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# ANKERSYN – A New Generation of Carbon-Bonded Magnesia Carbon Bricks

Based on a newly developed binder system, a new generation of carbon-bonded "low emission" magnesia carbon products with an extremely low toxic potential have been developed. Furthermore, the binder system is characterized by a very high carbon yield after carbonization that results in an extremely strong carbon bonding. Further significant advantages of this system are the high oxidation resistance of the highly-ordered carbon structure and the excellent stress-absorbing structure. This new generation of carbon-bonded magnesia carbon bricks is successfully marketed under the brand name ANKERSYN. ANKERSYN has been tested with success in a 270 metric ton (mt) basic oxygen furnace (BOF) at Sollac Atlantique (Dunkerque, France). ANKERSYN is a major milestone in high performance products that fulfil all technical and environmental requirements.

## Introduction

Resin- and pitch-bonded magnesia bricks are state of the art for the linings of BOFs, electric arc furnaces (EAF), and ladles [1]. Due to their high carbon residue, coal tar pitch and phenolic resins are the most suitable binders for magnesia carbon bricks, as detailed in Table I. In Europe, pitch-bonded magnesia carbon bricks are the most common brick types as they have proved to be less sensitive to the demanding conditions in European BOF vessels and ladles when compared to resin-bonded bricks.

The principal refractory development targets were a steady increase in performance, cost reduction, and an improvement in environmental aspects to meet customers requirements.

Especially during the last 15 years, the pressure to minimize the environmental pollution resulting from the production and application of refractories has increased significantly. Since all organic binders release volatiles during production and during the heating-up period of the BOF vessel or ladle, the manufacturers of pitch- or resin-bonded refractories, together with the suppliers of pitches and resins, have developed techniques to reduce the potential for environmentally critical emission levels, in parallel with a subsequent improvement in performance.

## Development of a New Low Toxic Carbon Binder

Coal tar pitch is still used in refractory production, for example in impregnation, because of its excellent carbon structure. However, in the last decade pitch has become an ever increasing discussion issue in the production and application of pitch-bonded products because of the carcinogenic potential of the polycyclic aromatic hydrocarbons (PAHs) contained in the pitch (Table I).

The uptake of harmful PAHs during pitch-bonded brick production is avoided by minimizing the dust and avoiding fumes at the production facilities (e.g., by the installation of exhaust and after-burning systems at the presses). By modernising the production facilities it is possible to minimize the benzo(a)pyrene (BaP) concentration in the air to a value lower than 0.002 mg/m$^3$ in the production of pitch-bonded bricks, which is the level recommended by the "Deutsche Gefahrstoff Verordnung". However, during the lining with pitch impregnated magnesia carbon bricks care must be taken to limit dust evolution.

To achieve a further reduction in the PAH emission levels, a new generation of carbon-bonded magnesia carbon bricks based on a new innovative carbonaceous-organic binder system were developed. An additional target of this new generation of binders was to replace the pitch impregnated brands.

| Binders for magnesia carbon bricks | Residual Carbon | BaP** (mg/kg) | Phenol (%) | Formaldehyde (%) |
|---|---|---|---|---|
| Coal tar pitch | 45-65* | 12000 | | |
| Pitch-bonded MgO-C 1st generation | | 300 | | |
| Pitch-bonded MgO-C 2nd generation | | 50-200 | | |
| Phenolic resin – Resole | 45 | - | 1-20 | < 1 |
| Phenolic resin – Novolak | 55 | - | < 1 | < 1 |
| Resin-bonded MgO-C | | - | Cresols, xylenols, and methylphenols | |
| * with dehydrogenating agents ** benzo(a)pyrene | | | | |

***Table I.*** *Binder systems for magnesia carbon bricks.*

The new carbon binder was developed by a German company and tested for refractory applications in close collaboration with RHI Refractories [2-4]. Considerable research was required to establish a suitable process route to transform coal tar pitch into the carbon binder that subsequently set a new environmental standard and is suitable for bonding high grade magnesia carbon products. The new production facility went into full scale operation in April 2002 .

