MAGNESIA-PLEONASTE BRICKS FOR ESSENTIAL REQUIREMENTS IN ROTARY KILNS

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ABSTRACT

The essential effect of iron ions in providing oxygen to the human body by valency change in hemoglobin is well known. In a similar way, iron oxide is recognized as essential compound in cement and lime kiln refractories for providing a satisfactory lifetime under varying kiln conditions. Investigations have shown that a defined amount of FeO_x in basic bricks is rather advantageous, e. g. for thermoplastic stress relaxation or coating formation, without affecting the necessary requirements regarding refractoriness, redox resistance, thermal shock resistance, etc. A measure for the thermoplastic behaviour is the deformation in the creep under compression test where the positive influence of iron oxide is shown. Early investigations describe the effect of chrome ore and hercynite, nowadays the Fe(II) and Fe(III) species containing pleonastic spinel show the most advantageous properties. This is due to the fact that the iron ions are stable bound in the microstructure. This is shown by the redox test, where strength and volume change after alternation of reducing and oxidizing atmosphere is determined. Although a dependency is obvious, a high cold crushing strength and modulus of rupture as well as the simultaneous presence of both iron oxide species is advantageous concerning thermoplastic stress relaxation and all other relevant properties. The graded presence of iron species in a series of pleonaste-containing refractories allows the selection of adequate refractory material regarding the requirement to cope with the influence of higher temperatures. It has to be concluded that a balanced presence of both iron oxide species is quite beneficial for the performance of rotary kiln bricks, in several cases they outperform refractories based on very pure raw materials, especially in kilns with a high mechanical load on the lining.

INTRODUCTION

Iron in its bivalent or trivalent form is essential for intelligent live on earth, as it is the only element enabling the transport of oxygen from the lungs to the cells in the body. Background is the structure of the heme b group in the blood with an iron ion in the middle, Fig. 1.

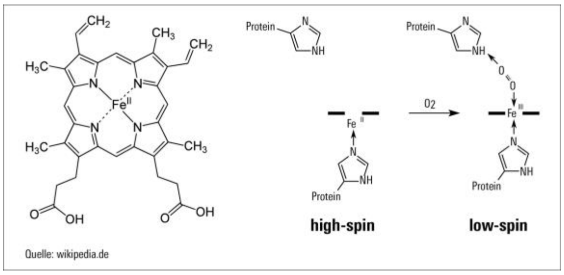

Fig. 1: Heme B group and mechanism of oxygen-bonding on hemoglobin
from: https://de.wikipedia.org/wiki/H%C3%A4moglobin

To tell in a very simplified manner, the transport of oxygen is assured by a pick-up of oxygen by the bivalent iron, so that it is oxidized into the trivalent state. At the user, e. g. a muscle, the oxygen is released, and the iron returns to its bivalent form, and the heme B is transported back to the lung in the blood circuit.

This necessity of iron for life on earth can also be transferred to industrially used refractories for better performance. Although iron and its ions are usually considered malevolent in this field of technology, contrarily the negative image of iron has to be revised not only in general, but especially for basic cement kiln refractories. A defined amount of iron in the brick will improve various properties, such as stress compensation, coating adhesion, and refractoriness. Also the valency change of iron in refractories, referring to redox resistance (= resistance to varying oxidizing and reducing atmospheres) should be considered.

STRUCTURE OF BASIC BRICKS FOR THE CEMENT INDUSTRY

In basic refractories for the cement industry, iron oxide is also found in its various forms. Bivalent iron is found e. g. in hercynite $FeAl_2O_4$ and in ferrochromite $FeCr_2O_4$, as well as in magnesia wustite (Mg,Fe)O. Trivalent iron is found e. g. in magnesioferrite $MgFe_2O_4$. Bi- and trivalent iron is found e. g. in magnetite $FeFe_2O_4$, chrome ore $(Mg,Fe)(Cr,Al,Fe)_2O_4$ and in pleonastic spinel $(Mg,Fe)(Al,Fe)_2O_4$.

Magnesioferrite can be reduced and will form magnesia wustite, on oxidation this reaction is reversed. This phase transformation is accompanied by a volume change of 6.7% due to an expansion resp. contraction of the crystal lattice, (2). In the end accelerated wear can be observed if the conditions seem to be too harsh, although it has to be considered that cement should be produced in an oxidizing atmosphere.

For the adjustment of optimized properties of basic cement kiln bricks the presence of oxidic iron ions can be thoroughly considered essential, while on the other hand a change in valency is rather undesirable (contrarily to the action in living bodies).

