Aspects of Elastification Reactions in Basic Cement Kiln Bricks

J. Södje, S. Uhlendorf, H.-J. Klischat

To increase the flexibility and elasticity of a basic refractory brick system, beneath the resistor MgO a second component is necessary, the so-called elastifier. Spinel minerals have proven to be an economically and technically suitable elastifier material. The behaviour of spinel minerals in the magnesia system are highlighted and focussed in this paper, as other (like zirconia) are of less importance nowadays. The behaviour of the crucial spinel types can be subdivided into three groups regarding their reaction potential with the basic brick material, the resistor MgO. The selection of the appropriate elastifier from the spinel group, its content and specific performance influences the properties and behaviour as well as the resistivity of the basic brick systems.

1 Introduction and historical background

The production of cement in highly efficient rotary kilns would not be possible today without the development of sophisticated elastified basic bricks. Only their installation offers a superior economic and ecological kiln lining. To further increase the productivity of cement production from the refractories side, refractory producers have put and continue to put efforts into the development of even more advantageous products.

Regarding the brickwork installation over the recent 100 year history of cement rotary kilns, fireclay bricks and high alumina bricks were primarily used in the hottest areas of the kiln until the 1940s.

Basic bricks were firstly installed approximately 75 years ago. First trials were carried out with magnesia and magnesia chromite bricks in the burning zone during the 1930s and 1940s. Magnesia chromite bricks became the standard basic brick in the hot section of the kiln, while magnesia bricks ex-hibited bad performance due to their poor structural flexibility [1]. The peak level of magnesia chromite bricks usage in the hot sections of the kiln was roughly between 1940 and 1990.

At the same time, dolomite bricks were installed in the main burning zone with similar positive results as magnesia chromite bricks in case of moderate climatic environmental conditions. Dolomite bricks are sensitive to CO_2, sulphur and humidity, which unfortunately affects their performance in hot climatic zones or when secondary fuels are used [2].

In the mid-seventies, trials with chromite-free magnesia spinel brick grades were carried out in Japanese cement rotary kilns, primarily in the coating-free transition zones [3]. Use of magnesia spinel bricks in Germany started in the early 1980s [4]. In this context, ALMAG® 85 became the most popular and successful magnesia spinel brick for cement rotary kilns. Although coating-friendly magnesia chromite bricks and dolomite bricks are still used in the burning zone, the environmental impact caused by refractory products containing chromite (hexavalent alkali chromate formation) resulted in an increasing demand for chromite-free basic bricks in the cement industry.
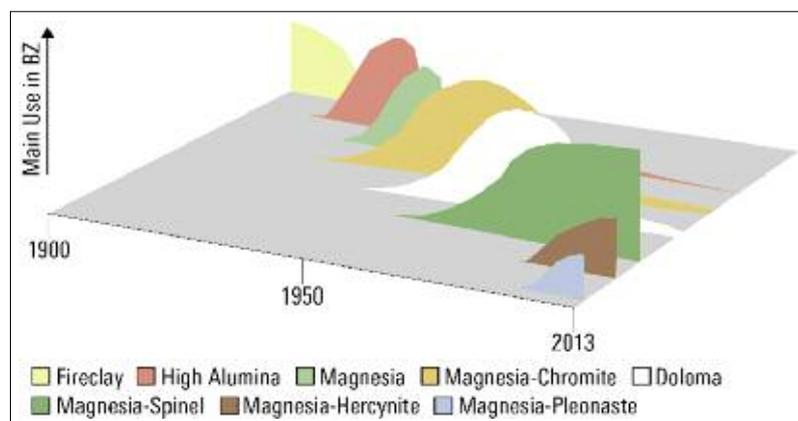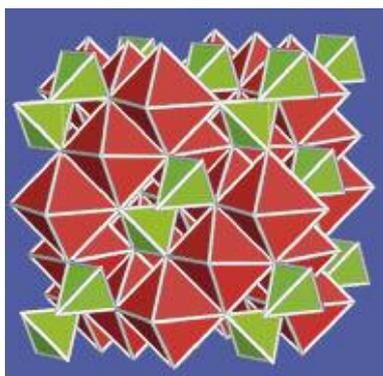
Fig. 1 Use of different brick grades in the main burning zone (BZ) of rotary cement kilns since 1900 (schematic diagram) (copyright: Refratechnik Cement GmbH)

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Fig. 2 General spinel structure
(source: ruby.chemie.uni-freiburg.de)

Consequently, the refractory industry introduced new chromite-free bricks with modified spinel types, structural properties and enhanced physical characteristics [5–12]. Some of these brick grades were optimized for specific kiln sections, like tire area, severely thermally loaded zones and the burning zone. Besides magnesia spinel bricks with varying spinel content and spinel types (sintered spinel, in situ spinel, fused spinel), magnesia hercynite bricks and magnesia pleonaste bricks have been developed for rotary kilns [8, 12, 13].

Fig. 1 schematically illustrates the use of brick grades in the main burning zone of rotary kilns since 1900.

2 Classification of spinel minerals

Spinel minerals have proven to be most suitable materials to act as elastifier in basic bricks. Various types of spinel are currently the most established elastifying component for basic brick grades in cement rotary kilns. Industrially important minerals of the spinel group are lithogenous and form deposits, like huge chromium ore deposits in South Africa, the Philippines and Finland. Spinel minerals possess a highly low-energy structure (cubic closed packed), which comprehends characteristic high hardness, high density, high melting temperature and high chemical resistance.

