

# Bonding of MgO-C bricks by catalytically activated resin

*REFRAFLEX technology comprises a catalytical activation of the graphitisation of ordinary phenolic resins in MgO-C bricks during coking. As a result the MgO-C bricks exhibit better thermo-mechanical properties in terms of hot strength, fracture toughness modulus of rupture and thermal shock resistance.*

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**M**agnesia-carbon bricks are well-established refractory products with particular properties for applications in converters, electric arc furnaces and steel ladles. In recent years the composition of high-duty magnesia-carbon bricks has been improved, especially in terms of the binders and additives used for better thermo-mechanical properties and improved ecological and economic benefits. The spalling resistance and thermal shock behaviour are of great importance during advanced secondary metallurgy, not only from possible failure of steel making aggregates, but also under steel quality considerations due to possible refractory impurities. MgO-C-bricks have gained acceptance as standard material for linings in BOF's, EAF's and ladles in the steel industry.

Carbon-containing materials are composite materials with totally different thermo-mechanical properties in comparison to conventional fired oxide ceramic materials. The special mechanical behaviour of carbon-containing materials is primarily influenced by the added carbon carrier and the bonding agent. Adding graphite flakes is generally applied for production of carbon-bonded bricks with typical carbon yields of 5 to 15 wt. %, e.g. Magnesia, Dolomite and Alumina-carbon bricks. In the past, bonding agents were thermoplastic coal tar pitch, with its graphite-like coke structure after heat treatment, and different kinds of thermosetting resins, which lead to a more brittle amorphous coke structure. New developments in bonding have also taken place. A successfully new developed bonding technology is bonding by catalytically activated resins, which, unlike normal resins, show graphitic structures from catalytically activated resins.

## CHARACTERISTICS OF MGO-C BONDING

In fired refractory products with ceramic bonding the only role of the binder that is blended in the mix before pressing is to maintain a specific strength for handling the ceramic body. This binder is removed while firing and

replaced by evolving ceramic inter linkages, formed mainly by solid state reactions at high temperatures. As long as the application temperature of these bricks does not exceed the firing temperature there will be no change in these linkages, thus the fired brick leaves the refractory plant in its final state.

This is completely different in MgO-C-bricks where the role of the binder is of greater importance and threefold:

1. The binder works as a glue, cementing the refractory particles together and giving `green-strength` to the brick
2. After curing and hardening (duroplastic binders) or solidification (thermoplastic binders) it provides the `as-delivered strength`, necessary for handling and bricklaying of the masonry. In a vessel such as a BOF the MgO-C-bricks in the lowest part of the lining have to carry the weight of the brickwork on top, which can be several hundred tonnes.
3. After being transformed into carbon due to the temperatures in the steelmaking process it works not only as a bonding agent but also as a non-wetting agent, so preventing slags from penetrating the brick.

This is why the binder of an MgO-C-brick has a significant impact on the refractory properties and subsequently on the performance of the brick in service. The binder changes into carbon at high temperatures and under reducing atmospheres. The organic bond is replaced by a carbon bond. In the refractory industry phenolic resins are state-of-the-art for bonding MgO-C-bricks.

Phenolic resins combine good workability and an acceptable environmental impact with good mechanical and chemical properties of bricks fabricated with it. Two types of phenolic resins are utilised: Resole and Novolac. Novolak resins are formed by a reaction between phenol and formaldehyde in a molar ratio between 1:0.4 and 1:0.9 under acidic conditions. Usually they are solid, thus have to be melted or dissolved in alcohols or similar solvents in order to work as a refractory binder. The main

Resistance to:	Brick property	Bonding property
Slagging	Open porosity Bulk density Work of fracture (WOF)	High portion of carbon residue after coking High oxidation resistance Good manufacture capabilities (wetting to MgO-grains and graphite-flakes during mixing) Non-wetting to slags
Thermoshocks	Hot Modulus of Rupture (HMOR) Young's Modulus	High flexibility High (hot-)strength
Abrasion/ Erosion	Crushing strength	High (hot-)strength

Table 1 Brick and bond properties

advantage of novolak compared to resole is its unlimited shelf life in the production of refractories due to hardening by reaction with hexamine. The main disadvantage is the required solvent to produce refractories at ambient temperatures, which lowers the carbon yield. Resole resins are formed by a reaction between phenol and formaldehyde in a molar ratio between 1:1 and 1:3 under alkaline conditions. Usually they are liquid at ambient temperatures, thus can work as a refractory binder without any melting or dissolving in alcohols or similar solvents. The main advantage of resole is the high carbon yield without hot pressing and the absence of solvents. The main disadvantage is its limited shelf life in production due to hardening without addition of a reactant.

