ISSN 2176-3135

ICSTI
6th International Congress on the Science and Technology of Ironmaking - ICSTI
42th Ironmaking and Raw Materials Seminar/ 42º Seminário de Redução de Minério de Ferro e Matérias-primas
13th Brazilian Symposium on Iron Ore / 13º Seminário Brasileiro de Minério de Ferro

VALUE IN USE OF THE DUNITE[1]

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Abstract

In this presentation we will review and analyse the several benefits that the rock "dunite" brings into the blast furnace process. While the general tendency is to analyze fluxing agents simply by comparing their MgO content and / or price per ton, we will show that this is a very incomplete and partial view, as the total effect of the material on the blast furnace process should be considered, which is what Pasek calls value in use of the dunite.

Key words: Value in use; Desulphuration; Alkali; Basicity.

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[1] *Technical contribution to the 6th International Congress on the Science and Technology of Ironmaking – ICSTI, 42nd International Meeting on Ironmaking and 13th International Symposium on Iron Ore, October 14th to 18th, 2012, Rio de Janeiro, RJ, Brazil.*

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1 INTRODUCTION

In this presentation we will review and analyze the several benefits that the rock “dunite” brings into the blast furnace process. While the general tendency is to analyze fluxing agents simply by comparing their MgO content and / or price per ton, we will show that this is a very incomplete and partial view, as the total effect of the material on the blast furnace process should be considered, which is what PASEK calls value in use of the dunite.

2 DISCUSSION

When considering Magnesia fluxes, we need to take into consideration all the characteristics of the mineral that justify its addition to the burden like:

- Hot and cold resistance to decrepitation and mechanical stresses (shatter - crushing - abrasion). This will control the production of fines and the overall permeability of the burden to the reduction gases, improving the overall operation.
- Softening points and melting characteristics, especially after the absorption of alkalis. These should be those of a flux, not the ones of a refractory.
- Capacity to absorb alkali vapours and Cyanide.
- Mineral analysis and content in reactive crystallites that form with Potassium vapours stable components that have the required melting point.

Different materials on the above characteristics affect may parameters in the blast furnace; some of the main ones are:

- Sinter productivity
- Sintering speed
- Sinter RDI
- Blast Furnace Productivity
- Coke consumption
- Sulphur & Alkalis content on the pig iron
- LTBT

We will see during this presentation how PASEK’s dunite has a positive impact in all of these parameters, which at the end has a bearing on the operational performance of the whole installation and is therefore economically positive.

2.1 Dunite as a Mineral

Dunite (Magnesium Iron Silicate) is a plutonic rock formed by several primary minerals frequently transformed into secondary minerals through different more or less complex geological processes. Dunite is chemically classified as a basic rock, with olivine being the main mineral contained in the rock.

Looking at the different mineral presentations of Magnesia Silicates and their use as Blast furnace flux we see that Talcum are too weak and fragile, Serpentines and Chlorites have such a high content of hydrates that they decrepitate or do not resist thermal shock and Amphiboles are too low in MgO. This is why the less transformed rocks such as Olivine and Dunite are the most commonly used fluxing additives for Magnesia in Sinter & Blast furnaces all through Europe and Japan. In this section we describe the mineral composition and physical properties.

2.2 Chemical and Mineralogical Analysis

Dunite has basicity index that is almost equivalent to the slag basicity index. It does contain more silica and alumina than other options and its moderate hydrate content is sufficient to leave a large porosity (20%) when heated above 800°C, but low enough for it not to decrepitate. The iron content in this mineral is high enough for the thermal re-crystallisation to produce reactive Bronzite and native Quartz associated with Hematite. Dunite has a very low alkali content.

When calcined, Dunite contains less than 50% Forsterite and its crystallites are more reactive to alkalis with lower melting points. These crystallized minerals include: Clinoenstatite, Bronzite and native Quartz associated to Hematite. Other possible fluxes are more refractory as they contain mostly Forsterite (83% after calcination), whereas Dunite contains 15/20% of Bronzite, an acid iron bearing silicate, and 60% of Chrysotile, less basic than Forsterite.