The spinel structure is based on a highest cubic sphere packing of O^{2-} ions. The cations in the spinel structure are encased in the octahedral and tetrahedral gaps. The general formula is AB_2O_4, and every elementary cell contains eight units of formula and exhibits different edge lengths between 8,09 and 8,64 Å depending on the chemical com-

position. Two types of occupation of the octahedral and tetrahedral gaps can be distinguished:

Normal spinel ($A^{2+}B_2^{3+}O_4$)

From the 24 cations per unit cell 8 A^{2+} ions are in the tetrahedral, and 16 B^{3+} ions are in the octahedral coordination.

Inverse spinel ($B^{3+}A^{2+}B^{3+}O_4$)

In this case, 8 B^{3+} ions are in the tetrahedral as well as 8 A^{2+} ions, and 8 B^{3+} ions are in octahedral coordination.

The "A" position is usually filled by bivalent cations (Mg^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.), and position "B" by trivalent cations (Al^{3+}, Cr^{3+}, Fe^{3+}, V^{3+}, etc.). Titan (Ti^{4+}) can be also embedded in the crystal structure, e.g. the spinel type ulvite (Fe_2TiO_4). Fig. 2 shows the general spinel structure.

All spinels form mixed spinel minerals, especially at high temperatures. Tab. 1 shows an overview of the most important minerals of the spinel group [14].

The variety of end members indicates that the spinel structure can incorporate cations with a wide spectrum of radii and valences. Additionally, a certain ratio of the octahedral and tetrahedral gaps can be unoccupied. This is named defect spinel. Defect spinels are formed at high temperatures and low pressures.

Regarding Tab. 1, some spinel grades from the spinel-gahnite series and the magnesiochromite-zincochromite series are utilised in the refractory industry producing elastified basic magnesia bricks, whereas the spinel grade chromite/magnesiochromite is the only one which occurs naturally and is industrially mined. The other utilised spinel grades, like MA-spinel and hercynite, have to be synthetically produced. The typical types of spinel which are used in basic brick grades are pre-synthesized sintered or fused spinel grades. The so-called in situ spinel or matrix spinel are formed in the texture of basic bricks during the manufacturing process (Chapter 3).

Currently, magnesiochromite (MCr), spinel (MA), hercynite (FA) and the recently developed and produced pleonastic spinel type ($[Fe_xMg_{1-x}]Al_2O_4$) are the principal spinel grades to elastify basic bricks. Basic bricks elastified with the spinel grades gahnite and

Tab. 1 Overview of the most important spinel group (endmember) [14]

Name	Formula	Type of Occupation	a [Å]
Spinel-Gahnite Series			
Spinel	$MgAl_2O_4$	normal	8,09
Hercynite	$FeAl_2O_4$	normal	8,13
Galaxite	$MnAl_2O_4$	normal	8,29
Gahnite	$ZnAl_2O_4$	normal	8,09
Magnesioferrite-Franklinite Series			
Magnesioferrite	$MgFe_2^{3+}O_4$	inverse	8,38
Magnetite	$Fe^{2+}Fe_2^{3+}O_4$	inverse	8,40
Jakobsite	$Mn^{2+}Fe_2^{3+}O_4$	normal	8,47
Trevorite	$Ni^{2+}Fe_2^{3+}O_4$	inverse	8,34
Cuprospinel	$Cu^{2+}Fe_2^{3+}O_4$	normal	8,37
Franklinite	$ZnFe_2^{3+}O_4$	normal	8,47
Magnesiochromite-Zincochromite Series			
Magnesiochromite	$MgCr_2O_4$	normal	8,36
Chromite	$Fe^{2+}Cr_2O_4$	normal	8,36
Manganchromite	$Mn^{2+}Cr_2O_4$	normal	8,47
Cochromite	$Co^{2+}Cr_2O_4$	normal	8,29
Nichromite	$Ni^{2+}Cr_2O_4$	normal	8,32
Zincochromite	$Zn^{2+}Cr_2O_4$	normal	8,35
Vuorelainenite-Brunogeieirite Series			
Magnesiocoulsonite	$MgV_2^{3+}O_4$	normal	8,38
Vuorelainenite	$Mn^{2+}V_2^{3+}O_4$	normal	8,48
Coulsonite	$Fe^{2+}V_2^{3+}O_4$	normal	8,30
Quandilite	$TiMg_2O_4$	inverse	8,40
Ulvöspinel (Ulvite)	$TiFe_2^{2+}O_4$	normal	8,51
Brunogeieirite	$Fe_2^{2+}Ge^{4+}O_4$	normal	8,41

galaxite were installed in the cement industry to a lesser extent.

3 Elastification in basic bricks

The main component of basic bricks is the resistor MgO, which is thermochemically resistant to attack by cement clinker or related materials. This resistor can be either extracted from natural magnesia-rich rocks (coarsely and finely grained magnesite) or synthetically produced from sea water and salt brines [15]. Unfortunately, products made only from MgO are characterised by a poor thermal shock resistance (due to their rigidity and high modulus of elasticity), a high thermal conductivity, and a high thermal expansion.

