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BENEFITS OF DUNITE AS MGO ADDICTION FOR SINTER AND BLAST FURNACE[1]

Roberto Caballero[2]
Raphael Vervenne[3]
Pablo Cuervo-Arango[4]
Javier Martinez[5]

Abstract

Quite a lot of plants are is using Dunite fines & lumps for long time, the reason for that are the following. In the sinter: The existing industrial experience for Sinter ranges has confirmed the following benefits: Higher reducibility of the sinter that translates to a lower coke consumption in the BF; Better hot strength or lower coke consumption at the same Hot Strength in the sinter plant; Better regularity of MgO in the slag; Higher productivity of the sinter plants; Lower percentage of screened off sinter before BF. In the Blast Furnace:_Better alkali evacuation by starting the capture in the upper part of the BF, this will have an effect on: Better operation of the Blast Furnace; Reduction of coke consumption; Reduction of sulphur in pig iron; Better alkali evacuation; the efficiency of the way MgO is added in the BF could improve the fluidity of the slag and it would mean a better desulphuration.

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2 *R&D Manager of Pasek Minerales*
3 *Raw Materials responsalbe of ArcelorMittal Gent*
4 *Innovation President Pasek Group*
5 *Managing Director of Pasek Minerales*

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Introduction

Magnesia Silicates are commonly used as Sinter and Blast Furnace fluxing additives, not only to adjust the MgO content, but also to promote Potassium elimination through the slag, limiting the harmful accumulation of Potassium in the stack.
Numerous analysis, investigations and laboratory tests have compared different Blast Furnace fluxes contributing to the understanding of the mechanisms of transformation of the minerals in the shaft and their capacity to absorb Potassium vapours.
The results of these investigations show that is more effective than other fluxes, for the following reasons:

- Hot and cold physical properties are superior.
- The softening and melting points lie within the temperature range of the lower shaft and the belly of the Blast Furnace;
- The hydrate content is high enough to leave room below 800°C (1470ºF) to a large porosity (20%) which insures the greater reactivity**;**
- With a lower basicity ratio it transforms, below 800°C, into minerals more reactive to K than other Forsterite based fluxes. It forms Clinoenstatite, Bronzite, native Quartz and Hematite, which readily form stable components with Potassium vapours.
- Laboratory simulations have shown that dunite is at least <u>two to three</u> times more effective than other fluxes in absorbing Potassium vapours in the shaft.

In Blast Furnace operation, the improvement of Potassium elimination enables the operator to use high basicity slags. This allows for a better control of the sulphur content in the pig iron.

- The diffusion of Potassium in dunite, very porous above 800°C, allows the use of coarse granulometries, 10-40mm mainly, while other fluxes need to be used as sand, 0-3mm to be effective.
- Fines are also an effective fluxing agent in the agglomeration of iron ore fines (sinter-pellets) because of their moderate softening and agglomeration temperatures that lie within the range normally used in sintering and pelletizing.

Despite the fact that the price is apparently higher when compared by MgO points; It turns out more economical, when all the <u>effective savings</u> brought by this mineral (desulphuration, slag basicity, reduced fines, lower cok consumption…) for Sinter & Blast Furnace, are taken into consideration.

Where Does dunite Add Value?

Magnesia silicates, quarried, crushed, sized and screened are added to the Blast Furnace in small quantities (15 to 35 kg/mt) to perform the following functions:

a) Magnesia addition, to fluidify the slag and adjust its MgO content to the optimum value (6 to 9%), required by its Basicity index and Alumina content.
b) Adjustment of the slag volume to its optimum value (290 to 360 kg/mt) above the slag Basicity index.
c) Improvement of the kinetics of primary slags formation (1200° to 1400°C) if the magnesia silicate used is indeed a Flux as it is for dunite. In this case

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slag desulfurization of pig iron is improved.

d) Absorption of Potassium Vapours in the lower shaft, and improvement of the kinetics of their fixation as K_20 in the slag. This makes sure that K is effectively flushed out of the hearth preventing its recirculation and accumulation in the stack.

It would be a gross and costly error when purchasing Magnesia Silicates, to take into consideration only the price of the MgO contained, and ignore its effectiveness as a flux to be loaded into the Blast Furnace. One should take into consideration all the characteristics of the mineral that justify its addition as a flux in the burden like:

- Hot and cold resistance to decrepitation and mechanical stresses (shatter - crushing - abrasion).
- Softening points and melting characteristics (after absorption of K_20 and Na_2O) which should be those of a flux, NOT the ones of a refractory.
- Capacity to absorb vapours of Potassium and Cyanide.
- Mineral analysis and content in reactive crystallites that form with Potassium vapours stable components with a low melting point.