Both resole and novolak lead to a resite (the cured and hardened material evolving from resole resin) structure after hardening and to a glassy carbon structure after coking. Resoles harden at temperatures of 180°C - 220°C mainly in tunnel kilns on the production site. At the same time, first the resite lattice forms with a C-content of about 80%. By choosing an appropriate resin the optimum three-dimensional lattice-like polymerisation of the resite is already given which is then transferred to the carbon lattice after pyrolysis. The carbon output of the

resite after pyrolysis is typically about 55 - 70%. During the pyrolysis under reducing conditions, gases (CO, H<sub>2</sub>, CH<sub>4</sub>) escape, as well as very low amounts of phenols, formaldehyde and aromates, whose concentration tend to the free content of these substances. There is no principle difference in the

emissions between resole resins and novolak resins.

Due to the chemical and structural properties of phenolic resins they change into isotropic glassy carbon after coking. Graphite can be achieved from resins only at temperatures above 2500°C. In contrast to the crystalline graphite, glassy carbon bonding has practically no way of compensating for excessive stresses other than by macro-cracks due to its hardness and brittleness. Moreover the oxidation resistance is lower because of its isotropic structure.

Table 1 shows how bonding affects the properties of an MgO-C-brick and thus its resistance to different wear-mechanisms:

### CATALYTICALLY SUPPORTED CRYSTALLISATION DURING COKING

As mentioned above the lower state of order of the crystal lattice of the isotropic glassy carbon is the reason for a higher brittleness. However, with the help of energy input the lattice can change into a higher state of order, thus can crystallise to form graphite. In the graphite industry, e.g. for the production of electrodes, the heat which is necessary to create crystalline graphitic carbon from various organic precursors is available by resistance or arc heating. In steel making vessels like BOFs, EAFs and teeming vessels the maximum process temperature is typically 1650°C-1750°C, and, moreover, these temperatures are present only at the surface (a few millimeters) of the bricks. These temperatures are not sufficient for proper crystallisation of organic resins. On the other hand it is well-known that reactions can be forced to take place at lower temperatures once a catalyst is involved in the reaction. E.g. hydrocarbons and other compounds burn to water and carbon dioxide in a catalytic converter installed in the muffler of automobiles, although the temperature is not sufficient for the reactions without the catalyst.

With catalytical activation (REFRAFLEX technology) it is possible to lower the graphitisation temperatures of phenolic resins to less than 1000°C; thus reaching those regions that are heated during preheating of ladles and

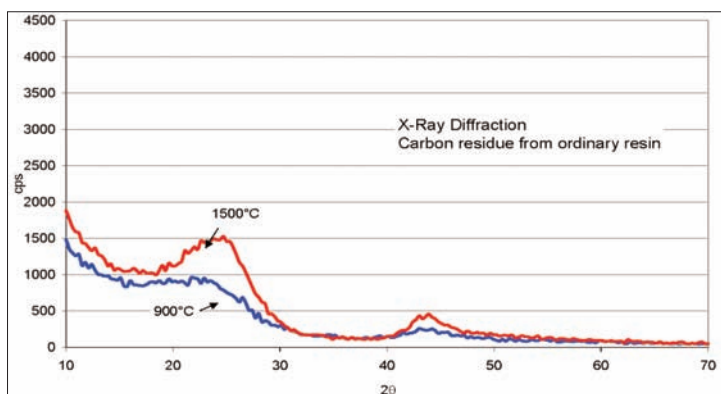


Fig.1 X-Ray diffraction pattern of coke originating from ordinary phenolic resin after different treatment temperatures

BOFs. The technology comprises the addition of catalytically active substances into the brick and a special manufacturing and curing process. The result is MgO-C bricks with superior strength, toughness and flexibility.

Figures 1 and 2 show X-ray diffraction patterns of isolated coke samples originating from ordinary phenolic resin and catalytically activated resin. X-ray diffraction patterns indicate the crystallinity of substances.

The peak of the catalytically activated resin at 26.5θ indicates very good crystallisation of the carbon from the resin pyrolysis. The ordinary phenolic resin shows only a broad and flat elevation of counts in the particular 2θ region, indicating a non-crystalline, amorphous structure. Obviously the activation energy for the creation of the crystal graphitic lattice was reduced significantly. The low graphitisation temperature of less than 1000°C guarantees that even after the first heat-up of a brick installed in a metallurgical vessel a substantial part of it will exhibit a graphitic structure, similar to a pitch-bonded brick.

