ADVANTAGES OF THE USE OF DUNITE IN SINTER MIX & BLAST FURNACE VS. DOLOMITE[1]

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Abstract

This documents demonstrates that the substitution of Dolomite by Dunite has several advantages that improves significantly the operation of blast furnaces. The data presented indicates that the LTBT improves, which means a lower sinter fines generation, the lower sinter fines returns improves the productivity of the sinter plants. The improved LTBT of the sinter produced means lower degradation in the upper part of the blast furnace, therefore the lower breakdown, generating less fines in the upper stack, thus an improved blast furnace permeability which in turn allows a constant blowing rate and smoother and stable blast furnace operations. Dunite has a lower melting point, this characteristic helps to have a thinner cohesive zone, again the effects are better permeability and more stable blast furnace operations. The DRI improves significantly; this has a positive effect for blast furnace operations and fuel rates. The accumulative benefits of improved LTBT and DRI and constant blowing with stable blast furnace operations has the effect of reducing the coke rates which in turns has the benefits of reducing the sulphur load to the blast furnaces. This reduction of the sulphur load has the effect of reducing the sulphur content of the hot metal, this very important effect must be noted when making an assessment of the benefits generated.

Key words: Dunite; Improvement; Properties; Blast furnace; Coke.

VANTAGENS DA UTILIZAÇÃO DA DUNITA NO SINTER OU DIRETAMENTE NO ALTO FORNO COMPARATIVAMENTE A DOLOMITA

Resumo

Este trabalho pretende demonstrar que a substituição da dolomita pela Dunita implica numa substancial melhoria no processo produtivo do alto forno. Na sinterização, a aporte de Dunita demonstra um melhor balanço do LTBT e os dados revelam menor geração de finos e aumento da produtividade de sinter. Conseqüentemente a degradação do sinter é menor na parte superior da cuba melhorando a permeabilidade e proporcionando um fluxo gasoso mais constante e a operação mais estável do forno. Com um ponto de fusão inferior a dolomita, a Dunita gera uma região coesiva menos abrangente permitindo melhor permeabilidade na parte inferior do forno melhorando substancialmente o DRI índex. Em função destes índices de LTBT e DRI, há uma diminuição do consumo de coque e do teor de S no gusa proporcionando uma importante redução nos custos. Estes benefícios deveram ser tomados em conta no calculo final das vantagens proporcionadas pela utilização da Dunita no sinter ou mesmo adicionada diretamente na carga de alto forno.

Palavras-chave: Dunite; Sinter; Alto-forno; Vantagens.

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1 INTRODUCTION

One of the most important and biggest integrated steel mill & blast furnace in EU contacted us to find a Magnesium Silicate that could be added to the feed in the blast furnace to economically replace the use of dolomite in the fusion beds of the blast furnace and also in the agglomeration.

Following their instructions we searched for a suitable mineral with optimum natural characteristics to improve the performance of the smelting load feed in the blast furnace, for example a rock/stone with a small loss on ignition to eliminate the risk of crumbling and other losses due to redundant volumes and dead loads, but above all to find an appropriate material that did not contain carbonate, given that all blast furnace operators know that CO2 that is released in the stack is “poison” for the performance of the blast furnace.

After having studied numerous Spanish and foreign magnesium silicates in the laboratory we chose dunite from a region in Galicia that met all the demands that we had for this new material.

After a period of testing spread out over almost 10 years of close work and in collaboration with the main steel producers in France, Belgium and Spain we have shown that the results of using dunite as the flux have been positive and interesting in the context of the improvements it brings to the blast furnace in the opinion of the engineers.

It is also worth noting that dunite, when well calibrated and adapted to the loading requirements, be it in rock form in the blast furnace or in fines in the agglomeration, gives a noticeable saving in coke in the slag.

Nevertheless, the most important criteria in the advantages of using dunite in the blast furnace or in the agglomeration is that it gives the user a base element that is stable and normal which you can rely on and that is vital for the good working of the blast furnace.

Dunite provides stability that gives reliable compositional quality in the slag.

According the requirements of the blast furnace operators, dunite is loaded directly into the blast furnace in rock form and/or dunite fines added to the agglomerate.

All the users of dunite fines have testified that replacing other additive MgO materials with dunite has improved the heat performance in the agglomerates and as a result given better performance of the agglomerates in the blast furnace and better operational performance.