As this paper demonstrates that it is superior in all these characteristics and functionalities. This clearly justifies its use as a Blast Furnace Flux when compared with other options, which have higher refractory characteristics.

Agglomeration With Dunite Fines (Sinter & Pellets)

Close control of the analysis of the gangue in 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)
- Reducibility at high temperatures (above 1050°C)

Besides, the MgO content of the agglomerate has to meet the needs of the slag to be formed, adjusting to its Basicity index and Alumina content, and also the required alkali removal capacity.

The MgO is added to agglomerates as Magnesia Fluxes with characteristics that are different for sinter and pellets.

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 scorification of the sinter with a severe loss of production and reducibility.

Magnesia Silicates have replaced dolomite successfully. But, among the various minerals which have been used:

- Serpentines MgO content is too low
- Other fluxes are too refractory and do not dissolve in the gangue or combine easily with the iron oxides

Softening and melting points are close to the normal agglomeration

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temperatures for iron ores and concentrates. In the sinter production the flame front temperature will be around 1300°C and sintering temperatures of pellets are about 1100°C.

Due to its silica content, grains dissolve quickly in slags rich in iron oxides (when other fluxes are not even attacked superficially by these slags at these temperature levels) and with proper crushing, grinding and screening you can produce a very constant grain size distribution of over time under a very narrow specification.

For sintering, fines without filler (washed) are ideal to improve the permeability of the sinter bed.

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, alkali vapours transported with the Blast Furnace reducing gases induce, during reduction, an excessive swelling of the pellets which makes them loose their mechanical resistance, and even crumble under their own weight.

Dunite pellets are far superior and should be preferred as it brings to the Blast Furnace mix all the benefits as an MgO flux described in this report.

5. Dunite Properties

If we look at the different mineral presentations of Magnesia Silicate 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, Amphiboles are too low in MgO. This is why it is one of the most commonly Magnesia Silicates used today in Sinter & Blast Furnaces as a fluxing additive. Let's see the properties of this mineral.

A. Chemical Analysis

it 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 so that it does not decrepitate.

The iron content is high enough so that the thermal re-crystallisation produces reactive Bronzite and native Quartz associated with Hematite. Its alkali content is very low.

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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%

B. Mineralogy

When calcined, it 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.

C. Cold mechanical properties

it 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.

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

Generates fines when produced at the quarry, upon crushing and sieving. While this is the end of fines production, for other fluxes more fines are produced upon handling and while the material is on the stockpile.
Other fluxes cannot be crushed and milled easily since abrasion produces a large quantity of fines. The edges in the lumps of these other fluxes are rounded off during abrasion resistance tests. This explains the problems encountered when these other fluxes are used in the Blast Furnace as a material supposedly of the correct size and free of fines.
In big sizes the delivery is stable and very compatible with Blast Furnace permeable burdens.

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D. Hot properties

It is only progressively, between 450° and 850°C that its hydrates are decomposed: this explains the good thermal shock resistance despite water content between 7 and 9%. As water from the surface of the grains evaporates, 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 stones when they have fallen on the burden at the throat of the furnace, keeps on degrading when going down the Blast Furnace stack.

The iron oxides contained and precipitated are reduced between 700° and 1100°C by the BF gases that diffuse through the open porosities left by dehydration. Iron oxides bonded in Forsterite cannot be reduced.

The weight variation at 1100°C under reducing conditions is higher by 3,3% and lower by 0,9% for other fluxes (compared to calcination under oxidizing atmosphere).

The open porosity 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 only has favourable effects.

Corrosion test by immersion of pieces of dunite and other fluxes in liquid primary slags have clearly shown that dunite is dissolved very quickly, while others stay intact, even up to 1350°C. This is explained because of the higher Forsterite content in the other fluxes that is an excellent material when used for the manufacturing of refractory bricks that resist oxidized slags.