For an appropriate performance of basic bricks, a second component has to be introduced into the structure, the so-called elastifier. This elastifier increases the structural flexibility of the lining, the ductility, and its fracture toughness by developing a microcrack network in the microstructure. This results in a high resistance to mechanical stresses by lowering of the modulus of elasticity E and simultaneously reducing the thermal expansion and the thermal conductivity. The formerly brittle MgO bricks turn into elastic, sometimes even thermoplastic high-tech products, which can manage the complex stresses prevailing in a cement rotary kiln. These are mainly mechanical stresses (by kiln shell ovality, thermal shocks, thermal expansion, condensing infiltrates), thermal stresses (by overheating), and chemical stresses (by cement clinker, redox conditions, etc.).

Spinel minerals have proven to be the most suitable materials to act as elastifier in basic bricks. They are compatible with the surrounding magnesia matrix, they induce a microcrack system in the brick, and are mostly highly resistant to chemical attack by cement clinker or related materials at regular service conditions and temperatures, although their resistance is naturally lower than that of MgO.

Known from the past, MA spinel ($MgAl_2O_4$) can be introduced into the brick matrix in two ways: as a presynthesized material (either sintered at temperatures of approx. 1700–1800 °C or fused at temperatures exceeding 2135 °C) or from an in situ reaction of alumina additives with MgO of the surrounding brick matrix during brick firing at 1500–1800 °C [16, 17].
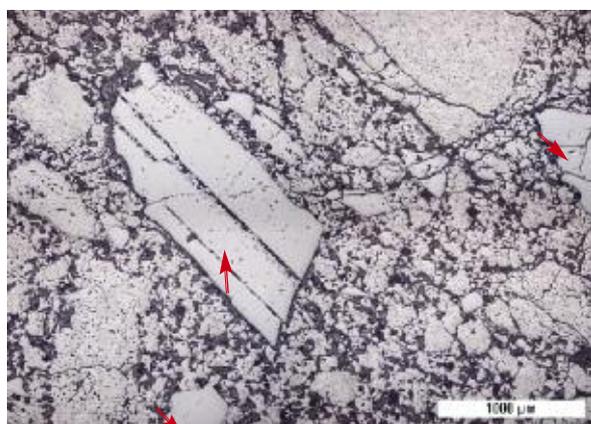
The performance of the elastifier in the magnesia matrix is highlighted by considerations, which focus only on the spinel minerals, as other elastifiers (like zirconia) are of less importance nowadays. As target values reflecting the structural flexibility, for the cold crushing strength σ ~70–80 MPa and for the modulus of elasticity E ~20–22 GPa are assumed, as bricks with these values are known to deal well with the mechanical requirements of typical rotary kilns.

Thus, the crucial spinels can be subdivided into three groups regarding their reaction potential with MgO, which also influences their content in the basic brick (Tab. 2).

Group I with the classical mineral spinel $MgAl_2O_4$ is characterised by little or no interaction between the elastifier and the MgO matrix, Fig. 3. Spinel is located, almost unaffected, beneath MgO. The elastification results from the thermal expansion mismatch between spinel ($8,8 \cdot 10^{-6}$ K^{-1}) and magnesia ($13,85 \cdot 10^{-6}$ K^{-1}) creating a microcrack system in the brick with a reduction of the modulus of elasticity (*Young*'s modulus) and a dramatic advance of the mechanical properties, like improved thermal shock resistance, lower thermal expansion, and less internal stresses in the brick.

Similarly, the newly developed pleonastic spinel is acting [12, 18]. As this pleonastic spinel contains a considerable amount of MgO, and alumina and iron are tightly bound in the crystal structure, the diffusion potential of ions is largely suppressed and the pleonastic spinel also elastifies largely by a thermal mismatch pattern (Fig. 4).

Because of absent reactions between resistor and elastifier, the elastifier needed

Tab. 2 Classification of spinel minerals regarding their reaction potential with MgO matrix (chrome spinel is a synonym for chrome ore in basic bricks)

| Group I no or Little Reaction with MgO Matrix	Group II Limited Reaction with MgO Matrix	Group III Complete Reaction with MgO Matrix
spinel $MgAl_2O_4$ pleonastic spinel $(Mg,Fe)(Al,Fe)_2O_4$	chrome spinel $(Mg,Fe)(Cr,Al,Fe)_2O_4$ hercynite $FeAl_2O_4$ galaxite $MnAl_2O_4$	alumina Al_2O_3

Fig. 3 Microstructure of a magnesia spinel brick with fused spinel grains (arrows) embedded in a magnesia matrix (copyright: Refratechnik Cement GmbH)
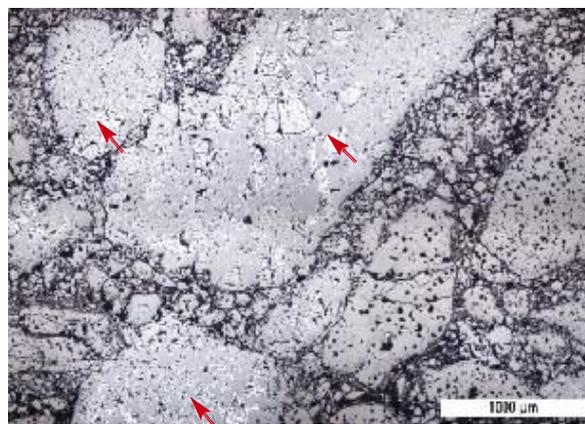