Some users have remarked on a gain in the cost of the agglomerates after replacing the other materials with dunite.

2 CHARACTERISTICS OF DUNITE

Table 1. Chemical Analysis & screening analysis of dunite fines

DUNITE 0/3 mm	Chemical Analysis								screening analysis					
	LOI	SiO2	Al2O3	Fe2O3	CaO	MgO	Na2O	K2O	> 5	4 / 5	3,15 / 4	1 / 3,15	0,5 / 1	< 0,5
MEDIA %	8,69	40,75	2,45	8,32	1,95	37,00	0,12	0,05	0,16	0,61	6,72	46,58	16,02	30,00
SDEV	0,58%	0,20%	0,16%	0,15%	0,17%	0,27%	0,02%	0,01%	0,08%	0,55%	2,02%	3,39%	1,53%	4,20%

Table 2. Chemical Analysis & screening analysis of dunite lumps

DUNITE	Chemical Analysis								Screening Analysis			
10/40 mm	LOI	SiO2	Al2O3	Fe2O3	CaO	MgO	Na2O	K2O	> 40	18/40	10/18	< 10
Avge %	8,19	40,98	2,50	8,33	1,92	37,06	0,12	0,05	0,26	75,47	21,38	2,56
SDEV	0,99%	0,33%	0,18%	0,13%	0,26%	0,49%	0,02%	0,01%	0,69%	3,93%	4,03%	0,56%

Table 3. Physical properties of dunite

Characteristic	Data
Crushing resistance (Baron)	1.400 kg / cm2
Abrasion indices (Baron)	4,5
Impact resistance (IRSID) in fines	< 10mm = 6%
Abrasion resistance (MICUM) 200 T. in fines	< 10 mm = 16%
Thermal shock resistance 200 T. in fines	< 10 mm = 5,3%
Swelling and contraction test at 1300º	Nil
Degradation test = CO2 at 1200º	Nil
Softening point (CENIM)	1350º
Fusion point	1450º
Real density	2,45
Apparent density	1,7

3 THE ADDITION OF MGO TO THE AGGLOMERATION IN THE FORM OF DOLOMITIC LIMESTONE

3.1 Agglomerate

Partial liquefaction of the load at that point, or the fusion temperature is only achieved locally and momentarily.

The CaO reacts with the SiO_2 and with the other components to form a pasty primary state that attacks the large granules. In contrary to the CaO, the increase in the MgO content does not diminish the fusion point despite the increase in the overall basicity.

A higher fusion point creates a less blended phase and delays a less rapid reaction so that the diffusion phenomenon, in being much slower, becomes more important in the solid state.

This higher fusion point from the contribution of MgO provokes a reduction in the reaction possibilities and reduces, as a consequence, the liaison between the MgO and the other components.

As a result more coke must be added to increase the temperature as required and to improve the reaction possibilities.

The increase in temperature will also reduce the lifespan of the agglomeration belt grills.

3.2 Cooling

A higher solidifying temperature and a narrower solidification zone will provoke greater cooling tensions and a greater number of cooling cracks (fissures). This will cause a disadvantageous effect in the mechanical resistance of the agglomeration.

Use of pre-heated air will eventually be able to solve this effect (though it is practically impossible).

3.3 The Influence of the Source of MgO

We assume that the MgO is always provided by dolomite ($CaCO_3$, $MgCO_3$).
Comparative studies between dolomitic limestone, olivine, semi-serpentine, dunite and dunite + heat, have been carried out by using an experimental stack.
Serpentine and dunite are Magnesium Silicates. Serpentine is a product of degradation (evolution) of dunite: it contains other minerals and more water. The serpentine in rock form that is commonly used as a source of MgO contains Magnesium Hydrate ($Mg(OH)_2$) and antigorite.
A lessening granular size will observe an increase in the reactivity (the best reactivity is for 0/1,25 mm), whilst as a mineral; it is dunite which gives the best results. An increasing ratio of MgO/SiO2 gives rise to a strong decrease in the return fines, a good improvement in the mechanical resistance and a reduction in the amount of coke consumed and in the quantities of dunite and semi-serpentine that have identical MgO contents.

