Thermal Cycling Tests on Dense Refractories

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Abstract

In the aluminium industry, the carbon anodes are baked in the anode baking furnace by means of the combustion of natural gas injected inside fluewalls made of dense aluminosilicate refractory bricks. These bricks are exposed across their lifetime to thermo-mechanical stress as well as chemical attacks. The nature of the anode baking process indeed imposes more than 100 thermal cycles lasting around 14 days and going from ambient temperature to approximately 1 200 °C.

The behaviour of the refractory lining and its condition at the end of its life have been widely analysed in the literature mainly through autopsies of used material. Thermal cycling has been studied only through thermal shock and therefore the effect of the sole (i.e. isolated from the chemical attacks and the mechanical loading) and "slow" thermal cycles such as the one imposed by the anode baking process is relatively unknown.

This paper describes the campaign of tests realized on four sources of anode baking furnace fluewall bricks to better understand the impact of thermal cycles on refractory material properties. Results show a similar evolution of all samples with, after 30 thermal cycles, a slight increase of the Young's modulus and a significant increase of the shear modulus. These evolutions lead to a decrease of the Poisson's ratio which is known in the scientist literature to be correlated with the resistance to thermal shock.

These observations are different than the ones observed for proper thermal shocks where the decrease in Poisson's ratio is more driven by a decrease on E modulus.

Keywords: Dense refractories, Anode baking furnace, Fluewalls, Headwalls, Thermal cycling.

1. Context

1.1 Baking Furnace Description and Refractory Quality

Green anodes are made with a mixture of petroleum coke, recycled anode butts and coal tar pitch, which are subjected to heat treatment in anode baking furnaces. The principal element in the anode baking furnace is the refractory flue wall, which separates the anodes from the flue gas during operation (Figure 1).

Figure 1: Anode baking furnace. Left: pits loaded with anodes, Right: top of fluewall under construction.

Flue walls are erected with bricks made of dense aluminosilicate refractory (chamotte and refractory clays). Typical chemical compositions are indicated in Table 1.

Table 1. Chemical composition requested.

Composition	Units	Typical values	Standards
Al_2O_3	% wt	46 to 54	NF EN ISO 12677
Fe_2O_3	% wt	< 1.5	
CaO + MgO	% wt	< 0.6	
$Na_2O + K_2O$	% wt	< 0.6	

1.2 Deterioration Modes of Fluewall Bricks

Anode baking furnace fluewalls usually last 5 to 8 years before being demolished and replaced. Vertical cracks followed by bending, as well as decomposition of the brick surface at the anode side usually trigger the demolition of the wall and its replacement.

The refractory bricks are exposed to high temperature and intensive chemical corrosion, leading to the alteration of thermomechanical properties. Two main root causes have been identified in previous works [1, 2].

The first origin is the gaseous environment surrounding the bricks on the anode side. The process of chemical corrosion is well understood [3] with the reduction of brick Si-based components on the anode side, and their recrystallisation in the degassing joints in the form of SiO_2.

The second root cause is the thermal cycling generated by the anode baking process. During each baking cycle, the refractory bricks are heated from room temperature to 1200 °C and cooled down in approximately 14 days in total. This thermal cycle is repeated 80 to 150 times over the lifetime of the fluewalls.

2. Objectives

The evolution of refractory bricks during their lifetime as well as the changes in their physical properties, composition and microstructures have been well documented mainly through autopsies and comparative analysis between new and used bricks [4, 5, 6]. These types of analysis did not, however, allow to discriminate the effects of the chemical corrosion and the effects of the thermal cycling.

More generally, the effects of thermal cycling on refractory and ceramic materials have been studied in previous works but only through the thermal shock measurement [7, 8, 9]. In thermal shocks tests, samples are heated to temperatures around 800 °C to 1000 °C and then quenched with water or air. Cooling rates generally used in such tests range from 230 °C/min to 10 °C/min. This is significantly higher than the cooling rates ranging from 5 °C/h to 10 °C/h applied by the anode baking process. Among other observations, drops in Young's modulus (E) and shear modulus (G) values accompanied by a decrease of Poisson's ratio (υ), which in some cases even reaches negative values [10] were observed in those conditions.