Fig. 4 Microstructure of a magnesia spinel brick with fused pleonastic spinel grains (arrows) embedded in a magnesia matrix (copyright: Refratechnik Cement GmbH)
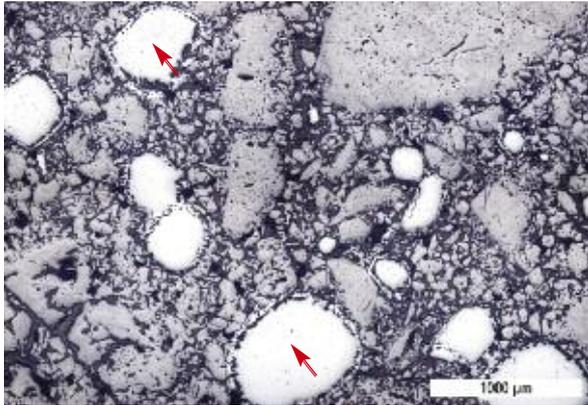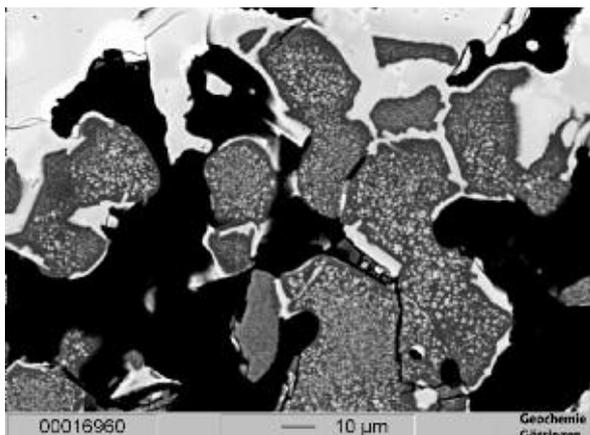
Fig. 5 Microstructure of a magnesia chromite brick with chrome spinel grains (arrows) embedded in a magnesia matrix; notable are the gaps around the chrome spinel grains (copyright: Refratechnik Cement GmbH)
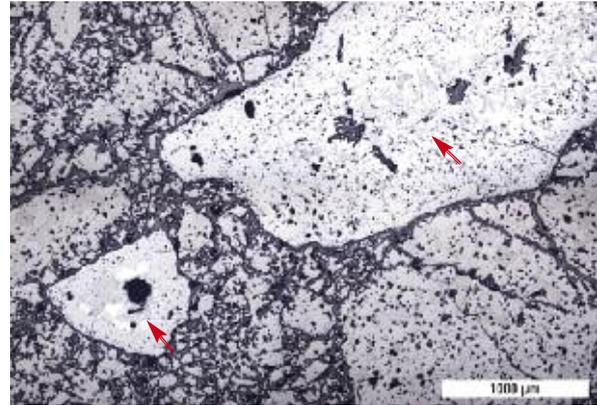

Fig. 6 Microstructure of a magnesia hercynite brick with fused hercynite grains (arrows) embedded in a magnesia matrix; notable are the holes in the hercynite grains due to diffusion of iron ions into the surrounding magnesia matrix (copyright: Refratechnik Cement GmbH)
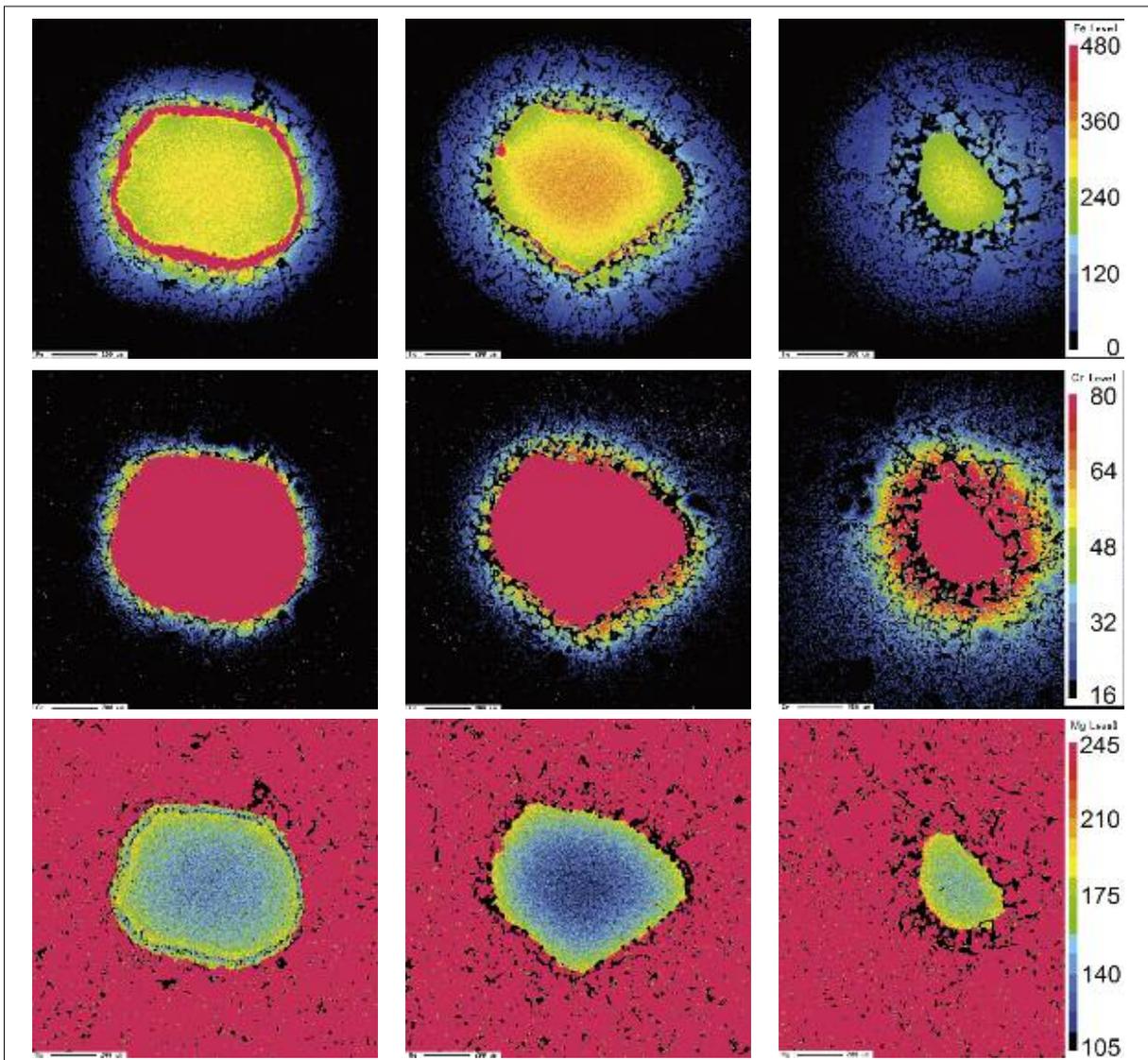
Fig. 7 Electron microprobe element maps for Fe, Cr and Mg of chrome spinel grains in an MgO matrix burned for 4 h at 1400 °C (left), 1500 °C (centre) and 1600 °C (right) illustrating the diffusion processes between chrome spinel and matrix as well as pore space formation around the chrome spinel grains [27]

