DETERMINATION OF THE GAS PERMEABILITY OF HYDRAULIC BONDED REFRACTORY CONCRETE

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During the solidification process of alumina and zirconia electrocast refractories – used for glass melting furnaces – dangerously sharp crystals can occur inside the shrinkage cavity. For the safe insertion of the blocks into the melting furnace, the shrinkage cavity must be sealed with refractory concrete.

The aim of our research was to determine the most important characteristics of refractory concrete: the mass and heat changes that take place during the first heat-up and gas permeability. Special laboratory measurements were carried out in order to determine the temperature and gauge pressure values in the shrinkage cavity sealed with refractory concrete during the first heat-up of the refractory block. The measurement data shows, that with 100 °C or above in the cavity (the boiling temperature of the water), the maximum overpressure was around 1300 Pascal. We can declare, that the gas permeability of the sealing refractory concrete allows the steam to leave released from the cavity at safe, low gauge pressure levels.

Keywords: electrocast refractories, solidification cavity, refractory concrete, gas permeability.

Introduction

In the solidification process of alumina and zirconia electrocast refractories melted in electric arc furnace, close to the point when the melted material is casted into the mould, dangerously sharp crystals would occur in the shrinkage cavity formed by the casting. For the safe building-in of the block into the glass melting furnace, this solidification hole must be covered with hydraulic bonded refractory concrete [1].

The aim of our research was to determine the most important parameters and conditions for the safe application of refractory concrete used for sealing of the solidification hole:

- the mass and heat changes occurring during the first heat-up;
- the gas permeability of the refractory concrete;
- the temperature measured in the shrinkage cavity;
- the gas pressure prevailing in the solidification hole covered with refractory concrete during the first heat-up of the refractory block.

The following types of refractories were examined:

- electrofused Aluminate-Zirconia-Silicate refractory block (AZS: Al₂O₃ = 66%, ZrO₂ = 21%, SiO₂ = 12%, Na₂O+Fe₂O₃ = 0,4%) [2, 3];

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hydraulic bonded refractory concrete made from cement Almatis CA 25-R, (Al₂O₃ = 81%, CaO = 18%, SiO₂ = 12%, Na₂O = 0.6%, Fe₂O₃+MgO = 0.6%), made with 16 m/m% of water) [4].

1. Mass changes and thermal processes during the first heat-up of the refractory concrete

1.1. Measurement method for the determination of mass change and thermal processes

While heating refractory cement Almatis CA 25-R (prepared with 16 m/m% of water) after two days of hardening and drying, the mass change of the material and different thermal processes have been determined using a “DERIVATOGRAPH-C” type instrument applicable for computing thermal analysis [5]. Three curves were produced from the test results:

- Thermogravimetry (TG, %), indicating mass change;
- Differential-thermogravimetry (DTG, %/°C), indicating the derivative of mass change;
- Differential-thermal analysis (DTA, °C), a curve of endothermal and exothermal thermal processes.

The derivatogram registered by the instrument during the measurement is shown in Figure 1. The results obtained by evaluating the derivatogram can be seen in Table 1.

![Figure 1. Derivatogram of cement Almatis CA 25-R (after two days hardening and drying). Mass change and heat processes during first heating depend on temperature](image-url)
### Table 1

Relevant values of the derivatogram belonging to sample Almatis CA 25-R cement

<table>
<thead>
<tr>
<th>Index in Fig. 1.</th>
<th>T, °C</th>
<th>TG, %</th>
<th>DTA, °C</th>
<th>DTG, mg/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95</td>
<td>-0.61</td>
<td>-1.261</td>
<td>-0.4</td>
</tr>
<tr>
<td>2</td>
<td>145</td>
<td>-2.05</td>
<td>-0.631</td>
<td>-0.213</td>
</tr>
<tr>
<td>3</td>
<td>215</td>
<td>-2.5</td>
<td>-0.361</td>
<td>-0.29</td>
</tr>
<tr>
<td>4</td>
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<td>-0.169</td>
</tr>
<tr>
<td>5</td>
<td>315</td>
<td>-4.08</td>
<td>-0.053</td>
<td>-0.126</td>
</tr>
<tr>
<td>6</td>
<td>735</td>
<td>-6.03</td>
<td>1.601</td>
<td>-0.069</td>
</tr>
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<td>7</td>
<td>910</td>
<td>-6.39</td>
<td>1.732</td>
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</tr>
<tr>
<td>8</td>
<td>1100</td>
<td>-6.41</td>
<td>1.807</td>
<td>-0.028</td>
</tr>
</tbody>
</table>

1.2. Summary of the thermo-analytical test results of the refractory concrete

Based on data of Table 1, we can say the following:

- The mechanical water mixed into the sample to adjust its plasticity continues to evaporate up until 120–125 °C.
- The most intensive water release occurs at the narrow temperature range of 95–105 °C. The rate of evaporation gradually decreases above 110 °C.
- At the temperature range of 215–315 °C, a second phase of water release can be registered.
- The dehydration process of the AH₃ bond is the most intensive around 230 °C.
- The degradation of the Ca₃AlH₆ bond terminates at 315–320 °C.
- The total mass loss of the refractory concrete at 320 °C is 5% on average.
- At temperatures above 320 °C, the very slow-rate degradation of more complex CₖAₘHₙ bonds occur in multiple steps, accompanied by steady mass loss [6].
- Mass loss processes end at 910 °C, with a total mass loss of 6.41 %.