The key production process is the treatment of coal tar pitch under vacuum at high temperatures, as illustrated in Figure 1. During this treatment most of the environmentally critical PAHs evaporate and are condensed, and the resulting condensate is principally used for the production of carbon black. The high molecular, high viscosity carbon binder residue is collected and liquefied with oils to guarantee a good binder workability during the subsequent refractory production.

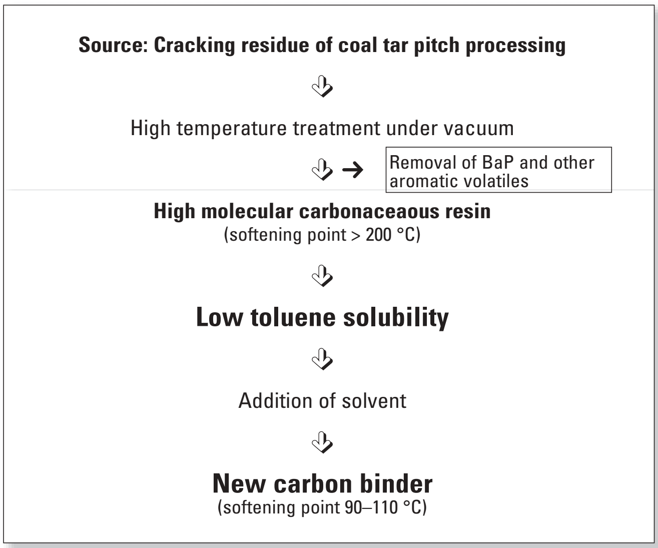


***Figure 1.*** *Process route for production of the new carbon binder.*

Due to this new innovative process route, the carbon binder has an extremely low content of toxic PAHs, substantially reduced emissions, and outstanding product properties, as detailed in Table II.

| | New Carbon Binder | Pitch |
|---|---|---|
| Softening point (°C) | 100 | 100 |
| Quinoline Insolubles (%) | 11 | 6 |
| Toluene Insolubles (%) | 40 | 20 |
| Coking residue (%) | 80* | 65* |
| Mixing temperature (°C) | 100-200 | 100-200 |
| Tempering Temperature (°C) | 300 | 300 |
| BaP (mg/kg) in binder | 300 | 12000 |
| BaP (mg/kg) in binder after tempering* | 10-40 | 4000-8000 |
| BaP (mg/kg) brick* | 10** | 100-200 |
| * with dehydrogenating agents | **recommended limit for BaP in Germany: <50 mg/kg [5] | |

***Table II.*** *Features of the new carbon binder.*

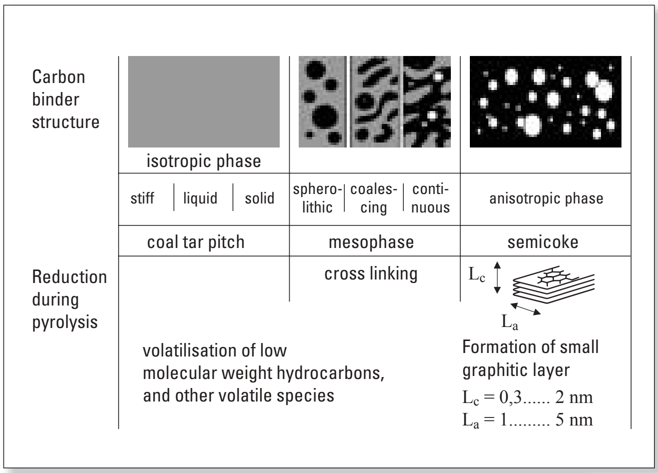


***Figure 2.*** *Pyrolysis of coal tar pitch to graphitized carbon.*

Due to the extremely high carbon yield of the binder which is in the range of 75-80% and its highly orientated graphite like structure (Figure 2) a strong carbon bonding can be achieved. The formation of liquid crystals, termed mesophase, that develop from the coal tar pitch and their mechanism of growth and coalescence determine the microstructure and subsequent graphitizability of the resulting carbon [6-9].

