# LONG TERM TEST OF COINJECTION OF SYNTHETICAL TIO<sub>2</sub> WITH PREMIXED PULVERIZED COAL FOR PREVENTIVE HEARTH PROTECTION OF ROGESA BLAST FURNACES IN DILLINGEN GERMANY<sup>1</sup>

Walter Hartig<sup>2</sup> D. Amirzadeh-Asl<sup>3</sup> D. Fünders<sup>4</sup>

#### Abstract

At ROGESA blast furnaces a mixture of pulverized coal and synthetic titanium dioxide is injected simultaneously in order to protect the hearth from premature erosion. Sachtleben has developed, in the form of RUTILIT, a fine-particle synthetic source of titanium dioxide which can be systematically injected into the zone of damage in the blast furnace hearth via the tuyeres. Thanks to its great particle fineness, RUTILIT has good rheological (flow) properties, permitting pneumatic conveyance. At The ROGESA-Ironmaking Plant a new technology has been developed in order to use the grinding and injection facilities not only for pulverized coal but also for titanium products. This achieves a quick and cost-effective repair of the damage of the hearth refractory, and thus a reduction of temperature in the hearth area. This paper is a common report from AG der Dillinger Hüttenwerke (Rogesa) and Sachtleben Chemie GmbH, Duisburg. It examines the benefits of a long term coinjection of pulverized coal and synthetic Titanium dioxide (RUTILIT) at Blast Furnace No. 4 and No. 5. **Key words**: Blast furnace; Titanium dioxide; Hearth protection; Repair; RUTILIT.

#### O PROLONGADO TESTE DE CO-INJECAO DE SINTETICO TIO₂ COM PREMISTURADO E ULVERIZADO CARVAO PARA PREVENTIVO PROTEÇAO DE CARDINHO DOS ALTOS FORNOS DE ROGESA /DILLINGER HÜTTE EM DILLINGEN, ALEMANHA

#### Resumo

Nos altos fornos da empresa Rogesa/Dillinger Hütte a mistura do pulverizado carvão e sintético Titanium- Oxide e injetada simultaneamente para proteger o cardinho contra erosão. A empresa Sachtleben Chemie desenvolveu uma possibilidade de injetar pequenas partículas de TiO<sub>2</sub> na área ferida do cardinho dum alto forno via ventaneiras. Por causa da pequena microestrutura das partículas , Rutilit tem muito boas condições reológicas, o que permitem boas possibilidades de transportes pneumaticos. A abrasão por causa dos transportes e operações é pequeno. Existem perfeitas condições para injeção via ventaneiras. No departamento de produção de ferro gusa da empresa Rogesa /Dillinger Hütte as unidades de moagens e insufliçao são usados não somente para insuflir PCI mas também produtos de Titanium. Por isso uma rapida e custo – reduzinda possibilidade de reparação de refractario do cadinho e construida e tambem para reduzir a temperatura no cardinho. Este apresentaçao e feito junto com Rogesa / Dillinger Hütte e Sachtleben Chemie em Duisburg. Sao analizadas as vantagens duma injecao a longo tempo duma co – injecao de PCI + TiO<sub>2</sub> (Rutilit) nos altos fornos 4 e 5.

**Palavras-chave**: Alto forno; Titanium dioxide; Proteçao do cadinho; Reparaçao; Rutilit.

- <sup>2</sup> General Manager Ironmaking ROGESA, walter.hartig@dillinger.biz
- <sup>3</sup> R&D of Sachtleben Chemie, Duisburg, Germany; d.amirzadeh-asl@sachtleben.de
- <sup>4</sup> GSR, Moers, Germany; synthetische.rohstoffe@web.de

<sup>&</sup>lt;sup>1</sup> Technical contribution to the 39<sup>th</sup> International Meeting on Ironmaking and 10<sup>th</sup> International Symposium on Iron Ore, November 22 – 26, 2009, Ouro Preto, MG, Brazil.

