Basic Refractory Mixes

EBT Taphole sand

Blast Furnace Slag conditioner

PASEK MINERALES

Aptdo. 1112

E- 33405, Asturias, Spain

www.pasek.es

javier.martinez@pasek.es

Tel: +34 985 50 04 44

INDEX

This document includes the following topics

1. INTRODUCTION TO PASEK MINERALES

PASEK MINERALES has been mining Dunite since 1972 in Spain. This mineral is processed on site and delivered via the local port or road to all our customers in Europe.

With over 21 million tonnes shipped and a capacity to produce 1 million tonnes per year, we are running one of the biggest Magnesia Silicate mines in the world.

On top of the uses directly related to the steel production that are covered in detail in this document, Dunite is also used as:

- Ceramic Filler
- Abrasives
- Water treatment
- Land filler and pH control
- Civil Construction
  (Sub-base, Ballast, Tarmac)

2. TECHNICAL REPORT:

Use of DUNITE in basic mixes for tundish working linings

A. Abstract

This report discusses the technical reasons for the use of DUNITE as an alternative to olivine in basic mixes for working linings in tundish. All conclusions in this report can be extended to any other basic mixes formulation used in steelmaking.

B. Scope

Data and conclusions can only be applied to DUNITE extracted by PASEK in its own open air mine located in Landoy (A Coruña) on the north western region of Spain.

C. State of the art

DUNITE is used in the making of pig iron using blast furnaces as a flux additive with a rate that can be anywhere in the range of 15-45kg/ton. This use is not exclusive of the DUNITE and some other natural magnesium silicates (like olivine) are being used in this process. There is a technical dispute between DUNITE and olivine in order to demonstrate which is better for the steel making operation as a whole and PASEK, through expensive scientific investigations can prove that DUNITE is better than olivine through the following data-based arguments:

- DUNITE softening and melting temperature is lower than olivine
- chemical water of DUNITE promotes an increase in porosity which enhances its reactivity

- DUNITE high temperature phases (clinoenstatite, bronzite and quartz), react with potassium steam forming more stable chemical compounds than the forsterite phase in olivine.

According to this know-how, PASEK supply DUNITE to some steel plants in the EU like ARCELOR MITTAL SPAIN, ARCELOR MITTAL GHENT, SALZGITTER FLACHSTAHL, DUFERCO CARSID or ARCELOR MITTAL BREMEN, and others.

On a different application, olivine has been added to the formulation of basic refractory mixes, in particular in the products for the working linings of tundish in continuous casting. Olivine addition to dead burned Magnesite for this application is between 20 and 30%. This has motivated a new effort in PASEK to investigate the possibility to replace it in these formulations by DUNITE, through a mineralogical comparison exercise between DUNITE and olivine.

D. DUNITE vs Olivine: Mineralogy

DUNITE is a plutonic rock formed by several primary minerals frequently transformed in other secondary minerals due to different geological processes more or less complex. Its chemical classification is basic being olivine the principal mineral in the rock. The most important difference between DUNITE and olivine is their geological classification, DUNITE as a rock and olivine as a mineral.

Spanish DUNITE, extracted by PASEK, has a primary mineralization of olivine, orthopyroxenes, (classified as enstatites) and clinopyroxenes (classified as diopsides). Different geological processes, principally hydrothermal alterations promoted by sea water contact, have derived in a secondary mineralization of lime amphiboles classified as hornblendes and serpentines[1].

[1] Corretgé, L. G. y Rubio, A.; Área de Petrología y Geoquímica – Universidad de Oviedo; “Geoquímica mineral de los procesos de serpentinización en las dunitas de Landoy”; 2008

Table nº1 shows the chemical composition of PASEK's DUNITE and its primary and secondary minerals. Olivine chemical composition is also shown in this table:

(%)	PRIMARY MINERALS OLIVINE	PRIMARY MINERALS DIOPSIDE	PRIMARY MINERALS ENSTATITE	SECONDARY MINERALS SERPENTINE	SECONDARY MINERALS HORNBLENDE	DUNITE PASEK	OLIVINE TUNDISH
MgO	34.4	16.4	32.8	39.0	17.8	37.2	49.0
CaO	<0.1	24.6	0.29	<0.1	12.5	1.8	---
SiO_2	34.5	53.5	56.2	43.6	46.1	40.7	41.8
Al_2O_3	1.7	2.4	2.8	0.7	12.6	2.4	0.56
Fe_2O_3	22.1	2.1	7.0	1.6	4.3	8.3	7.7
Na_2O	<0.1	0.15	<0.1	<0.1	2.2	0.1	---
K_2O	<0.1	<0.1	<0.1	<0.1	0.5	<0.1	---
L.O.I.	7.5	0.25	0.25	15.0	2.5	9.2	---

Table Nº1. Chemical composition of DUNITE.