Fig. 8 Backscattered electron image micrograph of the contact zone between chrome spinel (top, left) and MgO matrix (bottom, right) showing formation of secondary spinels in the periclase crystals and on grain boundaries [27]. Burning conditions were 4 h at 1600 °C
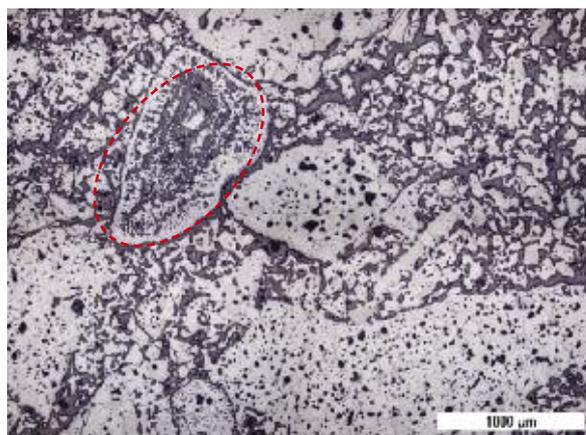
Fig. 9 Microstructure of a magnesia spinel brick with an in situ spinel grain (ellipse) embedded in a magnesia matrix; notable is the vacant core hole within the spinel grain due to diffusion of aluminium ions into the surrounding magnesia matrix with subsequent spinel reaction
(copyright: Refratechnik Cement GmbH)

for elastification typically amounts to 14–18 % and can even be as high as 28 % for special applications.

Group II, which is mainly represented by chrome spinel and hercynite as important spinels, is characterised by moderate reactions between the elastifier mineral and the matrix (Fig. 5, 6). These reactions are pronounced enough that a publication designates these minerals as active spinels [19].

When compared to the classical spinel ($MgAl_2O_4$) and pleonastic spinel (($Mg,Fe)(Al,Fe)_2O_4$) from Group I, chrome spinel and hercynite contain significantly less MgO. This leads to higher concentration gradients between elastifier and MgO matrix and thereby favours diffusion processes at high temperatures. Reaction tests with chrome spinel and magnesia exhibit diffusion of Fe(II)/Fe(III), Mn(II)/Mn(III), and/or Cr(III) ions from the elastifier into the matrix and, vice versa, the diffusion of Mg(II) into the elastifier [20–22]. These diffusion processes lead to further elastification in addition to the thermal expansion misfit.

In case of chrome spinel, a well-reviewed material, the interaction with an MgO matrix is described by various authors [23–26]. At typical burning temperatures (1400–1600 °C) significant amounts of Fe(II)/Fe(III) enrich in the contact area between chrome spinel and magnesia and subsequently diffuse into the MgO matrix (Fig. 7). The lack of FeO/Fe_2O_3 in the chrome spinel relic is partially substituted by MgO. But as mass transfer is mainly directed to the matrix, pore space is generated around the shrinking

chrome spinel grains (Fig. 7). This pore space is supposed to inhibit crack propagation and is therefore advantageous for the mechanical flexibility of the brick (reduction of Young's modulus). Cr(III) also significantly diffuses into the matrix, especially at temperatures above 1500 °C at which it increasingly turns into gaseous state. During cooling, the solubility of the iron and chromium ions in the periclase crystals of the magnesia decreases and secondary spinels [$Mg^{2+}(Fe^{3+},Cr^{3+})O_4$] precipitate on grain boundaries and inside periclase crystals, also contributing to brick elastification (Fig. 8).