# 1 ROGESA- Ironmaking facilities

# 1.1 No. 4 and 5 Blast Furnace Campaigns Before and After Its Enlargement

The company Roheisengesellschaft Saar (ROGESA), with a yearly production capacity of 4.4 million t of hot metal (HM), is a joint venture of the AG der Dillinger Huettenwerke, the major European heavy plate producer, and Saarstahl AG, one of the most important manufacturers of long products in the world. It is located at the site of Dillingen in the south west of Germany.

<b>U I</b>						
	BF No. 4	BF No. 5				
Year of construction	1974/2003	1985/1997				
Restart after relining	Oct.2003	Feb. 2006				
Reason of revamping	BF relining	interim repair				
Daily production	6200 t (metric)	7200 t				
Number of tap holes	2	2				
Working volume	2358 m <sup>3</sup>	2581 m³				
Hearth diameter	11,2 m	12 m				
Number of tuyeres	30	32				

Blast furnace No. 4 was restarted after enlargement in 2003. The BF No. 5 was relined and simultaneously enlarged from 11m to 12m in May 1997<sup>[1]</sup> and was restarted after interim repair in 2006. The reducing agents used are coke and pulverized coal, injected via a total of thirty lances at BF No.4 and thirty two lances at BF No. 5 at tuyere level.

## **1.2** Comparison of different methods to use titanium containing materials

The attempt for protection of blast furnace hearths by charging lump llmenite with the burden is the common practice for a number of decades.<sup>[2-4]</sup> However the results are often disputable. This purpose of the addition of Titanium compounds is based on the generation of high-temperature- and high-wear-resistant Ti(C,N) compounds, which exhibit temperature-dependent solubility in the hot metal. When the solubility limit is reached due to temperature decrease, which is the case at areas of damage in the hearth as a result of higher heat flux and loss of heat to the outside, the respective Ti(C,N) compounds are precipitated out of the hot metal and deposited in the more severely damaged zones of the masonry, with an intrinsic "hot-repair effect". <sup>[4]</sup>

The injection of fine-particulate  $TiO_2$  (RUTILIT) sources via the tuyeres directly in the vicinity of the hearth zone is a more effective method of importing  $TiO_2$  into the BF.<sup>[4-6]</sup> This technology offers a lot 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 well spotted and with low input quantities.
- The delay period before the reparative action occurs is much shorter, even in case of "hot spots" in the furnace wall.
- There is no accumulation of TiO<sub>2</sub>-containing materials in the blast-furnace shaft.
- The TiO<sub>2</sub>-containing materials are conveyed directly to the reaction site at tuyere level and in the hearth, where they are able to and direct influence with the gas, metal and slag phases, irrespective of the reactions occurring in the shaft and in the cohesive zone is possible.<sup>[7]</sup>

 Lower input rates and higher efficiency of conversion to Ti(C,N) compounds result in improved slag quality, thanks to lower TiO<sub>2</sub> contents in the slag, and therefore easier marketing of the ultimate blast furnace sand product.

	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	$AI_2O_3$	CaO , MgO	Moisture content		
	%	%	%	%	%	%		
RUTILIT								
NF	50-60	Max. 10	max. 25	max. 5	max. 8	22 - 28		
RUTILIT								
F50	45-55	max. 40	max. 20	max. 6	max. 6	< 2		
RUTILIT								
F85	80-85	max. 15	max. 15	max. 3	max. 6	< 2		

Table 2: RUTILIT properties

Due to their differing TiO<sub>2</sub> contents, the various RUTILIT products are suitable for a range of different uses, varying from preventative application (RUTILIT NF; RUTILIT F50) up to and including high-speed reactions to "hot spots" (RUTILIT F50 and RUTILIT F85) <sup>[8,9]</sup>

#### 2 DESCRIPTION OF THE PULVERIZED COAL INJECTION (PCI) INSTALLATIONS AND PREPA- RATION OF MIXTURE WITH RUTILIT NF

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 raw coal train unloading. 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 (Figure 1). 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 with a Paul Wurth injection plant:



Figure 1: Addition of RUTILIT NF to raw coal.

