Magnesia-spinel-carbon refractories for steel ladle slag zone applications

Magnesia-spinel-carbon refractories are widely used for steel ladle slag zones because of their resistance to slag attack. Optimisation of the spinel content through composition and processing control provides an optimum combination of thermal expansion and thermo-mechanical properties to further enhance in-service life.

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Resin bonded magnesia-carbon (MgO-C) bricks are widely used in the slag zone of steel ladles. Modifications to MgO-C bricks with higher MgO% and large grain sizes of fused magnesite and graphite are the first choice of refractory producers to reduce the detrimental effects of slag attack but, to further improve the characteristics of slag zone bricks, ancillary materials have been added in varying proportions and combinations for a long time. Metallic additives are the primary choice.

Recent developments involve resin bonded MgO-C with a spinel addition, such that the mix may be used either as pre-formed slag zone bricks or in-situ. The degree of formation of $MgAl_2O_4$ secondary spinel governs the expansion behaviour of the brick which is optimised to get just sufficient tightening of the joints to prevent liquid slag penetration. Excessive expansion may lead to development of stresses which causes structural spalling. The target expansion coefficient is approximately $10.1 \times 10^{-6}/^{o}C$. The spinel particles are formed at the periphery of the periclase grains and play a vital role in determining the refractory properties. The formed spinel microstructure minimises the open pores and this densification prevents slag penetration. The structural spalling resistance is increased due to the development of microcracks due to mismatch in the coefficient of thermal expansion between MgO ($13.5 \times 10^{-6} / ^{o}C$) and $MgAl_2O_4$ ($7.6 \times 10^{-6} / ^{o}C$) grains. A high rate of spinel formation can be detrimental because it is associated with substantial volume expansion, which may increase the degree of slag penetration. Thus, careful selection of MgO quality, the purity and fraction of the aluminous dopent, along with its quantity, are of prime importance to improve refractory performance. Details of work carried out to obtain the optimum properties are now described.

EXPERIMENTAL

Starting materials Fused and sintered magnesite, fused alumina and graphite were used as the base raw materials, the chemical properties of which are given in *Table I.*

	Magnesite	Fused alumina	Graphite
MgO%	97.5	-	-
Al_2O_3%	0.5	97.0	-
FC %	-	-	95.0
SiO_2 %	0.5	1.0	2.5

Table 1: Chemical analysis of starting material [FC is fixed carbon]

Concept, batch preparation and sample preparation. The basic concept was to observe the effect of addition of different types of dope materials on the hot properties of the slag zone MgO-C bricks such as slag corrosion resistance, hot strength, spalling resistance and thermal expansion due to different amounts of spinel formation. Keeping this objective in view, the selection of dopents and their granulometry were changed with different magnesite and graphite combinations (see *table 2*).

	P	Q	R	S
Fused magnesia, wt%	65	65	64	64
Sintered magnesia, wt%	10	10	10	10
Fused alumina, wt%	7	6	5	4
Graphite, wt%	12	13	14	15
Resin, anti-oxidants and other additives, wt%	6	6	7	7

Table 2: Batch formulation

The mixing was done in an Eirich mixer, following which the batch was allowed to age at ambient temperature for 0.5 hours. Bricks were pressed in a Laise press at a specific pressure of 200MPa. After pressing the bricks were tempered at 200ºC for 20 hours. The test samples were cut from the tempered brick as per the GB, ISO and Chinese National standards.

