ECONOMICAL EFFECTS OF THE METALLURGICAL USE OF SYNTHETIC TIO_2 PRODUCTS IN ORDER TO PROLONG THE CAMPAIGN OF A BF[1]

Walter Hartig[2]
Djamschi Amirzadeh-Asl[3]
Dieter Fünders[4]

Abstract

The use of titanium bearing materials is well known for the protection of the hearth against premature wear.The industrial application and different ways of input and effectiveness of lump ilmenite and synthetic TiO_2 (RUTILIT) will be described. There exist typical differences in the thermodynamically and kinetically behavior of the natural ilmenite-system and the synthetic RUTILIT-system. The result of this topics will be combined with the evaluation of economic conditions of the different TiO_2-systems, e.g. the market-prices of different product-systems, the specifical handling costs concerning e.g. the special input technologies, the metallurgical effectiv in the blast furnaces, the prolongation of the life time of the hearth of blast furnaces, and also the metallurgical effect on liquid iron and the slag by the added titanium containing material. The comparison of the industrial results of different applications shows the advantages of the use of the synthetic TiO_2 by injection technology. This paper is a common report from AG der Dillinger Hüttenwerke (ROGESA), Dillingen (Germany) and SACHTLEBEN CHEMIE GmbH, Duisburg (Germany) and shows the result of using titanium containing products in the blast furnace no. 4 and 5.

Key words: Blast furnace; Titanium dioxide; Hearth protection; Repair; Rutilit.

---

[1] *Technical contribution to the 43rd Ironmaking and Raw Materials Seminar, 12h Brazilian Symposium on Iron Ore and 1st Brazilian Symposium on Agglomeration of Iron Ore, September 1st to 4th, 2013, Belo Horizonte, MG, Brazil*

[2] *General Manager Ironmaking ROGESA, walter.hartig@dillinger.biz*

[3] *Metallurgy Engineering, Technical Director ES of Sachtleben Chemie, ABM member, Duisburg, Germany; d.amirzadeh-asl@sachtleben.de.*

[4] *Metallurgy Engineering, GSR, ABM member, Moers, Germany; synthetische.rohstoffe@web.de.*

1 INTRODUCTION

The hearth is the most severely exposed zone in the blast furnace. As a result of chemical attack, dissolution of the carbon bricks, flows of slag and hot metals, and thermal stresses(1) and generally determines the length of a furnace campaign. Therefore, methods which can lengthen the service life of the hearth and BF walls without interrupt the production are of significant economic and technical interest.

The current technological practice for reduction of wear and repair of damaged areas in the hearth is the input of ilmenite, a natural source of titanium,(1) which generates chemically and thermally stable titanium carbonitrides (Ti(C,N). These compounds accumulate primarily at the damaged points and have the effect of a so – called „hot repair“.(4,5)

In addition, TiO_2 contained in the titanium sources increases the viscosity of the slag and the hot metal thanks to the formation of intermediate oxides and Ti(C,N) with a favourable effect on temperature distribution in the hearth.(2,5) The addition of TiO_2 – containing material can also reduce the nitrogen content of the hot metal.(6)

Injection of titanium – containing materials via the tuyeres is the best solution, since these titanium sources are systematically transported to the target areas with no noticeable delay , thanks to the flows prevailing in the hearth. For this application, ilmenite has to be used in the form of ilmenite – sand. Due to the highly abrasive action of ilmenite sand, however, this method is suitable as a temporary measure in acute cases of damage only.(3,7,8) For this reason, long – term charging of titanium sources is accomplished via the furnace throat as a component of the burden. Lump ilmenite, or sometimes titanium-containing pellets, are generally used for this purpose.(5,7) In this case, the titanium has to travel the whole length of the blast furnace shaft and therefore has a delayed reaction. This method has been applied as a preventative measure since the 1960’s.

One disadvantage of this technique is the uniform distribution of the titanium throughout the cross – section of the blast furnace, despite the fact that it is needed only in the wall zones of the hearth. This necessitates higher input quantities and has a detrimental effect on slag quality.(3) In addition, feeding of titanium – bearing materials via the furnace throat may also cause obstructive depositions in the shaft and disrupt blast furnace operation.