Table 1. Chemical composition of the Dunite Mineral

Component	% weight
MgO	37%
SiO_2	40,5%
Fe_2O_3	8,3%
Al_2O_3	2,5%
CaO	1,9%
$Na_2O + K_2O$	<0,20%
L.O.I.	8,5%

2.3 Cold Mechanical Properties

Dunite is a homogeneous, fine-grained, hard stone of volcanic origin with few cracks. Careful extraction and selective crushing yield a material stable under the physical stresses of handling, transport and stock piling.

Table 2. Main Physical Properties of Dunite at ambient temperature

PHYSICAL PROPERTY	Typical Values
Bulk density	2,8 g/cm^3
Apparent porosity	<1,5%
Cold crushing strength	90MPa
Hardness	6,5/7Mohs scale

Dunite will generate fines when produced at the quarry, upon crushing and sieving where these can be properly screened. While this is the end of fines production for Dunite for other fluxes more fines are produced upon handling and while the material is on the stockpile. The edges in the lumps of these other fluxes are rounded off during abrasion resistance tests. This explains the problems encountered when testing these other fluxes to be used as a direct feed in the Blast furnace, as the material needs to have the correct grain size and needs to be free of fines. In big grain sizes (10-40mm) Dunite granulometry is very stable through the complete process and this makes it very compatible with Blast furnace permeable burdens.

2.4 Properties at Higher Temperatures

Dunite is a mineral that is made up of Olivine in more than 90%. The geological processes that the material underwent during its magmatic formation process changed its characteristics adding additional water in its chemical structure and reducing its sintering point to 1325ºC and its melting point to 1425ºC. When heated up from ambient temperature it is only progressively, between 450° and 850°C that Dunite´s hydrates are decomposed;(1) this explains the good thermal shock resistance despite its chemical water content between 7 and 9%. As the combination water is removed from the different mineral phases, it leaves behind a large open porosity that lets internal steam escape without resistance: there is no decrepitation. This porosity increases considerably the reactive specific surface of the magnesia silicates contained. Abrasion and crushing tests show that the decomposition of its hydrates does not weaken appreciably the grains that retain their excellent resistance to fragmentation and abrasion. Even when calcined, Dunite has physical properties that are equal or superior to the best burden materials (ore, sinter or pellets). These higher physical properties do not apply to other fluxes that behave like compressed sand where cracks propagate easily upon heating. Excessively refractory, these others fluxes do harden by sintering, but only above 1400°C. Thus, what is left of the other fluxes big size grains (>10mm) when they have reached the burden at the throat of the furnace, keeps on degrading when going down the Blast furnace stack.
The open porosity after calcination exceeds 22% (under reducing atmosphere), whereas it is limited to 4-5% for others. As the decomposition of hydrates happen below 800°C the produced steam cannot take part in the "solution loss" reactions (that are detrimental to coke consumption), because these take place above 900°C. This means that the decomposition of the hydrates contained in Dunite only has favourable effects.

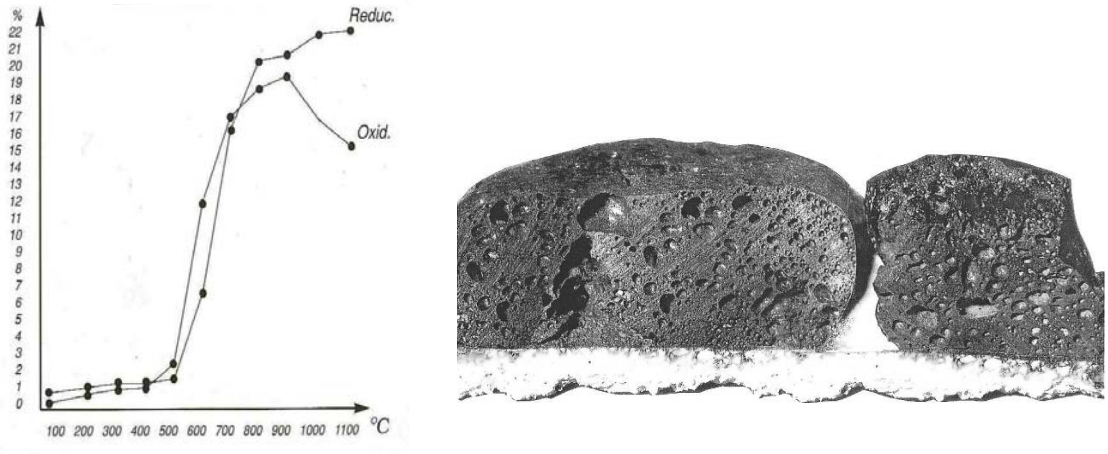

Figure 1. Evolution of % of Porosity in Dunite with Temperature on different ambient conditions. Image of Dunite at 1430^{o}C.