In case of hercynite and galaxite, the diffusion of Fe(II)/Fe(III) or Mn(II)/Mn(III) into the MgO matrix can be observed as well and also leads to the formation of secondary spinel in the periclase crystals. The loss of FeO in the hercynite or of MnO, respectively, in the galaxite is compensated by MgO from the magnesia matrix, which results in some kind of thermochemically more stable pleonastic spinel according to the reaction:

$$FeAl_2O_4 + MgO \rightarrow (Fe,Mg)Al_2O_4$$
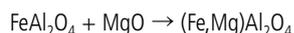
In case of galaxite in the brick, the following reaction can take place:

$$MnAl_2O_4 + MgO \rightarrow$$
$$(Mn,Mg)Al_2O_4 + MgAl_2O_4 \text{ [28]}.$$
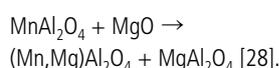
The mass transfer is lower compared to chrome spinel and usually does cause only a little pore space formation around the hercynite grains.

Because of the thermochemical reactions between resistor and modifier, the elastifier needed for sufficient elastification typically amounts to 6–10 %. For special applications, magnesia chromite bricks may even contain 15–25 % chrome spinel (the use of chrome spinel in cement kiln refractories is decreasing due to environmental aspects). Although a reaction takes place, the original elastifier is still present in the most part of the core area of the elastifier (topochemical reaction).

Group III is characterised by extensive reactions between the elastifier mineral and the matrix. Typically, no considerable amounts of the original elastifier substance remain, a complete mineral conversion takes place (Fig. 9). Even if some original alumina is left, the thermal mismatch between alumina and magnesia still provides a sufficient elastification due to the similar thermal expansion coefficient of alumina and spinel. Up to now, of economic importance is only the addition of alumina (Al_2O_3) to an MgO-based brick, the reaction product is magnesium alumina spinel. Due to the diffusion paths of Al_2O_3 into the MgO matrix, even hollow grains can be formed, with a pore on the site of the former alumina grains, surrounded by a shell of the newly formed spinel. Sometimes the core of the spinel shell is filled with low-melting reaction products from secondary minerals of the magnesia with alumina, in most cases calcium aluminates.

The reaction formula is simple:

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4$$
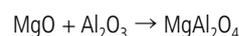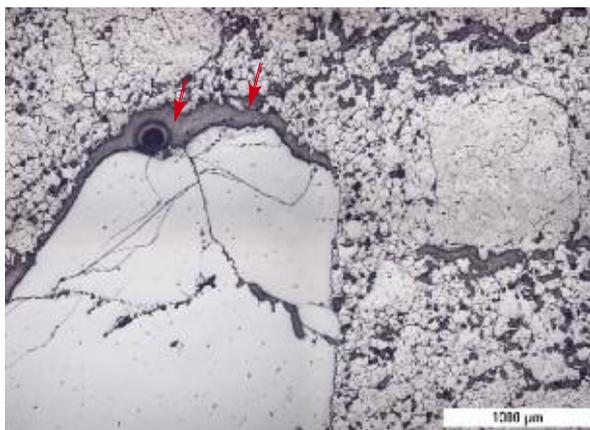
Fig. 10 Initial corrosion of a fused spinel grain leaving a pore near the corrosion area (~3–5 mm from the hot face side, arrows) (copyright: Refratechnik Cement GmbH)
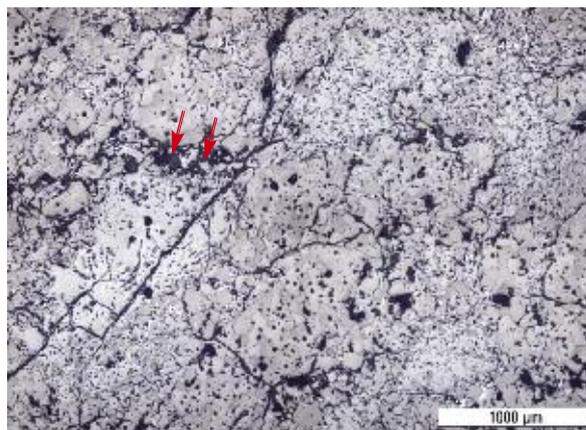
Fig. 11 Initial corrosion of a pleonastic spinel grain leaving secondary melts in the surrounding magnesia matrix; only initial pore formation is observed (~3–5 mm from the hot face side, arrows) (copyright: Refratechnik Cement GmbH)

The use of other X_2O_3 sesquioxides like Fe_2O_3, Y_2O_3, or even Mn_2O_3 and Cr_2O_3 instead of Al_2O_3 did not serve to create bricks with properties suitable for rotary kiln installations.

Because of the intensive reaction between resistor and modifier, the elastifier needed for elastification typically amounts to only 3–5 %. With this technology, the MgO content of the brick can be increased up to 95 %, but also with the disadvantage of a higher thermal conductivity and a higher thermal expansion. This has to be considered when installing bricks or a thermal insulation or when providing space for expansion.

By adding spinel minerals to a coarse- and fine-grained magnesia matrix, it is possible to create bricks, which can withstand the mechanical tensions in hot rotating units. By means of the appropriate mineral from the spinel group, also the thermochemical resistivity of a brick can be adjusted.

