

# An expansive Route to Produce High Refractoriness Insulating Refractories

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**Abstract:** This work presents a simple route to develop an enveloped porosity, contained by a low permeability surface, aiming the production of insulating refractories able to work as thermal insulators at very high temperatures (>1500°C). The process used consisted in using a controlled expansive route, by slip casting a Magnesium oxide ceramic slip charged with an expansive polyurethane reaction. The expansive reaction was developed under conditions of pressurization or not.

**Keywords:** Insulating Refractories – MgO- Casting Slip - Polyurethane

## 1 Introduction

Insulating refractories to work at very high temperatures (>1500°C), are generally produced from high refractoriness oxides (Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub>). In addition to insulating ability, it is highly desirable a low permeability for the material. This last property can be achieved if the material is produced with a strong dense surface, enveloping a porous but inherently weak bulk.

The insulating ability of a material is directly related to its thermal conductivity, which is a property linked to microstructure features of the solid [1].

The most important aspects to consider in relation to the effective thermal conductivity of the porous material, are; shape, orientation, pore volume fraction and the pores character (closed or open).

In this manner good thermal insulating materials should have two basic characteristics:

- High volume fraction of total porosity (>40%).
- The porosity should be formed eminently by closed pores of small sizes (<100μm).

Pores in ceramics generally are developed through the following routes [2,3,4]:

1 – Addition of combustible materials to a base refractory mix, which during the firing step vaporizes leaving pores behind. To do this one can add sawdust, powdered charcoal, rice husk, benzene or expanded polymers like expanded polystyrene

2 – Development of gaseous products through a chemical reaction, such as the acid or base attack in metallic powders chips or fillings, mainly of aluminum.

3 – Firing till bloating as is made to produce expanded clay.

4 –Through expansive polymerization reactions (polyurethane reaction).

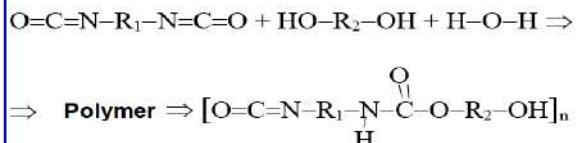
The refractory bricks prepared by the expansive method have the characteristics of large linear shrinkage after the first firing and low linear shrinkage under service conditions. The main reason is that in this case the structure is more uniform and evenly densified, and the pore size distribution is generally of a bimodal type.

In this work, the polyurethane expansive route was applied to make a MgO high temperature insulating refractory.

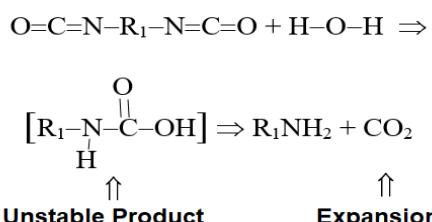
The polymerization expansion of polyurethane is accomplished by the reaction of a pre polymer with a polyol in the presence of water, as shown schematically in Figures 1, 2 and 3.

- - Prepolymer  $\Rightarrow O=C=N-R_1-N=C=O$
- - Ethylene Glycol  $\Rightarrow HO-R_2-OH$
- - Water  $\Rightarrow H-O-H$

**Figure 1** – Reactants used in the expansive reaction of a polyurethane.



**Figure 2** – Polymerization reaction.



**Figure 3** – Final expansive reaction.

From the previous figures, it can be concluded that the polymerization reaction provides the substrate and the subsequent hydrolysis promotes the expansion up on the liberation of  $\text{CO}_2$ .

The proposed approach of this work, consisted in the application of controlled pressurization to a polyurethane expansive reaction, in order to develop a porous bulk cellular structure confined by a somewhat densified surface peel.