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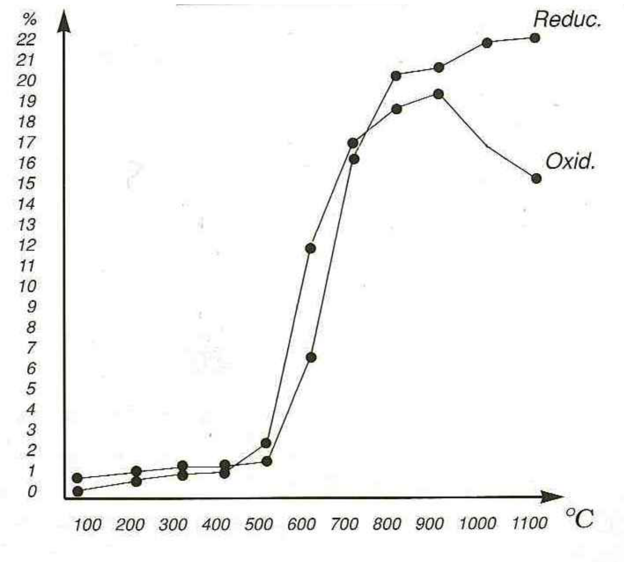
DUNITE OPEN POROSITY vs Temperature



DUNITE at 1430ºC: porous foamy

These test demonstrate that all the dunite charged as lumps and in the Sinter with the burden are molten as a flux in the belly and upper bosh of the blast furnace. Other more refractory fluxes stones 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 higher temperatures at the bottom of the Blast Furnace, the fusion takes place with considerable swelling and, as a foam, increases further the reactivity of primary slags.

Potassium Elimination From The Blast Furnace

1. Recirculation mechanism

The mechanisms of recirculation and elimination of Potassium from the Blast Furnace can be described as follows:
The bigger part of Potassium is charged 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 high temperatures (1700-2000°C) under extremely reducing conditions, which liberates Potassium Vapours and mixes them with the reducing gases (CO and SiO).

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The mineral burden (ore - pellets - sinter) contains smaller quantities of Potassium. It forms with the fluxes the primary slags after a certain degree of pre-reduction is reached when it melts down. The primary slags trickle on the hot coke, where the last direct reductions are completed.
The slags that run down into the hot zones behind the raceways are brought to very high temperatures (above 1600°C) where the coke reduces the Potassium silicates as Potassium vapours entrained with the bosh gases. The slags which trickle down colder zones in the hearth (between tuyeres and at the periphery of the "dead man") carry along with them dissolved K_20, because the reduction and vaporisation kinetics are too slow at these temperatures.
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 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 K vapours react with refractories that are attacked and prematurely damaged (swelling, disaggregation and smelting). They also attack the pellets in which they induce heavy swelling and the acid ashes of the coke that become weaker. At lower temperatures, they may even produce carbides in the coke.
The greater part of the vapours (K and KCN) is thus re-circulated with the descending burden. But, when the burden distribution is controlled and adjusted to create a permeable centre, the gases, which concentrate there, leave the burden still very hot (450°C), and carry along fine dust particles laden with Potassium carbonate.
Thus, some of the charged 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 K elimination mechanism but the elimination of Potassium with the slag can be much more massive and it can be promoted by:

- Adjusting the slag volume, which dilutes 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 reduces the formation of vapours when the slag trickles on the high temperature coke.