This study aims to evaluate impacts of the sole thermal cycling with heating and cooling rates and maximum temperature in the range of those observed for the anode baking process. This will enable to determine if the traditional thermal shocks methods, i.e., quenching with air or water, can be used to evaluate refractory bricks performance for an anode baking furnace usage. Samples from various sources used by operating plants have been tested to have a comparative look at the evolution of key properties depending on the sourcing of the material.

3. Experimental Methods

3.1 Sample Preparation

Samples have been cut from bricks (Figure 2) selected from known and new suppliers in the same range of products, i.e. bricks used for fluewalls erection.

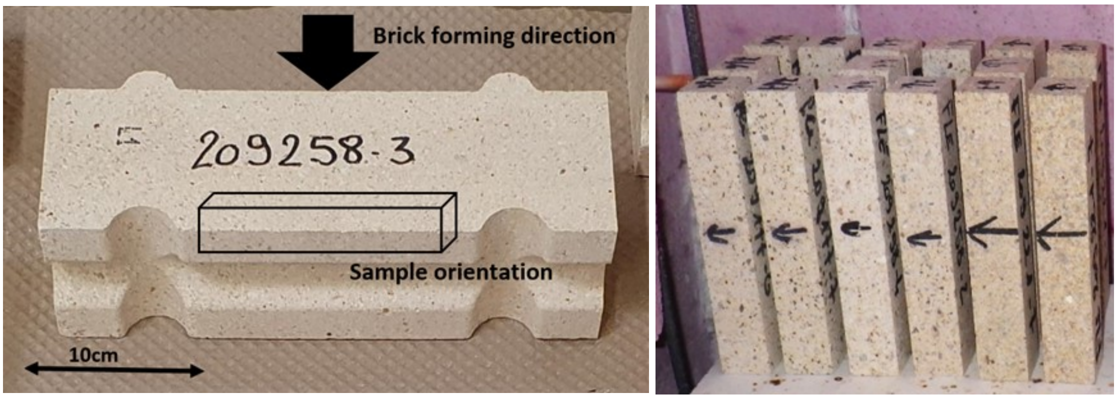

Figure 2: Left: brick samples orientation, Right: Samples from various origins.

Having several sources of material enable to have a view on the variety of quality the worldwide market currently proposes. Quality #1 and #3 are from known suppliers used since several decades on Rio Tinto furnaces. Supplier #3 is recognised as a good supplier by end users with fluewalls reaching good life duration. Supplier #2 is a recent supplier only being used for a few years and Supplier #4 is a brand-new supplier. As operating conditions can vary from one plant to another, performance collected on operating facilities, even though they are of good indication, must be taken with care.

3.2 Thermal treatment

The heat treatment applied to the various materials consists of the heating of the brick from room temperature and a succession of cycles between 1 200 °C and 600 °C at a rate of 1 cycle every 8 hours (Figure 3).

Heating and cooling rates are in the range of 75 °C/h which is significantly lower than heating rates of 10 °C/min used for low intensity thermal shocks. The fact that it still does not reach the real anode thermal cycle of 10 °C/h and samples do not come back to ambient temperature is for practical reasons to optimize tests duration.