The test carried out and the extensive practical experience over the years clearly indicate that all the Dunite added to the Blast furnace burden melts as a flux in the belly and upper bosh. Other more refractory fluxes have higher activation and melting points so they do not have much chance to melt down and react before they reach the very high temperature zones in the lower bosh (above 1450°C). At this point it is too late to carry out effectively most of the functions for which fluxes are introduced. At the higher temperatures at the bottom of the Blast furnace, the fusion of Dunite takes place with considerable swelling and, as foam the mineral increases further the reactivity of primary slags.

The iron oxides contained in Dunite will precipitate and get reduced by the BF gases that diffuse through the open porosities left by dehydration between 700° and 1100°C, again in the higher part of the furnace shaft. Iron oxides bonded in Forsterite cannot be reduced.

Corrosion test by immersion have shown that Dunite dissolves very quickly in liquid primary slags, while other flux materials stay intact, even up to 1350°C. The higher Forsterite content in the other traditional MgO addition fluxes explains this difference. Forsterite is an excellent material when used for the manufacturing of refractory bricks that resist oxidized slags.

2.5 Use of Dunite in the Blast Furnace

The main reason to add fluxes into the Blast furnace burden is to remove those unwanted materials like potassium or sulphur that are brought in mixed with the ores or the coke. To avoid the concentration of such materials in the stack or the need for costly cleaning operation of the steel further downstream, the right fluxes need to be added into the mix. These fluxes also act as slag generators through their affinity with the iron ores gangue, achieving the practical separation of the hot metal from all the other impurities. For this purpose, the main additions required in the Blast furnace are CaO and MgO.

In the following sections we will review the mechanisms involved in the potassium cycle and also the influence this has in the control of the level of sulphur in the hot metal. Finally we will develop the characteristics provided when Dunite is added through the agglomerates present in the burden. You can see a graphical representation of the alkali cycle in the figure below.

