RAW MATERIALS BASED ON MAGNESIUM OXIDE: STUDY OF PERFORMANCE, DEFINITION OF THE BEST FIELDS OF USE AND APPLICATION IN THE REFRACTORIES

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ABSTRACT

Raw materials' choice for the magnesite-carbon refractories products is fundamental to allow high performance in every field of use in steel mills. In the first part of this paper the main properties of the most used classes of magnesia (dead burned, "seawater" and electrofused) have been studied. Chemical and physical-mechanical analysis were performed on specimens integrally formed from each raw material. The data obtained gave us interesting information in particular for dead burned and "seawater" magnesia. These materials showed good properties of resistance to chemical and mechanical stress comparable in some cases to the performance guaranteed by the electrofused. At the same time, the results obtained for electrofused are useful to discriminate which magnesia use in relation to the application. In the second part of the work were tested the actual performance in real application of the raw materials with the best theoretical properties. They were introduced in bricks formulas commonly used in steelworks. The main chemical and physical-mechanical features were evaluated performing tests such as refractoriness-under-load, resistance to thermal shock, thermal expansion, X-Ray Fluorescence (XRF), resistance to alkali corrosion. The results showed interesting improvements. Some formulations of new products appear to be attractive for a subsequent use at the industrial level.

Keywords: magnesia; basic refractories; raw materials; mag-carbon bricks; steel industry.

INTRODUCTION

The need to produce high quality but low cost magnesite-carbon refractories materials, leads us to evaluate the importance of the raw materials' choice for these products depending on the application in iron and steel industry. Despite the wide use of magnesia raw materials, there are no recent studies that critically analyze their actual performance related to their properties. In this work, a preliminary study was carried out to investigate the most used raw materials based on MgO in refractory field [1,2]. Chemical and physical-mechanical analysis were performed on specimens integrally formed from each raw material. Three classes of magnesia have been analyzed: dead burned (DBM), "seawater" and fused magnesia. A comparison of the results was made and it has been defined in theory the ideal field of employment of these materials in steel industry. To verify the actual performance in real application, the bricks formulas most commonly used and marketed in steelworks were reproduced in laboratory introducing the raw materials with the best theoretical properties [3].

EXPERIMENTAL PROCEDURE

The raw materials used for this work were three fused magnesia (FM1, FM2, FM3), two "seawater" magnesia (SM1, SM2), one dead burned natural magnesia (NM), graphite, pitch powder, carbon black, anti-oxidant additives and phenolic resin.

Tab. 1: Chemical composition and physical properties detected on magnesia raw materials.

	FM1	FM2	FM3	SM1	SM2	NM
MgO	98.2	97.3	96.8	98.3	97.0	97.0
SiO_2	0.20	0.53	0.66	0.10	0.24	0.75
CaO	1.24	1.41	1.61	0.73	2.18	1.23
Fe_2O_3	0.15	0.41	0.56	0.52	0.20	0.70
BD[g/cm^3]	3.53	3.51	3.48	3.42	3.40	3.31
D_{cris} [µm]	2300	1090	890	95	130	98

Sample preparation

For the characterization of magnesia sintering and related properties, the samples were prepared mixing each type of magnesia with a ligninsulfonate binder, then the mix was pressed in cylinders (Ø50 x h50)mm which were fired at 1620°C for 5 hours.

For the characterization of the bricks industrial formula, a lab mix of 20 kg for formula was prepared and then 3 bricks for formula were pressed in an industrial plant. The bricks so obtained were tempered above 200°C.

Physical and mechanical tests

Open Porosity (OP) and Bulk Density (BD) were measured in accordance with standard testing method UNI EN 993-1.

Cold Crushing Strength (CCS) were measured in accordance with standard testing method UNI EN 993-5.

Module of Ropture (MoR) and Hot Module of Ropture (HMoR) were measured in accordance with standard testing method UNI EN 993-6 and UNI EN 993-7.

Resistance to abrasion test was performed according to UNI EN 993-20.

Permanent linear change was determined according to UNI EN 993-10.

Thermal shock resistance was determined according to PRE/R5.

Resistance to alkali test

On raw material sintered samples, resistance to alkali test was performed making a hole in the cylindrical specimens, putting inside 8g of Na_2CO_3 and heating the specimens for 5 hours at 955°C. Three cycles of heating with Na_2CO_3 were performed.

On brick samples, resistance to alkali was performed obtaining a cube of 100mm per side with a hole of Ø50mm x h50mm. 20g of Na_2CO_3 were put in the hole and the specimens were heated at 955°C for 5 hours.