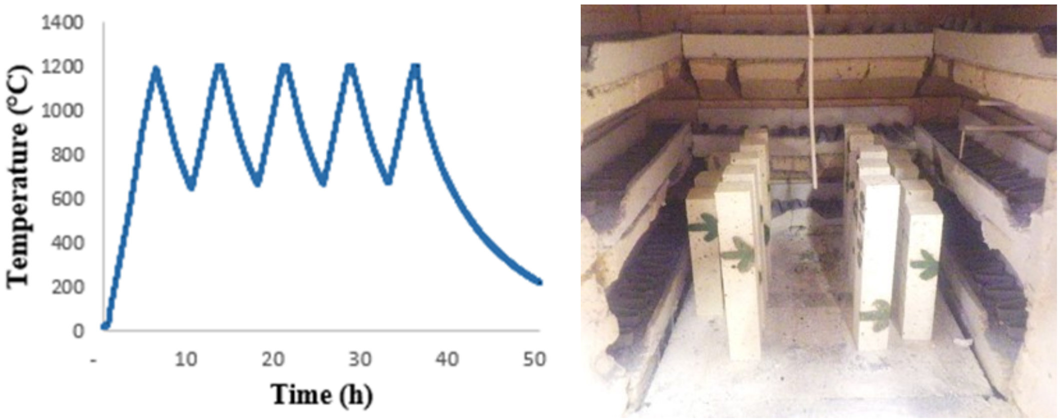

Figure 3. Thermal treatment.
Left: 5 thermal cycles graph, Right: samples arrangement inside the kiln.

Cycles are repeated 40 times, and stops are made after 5 cycles (C5), 10 cycles (C10), 20 cycles, (C20), 30 cycles (C30) and 40 cycles (C40). The specimens are mixed between each cycle, so as not to favor the specimens on the edge of the kiln over the ones in the center of the kiln.

3.3 Properties Measured at Different Cycles

The hot modulus of rupture (HMOR) is the only measurement made at 1 200 °C (Figure 4). It is realized on a 3 points bending bench with a load rate of 0.15 MPa.s^{-1} and gives an indication on the capacity of the refractory bricks to resist to mechanical forces and especially bending. As per standard ISO 5013, the tests were carried out on 4 bars (25 mm × 25 mm × 150 mm). The HMOR is measured before the first thermal cycle and after 20 and 40 thermal cycles.

Figure 4. Hot modulus of rupture device. Left: at ambient temperature, Right: at 1 200 °C.

Young’s modulus (E) and shear modulus (G) are determined from the natural resonance frequency of each sample in each of the different mechanical stress modes. This resonance frequency is obtained using a pulse excitation method. To do so, the sample is struck with a hammer weighing just a few grams (Figure 5). The resonance frequency of the bending and compression modes gives the Young's modulus (E) which gives an indication on the linear elasticity of the material. The resonance frequency of the torsion mode gives us the material's shear modulus (G) which is a measure of the elastic shear stiffness of a material.

Figure 5. Grindosonic® Acquisition System.

Resonance frequency is measured before the first thermal cycle and after 5, 10, 20, 30 and 40 thermal cycles.

Poisson's ratio (υ) is obtained by calculation from Equation (1). It is known in the scientist literature that the resistance to thermal shock of refractory materials is correlated to the Poisson's ratio to a certain extent. The higher this coefficient is, the greater the risk of reaching a rupture stress due to thermal shock.

$$\upsilon = \frac{E}{2G} - 1 \tag{1}$$

4. Test results

Measurements made before any thermal cycling are presented in Table 2.

Table 2. Samples properties at C0.

	Supplier 1	Supplier 2	Supplier 3	Supplier 4
Volumetric mass (kg/m3)	2 332	2 387	2 280	2 479
HMOR (Mpa)	13	11	10	18
E (Gpa)	32.0	30.7	23.5	49.6
G (Gpa)	13.7	12.7	11.0	21.4
υ	0.17	0.21	0.07	0.16

It can be observed that Supplier #4 bricks have significantly higher density and HMOR. Young's modulus and shear modulus are also higher for these samples. This is most probably due to the forming process realized with more pressing force giving a denser and more rigid material. On the opposite side, Supplier #3 is probably made with less force the volumetric mass which gives the lowest values of the entire test campaign. Supplier #1 and Supplier #2 are of similar quality between the two others.

Figure 6 presents the volumetric mass evolution for the four suppliers.