3.3.1 For MgO/SiO_2 = 1,4 we obtain

a1. For dunite 0/5mm: Less good resistance and lower consumption of coke by the lime agglomerates, but a higher speed of agglomeration at the same coke content in the mix;
a2. for dunite 0/1,25 mm (in a 0-3mm dunite a large part is <1,25mm): Better resistance and a lower consumption of coke than with the lime agglomerates;
a3. with serpentine 0/5mm: An important reduction in the mechanical resistance compared with the lime agglomerates;
a4. with dolomitic limestone <1,25mm: We have never achieved an improvement vis à vis the lime agglomerates.

3.3.2 For MgO/SiO_2 = 1,7

b1. With dunite < 1,25mm: A greater mechanical resistance and a lower consumption of coke than with a2;
b2. serpentine < 1,25mm: An important increase in the speed of agglomeration.

The laboratory tests have been confirmed in industrial application and it appears that dunite (< 1,25 mm) as well as the serpentine is rock form work well.
They increase the mechanical resistance and decrease the consumption of coke.

4 CONCLUSIONS CONCERNING THE MECHANICAL PROPERTIES DURING REPLACEMENT CAO BY MGO

If we use dolomite as an additive in place of limestone during agglomeration we obtain the following results:

- ASTME indices equivalent to those for limestone if we increase the content of coke during the agglomeration, this is valid:
  - for all the agglomerates with a high level of MgO (> or = 4%);
  - from $i_1 = CaO/SiO_2 > 1,2$ for limestone agglomerates with < 3% MgO.
- Better LTBT values compared with limestone agglomerates. Given that dunite provides SiO2, the LTBT values are even better.

If we use dunite as an additive or serpentine in rock form in place of the limestone, we can obtain properties equivalent to those for limestone if the granular size and the moisture content of the agglomeration load are adjusted.

5 EVOLUTIONARY CHARACTERISTIC OF DOLOMITE

Table 4. Dolomite properties

Parameters	**Constant i_2**	**Variant i_2**
Mechanical characteristics	Constant coke content MgO/CaO	Constant coke content MgO/CaO constant
Resistance to abrasion	Reduced	The minimum to get by in comparison with the limestones, towards higher basicity indices
Resistance to abrasion at higher Tº and under reduction conditions	Increased	The minimum to get by in comparison with the limestones, towards lower basicity indices. The evolution (LTBT index in function de i_2) is higher than for limestones. (better LTBT index).
Reduction properties	Reduced between 1,3 - i_2 - 2,5	Continual increase until $i_2 = 2,5$
Porosity	Increased	The minimum to get by towards higher basicity indices.

Within the basicity interval 1,3 <= CaO/SiO_2 <= 2,5 the agglomerates seem to have a better reduction properties. In practice we most often work with basicity indices within this interval.

The contribution of CaO from the dolomitic limestone is a poor CaO reactive due to the fact that crystal size of dolomitic limestone is 4 to 10 times larger than for normal limestone and also that this CaO requires more coke to carry out the necessary reactions. The dolomitic limestone provides both CaO and MgO.

By adding CaO and MgO separately we avoid the formation of CaO, MgO, SiO2 (monticellite) and we achieve better mechanical resistance characteristics.

Dunite provides SiO_2 and MgO to the fusion and practically no CaO. These CaO and MgO elements are already combined.

6 DESULPHURISATION ON THE AGGLOMERATION BELT

Sulphur is principally a fuel issue. Other sources we could mention include FeS2, FeS, CuS, ZnS, $CuFeS_2$.

The released sulphur is oxidised during the agglomeration in SO_2, while the sulphides give rise to SO_2 and oxides. A part of the SO_2 formed in the way combines with the lime in the form of CaSO4.

The influence of replacing a part of the CaO with MgO is favourable: Khoklov notes improved desulphurisation.

Given that the agglomerates that contain MgO have less CaO, we can take as a hypothesis that the SO_2 has less chance to react with the CaO.

Given that the CaO is the only oxide that can bind SO_2 ($FeSO_4$ and $MgSO_4$ are not stable at the temperatures being considered whilst CaSO4 is stable between 208º and 1.200º K) there is more SO_2 sucked up into the “agglomeration cake”. Therefore less sulphur will be left in the agglomeration itself.

Therefore, an increase in the content of MgO is favourable for desulphurisation on the agglomeration band.

7 THE PRODUCTIVITY OF THE AGGLOMERATION BELT

The speed of agglomeration seems to peak around 1,3% MgO. This is equivalent to the speed of agglomeration of the limestones with an MgO content between 2,5% and 3,3%. Above 3,3% of MgO it [the speed] is lower.

