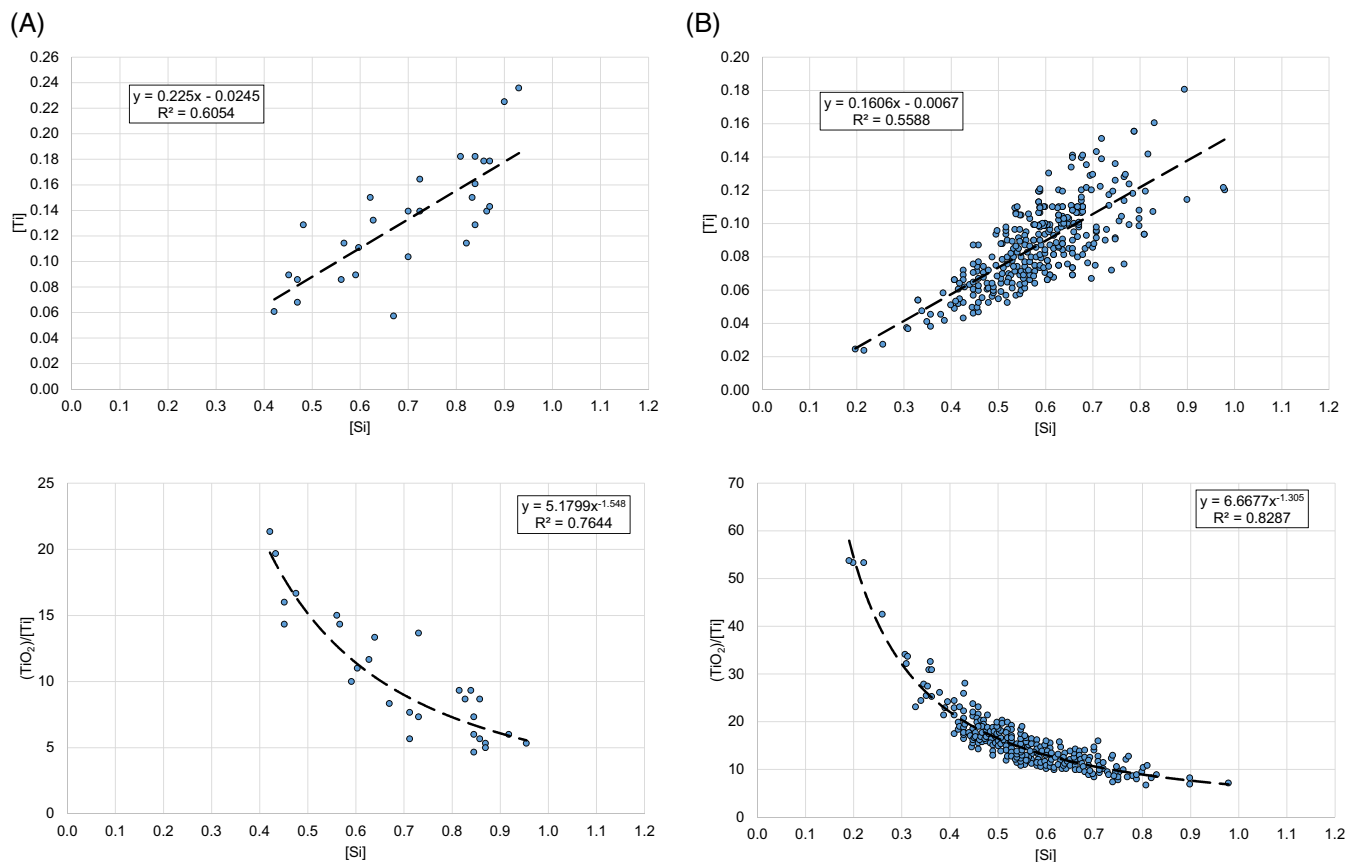


FIGURE 7 Dependence of the titanium content in cast iron [Ti] on the silicon content [Si], as well as a characteristic change in the distribution of titanium between cast iron and slag (TiO₂)/[Ti] depending on the silicon content [Si] in cast iron when titanium-containing materials are used in the charge (load up to 4.5–6.5 kg/t of cast iron) and with periodic monitoring of the titanium content in the smelting products (A), compared with the melting of a charge naturally alloyed with titanium and with constant monitoring of the titanium content in the smelting products (B).

An increase in the consumption of titanium-containing charge materials does not lead to a qualitative change in the transition of Ti to cast iron, therefore, for a rational and more complete process of scull formation, it is necessary to withstand increased heating of cast iron. With insufficient heating, the TiO₂ content in the slag increases, causing an increase in its viscosity and difficulty in processing the release of smelting products. Also, with insufficient heating and the transition of Ti into cast iron, the efficiency of using ilmenite raw materials decreases, regardless of the background level and its consumption in the BF charge.

The effectiveness of using titanium-containing materials at the level of 0.2 tons per supply on an ongoing basis is confirmed by the reduction in thermal loads on the coolers of the hearth, upper and lower flange BF-1 M of PrJSC “Kamet-steel” in October 2022 (Figure 8).

