
MAGNESIA-CARBON REFRACTORY LINING FOR FERRONICKEL CONVERTERS - OPTIMIZATION AND LINING IMPROVEMENT AT NEWCO FERRONIKELI (KOSOVO)

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ABSTRACT

During pyrometallurgical processing the converter is one of the most important aggregates to produce and to refine ferro-nickel. The oxygen blowing process is necessary to decrease the sulphur, phosphorus, carbon, silicon and the iron content in the FeNi-metal to the requested levels. This process is characterized by very long treatment times and very aggressive slags. The conventional way to line the converters was based on fired magnesia or magnesia-chromite bricks. However, by introducing magnesia carbon bricks the life time of the converter lining can be increased significantly. In this report theoretical aspects as well as practical experience are presented. Special emphasis is made to the FeNi-production at NewCo Ferronikeli (Kosovo) and on the optimization of the MgO-C refractory lining of the converter.

KEYWORDS: Ferro-nickel, FeNi, nickel, refractories, magnesia carbon, MgO-C.

1. INTRODUCTION AND USAGE OF NICKEL AND FERRONICKEL

Nickel and nickel-compounds play an important role in many different industries and applications. Possessing the high strength over a wide temperature range, the high corrosion resistance in acidic and basic environments is one of the main advantages of such alloys. The major use of nickel is in the production of stainless steel. These special stainless steel grades contain between 8-10 % nickel. In total nearly 70 % of the worldwide nickel production is consumed to manufacture stainless steel. About 20 % is used in other steel grades and special non-ferrous alloys. The smallest portion of about 10 % of the nickel production is used in plating and other special uses like coins, electronic and batteries [1, 2].

The main nickel deposits are commonly present in two forms: laterite or sulphide. About 70 % of the world land based nickel resources can be found in laterites, but they account for only 40 % of the worldwide nickel production. Noticeable laterite resources are located in Indonesia, Columbia and New Caledonia. Usually the laterite can be mined in open-cast mines, but the separation of the nickel-laterite is quite complicated and work-intensive. Therefore, the majority of the worldwide nickel production is based on sulphide ores which are easier to process than laterite. Important deposits are known in Canada, Russia and Australia. But due to an increased demand for nickel and nevertheless due to improved process techniques, a trend to a higher share of laterite sourced nickel is expected and visible [3, 4].

2. FERRONICKEL PRODUCTION AT NEWCO FERRONIKELI (NEWCO)

NewCo Ferronikeli includes a nickel production plant as well as two mines with an average of 1.1 % Ni. As a result of damage during the Kosovo conflict the plant, located in Drenas (Kosovo), was in a state of disrepair until 1990's. After the privatization and the acquisition by Cunico Resources NV the plant has been refurbished. On 2011 has reached a historic high of 9143

to of Nickel or 36500 to FeNi with average content of 25.4 % Ni. Based on the current plant dynamics and intended projects, the yearly production will increase to more than 10000 tons. In figure 1 a view on the plant in Drenas is given.



Figure 1: NewCo Ferronikeli production site

The nickel ore is supplied to the plant from Cunico Resources' Qikatova, Gllavica and Guatemala. The mines are exploiting with surface extraction method (open pit). The ore from Qikatova is transported to the smelter complex by dumpers whilst that of Gllavica is by railway. A scheme of the FeNi-production process at NewCo is shown in figure 2. Hammer crushers are crushing all ores received in fraction -60 mm. The prepared ore is transported by different conveyor belts and piled up in different stock piles. The metallurgical process starts by blending the lignite ores with solid fuels (steam coal). After passing the rotary kiln where the reduction and calcination takes place, the calcined ore is moved into the electric reduction furnace. In the EAF approximately 50 % of the sulphur in the iron/nickel alloy is removed and a metal with an average Ni-content of 13 % is produced. The remaining sulphur, silicon and carbon are removed from the liquid metal in the LD converters, and the iron/nickel alloy with a Ni-content of 17-22 % is then cast into ferronickel ingots.