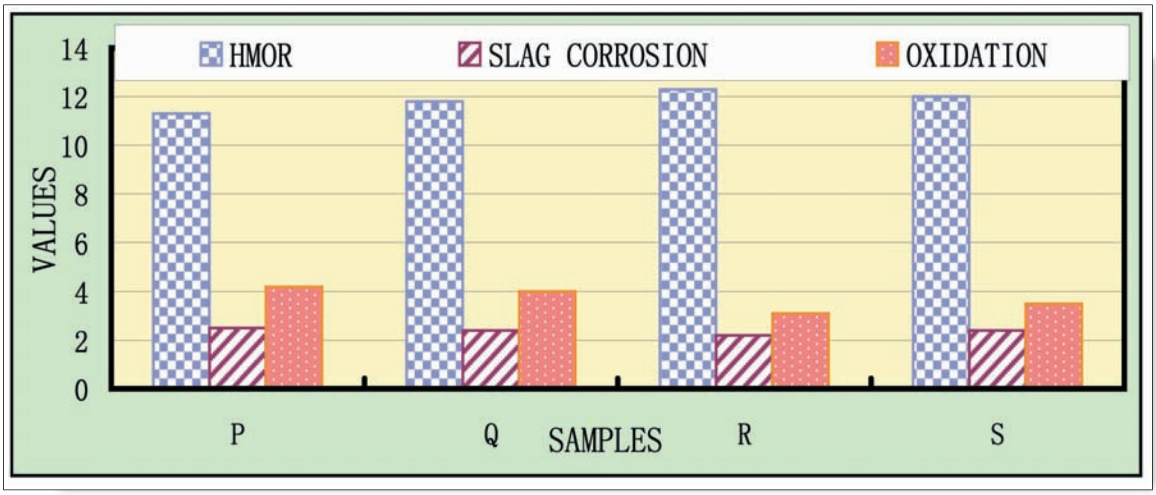


Fig.1 Test data

Test properties

All the tests as per the parameters shown in *Table 3* were conducted in the in-house laboratory.

	P	Q	R	S
Apparent porosity (AP) %	3.3	3.0	2.6	2.7
Bulk density (BD), g/cc	3.04	3.03	3.03	3.02
Cold compression strength (CCS), MPa	46.0	44.1	42.7	40.5
Coked AP after 1100ºC for 2hr, %	9.5	9.2	8.8	8.1
Coked BD after 1100ºC for 2hr, g/cc	2.99	2.97	2.96	2.94
Residual carbon, %	14.1	13.9	14.8	15.6
Slag corrosion, mm corroded	2.5	2.4	2.2	2.4
Oxidation resistance, mm oxidised	4.2	4.0	3.1	3.5
Modulus of rupture (MOR) MPa	14.6	15.1	15.4	14.7
Hot MOR MPa (1400ºC for 0.5hr	11.3	11.8	12.3	12.0
Permanent linear change PLC) % at 1600ºC for 2 hr 1st cycle	+0.62	+0.51	+0.42	+0.38
2nd cycle	+0.57	+0.45	+0.39	+0.31
3rd cycle	+0.43	+0.41	+0.31	+0.26

Table 3: Test properties of bricks

RESULTS AND DISCUSSION

Figure 1 shows the comparison of HMOR, oxidation resistance and slag corrosion. The effect of a gradual increase in graphite reflects in the residual carbon test results. It is expected that such an increase will improve spalling resistance. The oxidation resistance and hot strength are better with batch R than batch S due to a higher anti-oxidant : C ratio. The amount of anti-oxidant present in batch S might not be sufficient to arrest oxidation with still higher C%.

Figure 2 shows the PLC test results on repeated firing. Batch R shows a controlled variation in PLC on repeated firing. The high PLC values in batch P and Q are due to greater spinel formation. The higher PLC may create excess stress between adjacent bricks during operation which may lead to lining failure. Batch S shows less expansion which may not be optimal for making the brick joints tighten enough to prevent the slag penetration.

Based on these observations, batch R was selected for use, in spite of higher AP in all the batches. Attempts were made to control the coked AP by controlling the rate of spinel formation. This can be done through changing the granulometry of the dopent. Batch R was split into four fractions R1 to R4. The fused alumina part was taken into finer fraction to coarser fraction from R1 to R4. *Table 4* shows the batches prepared in same way as earlier and *Table 5* shows the properties achieved.

	R1	R2	R3	R4
Fused alumina, wt%	5	5	5	5
Fraction of fused alumina	Finer	Combi-1	Combi-2	Coarser

Table 4: Batch formulation

Table 5 and *figure 3* show that the PLC values reduced with changes from finer to coarser fraction of fused alumina. On repeated firing the maximum changes are observed mainly in the first firing for finer fractions than the coarser fractions in the batch combinations.