For cement kiln refractories, the iron oxide content in the resistor (low-iron magnesia with $Fe_2O_3 < 0.9$ %, iron-rich magnesia with Fe_2O_3 1-9 %), (2), and in the elastifier (usually a mineral from the spinel group, like low-iron MA-spinel with $Fe_2O_3 < 2\%$, or iron-rich pleonastic spinel or hercynite with $Fe_2O_3 > 25\%$) has to be considered, Fig. 2.

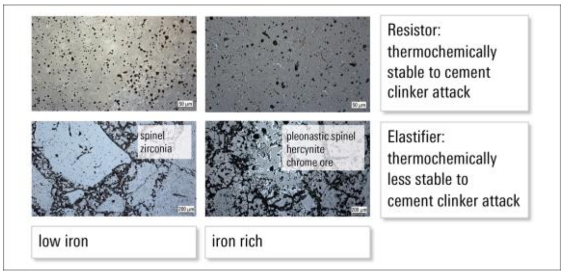

Fig. 2: Design of low-iron and iron-rich basic bricks with resistor magnesia and elastifier (usually a spinel mineral or zirconia containing mineral)

These mineral groups can be combined to produce elastic basic bricks being suitable for the installation in a rotary kiln, although it was found out that iron-rich magnesia and low-iron MA spinel in combination are not refractory enough for cement producing purposes. The diffusion potential of iron ions within the brick's microstructure can be significantly lowered if both structural elements contain this compound, such as in magnesia-pleonaste bricks and magnesia-hercynite bricks, allowing the use of iron-rich magnesia as resistor.

Furthermore, it has to be considered that cement should be produced in an oxidizing atmosphere to guarantee the correct formation of the desired clinker minerals, but the increasing use of alternative and secondary fuels and raw materials has led temporarily to at least reducing or reducing/oxidizing (redox) conditions in some sections of the rotary kiln.

IRON-INDUCED PROPERTIES OF CEMENT KILN REFRACTORY BRICKS

THERMAL EXPANSION

Iron oxide is essential for cement kiln refractories due to its influence on refractoriness and ability to cope with mechanical tensions induced by thermal expansion of the refractory lining and the permanent rotation of the kiln.

Thermal expansion in a brickwork always results in mechanical stresses according to Hooke's law $\sigma=\alpha\cdot\Delta\vartheta\cdot E$, which shows the influence of the thermal expansion coefficient α, the temperature difference $\Delta\vartheta$ and Young's modulus E.

For refractory linings, α can in a first approach be described by the maximum expansion measured in the refractoriness under load (RUL) test according to DIN EN ISO 1893:2008-09 [3]. As a comparison in Fig. 3, the typical curve of a low-iron non-elastified magnesia brick is shown as well as magnesia-pleonaste bricks with iron-rich and with low-iron magnesia.

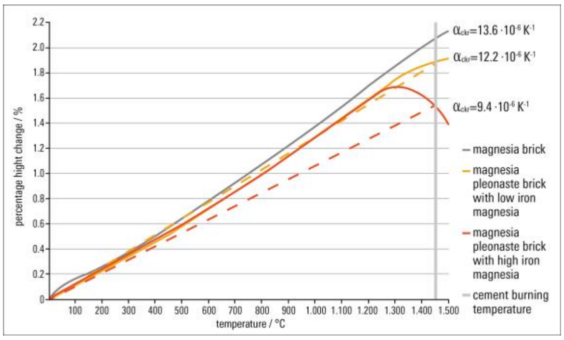

Fig. 3: RUL curves for magnesia and magnesia-pleonaste bricks

Although the thermal expansion up to 1300 °C of both pleonaste brick types is similar and favourably significantly lower than the expansion of the pure magnesia brick, at high temperatures (1450 °C as the cement burning temperature) the maximum expansion due to the softening of iron-rich magnesia is lower, which gives according to Hooke's law a lower stress at the hot face of the lining; the risk of spalling due to mechanical action is reduced. The "calculative" thermal expansion coefficient for cement kiln refractories α_{ckr} 20 °C/1450 °C is reduced from 16.6 $10^{-6}\,K^{-1}$ for a pure magnesia brick down to 12.2 $10^{-6}\,K^{-1}$ resp. 9.4 $10^{-6}\,K^{-1}$ for magnesia-pleonaste bricks due to the iron content in the magnesia, usually present as magnesioferrite precipitations in the periclase crystals resp. in the elastifier. A similar behaviour is observed in magnesia-hercynite bricks.