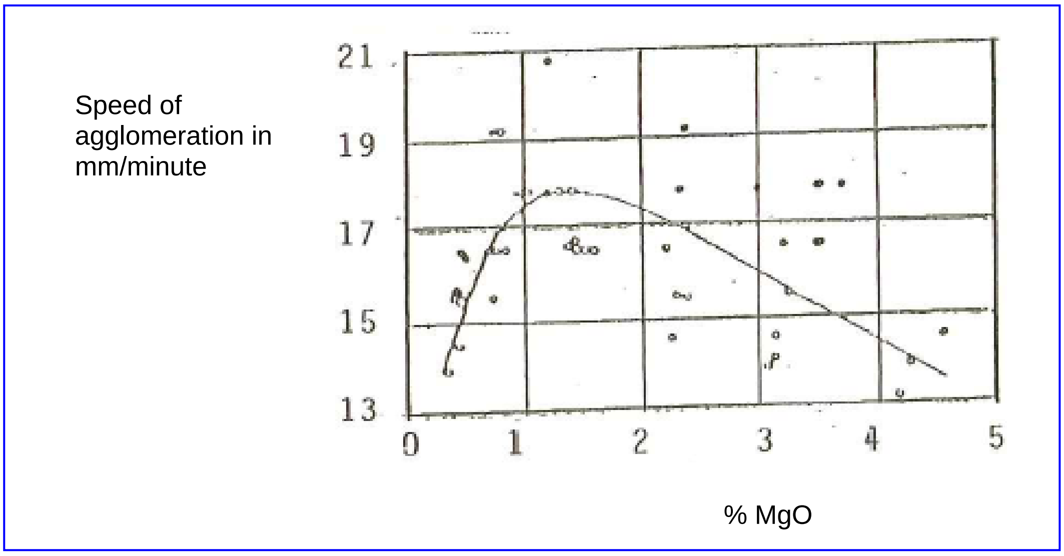

Figure 1. Vertical Speed of the Grill.

The influence of the MgO in the speed of agglomeration shown here is the vertical calcination speed for a load of agglomerate. During the monitoring that produced the above graph the basicity was kept constant. The increase in the percentage of MgO was obtained by replacing part of the limestone with dolomite (Figure 1).

Euler, Lackmann and Schwiete obtained other results while increasing CaO + MgO/ SiO_2:

- the production of agglomerates (ton per m2 per day) is always lower with dolomite than with agglomerates that have limestone as the additive.
  We would like to point out that all the agglomerates were made with the same quantities of coke (same quantity in Kg per 100 kg of mineral + basic additives)
  An increase in the coke content during agglomeration with dolomitic additives does not produce lower production figures in the dolomitic agglomeration;
- for basicity indices of B > 1,2, the agglomerations with dolomitic additives show a very marked reduction in production, in contrary to the limestone agglomerates.

An increase in the content of coke for the agglomerates with dolomitic additives had little effect; the same very marked reduction was noted for A > 1,2.

7.1 Increase of (CaO + MgO)/SiO_2 in the Lime

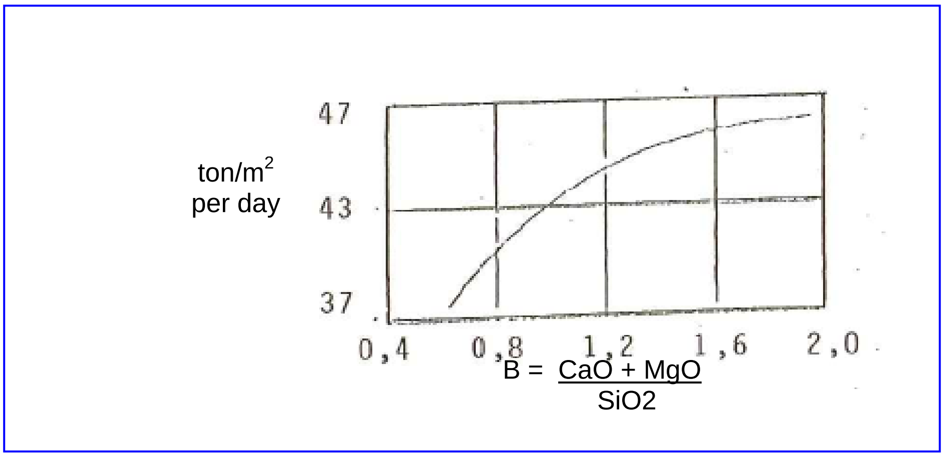

Figure 2. Production of Agglomerate.

