INFLUENCE OF FLEXIBILISERS ON BASIC CEMENT ROTARY KILN BRICK PROPERTIES

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ABSTRACT

Basic refractories for cement rotary kiln applications contain in addition to magnesia (MgO) a flexibiliser to optimize thermomechanical behaviour. In order to allow a direct comparison of cement rotary kiln bricks based on different flexibilisers, lab trial bricks with hercynite, MA-spinel and pleonaste have been produced in laboratory scale and investigated regarding their most important properties considering linear elastic, crack propagation, thermomechanical, and corrosion behaviour. According to the test results hercynite is the most efficient flexibiliser leading to superior performance in application in cement rotary kilns.

REQUIREMENTS ON BASIC REFRACTORY MATERIAL IN OPERATION OF CEMENT ROTARY KILNS

For the lining of cement rotary kilns the base refractory material is selected considering temperature profile and chemical load, with respect to the chemical characteristic of the kiln feed. Fig. 1 provides an overview of available refractory oxides. Due to the high refractoriness with a melting point of ~2800 °C and the low chemical reaction potential with the highly basic cement clinker, magnesia (MgO) is the most appropriate base raw material for areas of high thermal load in cement rotary kilns.

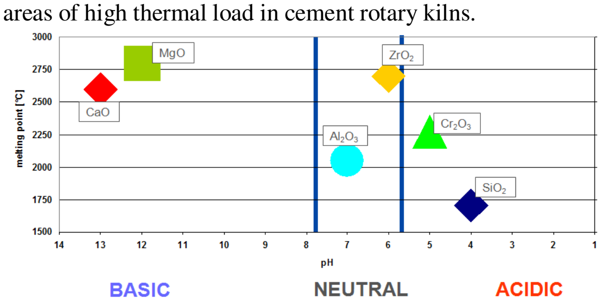

Fig. 1: Overview: Refractory oxides – melting temperature and chemical characterization.

However MgO is also characterized by physical properties such as high thermal expansion which leads to a low thermal shock resistance and brittle behavior. Under the unique operating conditions of a rotating kiln, the thermo-mechanical properties, especially high flexibility, are essential for the performance of refractories. In refractory product development the term flexibility is used to evaluate the ability of a material to prevent spontaneous cracking under mechanical stresses. Different additives are in use to increase the brick flexibility and reduce brittleness in cement rotary kiln bricks [1].

ADDITIVES INFLUENCING THE FLEXIBILITY OF CEMENT ROTARY KILN BRICKS

While magnesia seems to be an ideal material in the operation of cement rotary kilns from a refractoriness and chemical point of view, there is a requirement for additives to increase the flexibility. Historically chrome ore was the first additive that was used to increase the flexibility of cement rotary kiln bricks.

When chrome became environmentally questionable it was replaced by synthetic magnesium-aluminate-spinel (MA-spinel, $MgO.Al_2O_3$). Chrome free magnesia-spinel-bricks still are an environmental friendly solution for the lining of cement rotary kilns.

In the last years alternative fused, synthetic spinels were developed for the application in refractory products for the cement industry. The most important are hercynite, a Fe-Al-spinel, galaxite, a Mn-Al-spinel and most recently pleonaste, a Mg-Fe-Al-spinel.

The main effect resulting in flexibilisation, known as "thermal misfit", is quite similar for all types of spinels. The principle of thermal misfit is based on a lower thermal expansion of the flexibiliser compared to the surrounding magnesia (MgO) fines-matrix, which is shown in Fig. 2. During cooling of the brick firing, the matrix shrinks more than the flexibiliser grains. This leads to the formation of stress centers and microcracks in the surrounding the flexibiliser grains [2]. These stress centers and microcracks do not harm the brick structure, but ensure flexibility [1]. In addition to the thermal misfit (the difference in thermal expansion between flexibiliser and magnesia) the grain size of the flexibiliser also has an influence on the intensity of the stress centers.

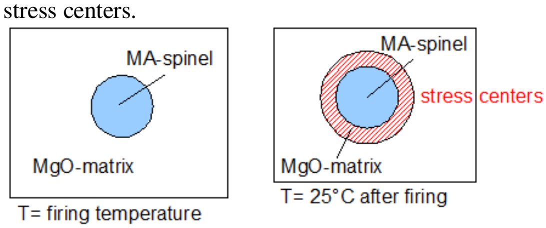

Fig. 2: Flexibilisation effect of thermal misfit.