Synthetical produced titanium sources in the form of the TiO_2 containing products Rutilit (Rutilit F 50, Rutilit NF etc.) which also offer an alternative in economic terms, have since many years become available on an industrial scale for many years. They differ from natural titanium sources in their significantly greater fineness, have scarcely any abrasive action, and therefore permit continuous feed via the tuyeres. Conditions for use in the blast furnace are therefore favorable, since these titanium sources can be systematically fed to the areas of damage in the hearth.

Since 2007 a new development of coinjection of synthetic TiO_2 with PCI was made in the blast furnaces in Dillingen (Germany) in close collaboration with Rogesa and Sachtleben Chemie GmbH.

1.1 BF Operator's Needs

In addition to the higher-level concerns of prolongation of the BF campaign, constant operation at production rates ranging up to the possible maximum is desirable, a target which can be viewed in conjunction with the reduction of maintenance costs. In addition, it is, of course, necessary to adhere to the hot metal and slag quality specifications.

2 MECHANISM OF CHEMICAL REACTIONS OF TIO_2 IN METALLURGICAL SYSTEMS

In order to determine the effect of the various titanium bearing materials on HM, slag and carbon bricks under the prevailing condition in the BF hearth, crucible test were submitted in Figure 1.

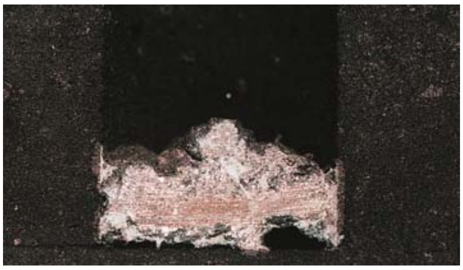

Figure 1. Rutilit test. Crucible containing Slag, Fe and fine particulate TiO_2 containing material.

Figure 2. Lump ilmenite test. Crucible containing Slag, Fe and lump ilmenite.

The mechanism of the formation of Ti(C,N) wear developed as follows:(8)
Metallic iron is required as the catalyst for conversion of TiO2 to Ti(C,N). By addition of TiO_2 into a metallurgical system TiO2 will be dissolved in the slag phase and reduced to metallic Ti by Si or carbon at the phase-interface HM and slag.

$$TiO_2 + C = Ti + CO_2 \quad \text{and/or} \quad TiO_2 + Si = Ti + SiO_2$$

Then, this formed Ti dissolves (high solubility) in hot metal immediately. The titanium enriched in the hot metal will be transported with the HM flow to the damaged zones of the hearth. The dissolved metallic Ti reacts with the C and N dissolved in the hot metal to form Ti(C,N) compounds which precipitate at the locations with lower temperatures (High heath flow) when Ti(C,N) solubility is in hot metal exceeded (L<0,01 %, low solubility in hot metal).

$$xTi + yC, zN = TiN, TiC \text{ and } Ti(C,N)$$

Figure 3 shows schematically the mechanism of formation Ti(C,N) protection layer in the BF hearth. Figure 4 shows a protection layer of titanium carbonitride on the hearth from the blast furnace after stop for relining. In this blast furnace synthetic titanium dioxide was injected for repair of hot spot.

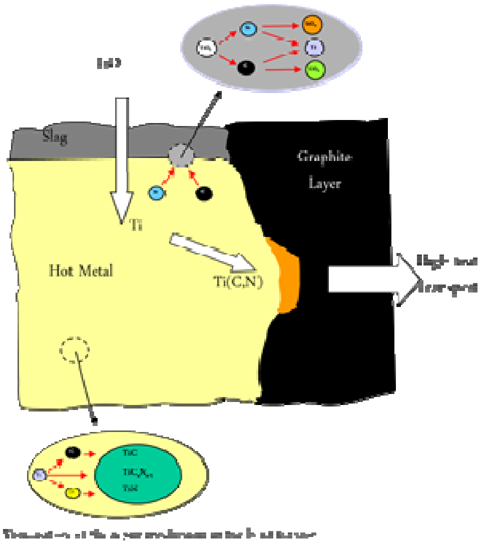

Figure 3. Visualization of formation Ti(C,N) protection layer in BF Hearth.

Figure 4. Pieces of TiN, TiC, Ti(CN) protetion layer from BF.