The influence of the CaO content in the agglomeration production (ton/m2 per day). The increase in the Basicity index B = (CaO + MgO)/ SiO_2 was achieved by adding limestone solution or charred lime (Figure 2).

7.2 Increase of (CaO + MgO)/ SiO_2 in the MgO

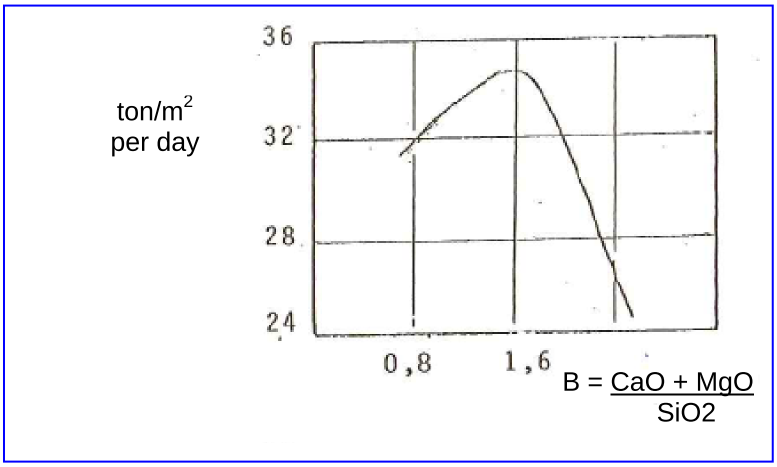

Figure 3. Production of Agglomerate.

The influence of the CaO content in the agglomeration production (ton/m2 per day). The increase in the basicity index B = (CaO + MgO)/ SiO_2 was achieved by adding raw dolomite. There was no lime added (Figure 3).

All these figures are valid when dolomite is used as the source of MgO.

Testing with dunite and serpentine has given better results (Meunier). While using fine granules (0/1,25 mm) the best results have been achieved for dunite and serpentine.

At the same time dunite provides MgO and SiO to the (CaO + MgO)/ SiO_2 ratio.

It does not increase the necessary fusion point and therefore does not increase the amount of coke consumed.

This has been proven in industrial application: use of dunite or serpentine give higher production figures than those achieved when using limestone. Lower production figures while using dolomite as the source of MgO have also been proven in industrial applications.

8 DISCUSSION OF THE STUDY OF THE STRUCTURE OF DIFFERENT AGGLOMERATIONS CONTAINING MGO

Devitrification in the growing vitreous phase, thanks to the (FeMg)1,3 $CaSiO_4$ type olivine breaks the glass matrix (die). The vitreous flexible mater is therefore replaced by a grid of olivine that never fully changes from crystalline form when MgO/CaO >= 1.

During the “destruction” of this vitreous frame it is normal that the mechanical resistance is reduced (Shatter index, Tumbler index). From a value of MgO/CaO >= 1 the mechanical impact resistance stabilises. The grid of olivine is fully transformed from the crystalline form.

Nevertheless, the mechanical resistance of the agglomeration for MgO >=1 is on net lower for limestone agglomerations. The hypothesis could be made that the grid of olivine does not guarantee the mechanical resistance of a MgO agglomeration due to the difference in fusion point and in the thermal dilation coefficient with the nearby phases.

At constant coke content and an increasing MgO/CaO, the mechanical resistance descends more because the fusion point for the first paste formation phase during the agglomeration is higher. Therefore, by having equal coke content, the agglutination of the particles in the MgO mix is lower than in a limestone agglomeration.

Carrying out optical microscopic analysis we find more constituents of mineral origin than in the limestone agglomerations. When adding dunite, the fusion point of the first paste formation phase does not rise. It is not necessary to increase the quantity of coke in the mix.

9 THE EVACUATION OF ALKALIS IN THE BF USING DUNITE

It has been established that an acid slag is good at evacuating the alkalis due to the activity of the silica but that at the same time the desulphurisation properties of said slag within the blast furnace are reduced.