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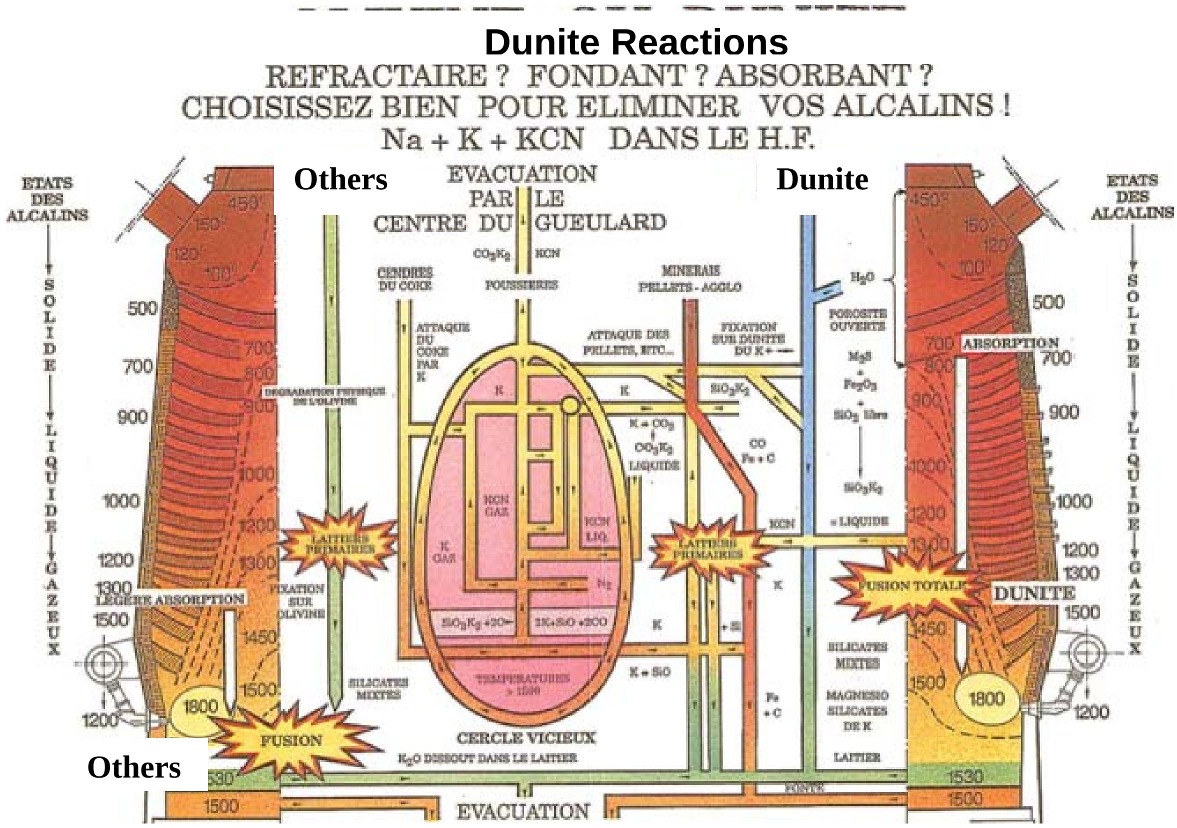

2. Elimination mechanisms

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 could accumulate during the operation. You can see a diagram of the Alkali (K, Na and KCN) evacuation mechanism in the figure below. Here are the details of how this works:

Water from hydrates (Chrysotile) 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 it swells appreciably, and thus further increases its Potassium absorption capacity.

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.

Potassium is locked away in the slag as stable components (complex silicates of Potassium, Magnesia and Alumina). They run down with the slag in relatively

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cold areas of the hearth (between the tuyeres and around the "dead man") and are flushed out with the slag accumulated in the hearth at a temperature low enough that there is no appreciable vaporisation of Potassium.
Slag is the best vehicle for Potassium elimination.

Iron Sulphur Control

Raw materials for pig iron production (coals, 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 sulfur partition coefficient, and an increase of iron sulfur 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 addition as a flux to the burden plays a decisive contribution to sulphur control.
We should also note that two of the effects of its addition have a direct favourable effect on desulphuration:

- increases the slag volume which helps dilute the Potassium to be eliminated with the slag and a correct slag basicity level
- it also favours the formation of primary slags, foamy and fluid, and thus more reactive.
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Conclusions

With a good level of MgO content and high hydrate content, Dunite fines and lumps are very advantageous Magnesia addition to the Blast Furnace burden.
Specifically:

- Fine-grained it is hard and withstands better the mechanical stresses during handling, transport, stockpiling and charging in the Blast Furnace. It retains its excellent properties at high temperature.
- Less basic, it contributes to the formation of more Magnesia slag that helps dilute and absorb K_2O and decreases its activity in the Blast Furnace. it melts down at low temperature to form primary slags.
- It should be mentioned that the other fluxes, when calcined into Forsterite, behave in contact with ferrous slags as an excellent refractory. Forsterite is used to manufacture high temperature bricks and refractory sand used in iron and steel foundries.
- Upon heating, it becomes very porous and transforms into Clinoenstatite, Bronzite and free Quartz associated to Hematite. Dunite swells when it absorbs K_2O.
- it absorbs Potassium and forms stable components that are transferred to primary slags. This mechanism improves the elimination of Potassium with the slag, limits its excessive recirculation and accumulation in the stack (as KCN and $C0_3K_2$). This accumulation is severely detrimental to proper operation of the furnace and lining life.

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- With an improved elimination of Potassium, the operator can increase the slag basicity; improving sulphur control and sulphur level of the pig iron.
- Fine, which softens in the temperature range of agglomeration of iron ore fines is an ideal flux to control the Magnesia content of sinter as well as pellets, and it improves their hot properties.
- it is one of the most economical MgO addition form for the Blast Furnace burden. Other fluxes are too refractory, produce CO_2 and are less reactive.