Mineral composition of the rock will determine the DUNITE behaviour at high temperature. Mineral distribution of the rock fired at 1100ºC is shown in Table Nº2 together with Olivine mineral phases.

(%)		DUNITE PASEK	OLIVINE TUNDISH
FORSTERITE	$2 \cdot MgO \cdot SiO_2$	47	83
CLINOENSTATITE	$MgO \cdot SiO_2$	27	5
BRONZITE	$[MgO,FeO] \cdot SiO_2$	19.5	7
QUARTS	SiO_2	1.5	---
AMORFOUS		5	5

Table Nº2. Mineral distribution of DUNITE.

The differences between DUNITE and olivine, based in olivine being a mineral opposite to the DUNITE being a rock, will still deliver a similar behaviour at high temperature in combination with dead burned Magnesite due to a general solid solution with the periclase of the Magnesite. The combination of DUNITE and Olivine with this periclase will be stable in both cases.

E. Solid phase relationships in basic refractories

The chemistry of periclase based refractories lays in the system CaO-MgO-FeO-Fe_2O_3-Al_2O_3-Cr_2O_3-SiO_2, in which magnesio-wustite, a solid solution of FeO and other oxides into the periclase, appears as a single phase. The prevalence of solid isomorphous replacement allows a general interpretation based in the CaO/SiO_2 ratio and in the R_2O_3 content[2].

In Table Nº3 below, the calculated or estimated temperatures of initial liquid formation are shown.

CaO/SiO_2 Ratio	Phase present	Approximate temperature of initial liquid formation (ºC)
Low Al_2O_3 and Fe_2O_3		
<0.93	MgO, $2MgO{\cdot}SiO_2$, $CaO{\cdot}MgO{\cdot}SiO_2$	1,487
0.93-1.40	MgO, $CaO{\cdot}MgO{\cdot}SiO_2$, $3CaO{\cdot}MgO{\cdot}2SiO_2$	1,487
1.40-1.,86	MgO, $3CaO{\cdot}MgO{\cdot}2SiO_2$, $2CaO{\cdot}SiO_2$	1,576
1.86-2.80	MgO, $2CaO{\cdot}SiO_2$, $3CaO{\cdot}SiO_2$	>1,900
High Al_2O_3 and Fe_2O_3		
<0.93	MgO, $2MgO{\cdot}SiO_2$, $MgO{\cdot}Al_2O_3$, $MgO{\cdot}Fe_2O_3$	1,565
0.93-1.40	MgO, $CaO{\cdot}MgO{\cdot}SiO_2$, $MgO{\cdot}Al_2O_3$, $MgO{\cdot}Fe_2O_3$	1,399
1.40-1.86	MgO, $3CaO{\cdot}MgO{\cdot}2SiO_2$, $MgO{\cdot}Al_2O_3$, $MgO{\cdot}Fe_2O_3$	1,370
>1.86	MgO, $2CaO{\cdot}SiO_2$, $MgO{\cdot}Al_2O_3$, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, $CaO{\cdot}Al_2O_3$, $CaO{\cdot}Fe_2O_3$	1,290

Table Nº3. Temperature of the initial liquid phase formation.

These different phases correspond to a theoretical state of thermodynamic equilibrium and the real case delivers a massive combination of complex solid solutions. All the temperatures have been determined through laboratory trials so they will be accurate.

According to this description, it will be very useful to consider this analysis as a tool for melting point prediction in function of CaO/SiO_2 ratio. As an example, in Table Nº4 below a typical composition of working lining mix for tundish, formulated with 80% of dead burnt Magnesite plus 20% olivine or DUNITE is considered.

[2] Kappmeyer, K. K., Hubble, D. H.; "Pitch-Bearing MgO-CaO Refractories for the BOP Process"; High Temperature Oxides. Part I: Magnesia, Lime and Chrome Refractories, Academic Press (1970)

	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	CaO/SiO_2
TYPICAL CHINESE 90 MAGNESITE	2.1	93.1	2.7	1.1	---	---
TYPICAL OLIVINE	---	49.0	41.8	7.7	0.6	---
PASEK'S DUNITE	1.8	37.2	40.7	8.3	2.4	---
80/20 MAGNESITE/OLIVINE	1.7	84.3	10.5	2.4	0.1	0.16
80/20 MAGNESITE/DUNITE	2.0	81.9	10.3	2.5	0.5	0.20

Table Nº4. Chemical composition of a typical working lining mix for tundish.