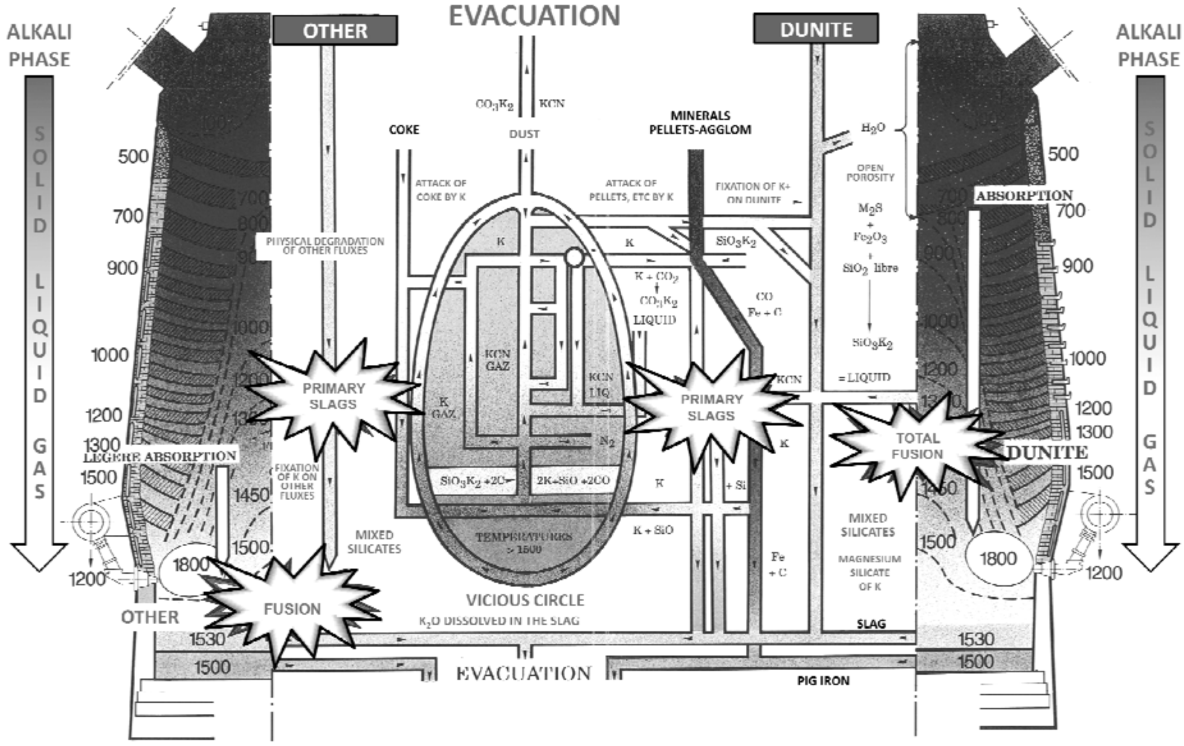

Figure 2. Potassium cycle in the stack and the effects of MgO fluxes

2.6 Potassium Recirculation Mechanism

The bigger part of the Potassium present in the stack is added with the coke ashes as Iron and Potassium Alumino-Silicates. The coke takes down to the tuyeres level these very stable compounds. Behind the combustion zone they are brought up to very high temperatures (1700-2000°C) under extremely reducing conditions. This liberates Potassium Vapours and mixes these with the reducing gases (CO and SiO), travelling with them on their way up through the stack. The mineral burden (iron ore - pellets - sinter) also contains smaller quantities of Potassium.

On their way up and in presence of coke, the K vapours react with the nitrogen of the gases forming vapours of Potassium cyanide (KCN). At 1100°C, the partial pressures of K and KCN are about equal. When they reach colder solids, the vapours condense, and the liquid moves down the furnace with the descending burden. When it reaches the high temperatures of the bosh, the liquid is vaporized and Potassium is re-circulated.

In the upper stack, the vapours are oxidized and carbonated by the CO_2 produced by the indirect reduction of iron oxides. The K_2CO_3 thus formed is deposited on the burden and moves down with it. When it reaches the high temperatures of the bosh, the coke reduces it to vapours, which are also re-circulated.

Since the Potassium can be re-circulated 5 to 10 times (and more under unfavourable conditions) through these mechanisms, it does accumulate in excessive quantities in the stack in liquid and solid form. This deteriorates not only the homogeneous porosity of the burden, but also the thermal and chemical operation of the furnace. There are also harmful side effects since the Potassium vapours react with refractories that are attacked and prematurely damaged (swelling, disaggregation and smelting). These vapours attack the pellets inducing heavy swelling and also the acid ashes of the coke that become weaker. At lower temperatures, they may even produce carbides in the coke.

All these effects make it clear that a mechanism that can gradually remove the alkali present in the burden and avoid their concentration will help in the overall productivity of the Blast furnace.

2.7 Potassium Elimination Mechanisms

As explained above there are several Hot properties of Dunite that are providing the Blast furnace burden with a mechanism for the elimination of alkalis that otherwise would accumulate during the operation. We will now discuss the details of how this mechanism works.

Water from hydrates present in the mineral (Chrysotiles) is progressively removed from 450º to 850°C leaving behind a large open porosity while the lumps do not decrepitate and retain their resistance to physical stresses. Simultaneously, the minerals are transformed into Forsterite, Clinoenstatite, Bronzite and fine Silica associated to Hematite, which precipitate in the open porosities. The Potassium vapours flow inside these porosities where they are oxidised and combined with Silica and Hematite to form silicates of Potassium, Magnesium and Iron that remain liquid in the range 900 to 1100°C. Alumina content can further lower the melting point of these complex silicates. These liquid phases progressively attack the various crystalline forms of precipitated Magnesia Silicates (Bronzite, Clinoenstatite and, finally, Forsterite which is less reactive and more basic). During this phase, Dunite swells appreciably, and thus further increases its Potassium absorption capacity through the increase in relative surface. Above 1100°C Dunite, with the absorbed Potassium (and Sodium), starts to soften and becomes part of the primary slags, where it readily dissolves at 1250°C. These primary slags trickle on the hot coke, where the last direct reductions are completed.

There is a part of these slags that run down into the hot zones behind the raceways are brought to high temperatures (above 1600°C) where the coke reduces the Potassium silicates as Potassium vapours entrained with the bosh gases. The remaining slags that trickle down colder zones in the hearth (between tuyeres and at the periphery of the "dead man") carry along with them dissolved K_2O, because the reduction and vaporisation kinetics are too slow at these temperatures.