4 Chemical stability of elastifiers in basic bricks against cement clinker

Known from numerous investigations on used basic bricks, in most cases the elastifier (=spinel mineral) is corroded whereas the resistor (=MgO) is rather unaffected.

Especially when alternative fuels are fired, high thermal und thermochemical stresses with increased temperature load to the lining are caused by abnormal burning conditions [29]. Also the use of low-grade coal can change the flame shape, which can cause local or general overheating. As a result thermochemical reactions between the cement clinker and the basic refractory brick, and here especially the elastifier (spinel types), are probable.

Minerals from Group I with the spinel $MgAl_2O_4$ are characterised by the formation of low melting calcium aluminates, mostly mayenite ($12CaO \cdot Al_2O_3$) or ye'elimite ($4CaO \cdot Al_2O_3 \cdot SO_3$, in the presence of sulphur oxide from the kiln gas atmosphere) on corrosion by overheated liquid cement clinker or unsuitable low-melting clinker composition. Primary (from infiltration) and secondary melts (formation of calcium aluminates) are absorbed by the surrounding brick structure and solidify during migration to the brick cold face or when the kiln is shut down. Cavities or pores remain on the site of the corroded spinel particles. In the centre of these pores may remain small relics of the original spinel grain. Due to the presence of primary and secondary melts, the brick structure at the hot face is highly densified, which results in spalling of the infiltrated area. The use of fused spinel may be advantageous due to less grain boundaries and higher primary crystal size (Fig. 10), whereas a sintered material provides a more homogeneous spinel phase, which may be better for elastification [30]. The selection of the spinel type also requires knowledge about the area and conditions of brick installation.

In case of pleonastic spinel, calcium aluminates may form as well, also the formation of calcium ferroaluminates $CaO(Al_2O_3,Fe_2O_3)$ is possible (Fig. 11).

As an important additional aspect, reactivity and surface area have to be considered: not only the chemical composition determines the corrosion behaviour, but to a similar extent also the structural properties do. Generally, fused materials with high grain size and a low porosity are more resistant to chemical attack than sintered ones with many grain boundaries (as first point of attack) and small crystal sizes.

In case of spinels, fused ones are increasingly used in cement kiln refractories to prevent a premature corrosion reaction, especially if the necessary amount for elastification is rather high. In case of iron-containing fused pleonastic spinel, the usually mobile iron ions are tightly bound in the crystal structure.

When bricks containing minerals from Group II (hercynite and chrome spinel), characterised by a mandatory amount of 6–10 % needed for elastification, are corroded by overheated cement clinker, the corrosion products are mainly dicalcium ferrite $2CaO \cdot Fe_2O_3$ (melting temperature 1435 °C) and/or $4CaO(Al_2O_3, Cr_2O_3)Fe_2O_3$, the latter in the event of magnesia chromite brick corrosion. This reduces the brick's refractoriness, and as a consequence of a subsequent densification a spalling of the infiltrated brick horizon and therefore a premature wear can take place (Fig. 12, 13).

In case of magnesia hercynite bricks, dicalcium ferrite and calcium aluminates, especially mayenite and ye'elimite (in the presence of SO_x), are the main corrosion products as well. Generally, a susceptibility of

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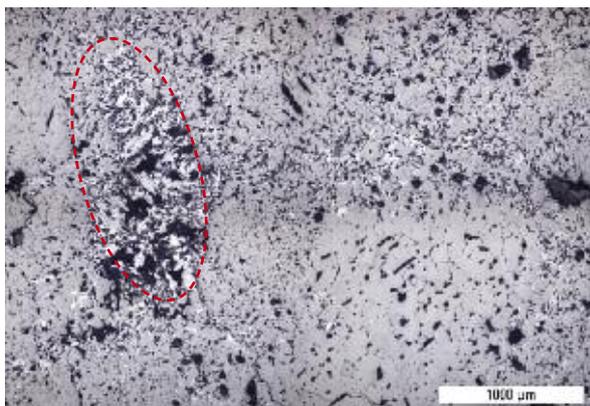**Castament® FS 60**
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Fig. 12 Corrosion of a hercynite grain leaving secondary melts, and calciumferritic melt in the surrounding magnesia matrix; notably, a significant pore formation is observed (~3–5 mm from the hot face side, ellipse), which gives rise to further infiltration and corrosion (copyright: Refratechnik Cement GmbH)
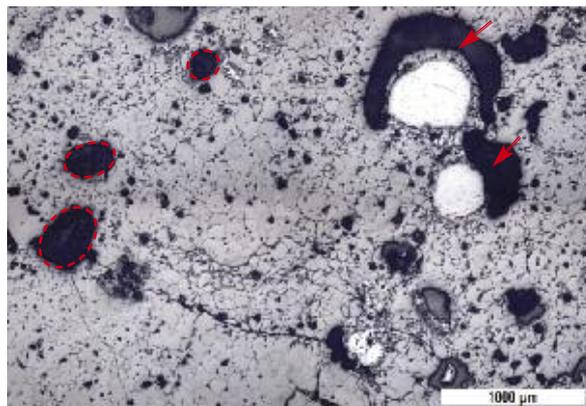
Fig. 13 Corrosion of chromite grains leaving chrome-containing secondary calcium alumino-ferritic melts in the surrounding magnesia matrix. Here, also a significant pore formation is observed (~3–5 mm from the hot face side, ellipses and arrows), which can promote further infiltration and corrosion (copyright: Refratechnik Cement GmbH)

hercynite (and galaxite) to the presence of SO_x is observed [31]: in several cases, $KFeS_2$ as reaction product of hercynite degradation according to the reaction

$$4MgO + 2K_2O + 4Fe(II)O \cdot Al_2O_3 + 8SO_2 \rightarrow 4KFeS_2 + 4MgO \cdot Al_2O_3 + 11O_2$$
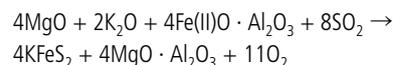
is found under reducing burning conditions.