Based on the highly oriented, graphite-like carbon structure, coal tar pitch bonded materials are advantageous with respect to their oxidation and spalling resistance.

The content of environmentally critical components in the binder of the tempered bricks is very low. Using high pressure liquid chromatography (HPLC) a quantitative analysis of the 16 characteristic PAHs was performed providing an indication of the PAHs released during the heating up of the bricks (Figure 3).

Figure 3 details the results of the two samples investigated. Sample A was a standard pitch-bonded magnesia carbon brick tempered at 270 °C with a BaP content of 50 ppm, whilst Sample B represented the newly developed carbon-bonded magnesia carbon brick with a BaP content of 7 ppm. The results indicated that the maximum release of volatiles occurred at 400 °C and that the standard pitch-bonded sample contained higher levels of volatiles. In particular, the concentration of all 16 Environmental Protection Agency (EPA) PAHs released during pyrolysis of Sample B was approximately half the level of the coal tar pitch bonded Sample A.

## Characteristics of the ANKERSYN Series

Based on the new innovative binder system, a new generation of magnesia carbon bricks, marketed under the brand name ANKERSYN were developed that demonstrated a great advance in performance and environmental requirements. As the bonding was based on a highly polymerized structure with a remarkably high carbon/hydrogen ratio, the bonding exhibits a semicoke-like structure, similar to a carbon bond. The typical properties of this newly-developed magnesia carbon generation are detailed in Table III.

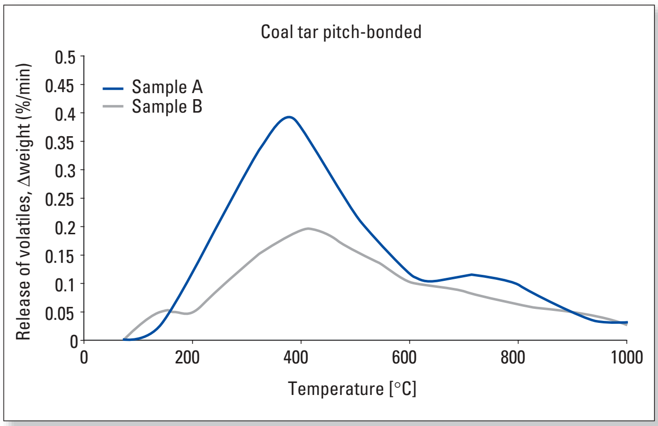


***Figure 3.** Release of PAHs during pyrolysis of a pitch-bonded magnesia carbon brick.*

Depending on the type of application the carbon-bonding can be adapted to the predominant requirements, for example BOF-trunnions, slag-lines, or scrap-impact zones (Figure 4). The matrix is densely packed with a strong carbon-bonding that results in excellent hot corrosion and hot erosion properties.

## Practical Experience

Commencing in 2002, a series of field trials with the magnesia carbon brands based on the new binder system were initiated in BOFs (e.g., Sollac Lorraine bottom of LWS converter, EAF, and ladles). In all cases there was no difference in performance between the coal tar pitch- and the carbon-bonded bricks with a trend towards a better performance with the new binder system.

An example that demonstrates the good performance of ANKERSYN is a large scale lining with ANKERSYN in the 270 mt BOF at Sollac Atlantique. The new grades were installed in the trunnions of converter 6, campaign number 337, concurrently with the equivalent standard materials that were coal tar pitch impregnated. This enabled a direct comparison of the products under identical in service conditions. The converter was put into operation on September 19, 2003, and taken out of service on February 27, 2004, after 3759 heats. The average weight of liquid steel per charge was 262 mt, giving a total of 984858 mt of steel processing. In the postmortem analysis no difference could be detected between the standard coal tar pitch impregnated and the new nonimpregnated materials. The in service potential in the trunnions, calculated from the measured remaining lining thickness after 3521 heats, was well over 4000 heats.

