

# INFLUENCE OF PHOSPHATE ON HOT PROPERTIES OF BASIC REFRACTORY BRICKS

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## ABSTRACT

The refractoriness of a basic brick is primarily defined by its interstitial phases. What matters in this respect is not only the absolute quantity of interstitial phases, but also particularly which type of phases they form. The most common by-elements in magnesia and magnesia products respectively are Ca, Si, Fe, as well as Al, and Cr. Depending on the bulk chemical composition these elements form different types of interstitial phases. In general the temperature of formation of melting phases decreases with an increasing number of elements. The effect of the different interstitial phases on the refractoriness of magnesia products is sufficiently described in literature. The target of the study described in the present paper was the improvement of the properties of magnesia products rich in iron oxide and alumina, especially at elevated temperature. In the course of a laboratory trial iron-rich magnesia bricks were produced and fired at different temperatures. With increasing firing temperature increasing values in refractoriness under load could be detected. The same effect was observed with iron-rich hybrid spinels containing magnesia bricks. On the other hand these bricks showed an increasing firing shrinkage with increasing temperature, which can cause severe problems in the production of refractory bricks. The target of the trials was to counteract this firing shrinkage whilst maintaining the high refractoriness of the bricks by incorporation of certain elements into the interstitial phases of the brick. The addition of phosphate has proven successful for a controlled modification of the interstitial phases in order to be able to produce iron-rich and alumina-rich bricks with improved refractoriness.

## INTRODUCTION

The refractory properties of fired magnesia bricks are strongly influenced by the interstitial phases.

Tab. 1. Phase existence in relation to lime/silica ratio <sup>[1][2]</sup>

	Melting point	C/S molar ratio		
		1.5-2	2	>2
	[°C]			
M	2825	yes	yes	yes
MF	1715 inc.	yes	yes	yes
M <sub>2</sub> S	1890			
CMS	1492 inc.			
C <sub>3</sub> MS <sub>2</sub>	1575 inc.	yes		
C <sub>2</sub> S	2130	yes	yes	yes
C <sub>2</sub> F	1449			yes
C <sub>4</sub> AF	1415			yes

Inc.: incongruent

The CaO/SiO<sub>2</sub> (C/S) molar ratio should be either  $\geq 2.0$  (see Tab. 1) or  $< 1.0$ . Experience shows that in case of a low molar lime to

silica ratio the refractory properties improve by lowering the C/S ratio.

Basic fired bricks with a low lime to silica ratio are mainly used as checker bricks for glass tank regenerators, for lime shaft kilns or as permanent lining in steel ladles. When the C/S molar ratio is between 1 and 2 monticellite and merwinite are formed. The melting point of these single phases is 1498 °C and 1575 °C. In combination as interstitial phases in a basic brick the temperature of occurrence of first liquid phases (invariant point) lies at 1490 °C, and in combination with additional oxides, such as aluminates or ferrite, this melting point is further decreased. Additionally depending on the absolute amount of these phases and with it the total amount of liquid phase the refractory properties of fired bricks with such a mineralogical composition are on a comparably low level.

However, in focus of the investigation in hand are fired bricks with a C/S molar ratio  $\geq 2.0$ . As long as there is no iron oxide or alumina it does not significantly affect the refractory properties if the lime to silica molar ratio is 2 or higher, since there is only dicalcium silicate respectively tricalcium silicate. But the situation changes if there is iron oxide and/or alumina available at C/S  $> 2$ . Then phases like dicalcium ferrite, brownmillerite or calcium aluminates (CA, C<sub>12</sub>A<sub>7</sub>, C<sub>3</sub>A) can occur, depending on the actual chemical composition. These phases influence the refractory and physical properties as well.