2. Measuring the gas permeability of the refractory concrete

2.1. Gas permeability measurement method

The rate of water evaporation from the refractory concrete in the shrinkage cavity during the first heat-up strongly depends on the gas permeability of the concrete. The method and the instrument of measurement tests were provided by the Department of Reservoir Engineering of the University of Miskolc.
Figure 2. Measurement setup for the gas permeability test.

1 – nitrogen tank, 2 – gas reducer, 3 – fine adjustment gas reducer, 4 – puffer tank, 5 – $\Delta p$ pressure transducer, 6 – voltmeter, 7 – flow meter, 8 – test sample in the HASSLER sleeve, 9 – pressure resistant container filled with water, 10 – pump to increase water pressure

Gas flow volume rate was calculated from the measured data in cm$^3$/sec units. From the measured values, the air and gas permeability values of the sample were determined for every increment of $\Delta p$ pressure change, using EXCEL software. The modified Darcy equation was used for the calculations:

$$k_g = \frac{q_{ga} \cdot p_a}{A} \cdot \frac{1000}{\mu_g} \cdot \frac{2}{p_1^2 - p_a^2} \cdot \frac{1}{1000 \cdot 0.9869} \quad [\text{mD}]$$  (1)

where:

- $k_g$ – permeability of the sample at a given pressure difference, (milliDarcy), mD;
- $A$ – cross section of the sample perpendicular to the gas flow, cm$^2$;
- $L$ – sample length, cm;
- $p_a$ – exit pressure of the gas flow (normal atmospheric pressure), bar;
- $q_{ga}$ – measured flow volume rate of the gas at the exit pressure, cm$^3$/s;
- $\mu_g$ – the viscosity of nitrogen gas, at average test pressure and temperature, cP, or mPa.s;
- $p_1$ – entry pressure of the gas, bar.

The pressure values registered in bars by the pressure transducer can be converted to atm by using a factor of 1000/0.9869, which allows to get the respective gas permeability values in the above formula in units of mD.

Equation (2) seen below was formulated by plotting each $k_g$ value of gas permeability (registered at $\Delta p$ pressure differences) against the reciprocal value of average test pressure ($1/p_{av}$) and by using the least squares method to fit a straight line onto the points. With this formula, the absolute (Klinkenberg) permeability of the sample and the constants ($k_{abs}, b$) of the Klinkenberg formula characterizing the gas permeability of the test sample can be determined:
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\[ k_g = k_{abs} \left( 1 + \frac{b}{p_{av}} \right) = k_{abs} + k_{abs} b \frac{l}{p_{av}} = k_{abs} + m \frac{l}{p_{av}} \]  

where

- \( k_{abs} \) – absolute (Klinkenberg) permeability, mD;
- \( b \) – Klinkenberg constant, bar;
- \( k_g \) – measured gas and air permeability, mD;
- \( p_{av} \) – average pressure of the measurement \((p_1 + p_a)/2\), bar.

Equation (2) defines a straight line, the axis crossing point of which is the absolute permeability of the sample \((k_{abs})\), while the \( b \) parameter of the Klinkenberg formula can be determined from its gradient:

\[ b = \frac{m}{k_{abs}} \]  

where

- \( m \) – the gradient of the straight line (directional tangent), mD/bar.

In some cases, Darcy’s law used to formulate the Klinkenberg formula (2) cannot be applied to describe the gas flow through the core samples. This occurs when gas flow velocity is too high and the flow behaviour of the gas changes from linear to turbulent. In such cases, average gas permeability can be determined by a more universal mathematical formula that applies to the full pressure range of the measurement.

The determination of average gas permeability should be based on the Forchheimer formula, a widely accepted equation describing turbulent gas flows:

\[ \frac{dp}{dl} = av + bv^2 \]  

where \( a \) and \( b \) are constants, and \( v = q/A \) is the leakage rate of the gas. Cornell and Katz replaced the constants in Equation (4) by the following physical parameters:

\[ \frac{dp}{dl} = \left( \frac{\mu}{k} \right) v + \beta \rho v^2 \]  

where

- \( \mu \) – gas viscosity, mPa.s;
- \( \sigma \) – gas density, g/cm\(^3\);
- \( k \) – permeability of the porous core, mD;
- \( \beta \) – coefficient for high velocity gas flow.