At the same time dunite contributes SiO_2 and MgO that gives a good fluid slag and no loss of pig iron. The MgO gives good desulphurisation properties and diminishes the SiO_2 activity (due to the fact that MgO is a weak base) for the capture of alkalis as is the case for CaO that comes from the gangues from the ferrous load. As the dunite is an orthosilicate (tetrahedrons of isolated SiO4) one molecule of silicon can bond with two base molecules. The silica that the dunite contributes is therefore more reactive on net, due to the capture of alkalis, than the silica that comes from the silicates in tetrahedron chains, leaves or bonded in three dimensional structures. The MgO and the SiO_2 from the dunite are available at the right place thanks to the decomposition of the alkali products in the ferrous load and the MgO and the SiO_2 can react with the alkalis in the coke ash that decompose later. That is not the case with other contributors of SiO2 such as gravel which melts too late, and olivine which contributes both SiO_2 and MgO but which has a fusion point that is too high/1.730ºC). Dolomite contributes CaO and MgO; the CaO diminishes the SiO2 activity and the fusion takes place a high temperatures. The decarbonisation of the dolomite impoverishes the gas. Further more products such as olivine, gravel and dolomite require supplementary coke consumption to such a notable level that it affects productivity and costs.

10 ADDITION OF MGO TO THE AGGLOMERATION IN A FORM OTHER THAN DOLOMITIC LIMESTONE

It has been shown that adding MgO in dolomitic limestone form had a negative effect on the quality of the agglomerate produced.

Thus we decided to study natural magnesium silicates such as olivine and serpentine as substitutes (CRM 45/72). From the mineralogical point of view these products are located in the following chain:

- olivine: pure magnesium silicate;
- dunite: a less pure magnesium silicate that contains more combined silica but which is more “smeltable” than olivine (1.730º compared to 1.450º for dunite) and that also contains some Fe content. Dunite is principally made up of olivine but having undergone serpentinasation;
- serpentine: dunite that has undergone a greater degree of serpentinisation;
- talc: talc is the last (lowest) element in this degradation chain.

Going into more detail about olivine and dunite, olivine is a pure crystalline rock whilst dunite is a crystalline rock with impurities and with water content.

These factors constitute the fundamental difference between these two products and at the same time explain their different behaviour during agglomeration.

The water content in the dunite more easily modifies its structure, and therefore it has less energy available. This combined with the impurities give dunite a greater reactivity and explains the difference in softening temperatures, +/- 1.500º for olivine and +/- 1.380º for dunite, and also the large difference in their fusion points, over 1700º compared to 1.450º.

Olivine extents the face of the flame on the agglomeration chain due to its refractory characteristics.

This allows us to draw a first very important conclusion: olivine needs to have a finer granular size than dunite while it is being used in the agglomeration mix.

In effect it is necessary to compensate the refractory characteristics and the lower reactivity with a larger surface area. Further more, preparing the different phases will be more difficult and a higher temperature at the flame front will be needed.

Due to the poor make up of the phases an agglomerate with a lower mechanical resistance for a higher Iso A 0/5 mm is created. The following conclusion can be made: to achieve an agglomerate with the same mechanical resistance the olivine needs to have:

- finer particle size (as previously mentioned);
- a higher calorific contribution so as to achieve a high enough temperature at the start of the phases.

Yet a higher agglomeration temperature also brings disadvantages.

Tests have proven that raising this temperature reduces the speed of agglomeration notably and increases the Iso A 0/5 mm in considerable proportions.

The diagrams in the Annex illustrate this phenomenon well:

Another consequence from raising the agglomeration temperature is on the influence on the reductability of the agglomerate.

In effect, the surplus of fuel; (in addition it has been shown that 20 Kg of extra coke in fines are needed when using olivine given the same particle size of olivine and dunite, and for the same mechanical resistance). However, this surplus of fuel results in an increase in bivalent iron of 3% in the agglomerate produced. In the blast furnace this agglomerate will need an additional 1% of coke as a consequence.

It is important to note that the use of olivine in a rich mineral fusion bed contains quartz smelted at 1.710º which requires of 5 Kg to 7 Kg per ton. As a result, additional supplement of coke fines is required which causes a reduction in the performance of the chain and a notable increase in the price of the agglomerate.