The use of a high iron containing flexibiliser such as hercynite or pleonaste has an additional effect, namely a diffusion process, shown in Fig. 3, superimposes the thermal misfit. The high iron content of the flexibiliser compared to the magnesia fines matrix and the high mobility of iron at firing temperatures results in a densified diffusion zone. This zone strengthens the stress center region, leading to an additional increase of flexibility. With increasing difference in Fe content between flexibiliser grains and the MgO matrix this effect intensifies.

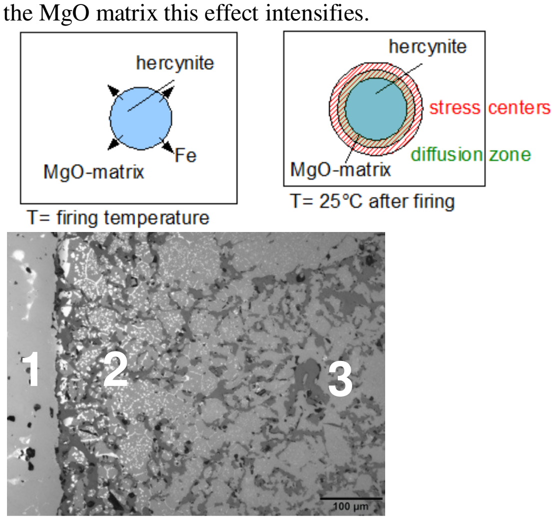

Fig. 3: Flexibilisation effect of thermal misfit superimposed by a diffusion zone of iron oxides. The micro image shows a detail of a hercynite grain (1) with a Fe oxide rich diffusion zone (2) and the surrounding magnesia matrix (3).

EVALUATION OF BRICK FLEXIBILITY

To evaluate the influence of different flexibilising additives on the flexibility of basic cement rotary kiln bricks, two different stages of the brick deformation process have to be distinguished: A linear elastic behavior and a crack propagation behavior.

Linear elastic behavior

The first stage of strain on a material is the so called linear elastic stage. In this stage stresses of a mechanical or thermo-mechanical origin occur within the brick, but no crack formation is observed. All deformations and stresses are within the linear elastic material behavior and totally reversible. In this stage the Young's modulus is the relevant material property. A typical material behavior is shown in Fig. 4. While a material with a high Young's modulus (e.g., a pure magnesia brick) shows a high stress level with a certain deformation, the stress level is reduced significantly with addition of a flexibilising additive.

The most simple test method is the indirect measurement of the Young's modulus with the ultrasonic method. This value is called dynamic Young's modulus and calculated as

$$E = \rho \cdot v^2 [GPa]$$

where ρ = density [kg/m^3] and v = ultrasonic speed [m/s]. The main advantage of the dynamic test method is the ability to obtain temperature dependent Young's modulus behavior in a short time period with a single measurement cycle. This is of importance because the Young's modulus is dependent on temperature

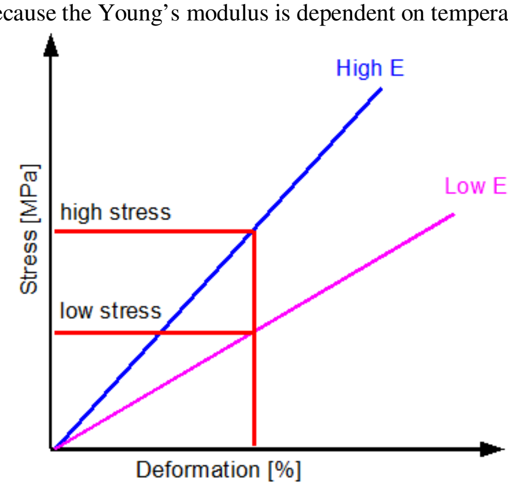

Fig 4: Comparison of materials with different Young's moduli.

