# IMPROVEMENT OF HYDRATION RESISTANCE OF BASIC BRICKS: A COMPARISON OF DIFFERENT METHODS

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## ABSTRACT

Hydration of basic refractory is a classic problem that can occur during different stages of production or during storage of finished products, the last one being the most critical. After their production, the basic bricks can be in storage for several months before being applied in industrial kilns, which increases the potential for contact with water. The hydration reaction occurs with high volumetric expansion, generating cracks and, in more extreme cases, the formation of dust. Thus, many solutions have been extensively tested by the refractory industry to improve the hydration resistance of basic bricks. One of them is to modify the recipe of basic refractories with additives that provide better protection. Others involve treating the bricks surface to improve resistance during storage. Therefore, in this study, three different methods of protection against hydration of basic refractory bricks are analyzed and compared.

### **1. INTRODUCTION**

The basic magnesia bricks tend to hydrate naturally due to the contact with liquid water or water vapor, where magnesia (MgO) and water (H<sub>2</sub>O) reacts to form magnesium hydroxide or brucite (Mg(OH)<sub>2</sub>). The hydration reaction is expansive, as there is a decrease in specific gravity from 3.58 g/cm<sup>3</sup> (MgO) to 2.36 g/cm<sup>3</sup> (Mg(OH)<sub>2</sub>), leading to crack generation which compromises the structure of the brick and, therefore, reduces its shelf life [1-3].

Based on hydration studies, Zhou [3] proposed a mechanism for basic bricks that takes place in three stages. In the first stage, the water goes into the open pores of the bricks and a brucite film is formed on the walls of the pores, followed by the second stage, when cracks are formed in the film. After crack formation, there is the third stage, in which new surfaces become accessible to water reaction, thus hydration accelerates and eventually leads to total disintegration of the refractory.

As can be observed, the hydration process starts in the open pores, which indicates that surface treatments on basic bricks can achieve good results in terms of hydration protection. These treatments usually involve the formation of a protective film, behaving as a physical barrier against the direct contact with water and therefore inhibiting the formation of a brucite layer. In addition to surface treatments, another option is the use of additives that provide resistance to hydration in refractory composition, but changes in properties should be investigated.

Since the treatments to improve the hydration protection of basic bricks have different approaches, the present work aims to analyze and compare three methods applied to magnesia-spinel bricks: one using an additive into the refractory recipe, and the other through two different surface treatments.

#### 2. EXPERIMENTAL METHODS

For the hydration studies, one magnesia-spinel composition was selected to prepare four variations of bricks at the laboratory. One variation was the typical brick with no treatment, named brick A. The other bricks were named brick B, which had the recipe modified by 0.25% of an anti-hydration additive; brick C and brick D were treated with a different surface treatment performed after firing brick A.

After firing (bricks A to D) and surface treatments (bricks C and D), the four variations were characterized in relation to bulk density (BD) and apparent porosity (AP) according to ISO 5017: 2015 standard, cold crushing strength (CCS) according to ISO 10059-Part 2: 2014 standard, permeability according to ASTM C577 standard, abrasion according to ASTM C704/C704M-09 standard, hot modulus of rupture (HMOR) at 1200°C for 3 hours and at 1485°C for 3 hours according to ISO 5013: 2012 standard, modulus of elasticity (MoE) according to ASTM C885 standard, chemical analysis by X-ray fluorescence using the PW2540 Philips spectrometer, and study of mineralogical phases by X-ray diffraction (XRD) using PANalytical equipment, X'Pert PRO model and the analysis was performed in the X'Pert HighSore Plus program using the JCPDS-International Centre for Diffraction Data as database.

The hydration tests were performed using two different methods. The first one was based on ASTM C 456-93 (2008) standard [4], but with some adjustments. In this methodology, three cubes sized 40 x 40 x 40 mm<sup>3</sup> were cut from each brick variation and placed inside autoclave with sufficient water to maintain 102°C for 5 hours, which represents one cycle of hydration. After drying at 110°C for 12 hours, the cubes were visually observed regarding crack formation, and weighed in order to obtain the mass gain. This process was repeated until reaching the complete disintegration of the cubes, limited to 10 cycles.

The other hydration test was performed in a climatic chamber at 70°C and 80% relative humidity, where three cubes sized 40 x 40 x 40 mm<sup>3</sup> of each variation were placed for 31 days. Every three or four days, the visual aspect and the mass gain were monitored. Figure 1 illustrates the equipment used for the hydration studies.



Figure 1: Equipment used for hydration tests: a) autoclave, b) climatic chamber.

## 3. RESULTS AND DISCUSSION

The properties of bricks A, B, C and D are reported in Table 1. Brick A has typical properties of a high-quality magnesia-spinel brick applied in cement rotary kilns: high density and mechanical strength, in addition to low porosity and permeability, with good levels of flexibility and strength under high temperatures. The alumina content of 12.5% suggests a spinel addition of about 20%, as well as the use of high-purity dead burned magnesia due to the CaO/SiO<sub>2</sub> ratio being higher than 2, which ensures the presence of the high-refractory  $C_2S$  phase.

Overall, the use of 0.25% additive to improve the hydration resistance of brick B maintained the same level of properties observed for brick A, but with a drop in HMOR at 1485°C. This drop is related to higher formation of the liquid phase when the additive is used in the recipe of brick B, which protects the magnesia grains against hydration but damages its refractoriness.