# 3 INJECTION CONDITIONS OF RUTILIT NF/PCI COINJECTION

First pilot Test:

- Injection period over 10 days from 3<sup>rd</sup> of March to 14<sup>th</sup> of March 2007

- Mixing of 20000 t raw coal and 100 t RUTILIT NF (moisture content 25 %); Quantity of RUTILIT NF 0,5 % referred to raw coal.
- After grinding and drying the mix was injected continuously into BF No. 4 and No. 5 via all tuyeres.
- Daily production: 6200 t HM BF No. 4 and 6700 t HM BF No. 5
- Total injection quantity pulverized coal and RUTILIT NF per day: 2000 t; 155 kg of pulverized coal specific/t HM; 0,4 kg RUTILIT NF/t HM
- Second pilot test:
- Injection period over 80 days (start: 15<sup>th</sup> of July to 4<sup>th</sup> of October 2007)
- Addition of RUTILIT NF to raw coal at various level in the range of 0.8 1.35 % referred to raw coal
- After grinding and the mix injected continuously into BF No. 4 and Nr. 5 via all tuyeres.
- Daily production: 6200 t HM BF No. 4 and 6700 t HM BF No. 5
- Total injection quantity of PCI and RUTILIT NF per day: 2000 t/day; 155 kg of pulverized coal specific / t HM; 0,6 1 kg RUTILIT NF/t HM
- Total injection quantity of RUTILIT NF in this period: 2130 t
- Third long-term test:

It was decided to stop the co-injection of RUTILIT NF beginning of October 2007 to assess the results and to observe the BF hearth wall and bosh temperature. After a time of constancy the hearth wall and bosh temperature started to rise again beginning of March 2008. In May 2008 ROGESA decided for prevention protection of hearth wall and bosh to start the co-injection with RUTILIT NF for a long-term period. Depending on the hearth wall temperature the addition of RUTILIT NF to raw coal varied between 0,5 and 1,5 % (0,6 – 1,11 kg RUTILIT NF/t HM).

Since September 2008 Rutilit NF is injected constantly together with the pulverized coal.

## 4 RESULTS

In March 2007 a pilot test was made to examine the feasibility of the technique. The test period lasted approximately ten days for the injection of 20000 t of pulverized coal. The normal input level of  $TiO_2$  in the burden was at 2,0 kg/t HM and was increased to about 3,0 kg/t HM depending on the added quantity of RUTILIT NF. It could be noticed that there was no detrimental effect over the entire coinjection period on the permeability of the Blast Furnace process because the overall pressure drop did not change (Figure 2).



Figure 2: Titanium input before and during injection period.

In order to force on the precipitation of Ti(C,N) in the BF hearth certain saturation has to be exceeded. When there is an additional input of  $TiO_2$  (by RUTILIT NF) of more than 0,8 kg/t HM, the increasing of Ti-content in the HM leads to a precipitation of Ti(C,N). The distribution of the Titanium between hot metal and slag depends on the thermal state of the Blast Furnace process. At "hot" conditions Titanium has a higher solubility in the hot metal, whereas when the process is "colder"  $TiO_2$  remains more in the slag.

The coinjection of pulverized RUTILIT NF and coal with a flow-rate 155 kg/t HM, i. e. 0,5 - 1 kg RUTILIT NF/t HM did not show any negative influence onto the reductants consumption of the hot-metal production. The HM-temperature has a constant level of  $1465 - 1485^{\circ}$ C (2669 - 2705 F). The slight fluct uation of the Ti-content in the hot metal, which has been in the range of 0,02 - 0,08 %, has been caused both by the thermal state of the blast furnace and by the RUTILIT NF coinjection (Figure 3). The TiO<sub>2</sub> content in the slag during RUTILIT NF co-injection was at any time maintained below 0,9 %, which is a significant quality criterion for processing and sale of the granulated slag as an additive for cement products (Figure 4).







Figure 4: Distribution of titanium dioxide in slag.