## RESULTS AND DISCUSSION

Initially two alternatives based on high in iron sintered magnesia and hercynite were produced at similar firing conditions in a laboratory test (see Tab.2). In order to decrease the C/S molar ratio the silica content was increased in alternative 1. The refractoriness under load test of both alternatives showed a negligible difference in T<sub>0</sub> due to the same phase composition, but a significant difference of almost 70 °C in T<sub>0.5</sub>, which is due to the different amount in which the phases are present.

Tab. 2. Laboratory trial with rich in iron bricks.

	Alt.1	Alt.2
DBM rich in iron	95%	95%
Hercynite	5%	5%
MgO	86.1%	85.9%
Al <sub>2</sub> O <sub>3</sub>	2.9%	3.0%
SiO <sub>2</sub>	1.0%	0.8%
CaO	2.1%	2.3%
Fe <sub>2</sub> O <sub>3</sub>	7.7%	7.8%
C/S [mol ratio]	2.1	2.9
T <sub>0</sub> [°C]	1305	1292
T <sub>0.5</sub> [°C]	1559	1493

Table 3 shows three alternatives which were fired in a lab kiln at a typical firing temperature ( $< 1550$  °C). The C/S molar ratio of all three alternatives is around 3.0. Alternative 3 has 10% hybrid spinels in the recipe, alternative 4 additionally phosphate (0.5-1.0%). Alternative 5 has an even higher content of hybrid

spinel (15%) and additionally the firing temperature was increased by 100 °C.

Tab.3. Laboratory trial with addition of phosphate and hybrid spinels.

	Alt. 3	Alt. 4	Alt. 5
Firing temp. [°C]	Stand.	Stand.	+100°C
DBM rich in iron	90%	90%	85%
Hybrid spinels	10%	10%	15%
Phosphate		<1%	<1%
MgO	82.3%	81.7%	79.2%
Al <sub>2</sub> O <sub>3</sub>	7.2%	7.1%	10.5%
SiO <sub>2</sub>	0.7%	0.7%	0.7%
P <sub>2</sub> O <sub>5</sub>		<1%	<1%
CaO	2.1%	2.1%	2.0%
Fe <sub>2</sub> O <sub>3</sub>	7.6%	7.6%	7.0%
C/S [mol ratio]	3.0	3.0	2.9
T0 [°C]	1289	1396	1440
T0.5 [°C]	1470	1527	1600

The higher alumina content leads to a decrease of the refractoriness of alternative 3 compared to alternative 2 but less than expected. Alternative 4 reveals that this negative influence of the spinels is counteracted by the addition of phosphate. T0 was approximately 100 °C higher compared to alternative 2. T0.5 showed a comparably smaller increase of 34 °C. The bricks with phosphate showed a much lower firing shrinkage, which suggests the firing temperature was too low. Therefore alternative 5 was produced with an increased firing temperature (plus 100 °C).

Alternative 5 contains 15% hybrid spinels as well as phosphate. The C/S molar ratio was again in the area of 3. The higher amount of hybrid spinels resulted in alumina content of approximately 10%. Nevertheless the refractoriness under load values showed a tremendous increase. A comparison of alternative 3 and 5 shows that T0 increased by 151 °C and T0.5 by 130 °C. Even alternative 1 with an adaption of the C/S molar ratio showed much lower RuL values compared to alternative 5. It must be pointed out that the alumina content of alternative 5 is approximately 3.5 times higher compared to alternative 1 and 2. It should be mentioned that the higher firing temperature without the addition of phosphate was not viable due to a very high firing shrinkage.

#### Bricks without spinels

In order to gain more information about the influence of phosphate to the refractoriness under load properties of basic bricks rich in iron oxide further trials without the addition of any spinels were carried out. Two alternatives have been produced, one without any adaption of the C/S ratio, the other one with the addition of phosphate. The bricks consist of iron-rich magnesia (typically 6-8% Fe<sub>2</sub>O<sub>3</sub>, 2.3% CaO and 0.8% SiO<sub>2</sub>), alternative 7 has additionally 0.5-1% phosphate.