The process is therefore, an interface reaction. It is necessary for the titanium to rise through the slag/hot metal-interface to achieve an effective reaction of the titanium sources. It is therefore advantageous to produce finely dispersed droplets of Ti with high quantity and high specific area as soon as possible. The results show the fine particulate synthetic titanium source of Rutulit products, with its TiO2 and non-fixed iron oxide. Therefore, it has been proved to be particularly favorable for the formation of high quantity of titanium carbonitrides. The larger Ti(C,N) crystals on the carbon blocks in the hearth can be attributed to the infiltration-induced concentration on the surface of the refractory material. This accumulation results in accelerated crystal growth and thus in stabilization of the depositions.

The lab test showed the synthetic titanium-containing materials exhibit advantages in terms of metallurgical effects compared with the natural materials. Thanks to the great fineness and the associated high surface area, the synthetic sources of titanium possess high reactivity, favoring the formation and deposition of the target titanium carbonitrides and therefore are a continuous feeding via the tuyeres directly to the damaged hearth wall zones suitable.

Table 1 shows some important characteristic properties of TiN and TiC compounds.

Table 1. Themo dynamical dates of titanium carbide and titanium nitride

Property	**TiC**	**TiN**
Density	4,93 g/cm^3	5,4 g/cm^3
Melting point	3157°C	2950°C
Thermal conductivity	29 W (m*K)	38 W (m*K)
Hardness (Mohs)	9	9
Hardnees (Knoop)	2470	1800
Solubility in hot metal (1400°C; 2552°F)	<0,01 wt%	<0,01 wt%
Cryslal type	Face centered cubic	Face centered cubic
Lattice spacings	0,4305 – 0,4327 nm	0,4223 – 0,4242 nm
Colour	Gray metallic	Copper coloured
Coefficent of expansion	7,3 * 10^{-6} K($a_{25/100}$)	7,3 * 10^{-6} K($a_{25/100}$)
Modules of elasticity (20°C)	320 GN/m^2	260 GN/m^2
Specific electrical resistance	7 * 10^{-5} W * cm	3 * 10^{-5} W * cm

3 TECHNICS OF FEEDING OF TITANIUM CONTAININGS MATERIAL PRODUCTS INTO THE BLAST FURNACE

Up to now, 3 methods exist to transport titanium containing material into a blast furnace.

3.1 Charging Lump Ilmenite or Ti Containing Pellets With the Burden

This method is hardly effective and has a lot of disadvantages.
Using this charging method, distribution occurs throughout the whole length of the shaft, and as a consequence there exists a delay in the reaction. Consequently, the quantities charged are higher than actually needed, compromising the quality of the slag and occasional deposits in the shaft (inactive burden).
Usually, titanium is uniform distributed throughout the cross-section of the BF. However, titanium is needed in the wall zones of the hearth only.
Therefore, higher input quantities are necessary and this has a negative effect on HM and slag quality. The increase of the titanium content in the pig iron from the increase in charging ilmenite, results in more TiO_2 contained in the slag and this could be a limiting factor in the use of slag as an additive in cement production.
Ilmenite is a natural ore which consists of iron titanate ($FeTiO_3$). It first needs to be broken down in the blast furnace into FeO and TiO_2 by means of the supply of energy (coke consumption 3 to 10 kg/t ilmenite) before the generation of Ti (C,N) compounds can occur.

3.2 Local Injection of Fine Particles Titanium Containing Material by Separate Injection Machine (Repair Action in Case of Hot Spot or Preventive)

The local injection of fine-particled TiO_2 sources via the tuyeres directly in the vicinity of the hearth zone is a more effective method of importing TiO_2 into the BF.(8-11,13)
This technique offers a whole series of advantages:

- injection occurs in the immediate vicinity of the endangered areas of the masonry. This means that best possible results can be achieved systematically by low input quantities;

- the delay period is shorter before the reparative action occurs, even in case of "hot spots" in the furnace wall;
- there is no accumulation of TiO_2-containing materials in the blast-furnace shaft;
- the TiO_2-containing materials are conveyed directly to the reaction site directly at tuyere level and in the hearth, where they are able to influence directly the interactions of the gas, metal and slag phases, irrespective of the reactions occurring in the shaft and in the cohesive zone;
- lower input rates and higher efficiency of conversion to Ti(C, N) compounds result in improved slag quality, thanks to lower TiO_2 contents in the slag, and therefore easier marketing of the ultimate blast furnace sand product.