STRESS RELAXATION

Another parameter for non-destructive thermomechanical stress relaxation is creep, simulated in the laboratory by means of the creep in compression (CIC) method shown in Fig. 4 [4], [5].

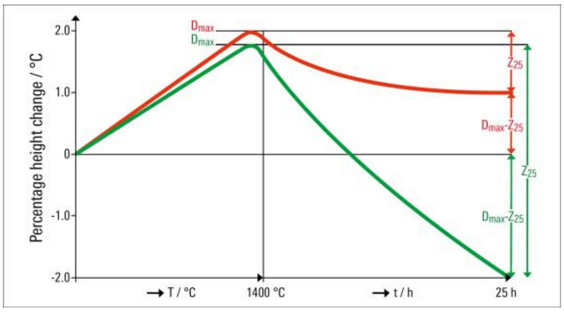

Fig. 4: CIC for various stress relaxation matters

With this method the deformation under constant pressure and constant temperature during a defined period can be measured, usually 25 hours. It is the art of the refractory manufacturer to adjust this to a balanced behaviour, as a low CIC does not reduce mechanical stresses due to missing non-destructive deformation, and a too high CIC value with simultaneously low refractoriness under load does not provide adequate resistance to higher thermal loads. In general, a $T_{0.5}\geq1450$ °C from the RUL test is required for the use of basic bricks in cement rotary kilns.

Fig. 4 shows typical curves of bricks with low and with increased CIC. Characteristic values for thermomechanical stress relaxation are D_{max} as maximum brick expansion – responsible for the level of generated stress – and D_{max}-$Z_{(25h)}$ as a measure for thermo-mechanical stress relaxation.

The calculated value of D_{max}-Z_{25} shows the ability of a refractory material to compensate mechanical stresses by non-destructive plastic deformation. The lower the value, the better is the stress relaxation behaviour. A comparison of the before mentioned brick grades clearly shows the influence of iron oxide, as the brick containing iron-rich magnesia can compensate better the thermomechanical stresses than the ones based on low-iron magnesia, Fig. 5.

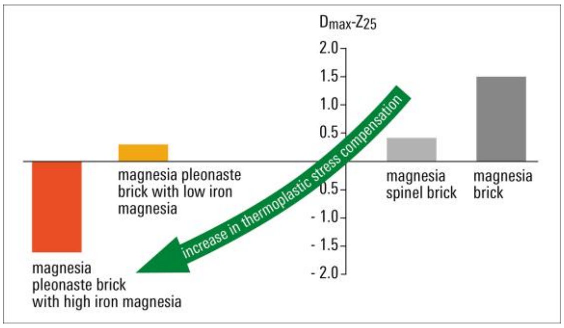

Fig. 5: Creep in compression of basic refractory bricks with different stress relaxation behaviour

Also it becomes clear that the iron content in the elastifier contributes to the stress relaxation behaviour as well, as the value for a magnesia-pleonaste brick is significantly lower than the one for a pure magnesia brick, similar to the well-established magnesia-spinel bricks. Simultaneously the refractoriness is kept at a high level to ensure a safe and smooth cement kiln operation. This is not only shown from a theoretical point of view, [6], but also by cement kiln installations, [7].

REDOX RESISTANCE

The redox resistance, i. e. the resistance to changing reducing and oxidizing conditions, is undoubtedly connected to the content of Fe_2O_3 (and of Mn_2O_3 to a lesser extent), (1). To simulate a redox load in a kiln, this can be experimentally realized by applying reducing conditions (embedding a burnt brick into a bed of graphite) and alternating with oxidizing conditions (by firing the brick in air), both at 1100 °C. As characteristic values, the shear modulus G and the change in volume are stated; as comparison, values of a low-iron magnesia-spinel brick are stated as well, Figs. 6, 7.

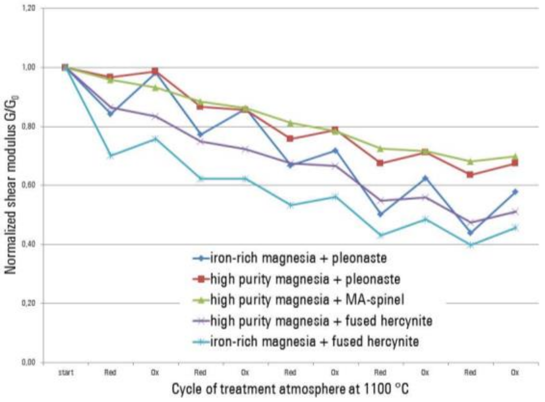

Fig. 6: Development of shear modulus G for various brick grades during redox test