In both formulations, CaO/SiO_2 ratio is lower than 0.93 so the prediction is very easy. Melting point of each single phase is the same, (as indicated in table Nº4) this means that the temperature of initial liquid formation is 1,487ºC.

	$2MgO{\cdot}SiO_2$ FORSTERITE 1,899ºC	$CaO{\cdot}MgO{\cdot}SiO_2$ MONTICELLITE 1,487ºC	[MgO·FeO] MAGNESIOWUSTITE 1,900ºC	$MgO{\cdot}Al_2O_3$ SPINEL 1,750ºC	MgO PERICLASE 2,800ºC
80/20 MAGNESITE/OLIVINE	20.3	4.8	3.0	0.1	70.8
80/20 MAGNESITE/DUNITE	19.1	5.6	3.1	0.7	68.7

F. Technical conclusions

- Related to the softening at high temperatures, the difference in the amount of Monticellite when DUNITE is used is less than 1%.

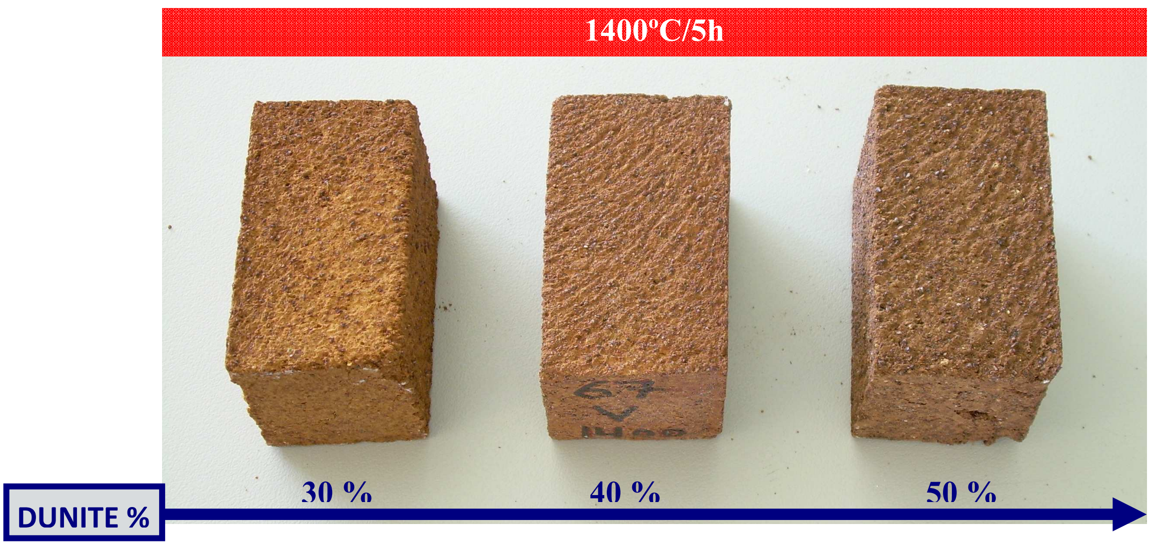
- Monticellite has a temperature of initial liquid formation of 1,487ºC so a dead burnt Magnesite with enough powder should be used. Below 100 microns the combination of DUNITE, or olivine, with the Magnesite will be fast during the heating. Maximum grain size of DUNITE, or olivine, will be 1mm due to the same reason.

- Phase and temperature of initial liquid prediction presented in the report don't include the additives needed in the formulation of working linings of tundish.

- Final assessment of DUNITE ability as olivine substitute will be done through laboratory and/or industrial trials.

