# Reducing the carbonitride formation risk with increasing titanium dioxide content in the blast furnaces charge of JSC EVRAZ NTMK

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**Abstract.** Analyse of the blast furnace charge chemical content changing with the JSC EVRAZ NTMK raw materials base alteration was carried out. That expected change would result in $TiO_2$ content increasing in the blast furnace slags. That increasing would lead to carbonitride formation in the upper levels of the blast furnace, which reduce technical parameters of the blast furnace operation by reducing effective volume of the furnace and derange regular charge moving. Possible ways of that problem solving was shown. It was proposed the complex technology, that affect 3 technological stages: agglomeration, blast furnace process and out-of-furnace treatment of steel. Converting of $TiO_2$ into $CaO \cdot TiO_2$ allows to delay carbonitride formation due to increasing required temperature for that process. In that case, carbonitride formation would move to the tuyere zone of blast furnace, where it increase lining durability. The proposed technology was industrially tested, and the main idea was proved. Few problems were found during industrial tests, but theoretical solving of them was proposed.

## 1. Introduction

At present, JSC EVRAZ NTMK processes titanomagnetites of the Gusevogorskoe field. In the near future it is planned to develop the actual Kachkanarskoe field (AKF) with processing of its ores [1].

In table 1, according to [1], a comparative chemical composition of the initial ore and concentrates of vanadium-containing deposits of the Urals is given.

**Table 1.** The material chemical composition of some Ural vanadium-containing deposits.

| Field | Content, mass. % | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | Ore | | | Concentrate | | |
| | Fe | $V_2O_5$ | $TiO_2$ | Fe | $V_2O_5$ | $TiO_2$ |
| Gusevogorskoe | 16.6 | 0.13 | 1.23 | 61.5 | 0.59 | 2.50 |
| Kachkanarskoe | 16.6 | 0.14 | 1.24 | 63.0 | 0.60 | 3.60 |
| Medvedevskoe | 24.0 | 0.25 | 7.00 | 60.0 | 0.7–0.8 | 10.15 |
| Kopanskoe | 36.7 | 0.45 | 9.90 | 54.60 | 0.7–0.9 | 8.13 |

In accordance with the table, after starting developing of the Kachkanarskoe field, the $TiO_2$ content in concentrate will increase from 2.5 to 3.6 mass. %. According to the same source, the IMET UB RAS carried out of blast furnace smelting calculations with using of Gusevogorskoe and Kachkanarskoe fields agglomerated concentrates of by the technology of JSC EVRAZ NTMK. The Results are summarized in figure 1 and table 2. According to the presented data, the $TiO_2$ content in the slag will increase from 10.53 % to 14.92 %.
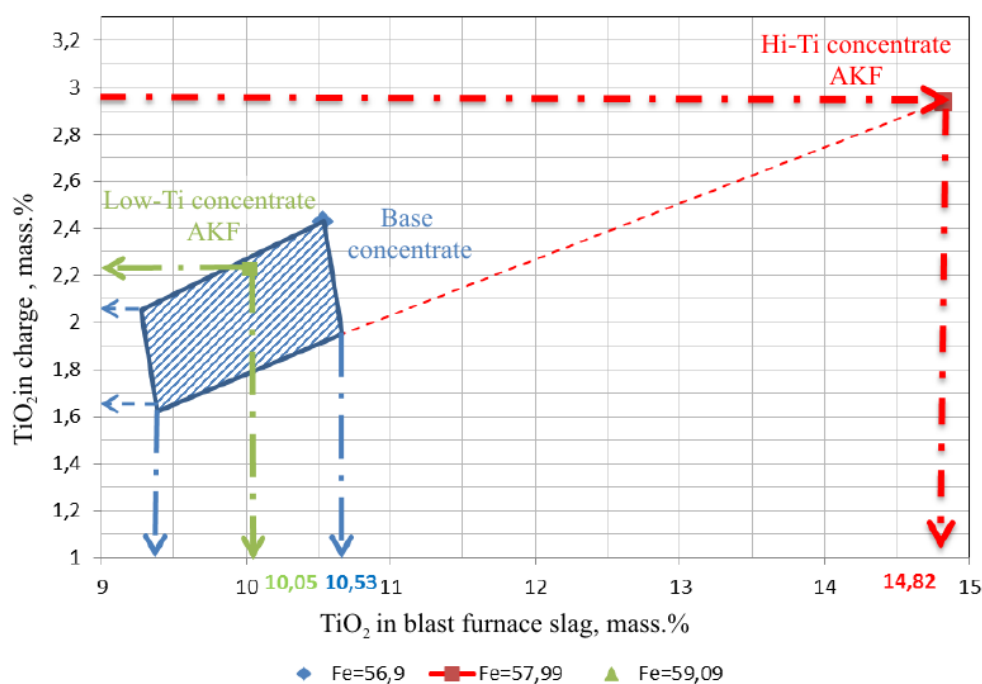