Slag corrosion resistance test

Static slag corrosion test was conducted by crucible method. The crucibles, shaped as the brick specimens for resistance to alkali, were filled with steel making slag, then heated at 1600°C for 5 hours. The crucibles were put in coke in order to avoid oxidation of the samples. At the end of the test the specimens were cut and the sections are visually compared.

Tab. 2: Chemical composition [%] of slag.

Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	Cr_2O_3	MnO	TiO_2
10.5	29.3	4.0	37.0	7.9	5.9	3.2	1.8

Tab. 3: Indices of basicity and MgO of saturation of slag. Note: IB2 = binary basicity index; IB4 = quaternary basicity index; IBopt = basicity optical index.

IB2	IB4	IBopt	$MgO_{sat.}$
1.25	1.13	0.693	19.22

This kind of slag was particularly aggressive to the basic lining due to the low IB2 value and the high MgO saturation [4] (Tab. 3).

RESULTS AND DISCUSSIONS

Magnesia sintering properties

The main results obtained on the specimens integrally formed by each kind of magnesia are shown in Tab. 4 and Fig. 1.

Tab. 4: Properties detected on cylindrical specimens.

	BD [g/cm^3]	OP [%]	CCS [MPa]	Thermal shock [N°cycles]
FM1	3.02	16.0	32.3	2
FM2	2.99	16.8	39.8	2
FM3	2.98	17.0	41.0	2
SM1	2.95	16.1	39.3	3
SM2	2.91	17.6	37.5	3
NM	2.91	17.1	51.3	4

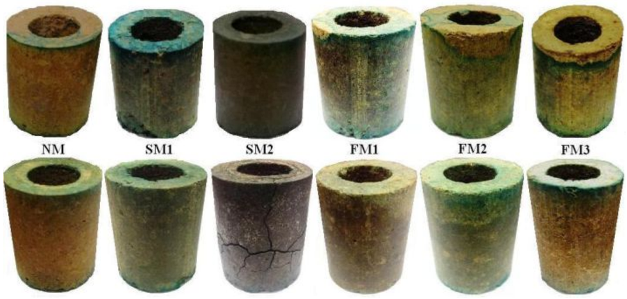

Fig. 1: Results of alkali resistance test after 1 cycle (above) and 3 cycles (below).

The BD of the specimens reflected the BD of the raw materials and the OP was roughly the same because of they were prepared with the same granulometric curve. There were interesting results in terms of CCS, thermal shock and alkali resistance for dead burned natural magnesia. In particular the behavior of the NM specimen showed:

- a better CCS, probably due to the presence of impurities that reduce the sintering point;
- a better thermal shock resistance;
- an alkali resistance similar to the fused magnesia.

Furthermore, SM1 showed a better behavior under alkali attack in comparison with SM2 (Fig. 1). After three cycles in fact the specimen SM2 was cracked, while the other kind of seawater magnesia SM1 appeared predominantly unattached.
Fused magnesia specimens showed similar physical and chemical characteristics despite their purity difference.
These results showed a good behavior of NM and significant difference between two seawater magnesia which was interesting to test in real products used in steelmaking. In particular, industrial formulas of the most commonly used products in converter, Electric Arc Furnace (EAF) and ladle have been modified.

Industrial formulas

In this second part of the study there have been modified standard formulas of products used in converter, EAF, ladle wall and ladle slag line.
Converter: SM2 used in standard formula A was replaced by NM in formula B and SM1 in formula C (Tab. 5).

Tab. 5: Converter formulas.

	A(STD)	B	C
FM2	X	X	X
SM2	X		
MN		X	
SM1			X
SM1(fine)	X	X	X
Antioxidant	X	X	X
Graphite	X	X	X
Carbon black	X	X	X
Pitch	X	X	X
Resin	X	X	X

Tab. 6: Physical and mechanical properties of converter products.

	A	B	C
OP[%]	5.4	6.2	4.7
BD[%]	2.92	2.91	2.95
CCS[MPa]	27.5	33.0	30.5
MoR[MPa]	10.8	8.4	9.4
Abr.Vol.[cm^3]	12.62	13.26	10.99
HMoR [MPa]	1.6	2.0	1.9
AFTER	**COKING**	**AT 1550°C**	
OP[%]	12.3	11.9	11.7
BD[%]	2.90	2.92	2.93
CCS[MPa]	25.3	29.2	23.3
MoR[MPa]	4.1	5.7	5.7
Abr.Vol.[cm^3]	18.95	21.81	18.94
PLC [%]	0.47	0.13	0.20

The introduction of NM instead of SM2 showed an improvement of hot characteristics (Tab. 6). In fact after coking at 1550°C, there was an increase in BD, a lowering in OP, an higher CCS and MoR than standard formula. Furthermore, the lower PLC detected in products B and C underline their better thermal stability.
Moreover, as shown in Fig. 2, product B had a comparable slag attack resistance than standard formula, while conversely product C absorbed all the slag.