G. Commercial considerations:

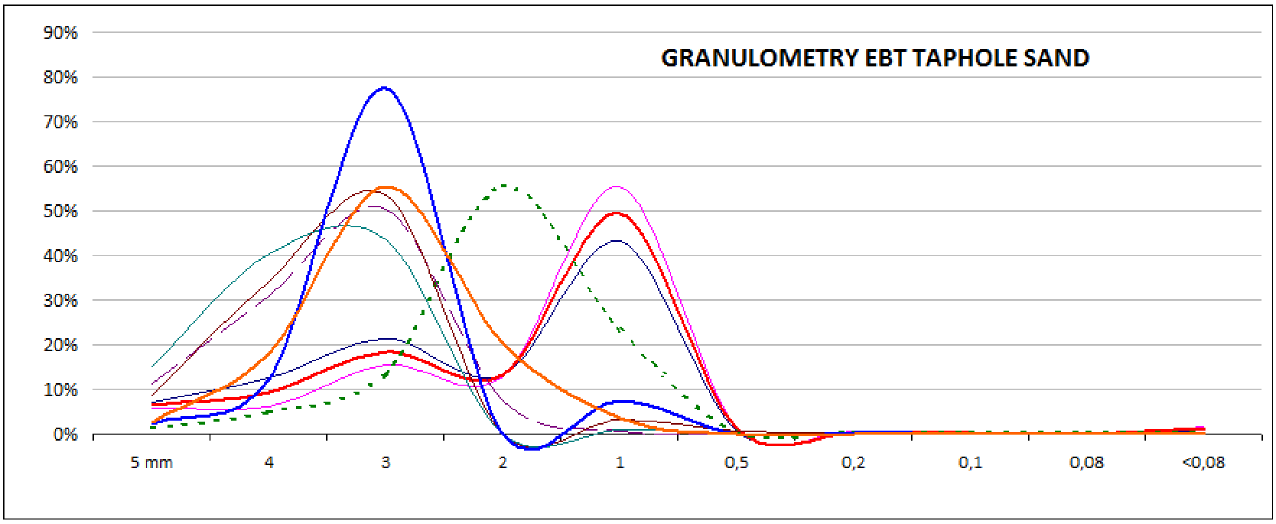
- DUNITE use in refractory applications is not new in the market. Over several years since our mine is in operation, PASEK and other refractories suppliers have been successfully formulating basic mixes for tundish with DUNITE percentages between 20 and 30%. Further advanced products with higher DUNITE percentages are currently being successfully tested.
- The annual amount of DUNITE 0/1 that is being commercialized by PASEK for tundish mixes is currently at around 5,000 tons. This considerable yearly amount can be taken as a guarantee of good behaviour of the DUNITE for refractory applications when properly formulated.
- Last but not least, using DUNITE in the basic tundish lining mixes provides a considerable saving which makes it really interesting in the present market conditions and also a good solution to offset other refractory raw materials price increases in the formula.
- DUNITE is a raw material mined and processed within the EU. This guarantees the stability on supply and quality though time and as a totally integrated supply chain, from the mine to your warehouse PASEK can guarantee the delivery times and be a flexible and reliable supplier for your raw material need of DUNITE type products.



3. DUNITE AS EBT TAPHOLE SAND

- Dunite has been used as Taphole sand filler for Electric Arc Furnaces that use Eccentric Bottom Tapping (EBT).
- This type of bottom tapping requires a material that can deliver a consistent level of fines that make sure there will not be any problem during the opening of the furnace. The hardness and mechanical resistance of Dunite make it excellent as filler.
- The mineral composition and fusion point give Dunite its condition as a flux that makes sure it will open the furnace without affecting the steel.
- Some of the most efficient EAF steel plants in Spain use Dunite as EBT Taphole sand.

Grain size can be customized as per customer requirement



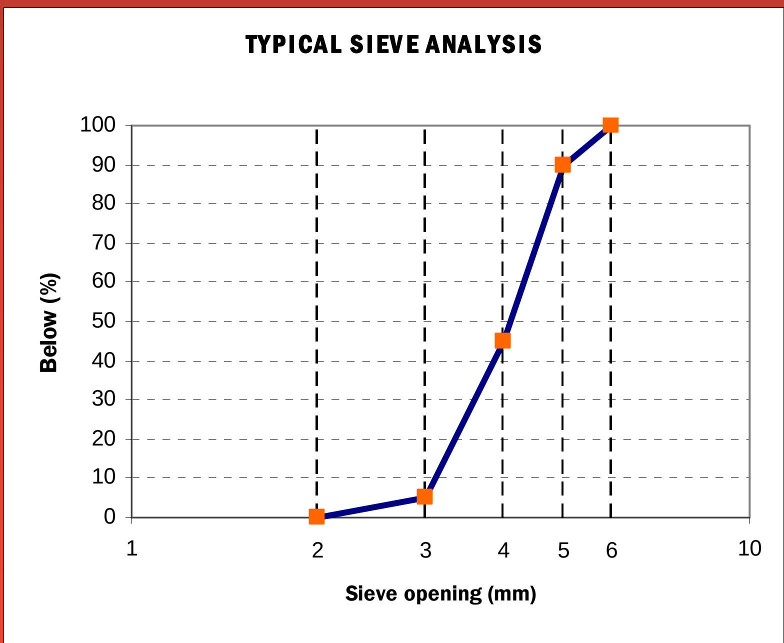
PASILMAG

EBT TAPHOLE SAND

Physical properties	
Absolute density	3.30 g/cm^3
Bulk density	1.67 g/cm^3
Melting point	1450 ºC
Colour	Grey
Petrologic name	Dunite