Fig. 5 shows the typical behavior of a magnesia brick without flexibiliser (green line) and a magnesia brick containing a flexibiliser (red line). While a pure magnesia brick shows an almost constant Young's moduli progression at a high level, with the inclusion of a flexibiliser, the Young's modulus starts at a low level, increases slightly during heating and shows strong increase in the first stage of cooling to ~1000 °C. The flexibilisation effect occurs during cooling at temperatures below 1000 °C, lowering the Young's modulus significantly. The Young's modulus level provides an indication of the ability of an additive to flexibilise a magnesia brick.

Crack propagation behavior

If the maximum stresses in the lining exceed the material strength, the state of linear elastic material behavior is exceeded and cracks will form. After initiation the crack propagates through the sample until destruction. The crack propagation behavior of refractory material can be measured using the wedge splitting test. Based on results of the Young's modulus determination a test temperature of 1100 C was chosen because at this temperature level the lowest material flexibility is expected. In the wedge splitting test the specimen is split with aid of a ceramic alumina wedge. The specific crack initiation energy G_C and the specific fracture energy G_F are measured [3]. The specific crack initiation energy (in J/m^2) can be explained as stored elastic energy until the crack is initiated while the specific fracture energy (in J/m^2) is the total energy required for the destruction of the sample.

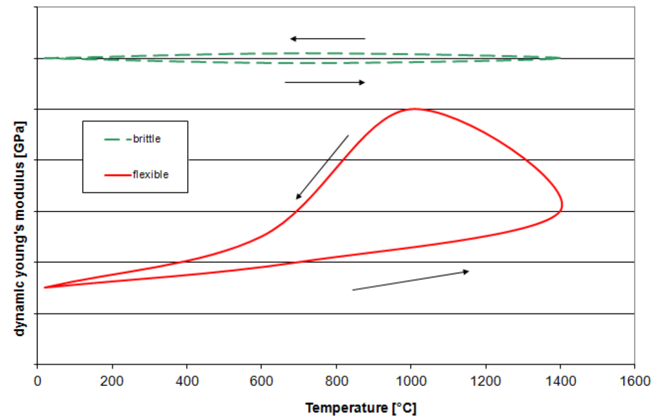

Fig. 5: Typical Young's modulus progression of a pure magnesia brick (green) and a magnesia brick containing a flexibilising additive (red).

A high value of G_F indicates a greater requirement of energy for destruction of the material while high absolute values of G_C indicate that at the moment of crack initiation a high level of elastic energy is stored, resulting in the spontaneous destruction of the specimen. In product development it can be assumed that materials show the highest flexibility if they have a high specific fracture energy G_F combined with a high G_F/G_C ratio (slow crack propagation). Fig. 6 shows a comparison of a brittle material (blue curve) with a flexible (ductile) material (magenta curve). While a brittle material shows a crack initiation at a high level resulting in the release of the stored high elastic energy G_C at crack initiation, followed by rapid crack propagation, in a flexible material, crack initiation occurs at a low stress level (low G_C) followed by a slow crack propagation and a high specific fracture energy G_F.

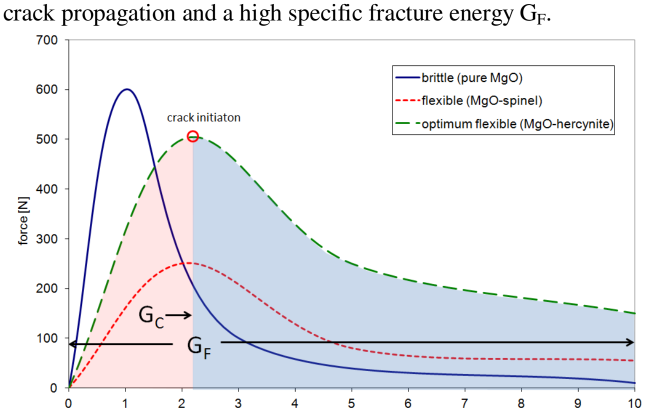

Fig. 6: Wedge splitting test curve for a brittle and a flexible material.