The industrial use of the synthetic source of titanium dioxide (Rutilit products) indicates a significant reduction of temperature upon systematic injection into critical BF hearth zones. Precision injection of Rutilit permits a rapid repair of the damaged point if a "hot spot" occurs.(10,11,13)

An injection system (Figure 5) is necessary for the use of Rutilit products.

This system consists of a storage-bin, a pressure lock, a feed vessel, a rotary feeder with an ejection-nozzle, and correspondingly dimensioned conveying lines for simultaneous delivery to up to 4 tuyeres.

The delivery rate should be around 10 to 60 kg/minute.

Figure 5. Injection system and silo for Synthetic TiO_2 products.

Figure 6. Injection lances for RUTILIT Products at the blast furnace.

The most appropriate tuyeres can be selected and supplied, depending on requirements and needs (Figure 6).

The automation concept enables entirely automated operation possible, with the exception of filling of the storage-bin.

An example of the results is shown in Figure 7 of Rogesa blast furnace no. 5 in the year 2005. There, it is shown the development of the hearth temperature as a function of the input of lump ilmente and / or synthetic TiO_2 containing material at the BF 5 of Rogesa, Dillingen, Germany.(13)

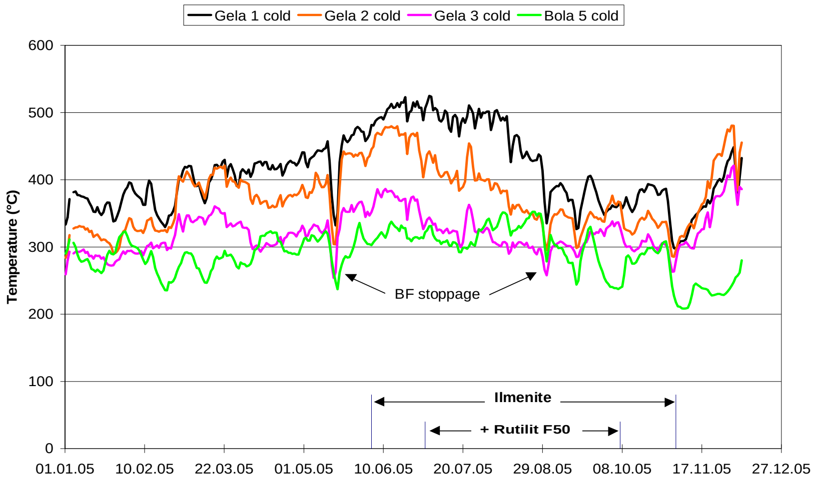

Figure 7. Hearth temperatures blast furnace 5 as function of the input of Ilmenite/ Rutilit.

3.3 Coinjection of Synthetic TiO_2 (RUTILIT) and Pulverized Coal

This new technique of coinjecting TiO_2 containing products together with pulverized coal through the tuyeres (360°) offers several of advantages:(14-17)

- in order to get a homogenous mixture, Intensive mixing of PCI and synthetical TiO_2 products (Rutilit) is possible;
- simple techniques and therefore low investments;
- the addition rate of TiO_2/t hot metal can be precisely controlled;
- the injection can be realized by all tuyeres around the BF hearth;
- this new method is particular for the general prevention combined with very low addition-rates;
- specific consumption of synthetic titanium dioxide containing products for elimination of hearth damage is significantly lower than using natural ilmenite ore is used;
- in addition, due to the lower specific input compared to lump ilmenite, the slag and hot metal quality will improve.

4 PRODUCTION TRIAL AND RESULTS OF THE USE OF TiO_2 CONTAINING PRODUCTS

The PCI plant at ROGESA Dillinder Huettenwerke offers the opportunity to blend TiO_2 containing materials into the raw coal, so that a mixture with a defined TiO_2 content can be injected into both blast furnaces.

The plant for preparation of the pulverized coal consists of two bedding yards of raw coal with a capacity of 20.000 t each. The addition of Rutilit NF is made from a truck unloading bin on the belt conveyor during the unloading process of the raw coal train. On the bedding yard a homogenization takes place. This results in a constant concentration of Rutilit NF in the fed raw coal. After the transportation of the mixture to the raw coal bin, a simultaneous grinding, drying and further mixing of the two components occurs in a vertical Loesche mill (Figures 8 and 9). The ground mixture is separated in a bag house filter and fed into storage bins by sending vessels. The injection into the blast furnaces takes place by single line controlled quantity for each tuyère by a Paul Wurth injection plant (Figures 8 and 9).