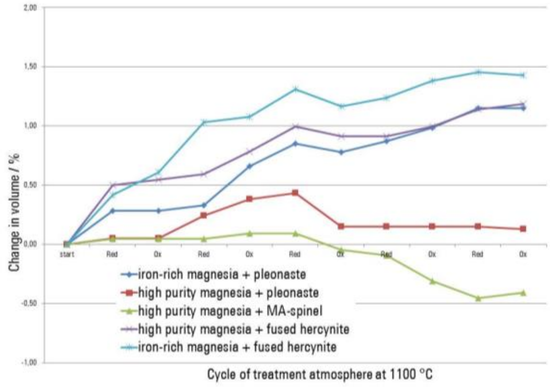

Fig. 7: Development of volume change for various brick grades during redox test

Unsurprisingly, the magnesia-spinel brick based on low-iron magnesia shows the least influence of redox cycles on the shear modulus. Magnesia-pleonaste bricks, based on low-iron magnesia as well, are also very stable in their redox resistance, which shows that the iron in the pleonastic spinel $(Mg,Fe)(Al,Fe)_2O_4$ is well-bonded and that only a small amount is diffusing into the surrounding magnesia matrix. Magnesia-pleonaste bricks and magnesia-hercynite bricks based on iron-rich magnesia are more affected by the redox cycles. That means that the iron in the magnesia is more susceptible to redox conditions. The bonding of the iron in the pleonaste seems to be more stable than the bonding in the hercynite, which may be attributed to the presence of MgO in the pleonastic spinel itself, and the absolute lower amount of iron in hercynite (ca. 42%) compared to ca. 25% in pleonastic spinel.

COATING ABILITY

Known from experience, bricks containing iron oxide in the elastifier and in the magnesia matrix exhibit a better coatability than low-iron natural or synthetic sintered magnesia (Fig. 8).

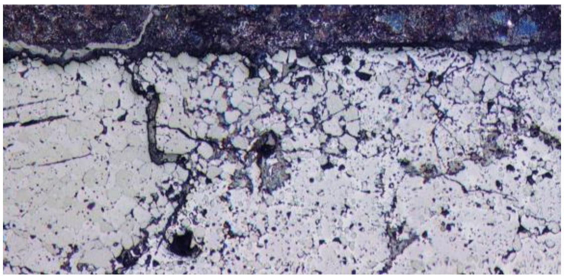

Fig. 8: Coating adhering on an iron-rich magnesia-pleonaste brick

Due to the presence of pleonastic spinel, magnesioferrite, and also belite, the coating behaviour of magnesia-pleonaste bricks based on ferrous sintered magnesia is significantly enhanced. The presence of highly viscous calcium ferrite and calcium aluminate compounds due to reactions between kiln feed and brick constituents, promotes the formation of a cement clinker coating on the refractory lining [8].

CONCLUSIONS

The results show the positive effect iron oxide on the properties of basic bricks for rotary kilns. The iron oxide reduces the stress sensibility of the lining, which is exposed to mechanical stresses by kiln rotation and thermal expansion. Due to the presence of bi- and trivalent iron oxide in the magnesia and the elastifier, the stress compensation ability of basic bricks is increased significantly. Despite of the presence of iron oxide up to 10%, the refractoriness for cement kiln applications is easily maintained, while the reliability for thermomechanical loads is significantly increased. Products containing low and elevated amounts of iron oxide are available, so that all demands for a cement kiln can be met. Even in case of redox loads, which should theoretically not be present in cement kilns, iron-containing magnesia-pleonaste bricks can perform satisfactorily, while for extreme conditions still the use of low-iron magnesia-spinel bricks is state of the art.

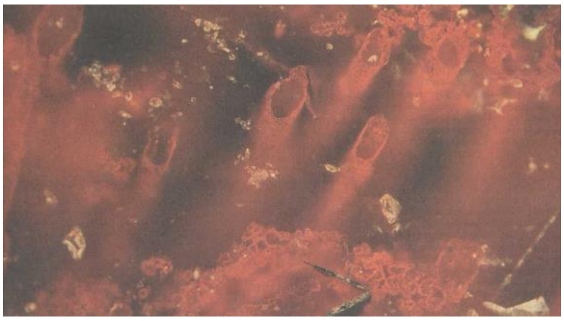

Fig. 9: Hematite tubules as possible relics of former bacteria [9]

It is evident that iron and its oxides plays a major role in today’s refractory technology when applied in latest sophisticated brick and lining concepts, just as it does in animate being (allowing oxygen transport and storage for life), and maybe even did in development of live [10].

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