EVALUATION OF THE FLEXIBILISING EFFECT OF DIFFERENT ADDITIVES

To evaluate the flexibilising effect of different additives, bricks with addition of 5% of MA-spinel, hercynite and pleonaste have been produced in laboratory scale. In order to ensure comparability the bricks are based on the same type of magnesia and flexibiliser grain size distribution and have been produced under the same firing conditions. The bricks were investigated with regards to the physical properties. Furthermore alternatives with 15% MA-spinel and pleonaste were produced. The dynamic Young's modulus and the wedge splitting test behavior were investigated to evaluate the flexibilisation behavior relative to additive type and amount.

Linear elastic behavior

In the production of basic cement rotary kiln bricks, flexibilisation occurs during cooling from highest firing temperature through thermal misfit. This procedure can be determined by dynamic Young's modulus. Fig. 7 shows that with an addition of 5% hercynite, a Young's modulus level of 26 GPa can be achieved, while an addition of 5% MA-spinel or pleonaste results a Young's modulus of 51 and 37 GPa, respectively

To obtain the required flexibilisation effect with MA-spinel and pleonaste the amount had to be increased to 15%. With this addition, the Young's modulus could be decreased to 25 GPa which is a similar to the level that can be reached with 5% hercynite.

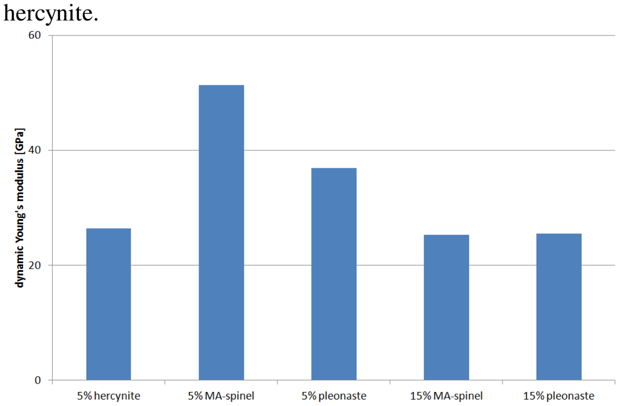

Fig. 7: Linear elastic flexibilisation effect: influence of different flexibilisers and their content on the dynamic Young's modulus.

Crack propagation behavior

To evaluate the crack propagation behavior wedge splitting tests at 1100 °C were carried out, test curves and data are shown in Fig. 8 and Fig. 9.

A comparison of the 5% alternatives show that regarding the consumed specific fracture energy G_F, hercynite shows the highest level, followed by pleonaste and MA spinel. With an increase of the flexibiliser amount to 15%, the G_F of the MA-spinel and pleonaste alternatives can be increased, however for pleonaste G_F is still lower than for 5% hercynite. Nevertheless, even with 15% of MA-spinel and pleonaste the wedge splitting test curve shows a faster decrease than that of 5% hercynite leading to a lower G_F/G_C ratio. This means faster crack propagation through the brick and consequently a lower flexibility.

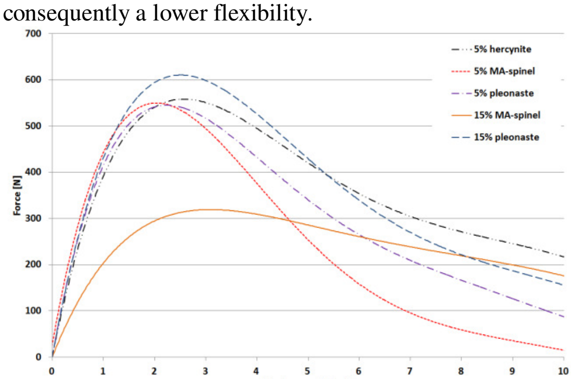

Fig. 8: Wedge splitting test curves (fit data) of the test alternatives at 1100 °C.

The crack propagation behavior of a brick containing 5% hercynite is superior due to the most appropriate combination of specific fracture energy G_F and G_F/G_C ratio. When the flexibiliser is increased to 15%, bricks containing pleonaste have a comparable specific fracture energy G_F but a lower ratio G_F/G_C, while MA spinel contain bricks typically have a lower G_F value, but high G_F/G_C ratio.

An overall evaluation of the thermo-mechanical behavior is shown in Fig. 10. A summary of the discussed properties indicates that magnesia-hercynite bricks show a superior behavior, followed by magnesia-pleonaste and magnesia-spinel bricks.