Fig. 2: Slag corrosion resistance of converter products.

EAF: FM3 used in standard formula D was replaced by FM2 in formulas F and G; SM2 used in standard formula D was replaced by NM in formula E and G (Tab. 7).

Tab. 7: EAF formulas.

	D(STD)	E	F	G
FM3	X	X		
SM2	X		X	
NM		X		X
FM2			X	X
SM1(fine)	X	X	X	X
Antioxidant	X	X	X	X
Graphite	X	X	X	X
Carbon black	X	X	X	X
Pitch	X	X	X	X
Resin	X	X	X	X

Tab. 8: Physical and mechanical properties of EAF products.

	D	E	F	G
OP[%]	5.7	5.5	6.1	5.9
BD[%]	3.01	2.97	2.93	2.95
CCS[MPa]	31.2	31.2	30.8	31.2
MoR[MPa]	9.9	9.4	7.7	9.3
Abr.Vol.[cm^3]	9.18	9.55	8.04	6.86
HMoR [MPa]	2.0	1.8	1.1	1.5
AFTER	**COKING**	**AT**	**1550°C**	
OP[%]	11.4	12.1	12.0	12.3
BD[%]	2.98	2.94	2.94	2.92
CCS[MPa]	28.2	32.7	28.3	27.8
MoR[MPa]	5.6	5.7	5.2	5.6
Abr.Vol.[cm^3]	15.73	22.53	20.47	20.65
PLC [%]	0.59	0.32	0.49	0.26

Also in this case was introduced NM instead of SM2 and moreover the same substitution was tested on a variant of standard formula with a better fused magnesia.
Contrarily to the converter products, the increase of the hot characteristics did not occur in EAF products, probably because the quantity of SM2 replaced with NM is lower than previous case. However, the new products showed a lower PLC than standard one (Tab. 8).
The slag attack resistance of the new products were comparable with the standard (Fig. 3). The formulas F and G didn't show an improvement compared to D and E formulas.

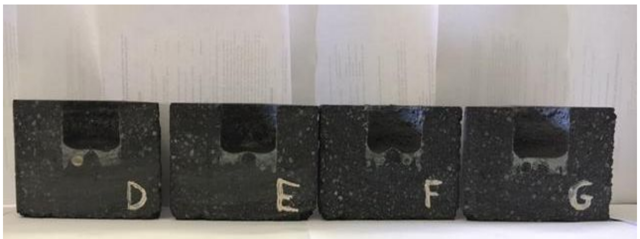

Fig. 3: Slag corrosion resistance of EAF products.

Ladle wall: SM2 used in standard formula H was replaced by SM1 in formula I and a mix of SM1 and NM in formula L (Tab. 9).

Tab. 9: Ladle wall formulas.

	H(STD)	I	L
SM2	X		
NM			X
SM1		X	X
SM1(Fine)	X	X	X
Antioxidant			
Graphite	X	X	X
Carbon black	X	X	X
Pitch	X	X	X
Resin	X	X	X

Tab. 10: Physical and mechanical properties of ladle wall products.

	H	I	L
OP[%]	4.3	4.0	4.8
BD[%]	2.99	2.99	2.92
CCS[MPa]	35.2	29.2	32.8
MoR[MPa]	8.3	8.8	7.9
Abr.Vol.[cm^3]	6.34	9.38	9.32
HMoR [MPa]	1.7	1.5	1.7
AFTER	**COKING**	**AT 1550°C**	
OP[%]	12.0	13.3	12.6
BD[%]	2.90	2.86	2.89
CCS[MPa]	20.7	18.5	21.7
MoR[MPa]	3.7	2.4	3.1
Abr.Vol.[cm^3]	27.36	30.36	27.04
PLC [%]	0.39	0.32	0.07

The replacement of SM2 with SM1 didn't lead to an improvement of mechanical properties, while the introduction of a quantity of NM produced an improvement of hot mechanical properties (Tab. 10). In particular, with NM there was a lowering of BD after 1550°C of 0.03 g/cm^3 in comparison of 0.09 g/cm^3 of standard formula and a lower PLC.
All formulas had been low slag attack resistance, as shown in Fig. 4.