The measuring levels 1 to 8 are shown in the sectional view of the hearth in Figure 5. The levels 1 and 2 are in the bottom region. The measuring levels 3 to 8 are in the hearth wall. The calculated wear of the ceramic cup is also shown. The sections 1 to 12 over the circumference are shown also in Figure 5.



Figure 5: Hearth design and section 1 to 12 of blast furnace No. 4.

Figure 6, 7, 8 and 9 show exemplarily during and after RUTILIT NF coinjection the behavior of the hearth wall temperature in two section (3 and 8) of BF No. 4 and in two section (1 and 2) between tap hole No. 1 and 2 of BF No. 5. During all the campaigns in 2007 and 2009 the coinjection rate of RUTILIT NF was varied between 0,4 – 1,11 kg/t HM. It was clearly to observe that with the increasing of RUTILIT NF-rats to 1,11 kg RUTILIT NF/t HM, how rapid the temperatures in the pre-damaged area declined with a time lag of only a few days. After coinjection has been finished, the temperature at the worn area kept nearly constant over four months. After this hold time temperature started to increased again.



**Figure 6**: Hearth temperatures at level 3 - 8 of BF No. 4, section 3. (Double thermocouples with the distance of 100 mm)

Temperatures in the hearth bottom are not influenced by the RUTILIT NF-Injection. The influence of a constant entrance cooling water temperature can also be clearly noticed.



Figure 7: Hearth temperatures at level 3 - 8 of BF No. 4; section 8

Highest temperatures are at the upper level of the hearth walls (level 7 and 8). In this region the ceramic cup is already worn out. At the hearth wall temperatures decrease during the coinjection period.

# 4.1 Long Term application of Rutilit at No. 5 Blast Furnace

Blast Furnace No. 4 was idled on April 28<sup>th</sup> 2008 with casting of the salamander due to the general reduction of production. In July 2009 a scheduled interim repair for changing the row of tuyère staves and one row of staves in the mid shaft was started. Concerning No 5 Blast Furnace, in the last two months of 2008 and in the following year 2009 the production was reduced and there were also some longer stoppings up to 120 h because of the steel crisis.

Therefore it is difficult to determine how the influence on the temperatures were caused by the RUTILIT NF/PC coinjection and by the stoppings. The stoppings and the reduction of the productivity have a significant influence.

Since June 2009 the increase of the hearth wall temperatures are related to the increase of the productivity and also to a deterioration of the coke quality which is shown in Figures 8 and 9.

BF No. 5, Section 1



Figure 8: Hearth temperature of level 1 - 6 of BF No. 5, section 1



Figure 9: Hearth temperature at level 1 - 6 of BF No. 5, section 2

The second and third campaigns indicate that the coinjection of RUTILIT NF with coal is also a suitable measure to build up a protective layer area in the bosh. The temperature profile of the bosh and the productivity at the BF No. 4 are shown in Figure 10. During the second period (start on 15<sup>th</sup> July 2007) the positive effect of the Rutilit NF/PCI coinjection could be detected, because the temperature started to decrease approx. 30 days after stat of the coinjection.



Figure 10: Influence of RUTILIT NF/PCI coinjection in the bosh at BF No. 4

Further examinations at both BFs indicated the same positive effect also in following parameters:

- Temperature in the hearth wall
- Temperature in the bosh
- Cooling effects of the different cooling systems.

## 5 QUANTITATIVE RESULTS OF THE USE OF RUTILIT NF/PCI COINJECTION FOR PREVEN-TIVE PROTECTION

A statistical analysis was made in form of a linear regression of measured values in the hearth wall to get a detailed quantitative description of the effect of the injection of Rutilit NF.

The equation is:  $\Delta T = a + b^* days$ 

The factor b is the effective coefficient, which describes how much the hearth – wall temperature is influenced by the injection of Rutilit NF.

In the following diagram (Figure 11) are some of the most important results:



Figure 11. Reactive coefficient of Rutilit NF on wall.