The two alternatives were fired at 1450 °C, 1560 °C and 1630 °C. It can be seen that the addition of phosphate has a significant impact on the RuL properties (see Tab.4) and on the hot modulus of rupture at 1400 °C as well. T0 of the phosphate free alternative shows only a low increase at the higher firing temperatures. However, alternative 7 shows a dramatic increase of T0 from 1381 °C to 1450 °C respectively 1564 °C. T0.5

shows at both temperatures a strong increase at higher firing temperatures. However the alternative with phosphate gives significantly better properties.

Tab.4. RuL values

Alt.6			
Firing temperature [°C]	1450	1560	1630
T0 [°C]	1306	1324	1341
T0,5 [°C]	1454	1482	1673
Alt.7			
Firing temperature [°C]	1450	1560	1630
T0 [°C]	1381	1450	1564
T0.5 [°C]	1560	1615	1700

The investigation of HMOR at 1250 °C and 1400 °C gave very interesting results. At 1250°C alternative 6 gave higher values. This can be explained by the lower refractory properties, because the sintering activity at the same firing temperature is higher compared to the phosphate alternative. But the temperature where the HMOR test took place (1250 °C) is below T0 (1306 – 1341 °C). The picture changes completely at 1400 °C. Here alternative 6 is above the T0 values and shows consequently very low HMOR (max. 1 MPa). On the other hand alternative 7 shows very clear the strong impact of phosphate to the hot properties. HMOR shows extremely high values (up to 11 times higher compared to alternative 6), also increasing with higher firing temperatures.

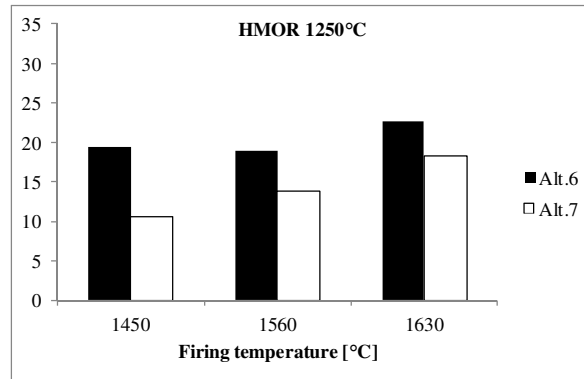


Fig. 1 HMOR 1250 °C

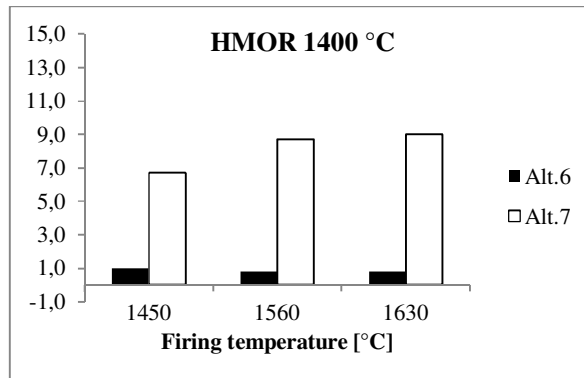


Fig. 2 HMOR 1400 °C

## **SUMMARY**

The investigation shows that the hot properties of basic iron-rich refractory bricks are strongly influenced by the C/S ratio and the addition of phosphate. This modification of the interstitial phases results in higher amounts of alumina phases, higher firing temperature, and tremendous improvement of the refractory properties.

Iron-rich products were until now not viable for some applications due to insufficient hot properties. As shown, the refractory properties of refractory products rich in iron can be significantly upgraded with small and easy to handle measures. So a new range of applications for these products has opened.

## **References**

- [1] E.F. Osborn and Arnulf Muan, "Phase Equilibrium Diagrams of Oxide Systems", Plate 2, American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960
- [2] A.S. Berezhnoi, Voprosy Petrograf. i Mineral., Akad. Nauk S.S.S.R., 2, 295 (1953).