**Figure 1.** Effect of $TiO_2$ content in a blast furnace charge on $TiO_2$ content in slag.

**Table 2.** Effect of TiO2 content in a blast furnace charge on TiO2 content in slag.

| Parameter<br>Blast furnace charge | Base concentrate<br>(Gusevogor skoe field) | Hi-Ti concentrate<br>(AKF, main pit) | Low-Ti concentrate<br>(AKF, west pit) |
|---|---|---|---|
| Agglomerate, % | 38.3 | 38.3 | 38.3 |
| Pellets, % | 52.3 | 52.3 | 52.3 |
| Iron-flux, % | 9.4 | 9.4 | 9.4 |
| $Fe_{all}$, % | 56.9 | 57.99 | 59.09 |
| $TiO_2$, % | 2.43 | 2.94 | 2.25 |
| Blast furnace slag | | | |
| $TiO_2$, % | 10.53 | 14.92 | 10.05 |

Table 3 shows the comparative chemical composition of titanic blast furnace slag of JSC EVRAZ NTMK according to 2016 data and the forecast for the transition to high-titanium raw materials.

Due to the increase in the titanium dioxide content in the slag, the titanium carbonitride formation risk in a blast furnace increases [2]. The technology of titanomagnetite processing with vanadium extraction operating at EVRAZ-NTMK JSC is unique. It is implemented only in this enterprise in Russia. At present, the problem of preventing carbonitride formation is solved by introducing a significant amount of fluorite into the blast furnace slag and monitoring the blast furnace lining thickness [3, 4]. Such a path requires constant monitoring of the lining condition.

**Table 3.** The chemical composition of blast furnace slag.

| Technology variant | Content, mass. % | | | | | | | | Basicity* |
|---|---|---|---|---|---|---|---|---|---|
| | CaO | SiO$_2$ | Al$_2$O$_3$ | FeO | TiO$_2$ | MgO | MnO | V$_2$O$_5$ | |
| Regular technology | 32.75 | 27.06 | 15.12 | 0.63 | 10.37 | 13.72 | 0.6 | 0.24 | 1.21 |
| Forecasting technology | 31.60 | 26.70 | 14.70 | 0.60 | 14.40 | 11.40 | 0.40 | 0.16 | 1.18 |

* – CaO/SiO$_2$

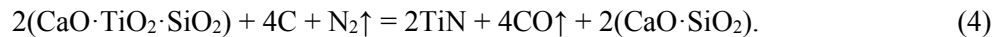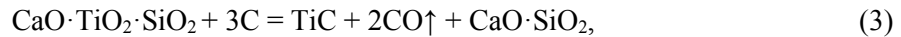## 2. Phase content and thermodynamic calculations

We propose a technical solution to prevent carbonitride formation by adjusting the slag phase composition. In the CaO-SiO$_2$-TiO$_2$ diagram, shown in Figure 2, with Al$_2$O$_3$ content of about 20 %, the JSC EVRAZ-NTMK blast furnace slags are currently located in region A. With the titanium dioxide increasing, they will shift to region B.
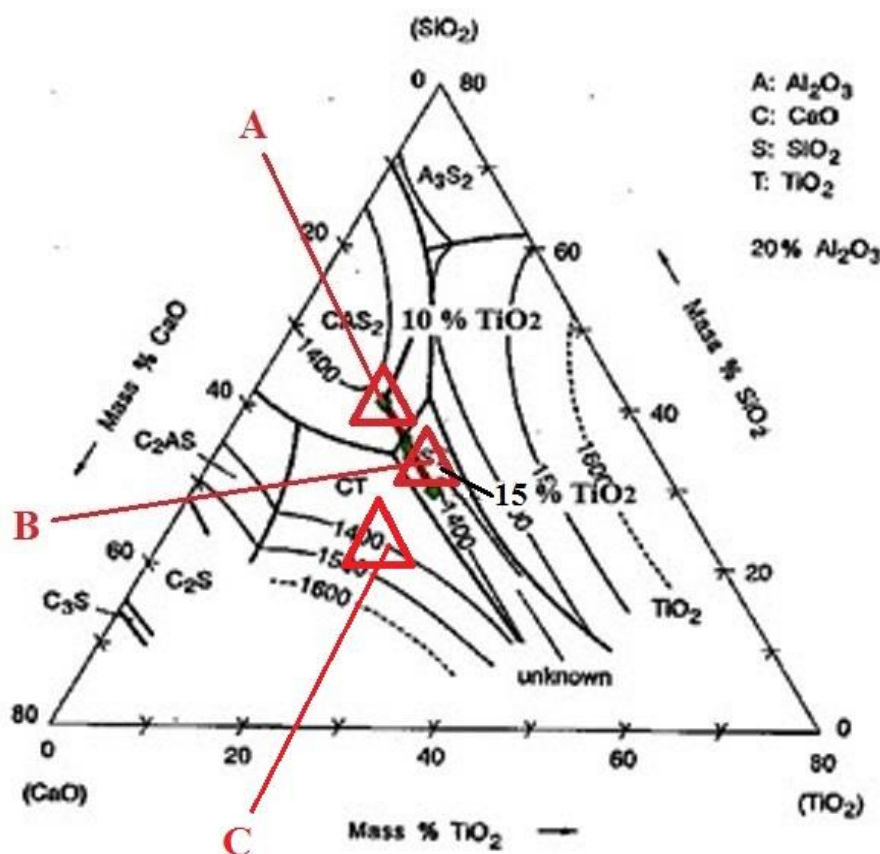