3. CONVENTIONAL LINING OF THE FENI CONVERTER

The conventional refractory lining of the FeNi-converters is based on fired, basic bricks. Some plants in the CIS region use a two-phase refining process in two different converters: an acid converter to reduce the Si-content in the FeNi-metal and a basic converter for the other refining processes. In this case the first (acid) converter is lined with fireclay or high alumina-bricks and the second (basic) converter with burnt basic bricks. Although there were different solutions in the different plants, most commonly was the use of magnesia-chromite bricks (60 % MgO, 20 % Cr_2O_3) or magnesia bricks with 95-98 % MgO for the slag line and some lower grade bricks with a lower content of MgO or Cr_2O_3 for the upper part of the converter lining.

In all plants we noticed a very heavy wear of the slag line with the typical wear pattern of burnt bricks, deep infiltration of slag and spalling of the bricks. Finally a so called "chess plate" wear pattern results, where a number of bricks in the lining were cracked, while other ones showed a good thickness. This wear pattern creates a number of problems for the operators; it is difficult to predict the end of the campaign and to arrange a new installation.

Due to the accelerated wear in the slag line area, a number of FeNi-plants are arranging an intermediate repair of the slag line, for example with smaller brick shapes.

Beginning of 2000, some first trials were made with carbon containing MgO-C bricks in the converter lining at Larco (Greece). There it was shown, that MgO-C bricks could work under the conditions of the refining of FeNi. The performance was better and the wear pattern synchronous. After this first trial a number of FeNi-plants start to use magnesia-graphite bricks for the converter lining.

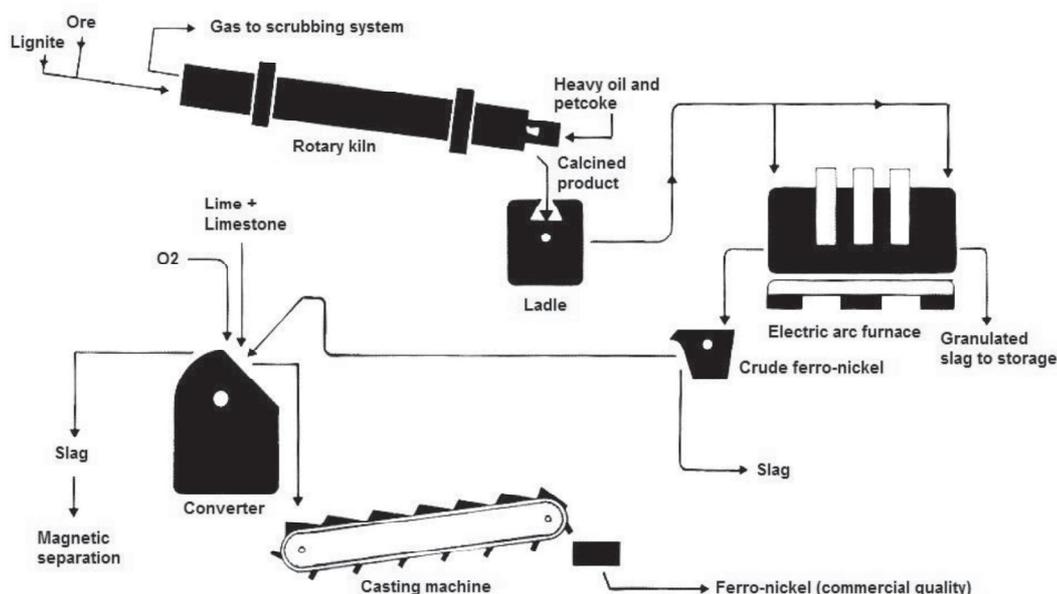


Figure 2: Ferro-Nickel production at NewCo Ferronikeli: flow sheet

4. INTRODUCTION OF MAGNESIA-CARBON AND TRIALS FOR OPTIMIZATION

When NewCo was restarted in 2007 the first refractory linings were installed with magnesia-chromite-bricks: the critical zone with a better, direct bonded grade and the bottom and upper part with a standard grade. This was the concept, which was used before the privatization of the company. The refractory consumption in 2007 was considerably high; more than 400 kg/t nickel with an average of 75 heats with a local repair (20 layers). The refractory bricks consisted of MgO-Cr₂O₃ with 17-20% Cr₂O₃.