Properties	Brick A	Brick B	Brick C	Brick D			
BD (g/cm³)	3.02	3.01	3.04	3.03			
AP (%)	13.35	13.80	12.00	12.15			
CCS (MPa)	90	93	120	110			
Permeability (cD)	11	11	0	0			
Abrasion (cm <sup>3</sup> )	14	14	10	7			
HMOR 1200°C-3h (MPa)	8.0	7.5	9.6	8.6			
HMOR 1485°C-3h (MPa)	2.0	1.3	1.9	1.8			
MoE (GPa)	34	33	82	85			
Chemical Analysis (%)							
MgO	85.73	86.41	85.81	85.41			
Al <sub>2</sub> O <sub>3</sub>	12.52	11.90	12.51	12.76			
CaO	0.83	0.81	0.81	0.82			
Fe <sub>2</sub> O <sub>3</sub>	0.53	0.49	0.49	0.47			
SiO2	0.26	0.25	0.26	0.27			
CaO/SiO <sub>2</sub> ratio	3.2	3.2	3.1	3.0			
XRD	MgO, MA,	MgO, MA,	MgO, MA,	MgO, MA,			
	$C_2S$	$C_2S$	$C_2S$	$C_2S$			

**Table 1:** Physical and chemical properties of bricks A, B, C and D.

The surface treatments for bricks C and D resulted in an increase in bulk density and mechanical strength, and a decrease in porosity, abrasion loss and permeability. In fact, the permeability reached zero value due to the filling of the open pores of the refractory during the surface treatment process, thus preventing the flow of the gas used in the test. However, these property changes are temporary, as the material which covers brick C decomposes in the range of 150 to 400°C. For brick D, the

decomposition occurs around 1000°C. Thus, the original properties of brick A are restored when the application temperatures of bricks C and D are above those described. The chemical analysis showed that the three treatments did not affect the values, also maintaining the same mineralogical phases of brick A.

The results of the first hydration test of bricks A, B, C and D performed in the autoclave at 102°C for 5 hours are shown in Table 2. The typical magnesia-spinel brick A presented the lowest hydration resistance, with crack formation after 2 cycles and complete disintegration by the third cycle. The use of the anti-hydration additive in brick B showed an improvement in the resistance since the crack formation occurred after 3 cycles and complete disintegration by the seventh cycle. However, substantial improvement in hydration resistance is observed in bricks C and D which have been surface treated. Brick C showed cracks only after 6 cycles of hydration, while brick D remained unchanged during all the 10 cycles. Furthermore, both bricks did not disintegrate until the end of the tenth cycle. Figure 2 illustrates the superior hydration resistance presented by bricks C and D.

Cycles	Brick A	Brick B	Brick C	Brick D
1	No changes	No changes	No changes	No changes
2	Cracks	No changes	No changes	No changes
3	Disintegration	Cracks	No changes	No changes
4	-	More Cracks	No changes	No changes
5	-	More Cracks	No changes	No changes
6	-	More Cracks	Cracks	No changes
7	-	Disintegration	More Cracks	No changes
8	-	-	More Cracks	No changes
9	-	-	More Cracks	No changes
10	-	-	More Cracks	No changes

**Table 2:** Evolution of hydration cycles of bricks A to D in the autoclave.



**Figure 2:** Visual aspect of the cubes from bricks A, B C and D after: a) 3 cycles, b) 6 cycles and c) 10 cycles of hydration in the autoclave (red arrows: cracks).

The graph presented in Figure 3 reveals that the crack formation of bricks A, B and C occurs when the mass gain is greater than 0.4%, and the disintegration when it reaches values greater than 1%. This observation is not valid for brick D, which does not present cracks, despite showing high mass gain during all the cycles. This behavior is related to the hygroscopic property of the material used for the surface treatment of this brick. Thus, the mass gain is related to the absorption of water by the material on the brick surface without brucite formation.





The results of the second hydration test of bricks A, B, C and D performed in the climatic chamber at 70°C and 80% relative humidity are shown in Table 3 and Figures 4 and 5. Although 31 days in the climatic chamber was not enough to crack bricks B, C and D, it is considered that the results obtained are in line with those of the autoclave, that is, all the treated bricks showing improved hydration resistance compared to the typical magnesia-spinel brick A, as illustrated by Figure 4.

Days	Brick A	Brick B	Brick C	Brick D
3	No changes	No changes	No changes	No changes
7	Cracks	No changes	No changes	No changes
10	More cracks	No changes	No changes	No changes
14	More cracks	No changes	No changes	No changes
17	More cracks	No changes	No changes	No changes
21	More cracks	No changes	No changes	No changes
24	More cracks	No changes	No changes	No changes
28	More cracks	No changes	No changes	No changes
31	More cracks	No changes	No changes	No changes

**Table 3:** Evolution of hydration days of bricks A to D in the climatic chamber.



**Figure 4:** Visual aspect of the cubes from bricks A, B C and D after: a) 6 days, b) 18 days and c) 31 days of hydration in the climatic chamber (red arrows: cracks).

The graph presented in Figure 5 shows lower mass gain compared to the autoclave due to the less aggressive hydration conditions performed in the climatic chamber, which also prevented the observation of crack formation for bricks B, C and D.



Figure 5: Mass gain in hydration test in the climatic chamber (Crack formation).

#### 4. CONCLUSIONS

Three different methods of protection against hydration of magnesia-spinel bricks were analyzed at the laboratory. A substantial improvement in hydration resistance was mainly achieved by bricks C and D which were surface treated. However, temporary changes in properties were also observed for both bricks. Thus, the choice of surface treatment to be used on the basic bricks will depend on their application. For rotary kilns, as in cement production, the treatment applied to brick C is more suitable due to the low decomposition temperature of the material, eliminating variations in properties along the thickness of the brick. For steelmaking equipment, for example, the treatment given to brick D is also a good option.

#### 5. REFERENCES

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