Figures 3 and 4 show the difference in the outer appearance of carbon originating from ordinary resin and that originating from the catalytically activated resin. While the coke from ordinary resin shows a uniform black lustre due to the glassy and isotropic structure of the carbon, the coke from catalytically activated resin has a shiny metallic appearance like pure natural flaky graphite. The different nature of these two types of carbon can be seen in more detailed with microscopic analysis as shown in figures 5 and 6.

**COMPARISON OF BRICK PROPERTIES**

It was interesting to find out how this catalytically activated crystallisation of phenolic resin during pyrolysis affects the properties of an MgO-C brick. Table 2 shows a comparison of properties of MgO-C bricks bonded by ordinary phenolic resin and REFRAFLEX bonding.

While the properties in the as-delivered state are more or less the same, significant differences emerge after the brick's bond is transferred into carbon by coking at 900°C according to ASTM C 831. Particularly in a hot state the catalytically activated resin bond shows enhanced strength (HMOR) and toughness (WOF). This is due to the superior properties of graphitic carbon in comparison to glassy carbon.

The interactions between graphite, binder and oxide grains in an MgO-C-brick cause a non-linear plastic-elastic behaviour under load. The three point bending strength test at room temperature is used for characterisation of the MOR and the mechanical behaviour (strain, Young's Modulus) (see Fig. 7). Due to the measurement of the strain as a function of different loads lower than the fracture load the `real flexibility performance` of a carbon bonded structure can be identified. High flexibility

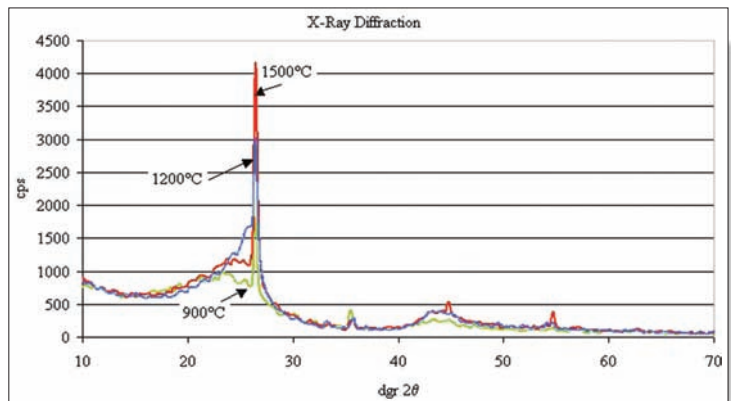


Fig.2 X-Ray diffraction pattern of coke originating from catalytically activated resin after different treatment temperatures.

leads to improved structural properties and a superior resistance towards thermally induced stresses. A higher flexibility is exhibited by the REFRAFLEX bonding with catalytically activated resin. Earlier research work has shown that higher strength at same displacement leads to better thermo-mechanical behaviour, including thermal shock and spalling resistance.



Fig.3 Coke from ordinary resin

Because of the plastic-elastic deformation of the curves, determination of Young's Modulus, (defined as a line originating at zero), is difficult. For better comparison of material behaviour, the Instantaneous Modulus - the rising of differential small sections of the load elongation curve, was introduced by Schacht. It can be understood as the first mathematical derivation of the load-elongation-curve in the range zero to maximum load. In the point of origin, both Young's and Instantaneous Modulus show similar values and consequently calculations given below are the same. Fig. 8 shows Instantaneous Modulus of different bricks as a function of the percentage of fracture load (applied load =100%).



Fig.4 Coke from catalytically activated resin

Apparently, the Instantaneous Modulus changes in a wide range. Below 30% of applied load a linear increase can be observed. The even curves indicate that no cracking takes place. It is a form of creep. After a local maximum of elasticity at about 25 to 30%, a sudden initiation of high scatter suggests that first cracks develop. After 35% load the Instantaneous Modulus permanently decreases with