In 2008, it was the first time when NewCo started to add dolomitic lime together with limestone. The specific refractory consumption decreased considerably by 250 kg/t nickel, the heats reached up to 100 heats with an average of 85 (with one partial repair). At the end of that year two linings with pure burnt MgO-bricks (97%) were tested. The results were disappointing: after 31 and 55 heats the wear was fast and extended till the upper cone of the converter. No partial repair was possible.

At the end of December 2008 NewCo made the first trial with MgO-C bricks. The lining lasted for 77 heats, the wearing of the bricks and the infected zone was much less. After a local repair of 12 rings (total rings for the converter are 52) with MgO-Cr₂O₃ bricks, another 36 heats were completed with total refractory consumption of 215 kg/t Ni and a result of 113 heats. Since this time mainly magnesia-graphite bricks were used for lining of the converter.

During 2010-12 NewCo ran a number of tests to reach a further improvement of the performance. The aim was to find an ideal composition of MgO-C bricks in order to get the best cost performance of the converter lining. Therefore different magnesia-carbon grades have been

tested. The main parameters are: kind and grade of the magnesia, carbon content and antioxidants. The results of the different material are shown in table 1.

The best performance in the slag zone has been reached with materials containing a 98 % fused MgO with an 8 % graphite addition. In general better results have been achieved with the following MgO-C modifications:

- lower carbon contents with an optimum of 8 %
- high grade fused magnesia with an MgO-content of > 98 %
- refraining from using all kinds of antioxidants

The construction of the converter and the refractory lining concept is illustrated in figure 3.

Table 1: Results (heats) of different refractory materials and grades in the slag zones of the NewCo FeNi-converter

| Grade | Refractory material | Composition | Result (heats) |
|-------|---------------------|---|----------------|
| A | magnesia-chromite | 60 % MgO, 20 % Cr ₂ O ₃ | 75 |
| B | burnt magnesia | DBM magnesia (97 % MgO) | 43 |
| C | MgO-C | DBM magnesia (97 % MgO), 6 % C | 76 |
| D | MgO-C | fused magnesia (98 % MgO), 8 % C | 124 |
| E | MgO-C | fused magnesia (98 % MgO), 10 % C, antioxidants Al | 119 |
| F | MgO-C | fused magnesia (98 % MgO), 10 % C, antioxidants Al, SiC, Si | 91 |
| G | MgO-C | fused magnesia (98 % MgO), 12 % C, antioxidants Al | 87 |
| H | MgO-C | fused magnesia (98 % MgO), 15 % C, antioxidants Al | 82 |

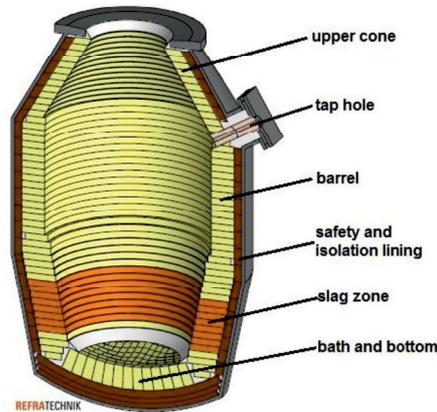


Figure 3: Construction and refractory material zoning of the FeNi-converter at NewCo Ferronikeli

5. WEAR OF MAGNESIA CARBON REFRACTORIES IN FENI CONVERTERS

In general the converter process can be characterized by two different process slags, which are presented in table 2.