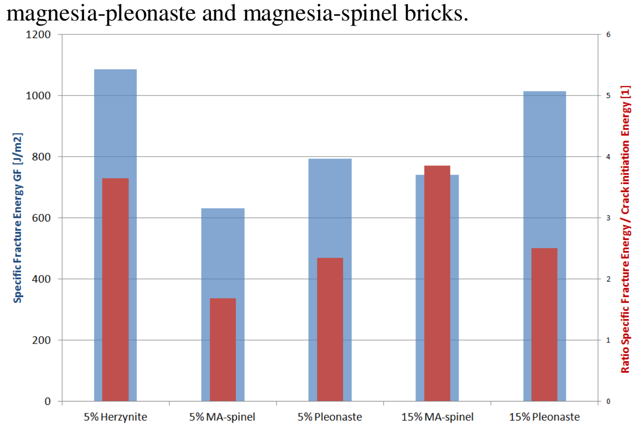

Fig. 9: Crack propagation - flexibilisation effect: influence of different flexibilisers and their content on wedge splitting test values.

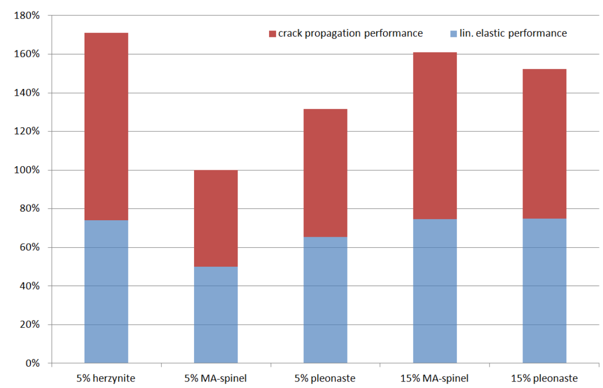

Fig. 10: Thermo-mechanical behavior of bricks containing different flexibilisers and their content, reference is a brick containing 5% MA-spinel.

CHEMOTHERMAL LOAD

An evaluation of post mortem investigations has shown that the most common wear factor for basic bricks in cement rotary kilns is the infiltration by alkali salts. In around 58% of all post mortem investigations alkali salt infiltration was identified as the dominant wear factor, followed by clinker melt infiltration with 20%. A study of the chemical environment shows that in the basic section of cement rotary kilns predominantly acidic or neutral compounds (49% of 280 post mortem investigations from all over the world) are present, while alkali surplus is only of minor importance.

From a theoretical point of view a chemical reaction of the flexibiliser grains (MA-spinel, hercynite, and pleonaste) with infiltrating alkalis is possible only in case of a particular strong alkali surplus in the kiln, but very rarely observed in real cement kiln operations. This reaction has been observed to a significant extent in laboratory scale crucible tests, independent of the type of flexibiliser used.

Consequently the main influence to reduce corrosion reactions is provided by the type of sintered magnesia and the strength of ceramisation. In practice the flexibiliser has only a very limited influence on the corrosion behavior in case of alkali salt attack.

Clinker melt infiltration

For the production of cement clinker a certain amount of liquid phase is needed in the production process. The average amount of liquid phase is ~25% and consists mainly of Ca aluminates and Ca ferrties. If the process temperature exceeds the standard level "overheating" or in case of an unfavorable composition of the raw meal, the amount of liquid phase increases and the clinker melt easily penetrates deep into the brick.

The corrosive attack of the supplied clinker melt initially affects the flexibiliser grains, independent of their type, by dissolution of the alumina and iron components. As a result the total amount of soluble components is of major importance regarding the severity of the effects of clinker melt attack. Consequently it is advantageous to minimize the amount of flexibiliser. Tab. 1 provides an overview of the amount of oxides from the flexibilising additives that can form liquid phases. Therefore hercynite is superior to other flexibilisers due to the lower required amount and therefore the lower total amount of oxides contributing to liquid melt formation.