Chemical Analysis	
MgO	37.2%
SiO_2	40.7%
Fe_2O_3	8.3%
$Na_2O + K_2O$	<0.2%

Sieve analysis	
6mm sieve pass	100%
5mm sieve pass	90%
4mm sieve pass	45%
3mm sieve pass	<5%



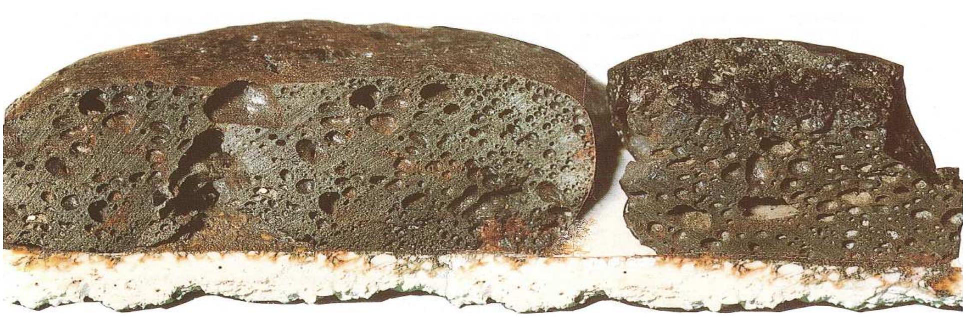
4. DUNITE AS BLAST FURNACE SLAG CONDITIONER

Blast furnaces all over the world require a number of fluxes to be added to the load. Dunite functions as a flux to improve the alkali evacuation and control the sulphur content in the pig iron.

The reasons why Dunite is such a good BF flux are:

- The hot and cold physical properties are very high.
- The hydrate content is high enough to leave room below 800ºC to a large porosity (20%) which insures the grater reactivity of Dunite.
- With a lower basicity ratio it transforms, below 800ºC, into minerals reactive to K which readily form with Potassium vapours stable components, with a low melting point.
- In BF operation, the improvement of K elimination with Dunite enables the operator to use a high basicity slag, which insures a better control of the Sulphur content in the iron.
- The diffusion of Potassium in Dunite, very porous above 800ºC, allows the use of a coarse size.
- Dunite fines are a very effective fluxing agent in the agglomeration of iron ore fines (sinter-pellets) because its moderate softening and agglomeration temperatures lie well within the range normally used in sintering and pellet production.

Blast furnaces all through Europe have been using Dunite for over 30 years.



DUNITE at 1430º C.

DUNITE

BLAST FURNACE SLAG CONDITIONER

Physical properties	
Apparent porosity	< 1.5 %
Bulk specific gravity	2.8 g/cm^3
Melting point	1450 ºC
Hardness Mohs scale	6.5 - 7
Cold crushing strength	90 MPa

Chemical Analysis	
MgO	37 %
SiO_2	40.5%
Al_2O_3	2.5%
Fe_2O_3	8.3%
CaO	1.9%
$Na_2O + K_2O$	<0.22%

Particle size distribution (%)

Dunite 0 - 3 mm

Sieve analysis	
> 3 mm	7%
1 to 3mm	43%
< 1 mm	50%

Dunite 10 - 40 mm

Sieve analysis	
> 40mm	1%
8 to 40mm	77%
10 to 18 mm	20%
< 10 mm	2%

Pasek

MINERALES

PASEK MINERALES Dunite mine in La Coruña (Spain)

Contact Details: **Javier Martinez**

T +34 985 50 04 44

M +34 629 84 17 87

E javier.martinez@pasek.es

Address: Aptdo 1112

E-33405 Asturias – Spain

www.pasek.es

SEGURIDAD Y SALUD LABORAL REGISTERED FIRM BM TRADA CERTIFICATION OHSAS 18001

REGISTERED FIRM BM TRADA CERTIFICATION ISO 9001:2000 UKAS QUALITY MANAGEMENT 012

REGISTERED FIRM BM TRADA CERTIFICATION ISO 14001:2004 UKAS ENVIRONMENTAL MANAGEMENT 012