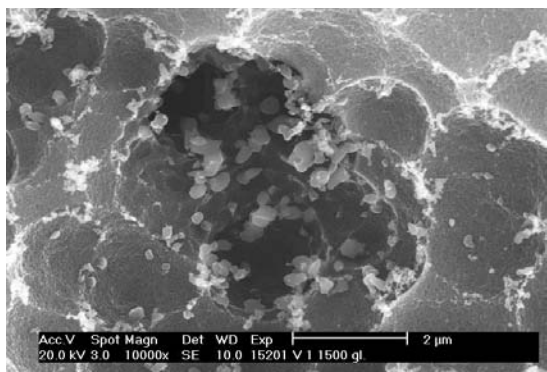


Fig.5 Resin without catalyst after coking at 1500°C

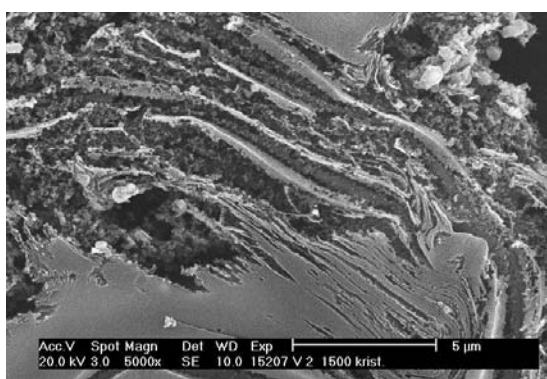


Fig.6 Catalytically activated resin after coking at 1500°C

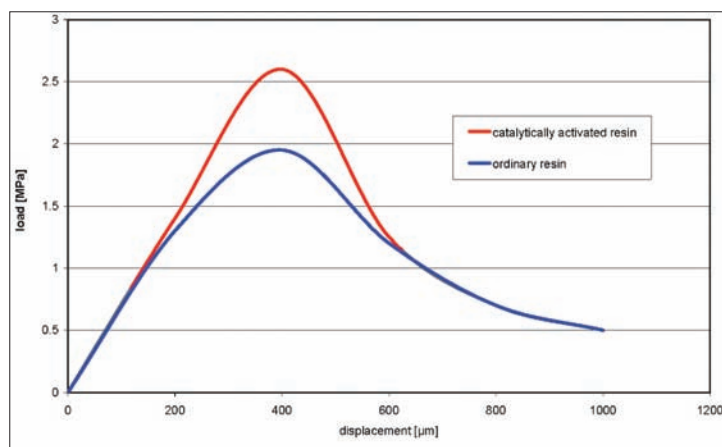


Fig.7 Load-displacement curves of MOR at 20°C

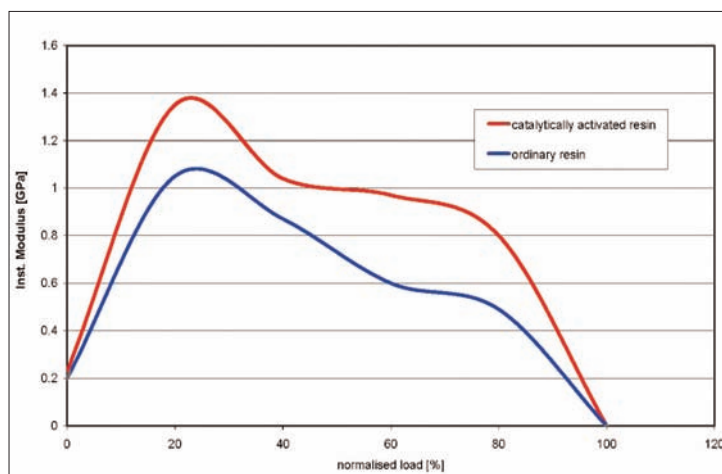


Fig.8 Instantaneous Modulus as a function of applied load

State: as delivered	Ordinary phenolic resin	REFRAFLEX catalytically activated resin
Bulk Density BD [g/cm <sup>3</sup> ]	3.09	3.06
Young's Modulus YM [GPa]	51.97	51.38
Open Porosity [%]	3.84	2.99
Cold compression strength CCS [MPa]	58.50	51.50
Modulus of rupture MOR [MPa]	16.25	15.90
State:after coking at 900°C (ASTM C 831)		
BD [g/cm <sup>3</sup> ]	3.03	3.02
YM [GPa]	10.44	11.12
Open Porosity [%]	10.39	10.16
CCS [MPa]	25.20	29.90
MOR [MPa]	2.81	3.83
HMOR [MPa]		
1000°C	4.41	6.23
1200°C	3.90	6.02
1500°C	2.71	3.81
Work of Fracture (WOF) [Nmm]		
1000°C	69.06	90.19
1200°C	61.34	149.52
1500°C	50.94	159.46

Table 2 Comparison of properties of a MgO-C brick (base FM 97, 10% flaky graphite) bonded by ordinary phenolic resin and bonded by the REFRAFLEX bonding

the decrease in the range of 40 to 80% of the applied load being quite linear.

The higher values of the Instantaneous Modules in the range 40 to 80% are caused by higher strength of catalytically activated resin during same displacement like without catalyst

### SUMMARY

REFRAFLEX technology comprises a catalytical activation of the graphitisation of ordinary phenolic resins in MgO-C bricks during coking. As a result the MgO-C bricks exhibit better thermo-mechanical properties in terms of higher hot strength, work of fracture and Instantaneous Modulus, and a superior thermal shock resistance.

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