As a result of the rather high sulphur content of ~0.5 % it is necessary to slag off the converter several times. Depending on the current sulphur content of the ferro-nickel crude metal the blowing periods of the converter are interrupted by 6-9 deslagging breaks. A special characteristic of the NewCo Ferronikeli crude metal is the rather high silicon content of average 2.2 – 2.8 %. Occasional peak values of 3.5 % silicon are possible. Due to this high Si-content of the crude metal the early

converter slag is highly acidic with a c/s-ratio of 0.4-0.5. This slag can be characterized by three main mineralogical forms which are diopside ($\text{CaMgSi}_2\text{O}_6$), wustite (FeO) and akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$). During the converter blowing process the amounts of the ferro-nickel metal on sulphur, phosphor, silicon and iron are reduced. Consequently, every de-slagging step increases the basicity of the slag. At the end of the converter process the slag has achieved a highly basic character (c/s ratio 50). Typical mineralogical main phases are magnetite (Fe_2O_3) and srebodolskite ($\text{Ca}_2\text{Fe}_2\text{O}_5$). Noticeable is the very high content on magnetite, caused by the intensive oxygen blowing process.

Table 2: Typical slags of a FeNi-converter

| | Early converter slag | Late converter slag |
|--|----------------------|---------------------|
| chemical composition [%] | | |
| SiO ₂ | 45 | 0.5 |
| Al ₂ O ₃ | 0.5 | 3 |
| Fe ₂ O ₃ | 20 | 60 |
| MgO | 12 | 2 |
| CaO | 20 | 25 |
| Cr ₂ O ₃ | 1 | 1 |
| SO ₃ | 0.5 | 2 |
| NiO | 0.5 | 0.5 |
| c-s ratio | 0.4 | 50 |
| mineralogical phase composition | | |
| diopside $\text{CaMgSi}_2\text{O}_6$ | ++++ | + |
| wustite FeO | ++ | + |
| akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$ | ++ | + |
| larnite Ca_2SiO_4 | + | + |
| magnetite Fe_2O_3 | + | ++++ |
| trevorite $(\text{Ni,Fe})\text{Fe}_2\text{O}_4$ | + | + |
| srebodolskite $\text{Ca}_2\text{Fe}_2\text{O}_5$ | | +++ |
| bredigite $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$ | | ± |

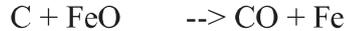
As the chemical character of the magnesia-carbon lining is basic, a rather high wear rate can be assumed during the first converter blowing periods. Within the first few minutes of the converter process the acidic slag causes very intense and destructive upon the MgO-C lining. The very high corrosion potential of the SiO₂-rich slag is intensified by the very low slag viscosity at the process temperature of ~1610°C (main component diopside with a melting temperature of 1391°C). Despite the rather high MgO-content of 12 % such acidic slags reveal a very high MgO-solubility of > 25 % [6]. The wear of the lining decreases with subsequent basic process slags. Figure 4 indicates the extreme corrosion and dissolution of the magnesia-carbon material. Regarding the total wear of the refractory lining the high iron oxide content and the rather high oxidation potential of the slag plays only a marginal role in this early converter phase.

With a continual converter process the slag is getting a more and more basic character. Due to the long blowing time of up to 45 min (6-9 x 5 min) the magnetite (Fe_2O_3) increases up to

> 60 %. Consequently, the slag reveals a very high oxidation potential against all carbon containing refractories.