This way Potassium is locked away in the slag as stable components (complex silicates of Potassium, Magnesia and Alumina) and these run down with the slag and are flushed out with the slag accumulated in the hearth at a temperature low enough so that there is no appreciable vaporisation of Potassium.

As mentioned above, the greater part of the alkali vapours travelling with the reducing gases are re-circulated with the descending burden. When the burden distribution is controlled and adjusted to create a permeable centre, the gases concentrate in this area and they leave the burden still very hot (450°C) carrying along fine dust particles laden with Potassium carbonate. This means that some of the original Potassium is not re-circulated and does not accumulate (provided the fine dust and the sludge of the gas cleaning plant are not recycled). This is a secondary Potassium elimination mechanism but the elimination through the slag that handles most of the original alkali load is a mechanism that can be promoted by:

- Adjusting the slag volume, diluting its K_2O content to acceptable levels.
- Decreasing the slag Basicity index. This stabilizes K_2O in the slag.
- Increasing the MgO content of the slag. For the same total basicity index, and for an identical sulphur capacity, this decreases the thermodynamical activity of Potassium.
- Using a cold operation (low silicon) and high top pressure, to slow down the reduction of Potassium. This lowers the formation of vapours when the slag trickles on the high temperature coke.

2.8 Iron Sulphur Control

Raw materials for pig iron production (coals and iron ores) contain alkalis (particularly K_2O) in quantities that may be detrimental to a good Blast furnace operation. The proper elimination of Alkalis from the Blast furnace does require adapted measures as mentioned in the previous point. The majority of these measures imply a degradation of the sulphur partition coefficient and an increase of iron sulphur content: this is particularly the case when using a lower slag basicity and colder operation that are the most effective ways to eliminate alkalis.

As Dunite addition to the burden improves the elimination of alkalis in the slag, this allows us to increase the basicity level of the slag ensuring a proper control of the sulphur content in the pig iron. This means that the addition of Dunite as an MgO flux to the burden plays a decisive contribution to sulphur control. In particular we should mention that two of the effects of this addition have a direct favourable effect on desulphuration: the increase in slag volume helps dilute the Potassium to be eliminated with the slag and provides a correct slag basicity level; Dunite also favours the formation of primary slags, foamy and fluid, and therefore more reactive.

2.9 Addition through Iron Ore Agglomerates

The mechanisms described above for alkali evacuation are of special relevance when Dunite is added directly to the Blast furnace as a coarse grain of between 10 and 40 mm. However, the mineral has also been used since the start as a flux to be added to the sinter in a finer grain of less than 3 mm. Finally there are currently tests going on for the production of acid pellets using Dunite as an MgO flux to take advantage of its low sintering temperature compared to other flux alternatives.

Close control of the analysis of the gangue that is provided in iron ore agglomerates has always been recognized as critical. The importance of the MgO content in this gangue has been demonstrated a focus point. Its effects are essential on Mechanical resistance at high temperature after reduction (RDI); Reducibility in the reserve zone (800 to 1000°C) and Reducibility at high temperatures (above 1050°C).

Dolomite fines were initially used with what was later proven to be poor results. Dolomite is very refractory and does not readily dissolve in the gangue unless very high temperatures are reached. If the agglomeration temperature is too low for the Dolomite (which are the normal operating conditions), the un-dissolved grains create weak points in the structure, and the mechanical resistance of the agglomerate is unacceptably low. It is necessary to adopt a higher agglomeration temperature: but this increases the fuel consumption and the harmful escorification of the sinter with a severe loss of production and reducibility.

Magnesia Silicates have replaced dolomite successfully. Among the minerals that are being used Serpentine’s MgO content is too low and Olivine fluxes are highly refractory and do not dissolve in the gangue or combine easily with the iron oxides. The softening and melting points of Dunite (sintering happens at 1325ºC and the melting point of the mineral is 1425ºC) are close to the normal agglomeration temperatures for iron ores and concentrates since in the sinter strand the flame front temperature will be around 1300°C and temperatures used in pellets ovens are about the same.

Due to its silica content, Dunite grains dissolve quickly in slags rich in iron oxides and with proper crushing, grinding and screening you can produce a very constant grain size distribution over time and comply to a very narrow specification. For sintering, fines without filler (washed) are ideal to improve the permeability of the sinter bed.