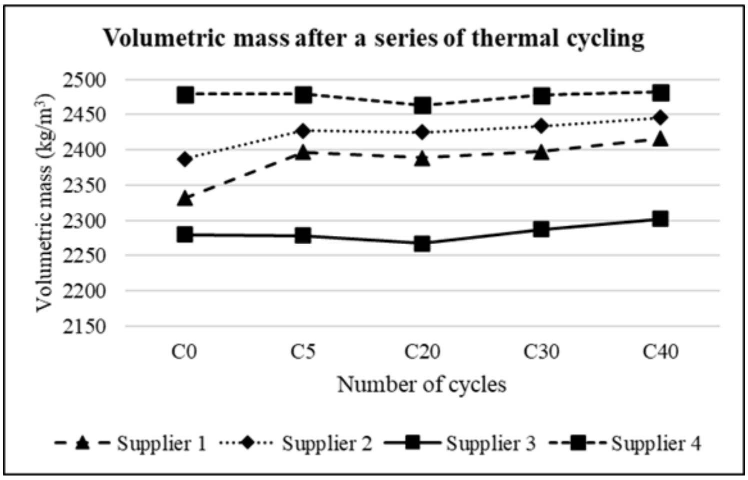

Figure 6. Volumetric mass.

A significant increase in volumetric mass is observed for suppliers 1 and 2 from C0 and C5. Then the volumetric mass slightly increases from C20 to C40. The evolution for suppliers 2 and 4 before 5 thermal cycles is probably correlated with an insufficient baking since the material reached a stable value for volumetric mass after 5 thermal cycles except for Supplier #3.

As presented in Figure 7, the Young's modulus E slightly increases for suppliers 1, 3 and 4.

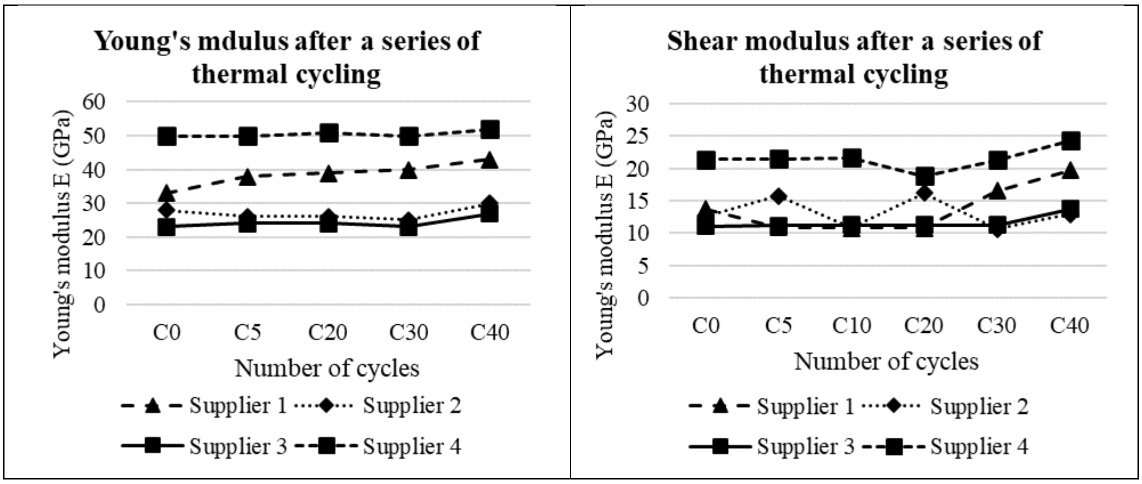

Figure 7. Left: Young's Modulus E, Right: Shear modulus G.

This observation goes in the opposite way as what has been observed in previous works [7, 8] where a drop in Young's modulus of approximately 20 to 30% was observed for proper thermal shocks, probably due to the lower heating and cooling rates in this study. It is also interesting to see that the shear modulus G increases after 30 cycles for all suppliers.

Figure 8 presents the evolution of Poisson's ratio.

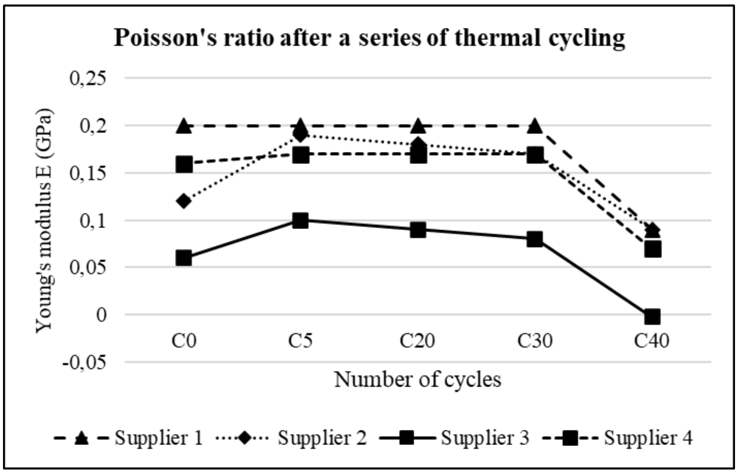

Figure 8. Poisson's ratio.