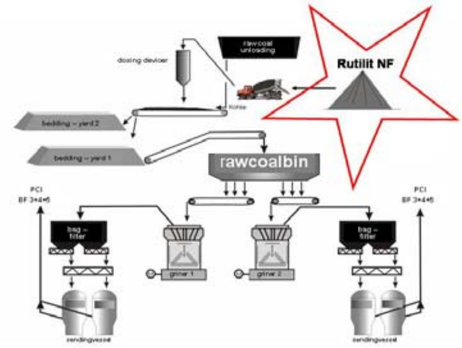

Figure 8. Addition of Rutilit nf to raw coal.

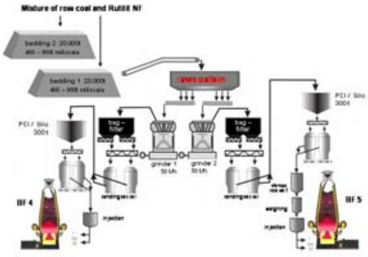

Figure 9. Grinding, drying and injection auf Rutilit NF/PCI in BF No. 4 and 5.

Table 2 shows a list of Titanium – bearing products:
The analysis of the injected material is shown in table 2. Rutilit F 50 and Rutilit NF are synthetic produced materials, which contain mainly Titanium dioxide.
The main grain size of the Rutilit products ranges between 5 and 70 µm with an average particle size of 20 to 30 µm.

Table 2. Main characteristics of the Titanium sources tested at blast furnace

Material	**TiO_2 (%)**	**Fe_2O_3 (%)**	**SiO_2 (%)**	**CaO (%)**	**Al_2O_3 (%)**	**MgO (%)**	**C (%)**	**H_2O (%)**	**Particle size analysis**	**Input**
RUTILIT F 50	45-55	< 40	< 28	< 8	< 6	< 5	--	< 2	20 µm	Separate Injection System
RUTILIT NF	38-52	< 15	< 15	< 4	< 4	< 4	30-40	21-25	20 µm	Co-injection with PCI
Ilmenite	33	< 36	< 25	< 3	< 8	< 5	--	6	10 to 40 mm	Charging with the burden

From July 2008 to July 2010 was injected a mixture of Rutilit NF and pulverized coal was injected into blast furnace no. 4 and no. 5. During this time the total injection quantity of PCI and Rutilit NF was 0,8-1,2 kg / t HM.

The coinjection of pulverized Rutilit NF and coal with a flow-rate 155 Kg/t HM, i. e. 0,8 – 1,2 kg Rutilit NF/t HM or 0,5 to 0,8 TiO_2/t HM did not show any negative influence on the reductants consumption of the hot-metal production. The HM-temperature has a constant level of 1465 – 1485°C (2669 – 2705 F). The slight fluctuation of the Ti content in the hot metal, which has been in the range of 0.02 – 0.08%, has been caused by the thermal state of the blast furnace and by the Rutilit NF coinjection. The TiO_2 content in the slag during Rutilit NF coinjection was maintained below 0.9% at any time, which is a significant quality criterion for processing and sale of the granulated slag as an additive for cement products.

Figure 10 and 11 reveals the development of the temperatures in the hearth of blast furnace 4 and 5 in relation to the additions of the co-injection of Rutilit NF and PCI since 2008.

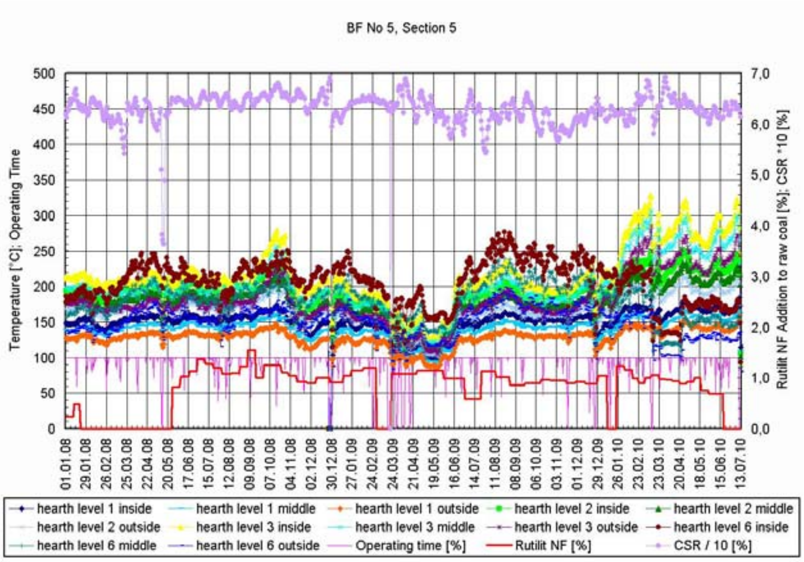

Figure 10. Temperature measurements and operation data (section 5).