## 2 Materials and Methods

### 2.1 Base Composition

**Table 1** presents the materials used to prepare the urethane+MgO slip base composition.

**Table 1** – Base Composition used to prepare the urethane ceramic slip

Dead burned MgO (<325mesh)	60wt%
Polyol	9wt%
Prepolymer	9wt%
Water	22wt%

### 2.2 -Mixing Sequence to prepare the Urethane Slip

- a) -  $\text{MgO} + \text{H}_2\text{O} \Rightarrow$  Mixing well
- b) - Adding Polyol  $\Rightarrow$  Mixing well
- c) - Adding the prepolymer  $\Rightarrow$  Mixing

### 2.3 Specimens Preparation

After preparing the urethane ceramic slip, 12 cylindrical specimens with a diameter of  $\Phi=1\text{cm}$  and height of  $h=8\text{cm}$ , were cast inside medical syringe flasks with a closed dead end. The internal walls of the flasks were lubricated in order to facilitate the extraction of the molded specimens. After filling with the ceramic slip, three of the flasks were left with one open end, in order to let the expansion reaction to proceed freely. The nine remaining flasks were actuated by means of closing plungers, and separated into groups of three. These three groups were submitted respectively to different external pressures applied to the plungers. The used external pressures of 0.5, 1.0 and 2.0 MPa were applied by an Instron Testing Machine. After the polymerization and expansive reaction, the molded specimens were extracted from de flasks dried at  $110^\circ\text{C}/12\text{h}$ , and fired under the following schedule:

- - From room temperature to  $400^\circ\text{C}$ , a heating rate  $5^\circ\text{C}/\text{min}$  was used, with a soaking time of one hour at this temperature.
- - From  $400^\circ\text{C}$  to  $1500^\circ\text{C}$ , a heating rate of  $10^\circ\text{C}/\text{min}$  was used, with a soaking time of 4 hours at this temperature.

### 2.4 Properties Evaluation

After firing the prepared cylindrical specimens were submitted to the following tests:

- a) Evaluation of the physical properties; Apparent Porosity and Apparent density by the immersion technique.
- b) Evaluation of Mechanical Strength by Flexural 3 Point Bend Test with a span of 6cm and loading rate of 1mm/minute.
- c) Microscopy observation of fractured surfaces by a stereoscopic microscope.

## 3 Results and Discussion

### 3.1 Physical Properties

The results of Physical Properties are presented in Figure 4. In the plots, each point is the average value of three tests. It can be observed that by using the expansive route it was possible to produce from 40% to 56% of volumetric porosity fraction, depending on the externally applied pressure by the plungers. Densities from  $0.88\text{g/cm}^3$  to  $1.26\text{g/cm}^3$  resulted, starting with the free expansion (atmospheric pressure), and ending at 2MPa plunger pressurization.

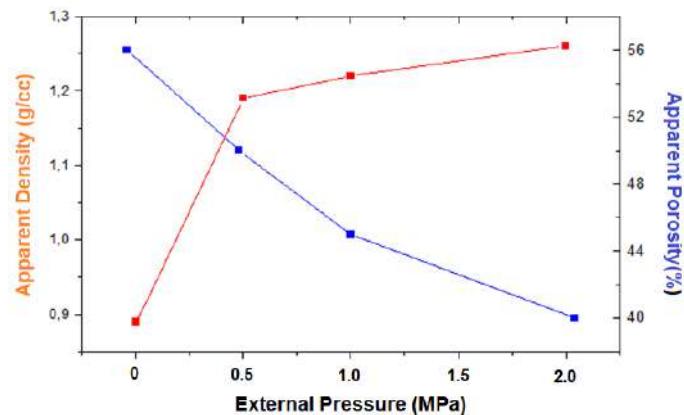


Figure 4 – Physical properties versus external pressure during the expansive reaction of the specimens fired at  $1500^\circ\text{C}/4\text{h}$ .

### 3.2 Flexural Strength

**Table 2** presents the results of flexural strength after three-point bending testing of the fired specimens ( $1500^\circ\text{C}/4\text{h}$ ). Each value is the average of three tests. It can be observed that the flexural strength increases sharply from the free expansion condition till the one of 1.0 MPa of applied external pressure, indicating a high increase in strength. This is obviously the consequence of microstructure change. The magnitude of 1.18MPa of flexural strength can imply from 10 to 15 MPa of compressive strength, which is an excellent strength for an insulating refractory with 40 to 50% of apparent porosity. This fact, also expresses the contribution of the densified surface layer and the decrease of pore size. It will be shown ahead that pore linking and

laminations, apparently caused the decrease in strength of the 2.0 MPa pressurized specimens. It is apparent that the pressurization of 0.5 MPa or 1.0 MPa, leads to a good combination of physical and mechanical properties.