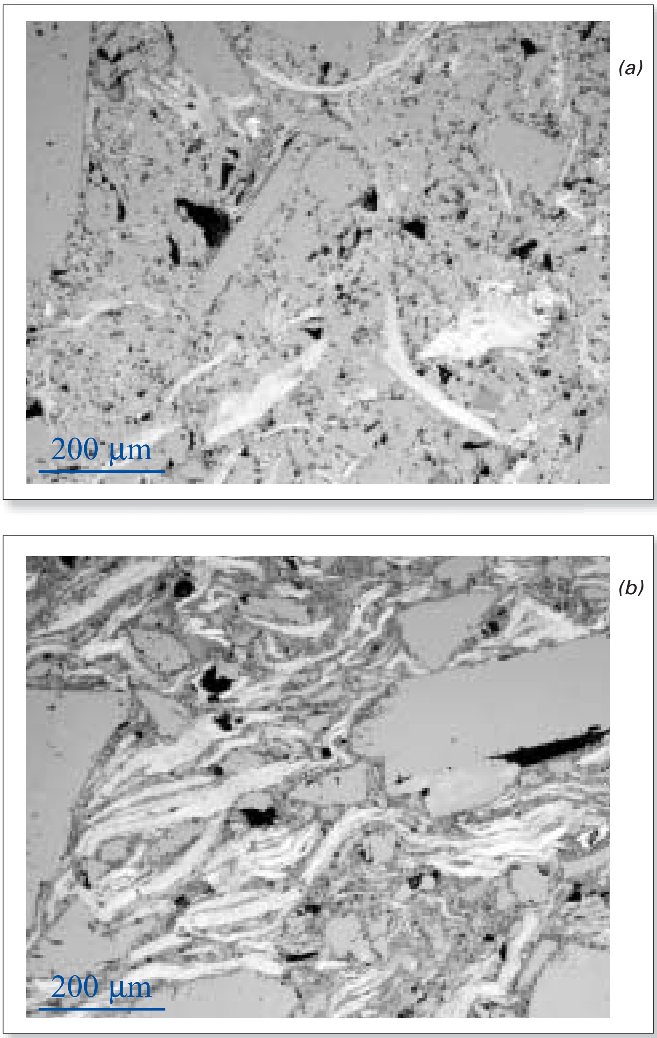


***Figure 4.** Microstructure of ANKERSYN bricks. (a) 5% residual carbon, and (b) 14% residual carbon.*

| Brand | ANKERSYN DX90 | ANKERSYN DX93 | ANKER DX90 | ANCARBON DX93 |
|---|---|---|---|---|
| Characteristics: | Carbon-bonded | | Pitch-bonded | |
| Residual carbon (%) | 6 | 14 | 6 | 14 |
| Physical properties as received: | | | | |
| - BD (g/cm³) | 3.20 | 3.05 | 3.18 | 3.03 |
| - OP (%) | 3.5 | 3.5 | 4.0 | 3.5 |
| - CCS (N/mm²) | 60 | 38 | 70 | 35 |
| Physical properties after coking at 1000 °C: | | | | |
| - BD (g/cm³) | 3.15 | 2.98 | 3.14 | 2.94 |
| - OP (%) | 7.0 | 7.5 | 8.0 | 8.5 |
| - CCS (N/mm²) | 80 | 37 | 70 | 30 |
| - HMOR (N/mm²) | 8.0 | 11.0 | 6.5 | 10.0 |
| Special features of ANKERSYN | → Low amount of volatiles – BaP <20 ppm<br>→ MgO- reinforced matrix – high ratio of MgO/C in the matrix | | | |

***Table III.** Characteristics of carbon-bonded magnesia carbon high grade bricks. Analyses include bulk density (BD), open porosity (OP), cold crushing strength (CCS), and hot modulus of rupture (HMOR) at 1400 °C.*