Thus, to intensify scull formation in the forge it is necessary:

1. Ensure the supply of titanium to the BF at a level of at least 4.5 kg per ton of cast iron;
2. Ensure that a mixture of iron ore materials with a total basicity of 0.85–1.15 units and a titanium-containing additive is charged into the peripheral zone of the top in an amount that ensures the titanium content in cast iron at the level of 0.15%–0.25% and which corresponds to the content (TiO₂) = 1.15%–1.30% in slag at $([Si] + 0.44 \bullet [Mn]) = 0.7\%–0.8\%$;
3. Limit the entry of iron ore materials and additives containing titanium into the central zone of the BF;
4. When using titanium-containing materials, before stopping the process, ensure that the titanium-containing additive is removed 6–8 h before stopping the process.^{29,30}

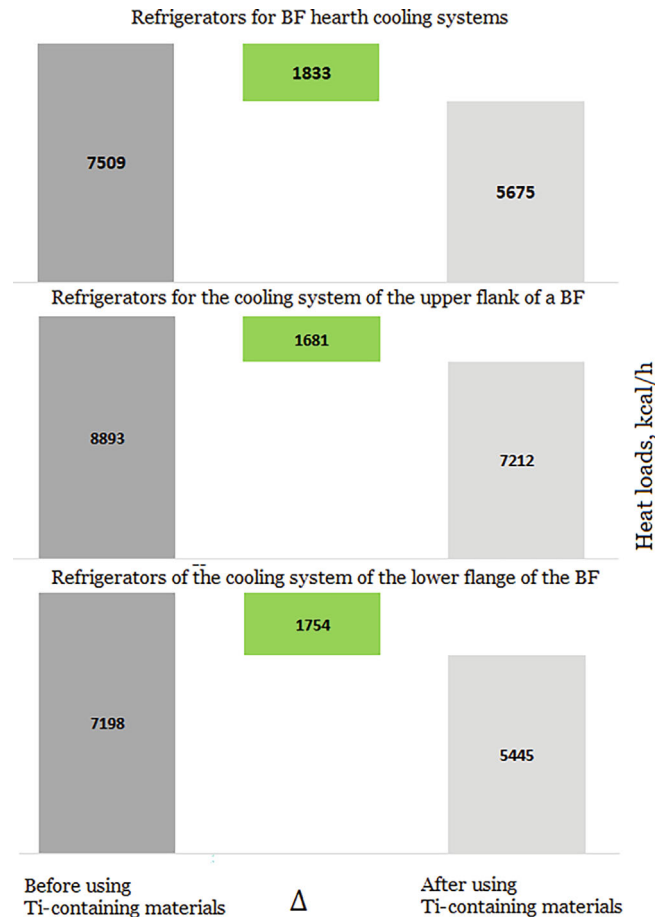


FIGURE 8 Change in thermal loads on the coolers of the hearth, upper and lower hearth BF-1 M of PrJSC “Kamet-steel” in October 2022 before and after the use of titanium-containing materials at the level of 0.2 tons per feed on an ongoing basis.

4 | CONCLUSION

The results of the development of stabilization measures aimed at removing zinc with smelting products and accumulating titanium in the blast furnace hearth are presented. The negative impact of zinc oxides on the condition of the blast furnace shaft lining, accompanied by the formation of deposits and excessive specific coke consumption, which occurs when zinc circulates in the blast furnace volume, requires measures to remove zinc with the smelting products. Measures are proposed, consisting of carrying out washings according to the proposed regulations during the operation of the blast furnace at the planned blast parameters and ensuring the necessary thermal reserve. In order to prolong the blast furnace campaign, one of the most common methods of protecting the lining of the hearth and flange is the periodic introduction of titanium-containing materials into the blast furnace charge. The supply of titanium oxides to the furnace is usually ensured by using ilmenite concentrate or specially prepared ilmenite briquettes with a high titanium content as part of the sinter charge, which can be added directly to the blast furnace charge. The experience of using titanium-containing materials as part of a blast furnace charge has been analyzed and measures have been formulated to intensify skull formation in the furnace.

AUTHOR CONTRIBUTIONS

Yurii Semenov: Conceptualization; methodology; data curation; writing – review and editing; writing – original draft; investigation. **Viktor Horupakha:** Investigation; methodology; validation; formal analysis; writing – original draft. **Serhii Vashchenko:** Formal analysis; visualization; investigation. **Oleksandr Khudyakov:** Formal analysis; validation; investigation. **Ievhen Shumelchik:** Formal analysis; visualization; investigation. **Kostiantyn Baiul:** Formal analysis; validation.

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CONFLICT OF INTEREST STATEMENT

Authors act as consultants for company PrJSC “Kamet-steel” mentioned in the article. Authors have no conflict of interest relevant to this article.

PEER REVIEW

The peer review history for this article is available at <https://www.webofscience.com/api/gateway/wos/peer-review/10.1002/eng2.12881>.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Yurii Semenov  <https://orcid.org/0000-0003-2299-5742>

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