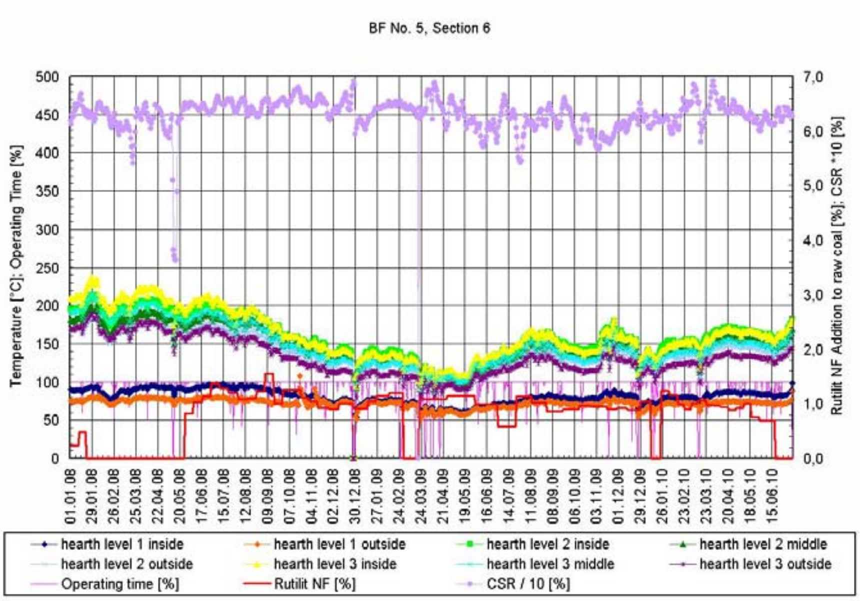

Figure 11. Temperature measurements and operation data (section 6).

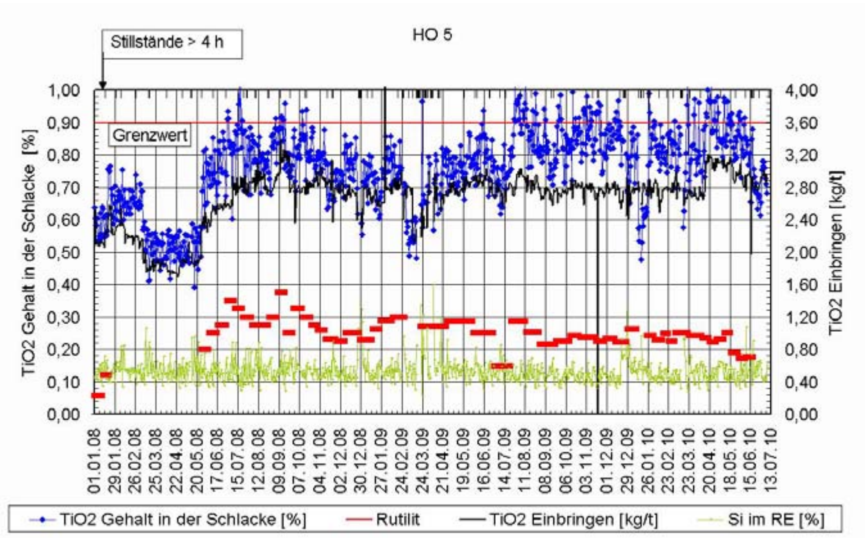

Figure 12. Distribution of Titanium dioxide in slag of BF 5.