From Figure 4 and Table 1 it can be concluded that the application of external pressures bigger than 1.0MPa does not improve the strength and cause a sensible decrease in the apparent porosity, which is not a good combination of properties for insulating purposes.

These aspects became clear through the microscopy observations to be treated ahead.

**Table 2-** Flexural strength in three-point bend test of the fired specimen, after being produced by expansive reaction under different external pressures.

Pressure	Flexural Strength (MPa)
Local Atmosphere	0.43
Pressurized Externally 0.5 MPa	0.83
Pressurized Externally 1.0 MPa	1.18
Pressurized Externally 2.0. MPa	0.98

### 3.3 Microscopic Observations of Fractured Surfaces

After the flexural strength testing, the fracture surfaces of the fired specimens were observed by a stereoscopic microscope.

**Figure 5** shows the transversal fracture surface of one specimen whose preparation was done under free expansion. It can be observed the following features:

- a) A thin densified external surface layer.
- b) Large volume fraction of pores of widespread diameter distribution, many with a diameter greater than  $>200\mu\text{m}$ .
- c) Regions of apparent pore coalescence and cracks.



1mm

**Figure 5** – Fracture surface of a specimen prepared under free expansion after firing at 1500°C/4h.

**Figure 6** shows the transversal fracture surface of one specimen whose preparation was done under the applied external pressure of 0.5MPa. It can be observed the following features:

- a) It is still visible a thin densified external surface layer but less porous than that shown in Figure 5.
- b) It can be observed a certain number of sparse densified zones and an apparent smaller volume fraction of porosity with pores of smaller equivalent diameter, and a closer size distribution than the one produced under the free expansion of Figure 5.
- c) Apparent absence of pore coalescence.
- d) It can be seen a crack and two laminations in regions closer to the external surface.



1mm

**Figure 6** - Fracture surface after firing at 1500°C/4h, of a specimen prepared under 0.5MPa external pressure.

**Figure 7** shows the transversal fracture surface of one specimen whose preparation was done under the applied external pressure of 1.0MPa. It can be observed the following features:

- a) It is visible that the densified external surface layer is a little thicker and less porous than that shown in Figure 6.
- b) The bulk of the specimen shows a more porous micro structure than in the regions towards the external surface, which is a consequence of the gradient opposition against the expanding gases towards the exterior. The bigger densification explains the increased apparent density and lower apparent porosity observed for the sample prepared under 1.0 MPa pressurization.

- c) The pores present a more isometric shape than the ones of the other samples.
- d) Pores coalescence zones are not visible but a few cracks are present.
- e) Pores are of smaller size.



1mm

**Figure 7** - Fracture surface after firing at 1500°C/4h, of a specimen prepared under 1.0MPa external pressure.

**Figure 8** shows the transversal fracture surface of one specimen whose preparation was done under the applied external pressure of 2.0MPa. It can be observed the following features:

- a) The dense external surface layer is much thicker than the ones observed for the other samples.
- b) The microstructure has no homogeneous distribution neither in relation to pores nor to densified zones.
- c) It seems that the use of 2.0MPa pressurization led to intense laminations which certainly contributed to the decrease in flexural strength; when compared to the 1.0MPa pressurization.
- d) Pores of smaller size and thicker densified zone towards the surface of the specimen.



1mm

**Figure 8** - Fracture surface after firing at 1500°C/4h, of a specimen prepared under 2.0MPa external pressure.

#### 4 Conclusions

Based on the results of this short investigation it can be concluded that:

- a) The use of the confined pressurization of urethane ceramic slip expansion reaction provides the means to produce differentiated microstructure in which dense external layer envelopes and sustain a porous bulk material upon firing.
- b) By changing the externally applied pressurization it is possible to change the size and morphology of the pores, as well as the physical properties and mechanical strength.
- c) The use of external pressurization of 1.0MPa seems to lead to a better combination of physical properties and mechanical strength.
- d) The process has a good enabling potential to be used in the production of insulating refractories based on high refractoriness pure oxides to be used at very high temperatures.

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