The wear mechanism during this second converter stage is dominated by two main wear mechanisms:

-oxidation of the carbide in the refractories matrix and binder system



-formation of magnesio-ferrite (MgFe_2O_4) and the loss on refractoriness

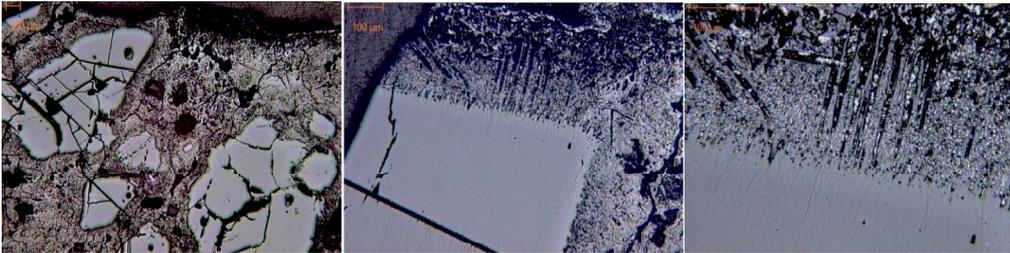
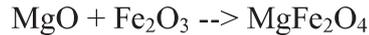


Figure 4: Microscope images of a magnesia-carbon brick in contact with a highly acidic slag of a FeNi-converter: the highly acidic slag possess a massive corrosion potential on the magnesia grains. The visible extreme dissolution of the periclase results in a very high wear rate

Magnetite containing slags are tent to oxidize the graphite in the magnesia-carbon refractories. Beside the graphite, the carbonaceous binder system of the MgO-C brick will be oxidized too. As a result the refractory materials lose the anti-wetting behavior and the opened up pores allow an intensified slag penetration. It is a well-known effect that iron oxide is capable of dissolving in the MgO-crystals [7]. Depending on the oxygen partial pressure magnesio-wustite ($[\text{Mg,Fe}]\text{O}$) or magnesio-ferrite (MgFe_2O_4) is formed. Both, the formation of magnesio-wustite and magnesio-ferrit result in the loss of refractoriness and therefore in an increased wear of the refractory lining. Figures 5 are showing the wear effect of FeO/ Fe_2O_3 -rich slags in contact to magnesia-carbon materials.

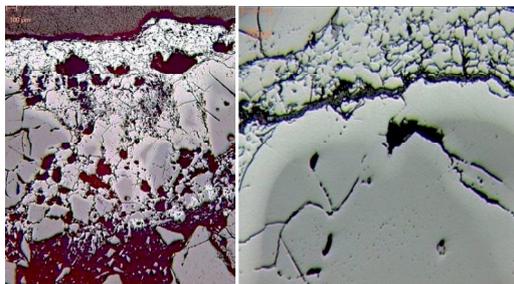


Figure 5: Microscope images of a magnesia-carbon brick in contact with a highly basic and iron oxide rich slag of a FeNi-converter: the main corrosion effect is the formation of magnesio-ferrite (MgFe_2O_4) and the loss on refractoriness. The absorption of the iron and the formation of magnesio-ferrite are visible by the typical bleaching of the magnesia grain boundaries. Bubbles in the frozen slag layer clearly indicate the oxidation of the graphite and/or the carbon binder from the brick

6. CONCLUSION

The special working conditions of the FeNi LD converter cause a very high corrosion potential against the refractory wear lining. In general the process can be described by two different converter slags:

- highly acidic early converter slag
- basic converter process slag rich in FeO

The MgO-Cr₂O₃ material that has been used for several years didn't meet the demands of the converter process, whereas the MgO-C lining proved their performance. Especially the highly acidic slag that occurs during the first stages of the converter process can cause a massive corrosion of the wear lining that can be a multiple of the later basic process slags. The second stage of the converter process is characterized by a basic but FeO-rich slag. Based on theoretical aspects as well as on practical experience the following principals for selecting MgO-C materials can be summarized:

- high quality fused magnesia with a MgO-content of >98 %
- big periclase crystals and a c/s-ratio of the silicate phases of >2.0
- carbon content of maximum 10 %
- avoidance of any antioxidants like alumina, silica or silicon carbide

With respect to these theoretical aspects and based on several practical trials the lifetime of the FeNi-converter has been increased by 75 % within 4 years.

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