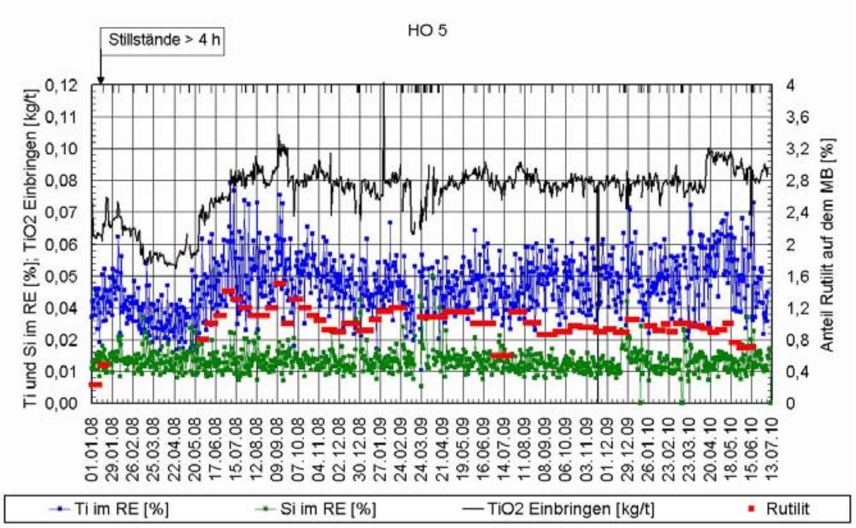

Figure 13. Titanium and silicon distribution in HM of BF No. 5.

5 ECONOMICAL ASPECTS OF THE USE OF TITANIUM CONTAINING PRODUCTS

5.1 Comparison of Charging Titanium (Ilmenite) via Burden and Tuyer Injection of TiO_2 (Rutilit)

During the trial at No. 5 BF at Rogesa the Ilmenite input with the burden with TiO_2 content of 31% was 12 Kg /t HM resp. 3,7 Kg /t HM. The increase of the Ti content in HM was 0,05%.

The input of 3 Kg Rutilit F 50/t hot metal which results in an TiO_2 input of 1,65 Kg per ton of hot metal leads also to a Ti content of 0,05% in the hot metal.

The efficiency of the solution of the TiO_2 in the hot metal at the use of Rutilit is three times higher as with lump ilmenite.

Additionally, it can be stated that the use of lumpy ilmenite leads to a higher TiO_2 content in the slag. In the case of 12 kg Ilmenite input per ton of hot metal the TiO_2 content in the slag rises from 0,5% to 1,4%. This may leads to problems in the selling the granulated slag.

5.2 Prolongation of the Campaign

Because of the use of tuyere injection of synthetic TiO_2 containing products for prevention measure or for local injection for repair of hot spot, the number of unusual production interruptions can be reduced significantly. This leads to a more continuous production rate, which reduces the cost of hot metal.

- the need of capital in relation to the benefits, because of postponement of the larger repairs of the hearths is postponed. By this capital interests are saved;
- less stops of the blast volume due to the reduced numbers of hot spots;
- reduction of cost for hearth maintenance (e.g. grouting);
- increasing of HM production because of no hot spot and less stop of the BF;
- the PCI- rate can be more often be kept on the target level;
- reduction of production rate because of hot spots;
- reduction of the negative consequences of plugged tuyeres.

6 CONCLUSION

The project “Hearth protection in BF by using of Ti containing materials” was focused on investigations of charging with the burden (lump ilmenite) and tuyere injection (RUTILIT) in order to assist the blast furnace operators to optimise the hearth protection, prolongation of campaign and economic effects of different technology for addition of Ti containing material.

The results show that the tuyere injection of synthetic TiO_2 products is much more effective than charging lump ilmenite with the burden. The efficiency of the solution of the TiO_2 in the hot metal at the use of Rutilit is three times higher as with lump ilmenite.

Additionally the tuyere injection can be used very effective as a preventive measure for hearth protection and also as local measure at acute damaged zones (hot spot) in the BF hearth.

The use of synthetic titanium products via tuyere injection instead of addition lumpy ilmenite via burden has significant advantages:

- less danger of hot spots in the hearth and less danger of hearth breakouts;
- higher availability and productivity of the blast furnace;
- prolongation of the campaign and therefore less capital costs;
- improved of selling the granulated slag to the cement industry.