Acid Pellets have better mechanical properties when Dunite ultra-fines are used. These ultra-fines are produced by washing the fines produced for sintering or by an additional milling step. Compared to dolomite, the increase of the MgO content of pellets with ultra- fines has a very favourable effect on their resistance to alkali vapours. When the MgO content is too low in pellets (usually only the amount provided in the iron ore gangue), alkali vapours transported with the Blast furnace gases induce, during reduction, an excessive swelling of the pellets which makes them loose their mechanical resistance, and even crumble under their own weight. Pellets containing Dunite as a flux should bring to the Blast furnace mix all the benefits as an MgO flux described in this report together with a good mechanical resistance all through the process.

2.10 Value in Use of Dunite

PASEK Dunite’s value in use at the pig iron manufacturing process is the result of the combination of the physical and chemical properties of the product:

- Its low melting point compared to other fluxing agents makes it a superb product for slag conditioning, fluxing activity and basicity control of the slag, which starts performing at an early stage of the process, instead of at the bottom part of the blast furnace.
- Its high porosity at medium ranged temperatures helps the capturing of alkalis, sulphur and cyanide compounds which are brought into the blast furnace by iron ore gangue, coke and other additives.
- Its low LTBT has a bearing on a very high level of permeability inside the blast furnace; as a result, a higher reaction degree between solids moving down and gases going up is achieved.
- This property also helps obtain an interesting RDI value of the sinter, when used as fine material in the sintering process.
- Its well balanced MgO / SiO_2 ratio.

Just to resume all this in one single point, the use of dunite both in the sintering process (as fine material) or directly placed inside the blast furnace means a very important overall economical advantage and operations improvement,.

3 CONCLUSION

With a good level of MgO content and high hydrate content, Dunite fines and lumps have proven to be a very advantageous form of Magnesia addition to the Blast furnace burden.

Specifically the characteristics of Dunite that help the Blast furnace operation are:

- In the form of grains above 10mm is hard and withstands perfectly well the mechanical stresses that happen during handling, transport, stockpiling and charging in the Blast furnace. It retains its excellent mechanical properties at high temperature. This allows for the direct addition of the MgO in the Blast Furnace, giving the option to the operator to avoid, where required, the presence of MgO in the sinter.
- With a low basicity ratio, it contributes to the formation of more Magnesia slag that helps dilute and absorb K_2O decreasing its activity in the Blast furnace. Dunite melts down at a relative low temperature to form primary slags. Other fluxes, when calcined into Forsterite, behave in contact with ferrous slags as an excellent refractory, requiring higher energy input and delaying the start of the alkali evacuation mechanism. Forsterite is used to manufacture high temperature bricks and refractory sand used in iron and steel foundries.
- Upon heating, becomes very porous and transforms into Clinoenstatite, Bronzite and free Quartz associated to Hematite. Dunite swells when it absorbs K_2O.
- When it absorbs Potassium it forms stable components that are transferred to the primary slags. This mechanism improves the elimination of Potassium with the slag controlling its excessive recirculation and accumulation in the stack (as KCN and K_2CO_3). This accumulation is severely detrimental to proper operation of the furnace and lining life.
- With an improved elimination of Potassium, the operator can increase the slag basicity; improving sulphur control and reducing the sulphur level of the pig iron.
- As a fine, with a sintering temperature in the range of the ones used in the agglomeration of iron ore fines, it is an ideal flux to control the MgO content of sinter as well as pellets because at the same time it improves their hot

properties.

- Despite having a lower MgO content per tonne than some other fluxes it is one of the most economical MgO addition form for the Blast furnace burden since these other fluxes are too refractory, produce CO_2 and are less reactive.

Acknowledgments

We would like to thank all our clients that have helped us to understand the details of the use of Dunite as an MgO flux over the past four decades and with their open minds and controlled risk taking attitude have helped to improve their process, reduce their operational costs and improve their product quality. A very special recognition goes to Mr. Ralph Vervenne, blast furnace load preparation manager at SIDMAR in Belgium that over the years worked to understand the economic added value of the different minerals involved in blast furnace production, specially dedicated to the study of Iron ores, Limes and MgO addition fluxes (Olivine, Dunite and Dolomite).

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