Good mechanical resistance in the agglomerate is absolutely necessary for the good working of the blast furnace. We can see the relation that exists between the permeability, the quantity of coke burnt up in the conduit and the resistance of the agglomerate (M10) by looking at the Table 5.

Table 5. Permeability, coke burnt up in the conduit and resistance of the agglomerate

M10	Kp (permeability) %	Ton coke/24 hours
45	100	100
48	127	127
51	133	133

Further more this increase in rate has been possible with the same % of coke.

In a blast furnace, fitted with staves, we have been able to measure that the degradation of the agglomerate increased notably the thermal loads of the staves and that this necessitates a slowing down of the process due to higher temperatures.

Dunite is further down the degradation chain than olivine, it behaves very differently to olivine in the agglomerate mix. It is more reactive, its lower fusion point is more in line with the phases of the agglomerate.

There is also an important gain in fuel requirement (20%) of the agglomeration and as such, improved reductibility in the blast furnace. Moreover, all things being equal, dunite gives an agglomerate with better mechanical resistance properties and therefore more profitable performance and production cost in the blast furnace.

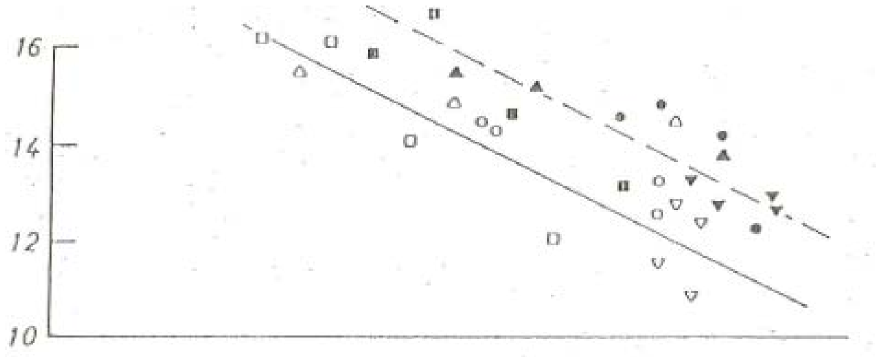

Figure 4. Speed of agglomeration mm/mm.

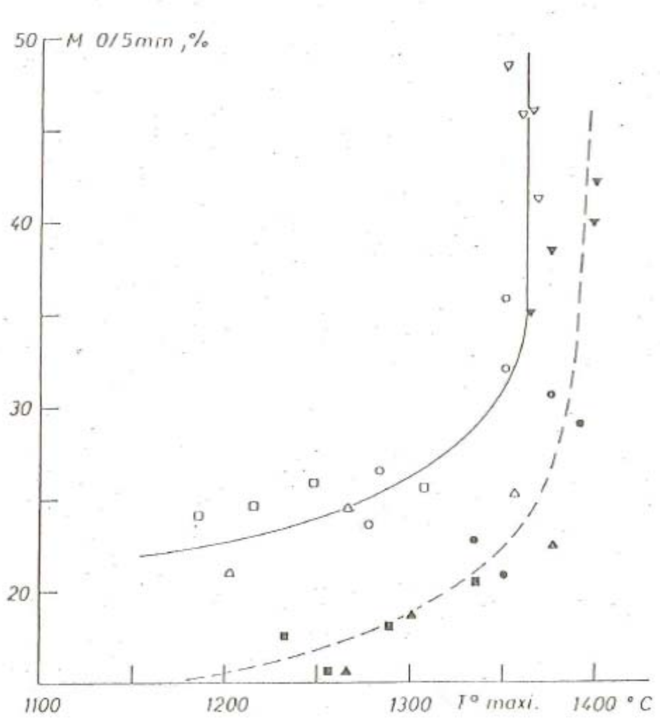

Figure 5. Relation between resistance, speed and maximum agglomeration temperature.

11 CONCLUSIONS

This report has made some observations about the increase of the % of MgO in the agglomerates. The results of different studies carried out many people are taken into account in this context. According to the needs of the blast furnace operators MgO must be provided in one form or another. Dolomite is always disadvantageous from the point of view of the coke consumption and/or the quality of the agglomerate produced.

In industry, all the consumers that have used our dunite fines (<5 mm) have stated that it is possible to increase the % of MgO of the agglomerates without encountering the terrible problems experienced by adding dolomite. On the contrary, there is a gain, above all in quality and in the amount of coke consumed.