**Figure 2.** Diagram of CaO-SiO$_2$-TiO$_2$.

In region A, the slag phase composition is represented by anorthite (CaO·Al$_2$O$_3$·2SiO$_2$) and titanium dioxide in the form of TiO$_2$. From such titanium, carbonitride formation proceeds by reactions (1) and (2).

$$TiO_2 + 3C = TiC + 2CO\uparrow, \qquad (1)$$

$$2TiO_2 + 4C + N_2\uparrow = 2TiN + 4CO\uparrow. \qquad (2)$$

Thermodynamic calculations indicate that reaction (1) is possible from 1300 °C, and reaction (2) – from 1200 °C. When slag compositions are moved to region B, titanium dioxide is converted to sphene ($CaO \cdot TiO_2 \cdot SiO_2$). The titanium carbonitride formation becomes possible by reactions (3) and (4).

$$CaO \cdot TiO_2 \cdot SiO_2 + 3C = TiC + 2CO\uparrow + CaO \cdot SiO_2, \tag{3}$$

$$2(CaO \cdot TiO_2 \cdot SiO_2) + 4C + N_2\uparrow = 2TiN + 4CO\uparrow + 2(CaO \cdot SiO_2). \tag{4}$$

In this case, the risk of carbonitride formation remains, since according to thermodynamic calculations, the start the titanium carbo-nitrides formation by reactions (3) and (4) is shifted to a higher temperature region by only 100 °C (reaction (3) – 1400 °C, and reaction (4) – 1300 °C).

## 3. Proposed technology

To reduce that risk, it is proposed to convert titanium dioxide to perovskite ($CaO \cdot TiO_2$) at the agglomeration stage. In that case, carbonitride formation will proceed according to the reactions (5) and (6)

$$CaO \cdot TiO_2 + 3C = CaO + TiC + 2CO\uparrow, \tag{5}$$

$$2CaO \cdot TiO_2 + 4C + N2\uparrow = 2TiN + 2CaO + 4CO\uparrow. \tag{6}$$

Reactions (5) and (6) are possible only above 1600 °C, i.e. carbonitride formation will shift to the tuyere zone of blast furnace. Here it could provide a positive effect by formation of a refractory slag coating (skull).

At the same time, the basicity of blast furnace slags will increase, and they will shift to the region of perovskite existence (region C). An increase in the slag basicity will lead to an increase in their melting point and heterogeneity, which can have a negative effect on the domain process.

According to [5], blast furnace slags should contain manganese oxides, which destroy titanium carbides by reaction (7).

$$2MnO + TiC = 2Mn + TiO + CO\uparrow. \tag{7}$$

In the same work, it is noted that the MnO effectiveness in the titanium carbide formation prevention can be improved by reducing the slag viscosity. That could be achieved by addition of liquifying additives into the mixture. For example, it could be a boron-containing materials.

## 4. Technology verification

Our group in cooperation with EVRAZ-NTMK JSC conducted tests to replace limestone with slags of ladle-furnace steel processing (LF-slags) during agglomeration [6]. This replacement provided:
- increase the specific productivity of agglomeration machines by 4.3 %;
- increase the strength index B $_{+5 \, mm}$ – by 0.3 %;
- reduce the consumption of coke breeze by 10 %.

However, these tests revealed the disadvantages of this method. LF-slags contain a significant amount of metal shots and large metal scraps. That hampers infusion of LF-slags into the agglomerate.

Our group have developed methods for the LF-slags complex stabilization [7]. In the case of using boron additives, that methods can not only stabilize the slag, but also reduce its viscosity. That will result in reducing of metal shots in LF slags. It is proposed to use processed slag during agglomeration. Along with the titanium dioxide conversion to perovskite, that approach will reduce the slag viscosity and heterogeneity.

## 5. Conclusion

The proposed technology affects three processes of JSC EVRAZ-NTMK: ladle-furnace steel treatment, agglomeration and blast furnace process; and allows to reduce the risk of carbonitride formation during the plant raw material base changing to high-titanium raw materials.

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