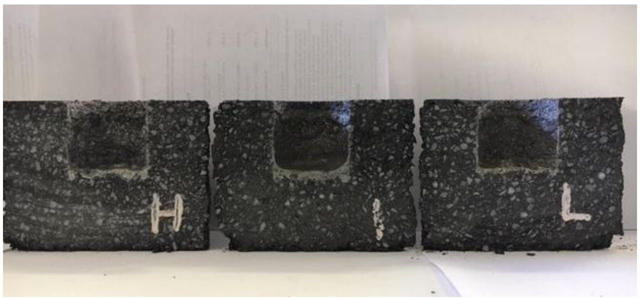

Fig. 4: Slag corrosion resistance of ladle wall products.

Ladle slag line: SM2 used in standard formula M was replaced by NM in formula N (Tab. 11).

Tab. 11: Ladle slag line formulas.

	M(STD)	N
SM2	X	
FM1	X	X
FM2	X	X
NM		X
SM1(Fine)	X	X
Antioxidant	X	X
Graphite	X	X
Carbon black	X	X
Pitch	X	X
Resin	X	X

Tab. 12: Physical and mechanical properties of slag line products.

	M	N
OP[%]	5.5	5.7
BD[%]	2.93	2.93
CCS[MPa]	27.3	27.8
MoR[MPa]	7.6	7.4
Abr.Vol.[cm^3]	12.34	13.71
HMoR [MPa]	2.0	2.0
AFTER	**COKIZATION**	**AT 1550°C**
OP[%]	12.0	12.5
BD[%]	2.90	2.87
CCS[MPa]	17.8	16.8
MoR[MPa]	2.8	3.3
Abr.Vol.[cm^3]	27.09	29.03
PLC [%]	0.56	0.26

In this case the SM2 was replaced by NM in a formula with a mix of fused magnesia with higher purity.
There was no particular variation in mechanical properties, while there was also in this case a lowering of PLC (Tab. 12), but it was found also a falling of slag corrosion resistance (Fig. 5).

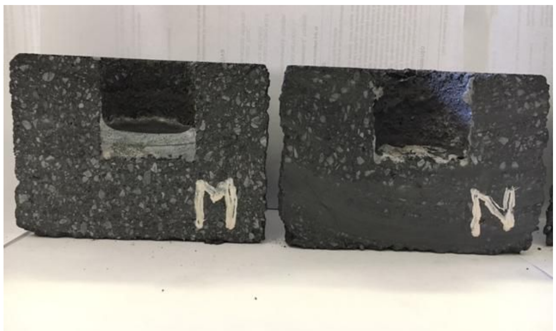

Fig. 5: Slag corrosion resistance of ladle slag line products.

CONCLUSIONS

A large number of data have been extracted from raw materials based on magnesium oxide and the most commonly used and marketed products in steelworks.

The main results obtained in this work showed that the replacement of seawater magnesia with natural dead burned magnesia offers an improvement in thermal stability, thus making this raw material especially suitable for that application with high thermal shocks. Moreover, this replacement usually leads to a slightly improvement of hot mechanical properties due to the easy sintering skill of this raw material. Conversely, NM gives a general lowering in abrasion resistance because of its low BD and small crystal, so it is recommended avoid the use of NM in application with strong flows of fluids and solids.

The chemical resistance tested in particular by slag attack resistance, showed that the behavior of NM is difficult to predict and can be affected from the other components in formula. Generally we found that NM has a similar or better behavior than SM1 (seawater magnesia with similar crystal size), while similar or worse behavior in comparison with SM2 (seawater magnesia with a larger crystal size). So, to obtain a good slag attack resistance it is important have a larger crystal size but also study the real mechanism of interaction with industrial slags.

The results obtained in this work emphasize the importance of thoroughly knowing the interactions between the refractory material components and the substances with which they interact in exercise.

Therefore, these interactions determine the effective performance of refractory material during its use.

REFERENCES

[1] Landy R. Magnesia refractories. In: Schacht CA. Refractories Handbook, chapter 5. Marcel Dekker, Inc: New York; 2004.

[2] Ewais EM. A review: Carbon based refractories. J. Ceram. Soc. Jpn., 2004; 112 (10): 517-532.

[3] Benavidez ER, Brandaleze E., Lagorio YS, Cass SE, Tomba Martinez AG. Thermal and mechanical properties of commercial MgO-C bricks. Materia. Rio de Janeiro, 2015 July/Sept.; Vol. 20 n.3.

[4] Pretorius E. Fundamentals of EAF and ladle slags and ladle refining principles. Bakers Refractories; 2015.