Tab. 1: Overview: major oxides in flexibilisers that contribute to liquid phases depending on the flexibiliser amount.

	hercynite	**pleonaste**	**MA-spinel**
Al_2O_3	49,5%	51,0%	66,5%
Fe_2O_3	47,0%	23,0%	0,2%
MgO	1,9%	24,0%	33,0%
CaO	0,2%	0,5%	0,2%
SiO_2	0,1%	0,2%	0,1%
Amount Flexibiliser	**5,0%**	**15,0%**	**15,0%**
Al_2O_3 sum.	2,5%	7,7%	10,0%
Fe_2O_3 sum.	2,4%	3,5%	0,0%
Oxides melt sum.	**4,8%**	**11,1%**	**10,0%**

THERMAL LOAD

In order to obtain information about the influence of different flexibilising additives on the thermal performance of the bricks, hot modulus of rupture (HMOR) tests according to DIN EN993-7 were performed. HMOR test values at 1400 °C are shown in Tab. 2. With a standard addition of 5% flexibiliser, bricks containing common MA-spinel show the highest HMOR at 1400 °C. The HMOR of bricks with iron containing spinels, hercynite, and pleonaste are on a lower, albeit similar level. As it is necessary to increase the amount of MA spinel and pleonaste in order to achieve the required flexibilising properties, a decrease in HMOR was observed.

Tab. 2: Hot properties – refractoriness under load acc. to DIN EN ISO 1893, HMOR acc. T_0. DIN EN 993-7.

	5% hercynite	5% MA-spinel	5% pleonaste	15% MA-spinel	15% pleonaste
RUL T_0 [°C]	1635	1685	1637	1538	1586
RUL $T_{0.5}$ [°C]	>1700	>1700	>1700	>1700	>1700
HMOR $_{1400}$ [MPa]	3.1	4.3	3.2	2.7	2.4

In addition to the hot modulus of rupture, the refractoriness under load according to DIN EN ISO 1893 was evaluated. Comparing the refractoriness T_0 and $T_{0.5}$ values for bricks with 5% flexibiliser, MA-spinel shows the highest values. Considering that a higher amount of flexibiliser is required for MA spinel and pleonaste to achieve similar flexibility levels as with hercynite, a drop in refractoriness was also observed. This is reflected in the refractoriness values for bricks with 15% MA-spinel or pleonaste.

CONCLUSION

Flexibilisation of the basic brick structure is the main purpose for adding different types of spinels, wherefore particular attention has been paid to thermo-mechanical properties. Additionally other influencing parameters taking place during operation in cement rotary kilns such as chemical attack by alkali salts and clinker melt as well as thermal stresses have been considered.

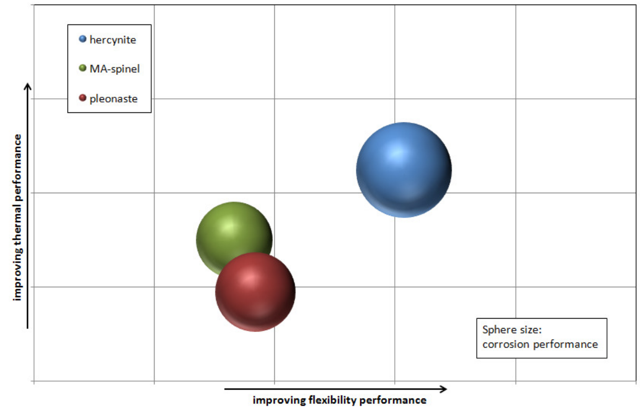

Fig. 11: Qualitative overall performance of different flexibilisers based on their performance level, x-axis: flexibility performance, y-axis: thermal performance, sphere size: corrosion resistance performance.

The general performance level of different types of basic cement rotary kiln bricks is shown in Fig. 11. The test series has shown that hercynite is the most efficient flexibiliser to increase brick flexibility, while if pleonaste or MA-spinel is used a high percentage of flexibiliser is required to achieve comparable brick flexibility. Based on numerous post mortem investigations the chemical resistance in cases of alkali salt and clinker melt attack should be considered equal. The disadvantages of corrosion effects observed in all types of flexibilisers can be reduced in case of hercynite due to the lower percentage needed to achieve required flexibility level. This lower amount has also an additional positive influence on refractoriness.

The performed investigations identified hercynite as the most suitable flexibilising additive. This is also confirmed through experiences over the past 20 years.

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