For magnesia galaxite bricks, a similar reaction may take place, with $K_2Mn_3S_4$ as corrosion product, although this mineral has not been explicitly found up to now. Although the corrosion mechanisms for these brick grades have not been investigated fully yet, it is possible that some low melting eutectics in the quaternary system MnO-CaO-Al_2O_3-SiO_2 (approx. 1150 °C) may occur resulting in a premature wear by loss of refractoriness. Although [28] mentions that a lower amount of the elastifier from Group II, compared to magnesium aluminium spinel from Group I, is needed to achieve a similar structural flexibility (which should give the brick also a higher resistance to chemical attack), it has to be considered that the elastification is lost more easily when the already reduced amount of elastifier is even more reduced by kiln feed corrosion.

In case of minerals from Group III (i.e. alumina, either sintered or fused), the lowest amount is needed for elastification, which also gives the lowest amount of elastifier (a.k.a. spinel) in the magnesia spinel brick. The reaction products are chemically the

same ones as for presynthesized spinel from Group I. Due to the in situ reaction, the newly formed spinel is rather fine-grained (crystal size <10 µm) and thus less corrosion resistant than e.g. a fused spinel. This can be also clearly seen by a post-mortem analysis of a used brick containing in situ formed minerals (Fig. 14): a complete corrosion of the in situ spinel took place and caused a complete loss of structural flexibility and brick spalling. The structure is infiltrated primarily by liquid cement clinker and secondarily by melts formed by spinel corrosion. The magnesia grains still remain chemically unaffected by cement clinker, as predicted by theory.

So although the amount of spinel as a primary point of attack is much lower than that of minerals of Group I, the degradation takes place much faster due to the smaller crystal size.

For performance of basic bricks, not only the chemical composition of the elastifier "spinel mineral" has to be considered, but also mineralogical, structural and steric reasons. For a high corrosion resistance, which is needed in thermally loaded transition zones of cement kilns, a dense material should be used to minimize a thermochemical attack by kiln feed. Usually, these are fused products essentially from Group I with a high crystal size and few grain boundaries. If only an elastification is needed without high requirements on the chemical resistance (e. g. for installations in the main burning zone with a stable protective coating), sintered/fused material from Group I or in situ material from Group II can be used. Materials from Group III, essentially spinel from a reaction of alumina with the surrounding magnesia matrix, nowadays are less common, also as both the spinel with its fine crystalline structure and the unreacted alumina relics show a low corrosion resistance to calcium-containing materials.
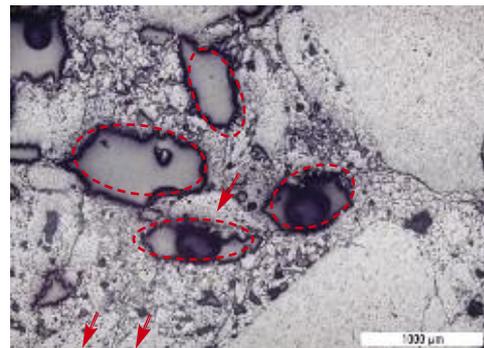
Fig. 14 Corrosion of in situ spinel grains leaving corrosion holes as big pores in the structure (~3–5 mm from the hot face side, ellipses). Simultaneously present presynthesized sintered spinel in the structure remains rather unaffected (arrows) (copyright: Refratechnik Cement GmbH)

An example shows the different reactivity of presynthesized and in situ spinel: Fig. 14 shows a brick which combined presynthesized and in situ elastification. Both elastification types are located right beneath each

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other. Due to corrosion by overheated cement clinker, the in situ spinel completely disappeared leaving only pores in the structure, whereas the presynthesized spinel remains rather unaffected in the structure.

For a proper selection of brick grades with the spinel minerals from Group I, II or III, beneath the selection of the resistor magnesia, the conditions in the kiln regarding the kiln itself, the raw materials and the fuel have to be known and analysed to install a brick lining with the highest efficiency and best performance.

5 Conclusion

In the past, the development of basic bricks was given a lot of attention by refractory manufacturers. New brick grades with specific properties for the various requirements in cement kilns, kiln zones and miscellaneous kiln conditions have been developed. The concept is mostly based on the combination of magnesia with at least one mineral from the spinel group. Spinel minerals can be introduced into the brick as presynthesized material, so that no interaction with the magnesia brick matrix takes place, as material with a limited interaction, and as material with a complete conversion reaction with the brick matrix. The amount needed for elastification is highest for the first group and lowest for the latter one. Regarding brick choice for cement kiln installation, not only the elastifying effect, reduction of Young's modulus, but also the thermo-chemical resistance to cement clinker attack has to be considered.

It goes without saying that research on basic bricks will not cease, but new products with new properties of the elastifier (not limited to minerals from the spinel group), designed to improve the ambitious process of cement manufacturing, for the benefit of the cement producer are in progress.

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