It is to be seen, that there exists a clear regularity of the injected quantity of RUTILIT NF and the decrease of the hearth wall temperature during different periods of approximately 2 weeks.

The effect is that the temperatures in the walls decrease quasi in all the periods. Even when the temperature is increasing, the value of the increase is reduced. But in most cases there exists a clear negative temperature trend.

One exception has to be noted in the two weeks, when the quantity of added RUTILIT NF are approximately 1,1 and 1,2 % of the PCI – coal.

The reason for this single exception is a period of bad coke quality which was used in that time and which created a lot of other metallurgical problems in the inner part of the blast furnaces.

# **6 CONCLUSION**

The preventive protection of hearth of blast furnaces by charging Ilmenite (titanium dioxide source) with the burden is a common but antiquated practice in BF operation. The long-term industrial test at blast furnace of ROGESA of the coinjection RUTILIT NF with the coal indicated a significant reduction of temperature at critical BF hearth zones and also at the bosh. This new method permits rapid repair of the damaged area if a "hot spot" occurs and prolonged significantly the life time of the BF hearth.

An economical evaluation and comparison of charging Ilmenite with the burden showed that the coinjection of synthetic titanium dioxide (RUTILIT NF) with the coal is a cheaper and more effective method for BF-hearth protection. In addition, due to the lower specific input and lower migration into the slag compared to Ilmenite, the use of RUTILIT NF coinjection also allows to stick within the desirable low titanium dioxide levels in the slag.

A very good common mixing, grinding and drying inclusive a perfect pneumatic conveying into the blast furnaces by all tuyeres has been done without any negative influence and abrasion problems and therefore is still continued.

The preventive protection with this new and simple technique increases the productivity while saving energy and raw materials costs.

At ROGESA the coinjection of RUTILIT NF together with coal will be a measurement to extend the BF-hearth life time.

### REFERENCES

- 1 F. Bordemann and W. Hartig, "Redémarrage du HF 5 de ROGESA après augmentation de creuset de 11 à 12 m et évolution des performances," ATS commission Fonte, Gent, Belgium, June 11-12, 1998.
- 2 Kowalski, W.; Lüngen, H.B.; Stricker, K.P.: Stahl u. Eisen 119 (1999) No. 4, pp. 119/128
- 3 Datta, K.; Sen, P.K.; Gupa, S.S.; Chatterjee, A.: Effect of titanium on the Characteristics for Blast furnace. Steel Research Vol. 64, (1993) p. 232/238
- 4 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), pp. 307/312
- 5 Bergsma, D.; Fruehan, R.J.: Fundamentals of titanium-rich scaffold in the blast furnace hearth. 60th Ironmaking Conf. Proc. (2001) pp. 297/312, Baltimore, USA
- 6 Dierich J.C.; Bauer W.; Amirzadeh-Asl D.; Fünders D.: Eigenschaften synthetischer titanhaltiger Materialien zur Verschleißminderung in Hochöfen. Stahl und Eisen 119 (1999) pp. 85/90
- 7 Bürgler Th.; Brunnbauer G.; Ferstl A.; Zeirzer Ch.; Pillmair G.: Injection for TiO<sub>2</sub> components and ironmaking byproducts at VASL BF A. Paper, Paris 2000
- 8 H.G. Grabietz, R. Altland, G. Schmucker, D.Amirzadeh-Asl, W. Bauer: "Injection tests of Rutilit AT as a TiO<sub>2</sub>-containing material at blast furnace A at HKM Duisburg"; Stahl u. Eisen special (Sep 2002); p 56
- 9 Amirzadeh-Asl D.; Restivo V.; Fünders D.: Properties of synthetic TiO<sub>2</sub>-containing materials for the blast furnace: Enhanced BF availability; The Iron and Steel Technology Conference; Paper; Cleveland, USA 2006
- 10 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
- 11 Hartig W.; Lin R.: Investigation of influential parameters on BF operations and wear conditions of No. 5 blast furnace after its inner volume enlargement; The Iron and Steel Technology Conference; Paper; Indianapolis , Ind., USA 2007