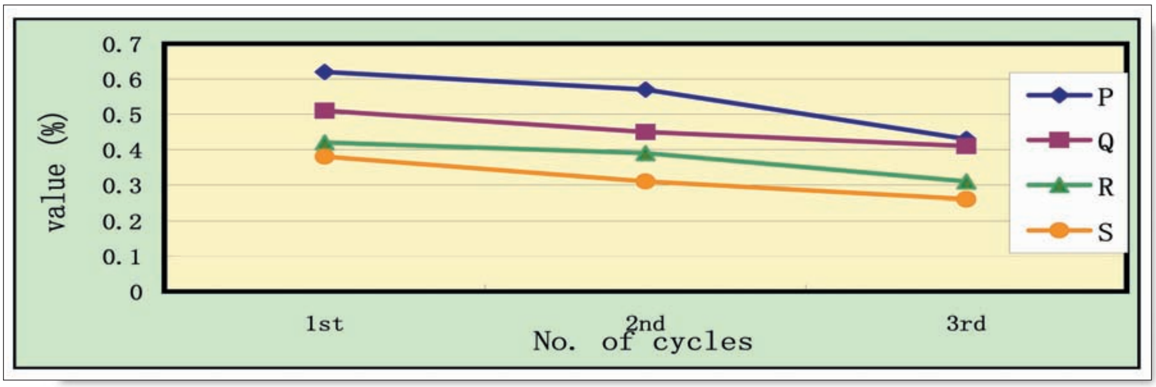
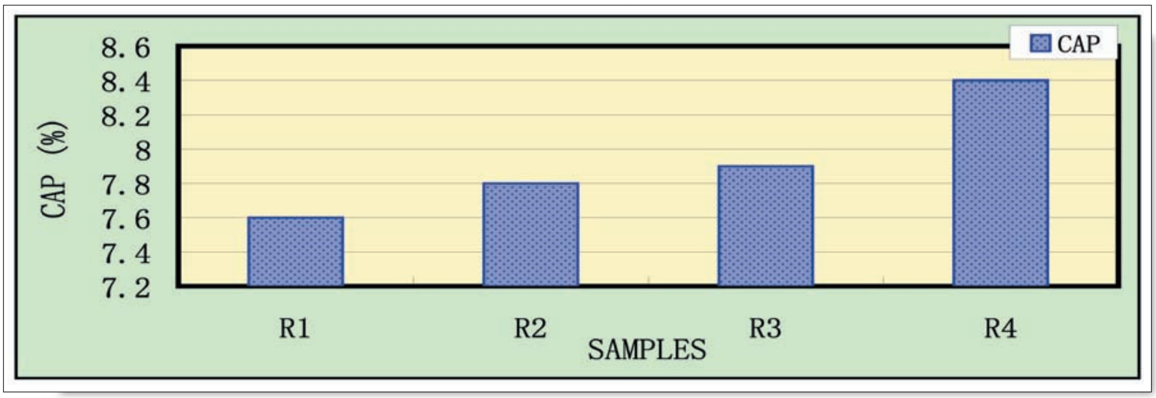


Fig.2 PLC data on repeated firing

Fig.3 Comparison of coked AP after 2 hours at 1100°C



	R1	R2	R3	R4
AP, %	2.4	2.5	2.6	2.5
BD, g/cc	3.01	3.02	3.01	3.03
Coked AP after 1100ºC for 2hr, %	7.6	7.8	7.9	8.4
PLC % at 1600ºC for 2 hr, 1st cycle	+0.51	+0.45	+0.41	+0.40
2nd cycle	+0.46	+0.42	+0.38	+0.38
3rd cycle	+0.40	+0.39	+0.35	+0.34

Table 5: Test properties

From the comparison, it is seen that batch R2 produces coked AP and PLC in the accepted range of +0.30 to +0.40.

FIELD APPLICATION

Bricks made with batch R2 in our China plant were sent to a European steel plant where they achieved an average life of 102 heats over a few ladles, compared to their normal ladle life of 90 heats. The steelmaking operational parameters are given in *Table 6*.

Ladle capacity	375 t
Average tapping temperature	1720ºC
Lining thickness (slag zone)	187 mm
Type of steel	Ultra low C
Secondary refining	LF-RHOB

Table 6: Steelmaking operational parameters

CONCLUSIONS

- The new brick has controlled expansion on repeated firing, which helps in tightening the joints between the bricks
- The improved quality of magnesia-spinel-carbon brick has better slag corrosion resistance than normal brick
- The life of the ladle could be enhanced due to better spalling resistance with new batch.

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ACKNOWLEDGEMENT

The authors are grateful to the management of ORIND Refractories Limited, China for sharing this data and publishing this paper.