\( \beta \) coefficient in Equation (5) is the parameter of the core sample that makes it possible to apply Darcy’s law:

\[ \frac{dp}{dl} = \left( \frac{\mu}{k} \right) q/A + \beta \rho \left( \frac{q}{A} \right)^2 \]  

Assuming that the flow is isometric during the test and the nitrogen gas used under laboratory conditions is an ideal gas, gas density can be determined by the following formula:
Substituting the appropriate density values in Equation (5) and performing the integration considering the limits \( x = 0, p = p_1, p = p_a \), we get:

\[
p_i^2 - p_a^2 = \left( \frac{2\mu L}{k A} p_a \right) q_g + \left( \frac{2LMP_a^2}{A^2RT_a} \right) q_g^2
\]  
(8)

Equation (8) is practically identical with the one applied to linear gas flow in porous media:

\[
p_i^2 - p_a^2 = A_0 q_g + B_0 q_g^2
\]  
(9)

Comparing Equations (8) and (9), it can be deduced that the constant \( A_0 \) in Equation (9) can also be defined by the formula below:

\[
A_0 = \left( \frac{2\mu L}{k A} p_a \right)
\]  
(10)

\[
B_0 = \left( \frac{\beta 2LMP_a^2}{A^2RT_a} \right)
\]  
(11)

The constants \( A_0 \) and \( B_0 \) can be determined with the least squares method. Average gas permeability for the porous matter can be determined from point \( A_0 \) of the straight line fitted onto the measurement points crossing the axis:

\[
k_{g,avg} = \left( \frac{2\mu L}{A_0 A} p_a \right)
\]  
(12)

Using the appropriate values in the formula, we get the following equation for the determination of average gas permeability:

\[
k_{g,avg} = \left( \frac{2000 \cdot \mu_g \cdot L \cdot 0.9869 \cdot p_a}{A_0 A} \right)
\]  
(13)

The average gas permeability \( k_{g,avg} \) of the sample can be calculated by determining the constants \( A_0 \) and \( B_0 \) of Equations (10) and (11) from the measured \( \Delta p_i^2 \) pressure differences belonging to \( q_g \) gas flow volume rates.

The test requires 30 mm high test samples with a diameter of 37 mm. The height of the test sample closely resembles the thickness of the refractory concrete layer generally used for sealing the solidification hole of the refractory blocks in industrial practice.
2.2. Summary of gas permeability test results

Based on gas permeability tests performed on refractory concrete test samples made of Almatis CA-25 R cement and AZS powder, the following conclusions can be drawn (see Figure 3):

- The concrete used to seal the cavity of the refractory block is not gas resistant. The increase in the gas permeability of the concrete is linearly correlated with the pressure difference registered between the two ends of the tested sample.
- Layers below the outer surface (facing the combustion chamber) of the concrete sealing of the shrinkage cavity shows significantly lower flow resistance against steam formation. This means that the steam formed during the heating process in the outer layers of the refractory concrete can escape at much lower pressure differences with higher volumetric flux.

![Figure 3. Average volumetric flow of concrete made from cement Almatis CA-25 R + grained AZS](image)

3. Determination of temperature and overpressure in the solidification hole

3.1. Laboratory method for measuring temperature and overpressure in the solidification hole with measurement data

Test samples were made of refractory AZS blocks, with the dimension of 170 x 250 x 120 mm. In order to simulate the conditions of hole formation in electrofused refractory blocks, 80 mm deep and 60 mm wide cylindrical cavities were made, sealed with a 30 mm thick layer of concrete. The samples were placed in an electric furnace and heated to 350 °C at the rate of 5 °C/h.
A piezo-resistance differential pressure sensor, type “NSCDANN 150 PGUNV” [7] was connected to the outer end of the copper tube with a thick, transparent plastic tube charged with silicone oil (heat-resistant up to 300 °C) to prevent the steam from condensation and excess overpressure. The externally visible outer surface of this thermo-oil served as a visual indicator of the rising steam pressure in the closed hole.

Figure 4. Schematic diagram of the measurement cycle for the monitoring of overpressure and temperature in the shrinkage cavity during the heat-up of an electrofused AZS (with a concrete-sealed solidification hole). 1 – refractory block, 2 – positioning copper mesh, 3 – tested refractory concrete, 4 – pressure sensor, 5 – heat-resistant silicone oil, 6 – copper tube, 7 – NiCr-Ni thermocouple, 8 – data collector

Figure 5. Average temperature and overpressure in the solidification hole, sealed with refractory concrete
3.2. Conclusions of the laboratory experiments

The following can be concluded from the laboratory measurement data:

- When the temperature inside the furnace and measured at the interior surface of the refractory is 250–260 °C, the solidification hole has a temperature of approximately 100 °C.
- Around 100 °C (i.e. the boiling point of water), the overpressure of the steam reaches its peak (max. 0.013 bar) for each tested sample. This means, that the gas permeability of the concrete allows the steam – formed from mechanical water – to release from the solidification hole at low pressure levels.

Final conclusions of the research

Based on the described complex analysis, it can be stated without a doubt, that the gas permeability characteristics of the refractory concrete made of cement Almatis CA-25 R + grained AZS, allows the steam, formed during the first heating up of refractory wall of glass melting furnaces, leave the block without further intervention.

The 0.02 bar overpressure – arising in the solidification hole – does not cause damage to the electrofused refractory blocks and the refractory concrete used for the lining of the solidification hole.

Acknowledment

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References

[1] MOTIM Fused Cast Refractories Ltd.: http://www.motim.hu/kadko/docs/felhasznalas.htm