REFERENCES

1 Kowalski, W.; Lüngen, H.B. Stricker, K.P.: Stahl u. Eisen 119 (1999) Nr. 4, S. 119/128

2 Datta, K.; Sen, P.K.; Gupta, S.S.; Chatterjee, A.: Effect of titaniaon the Characteristics for Blast furnace. Steel Research Vol. 64, (1993) p. 232/238

3 Okada, T.; Kuwano, K.; Schimomura, K.; Hori, H.; Miyatani, H.; Ochiai, Y.; Uemura, K.: Protection of Blast furnace Hearth Refractories by TiO2 Injection trough Tuyeres. 50th Ironmaking Conference Proceedings (1991), S.307/312

4 Bergsma, D.; Fruehan, R.J.: Fundamentals of titanium-rich scaffold in the blast furnace hearth. 60th Ironmaking Conf. Proc. (2001) p. 297/312, Baltimore, USA

5 Pochwisnew, A. N.; Abramow, W.S.; Krasawzew, N.I.; Leonidow, N.K.: Der Hochofenbetrieb, VEB Verlag Technik Berlin, 1954

6 Boone, A.G.; Jimenez G.; Castilli, J.: Titanium addition practice and maintance of the hearth in ASMSA´s blast furnace. 56th ironmaking Conf: Proc. (1997) p. 321/326. Chicago, USA

7 Bürgler Th.; Brunnbauer G.; Ferstl A.; Zeirzer Ch.; Pillmair G.: Injection for TiO_2 components and ironmaking by-produktsat VASL BF A. Vortrag, Paris 2000

8 Dierich J.C.; Bauer W.; Amirzadeh-Asl D.; Fünders D.: Eigenschaften synthetischer titanhaltiger Materialien zur Verschleißminderung in Hochöfen. Stahl und Eisen 119 (1999) S. 85/90

9 Bürgler Th.; Brunnbauer G.; Ferstl A.; Zeirzer Ch.; Pillmair G.: Injection for TiO_2 components and ironmaking byproducts at VASL BF A. Paper, Paris 2000

10 Amirzadeh-Asl D.; Restivo V.; Fünders D.: Properties of synthetic TiO_2-containing materials for the blast furnace: Enhanced BF availability; The Iron and Steel Technology Conference; Paper; Cleveland, USA 2006

11 Hartig W.; Amirzadeh-Asl D.; Fünders D.: Used of synthetic titanium products for protection of the hearth of ROGESA blast furnaces; Technical contribution to XXXVII Ironmaking and Raw Materials Seminar, September 2007, p. 456/469; Salvador-BA, Brazil

12 Hartig, W.; Amirzadeh-Asl, D.; Fünders, D.: Blast furnace hearth protection by simultaneous

13 Paper; Indianapolis, Ind., USA 2011 injection of pulverized coal and synthetic Titanium dioxide products. The Iron and Steel Technology Conference; Paper; St. Louis, USA 2009

14 Liceage, F; Vidales, G.; Mata, R.: 30 Million in the Hearth of Blast Furnace No. 5 at AHMSA Mexico. The Iron and Steel Technology Conference; Paper; Pittsburgh, USA 2010

15 Hartig W.; Amirzadeh-Asl, D.; Fünders, D.: Result of co-injection of PCI and synthetic Titaniumdioxide products for protection of the hearth at Rogesa No. 5 BF after stop for relining. The Iron and Steel Technology Conference; Paper; Indianapolis, Ind., USA 2011

16 Eisen, P.; Gertz, J.; Grabietz, G.; Tauchert, S.; Schulte, S.; Amirzadeh-Asd, Dj.; Fuenders, D.; Test of coinjection petrol coke containing synthetical TiO2 with premix pulverised coal for hearth protection of Hüttenwerke Krupp Mannesmann blast furnaces; 8th Ironmaking ConferenceIAS, 2011, Rosario, Santa Fe, Argentina

17 Santos, G. S.; Costa Manso, G. A.; Oliveira, M. A. G.; Fernandes, M. V.; Amirzadeh-Asl, Dj. Fuenders, D.; Hearth protection of blast furnace no. 3 of Usiminas by injection of titanium dioxide products; Technical Contribution to the 41st Seminar on Iron Mining Reduction, ABM, Vitória, ES, Brazil, September 12 to 15, 2011

18 Borego, J. A.; Villarreal, M.; Castro, L.; Veliz, J. A.; Teubl, W.; Improvment in control processand hearth maintenance in BF no. 5 at AHMSA; The Iron and Steel Technology Conference; Paper; Indianapolis, Ind., USA 2011