A further question was to determine if the operating conditions had been favourable to the behaviour of the refractories. To examine this issue the "CCRCT" coefficient was used, which gives the difference in terms of the number of heats between those calculated under normal standard conditions and those actually achieved. The CCRCT figure is a correlation coefficient which takes into account the following main factors that influence refractory performance, compared to the same factors under normal working conditions:

>> Temperature
>> Steel carbon content
>> Slag iron content
>> Raw dolomite added to the slag
>> Calcium oxide content
>> Number of heats per shift
>> Percentage of shifts with a low number of heats
>> Percentage of heats with high manganese or calcium silicon content

The CCRCT coefficient over the whole campaign was -98, (i.e., the lifetime in normal operating conditions should have been 3757 -(-98) = 3855 heats). This indicates that the actual working operations were harsher than under normal conditions. For example the average temperature was 1689.5 °C as opposed to 1680 °C under standard conditions.

The number of heats actually achieved in this campaign was above the average life time of 3519 heats for all the previous converters run at Sollac Atlantique since the beginning of 2003 and represents the best result for the last 12 years. This good performance was possible because of the day to day observations and effective cooperation between the various departments involved. Furthermore, it was achieved by fulfilling the following conditions:

>> Adaptation of working conditions to the status of the refractory lining.
>> Optimization of refractory maintenance in terms of gunning and slagging.
>> Optimization of the refractories to produce a well balanced lining.

This in service result indicates the new ANKERSYN products are suitable for the conditions prevailing at Sollac Atlantique.

## Conclusion

Through the introduction of a new innovative carbonaceous-organic pitch carbon binder system, in combination with special dehydrogenation additives and high-temperature tempering, the on-site emission of critical volatiles could be reduced to the lowest levels. Further significant advantages of this new bonding type are the exceptional oxidation resistance of the highly oriented carbon structure without the requirement for antioxidant addition. This produces an improved redox resistance, a more flexible brick structure, and outstanding fracture mechanical properties with a high shock absorbing potential.

This new binder type represents a milestone with respect to high performance products, fulfilling the increasing demands of operational requirements and environmental standards.

## References

[1] Buchebner, G. and Pirker, S. New high-performance refractories for BOF use. XXXIX International Colloquium on Refractories, Aachen; Germany, Sept 1996. *Stahl u. Eisen.* 1996, Special Okt., 40-45.
[2] Boenigk, W.; Schnitzler, D.; Stiegert, J.; Buchebner, G. and Grassegger, S. Carbores – A carbon speciality to improve the performance of refractories bound with phenolic resins. *EUROCARBON 2000*, Berlin; Germany, 2000; Abstracts pp 367-368.
[3] Boenigk, W. and Schnitzler, D. *EUROCARBON 1998*; Abstracts pp 129-130.
[4] Buchebner, G. and Samm V. EOSC´03, *Proceedings of the 4th European Oxygen Steelmaking Conference*, Graz, 2003 pp 135-143.
[5] Technische Regeln für Gefahrstoffe TRGS 551, Teer und andere Pyrolyseproduckte aus organischem Material, Ausgabe Juli 1999.
[6] Marsh, H. and Griffiths, J. *Ext. Abstracts International Conference on Carbon*; Toyohashi; Japan, 1982.
[7] Rand, B. and McEnaney, B. Carbon Binders From Polymeric Resins and Pitch. I. Pyrolysis Behaviour and Structure of the Carbons. *Br. Ceram. Trans. J.* 1985, 84, 157-165.
[8] McEnaney, B. and Rand, B. Carbon Binders From Polymeric Resins and Pitch. II. Structure and Properties of the Carbons. *Br. Ceram. Trans. J.* 1985, 84, 193-198.
[9] Franklin, R.E. The structure of graphitic carbons. *Acta Cryst.* 1951, 4, pp 253-261.
[10] Buchebner, G.; Neuböck, R. and Grassegger, S. Carbon-Bonding. A New Milestone on Low Emission Magnesia Carbon Bricks. UNITECR´01, Cancun, Mexico, 2001; 1, pp 324-335.

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