Because of the evolution of the Young's modulus and the shear modulus, the Poisson's ratio goes down after 30 cycles. It is known in the scientist literature that the higher this coefficient is, the greater the risk of reaching a rupture stress due to thermal shock. This change is due to the increase in the shear modulus G contrary to previous works [10] where the drop of the Poisson ratio is obtained through the increase the Young's modulus.

Figure 9 presents the evolution of the HMOR. Although results after 40 thermal cycles for suppliers 1 and 3 are not available, a similar evolution to all the suppliers is observed with an increase from cycles C0 to C20 of around 15% in average and a decrease after 20 cycles of around -33 % in average.

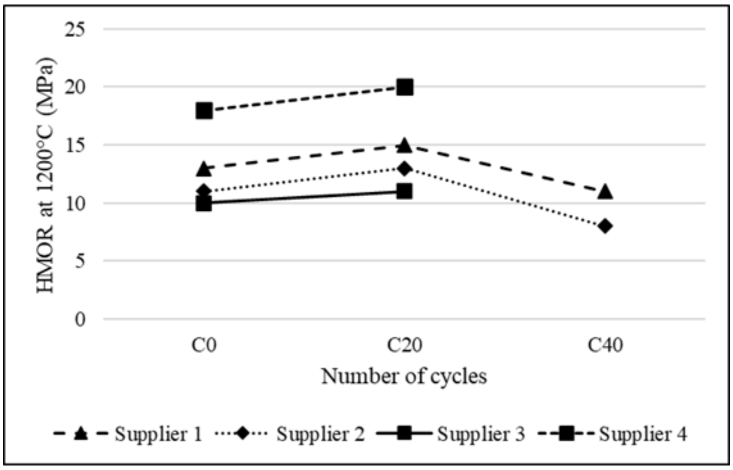

Figure 9. Modulus of rupture by bending.

5. Discussion

Beyond the measurements realized, Kingery [11] defined a soft thermal shock resistance called R' factor based on Equation (2).

$$R' = \frac{\sigma_r.(1-\nu).\mathrm{k}}{E.\alpha} \tag{2}$$

Where:

σ_r rupture stress
ν Poisson's ratio

k	thermal conductivity
E	Young's elastic modulus
α	coefficient of thermal expansion

This R' factor tells us qualitatively about the characteristics that a refractory material must have to maximize its resistance to temperature variations. As a result, a good resistance to temperature variations is obtained with a high rupture stress σ_r and thermal conductivity "k" and low Young's modulus "E", Poisson's ratio "v", and a low coefficient of thermal expansion "α".

Unfortunately, the coefficient of thermal expansion α has not been measured for supplier 2 and 4 as well as the thermal conductivity k for all suppliers. As a result, a direct calculation of the R' factor is not possible. However, and as presented in Table 3, the coefficient was still calculated without these missing parameters.

Table 3. Properties initial values.

	Supplier 1	Supplier 2	Supplier 3	Supplier 4
Rupture stress σ_r (N/mm²)	13	10.7	10.6	19
Young's modulus E (GPa)	38.5	26.7	24.5	50.5
Poisson's ratio υ	0.15	0.17	0.07	0.15
$\sigma_r\,(1-\upsilon)/E$	0.286	0.332	0.401	0.321
	71 %	83 %	100 %	80 %

The brick quality with the better resistance to thermal stress is supplier #3 with a lower E and G and a lower density. Brick supplier #4 is better resistant to pure mechanical load.

6. Conclusion

The tests realized on different qualities of refractory materials show a similar evolution of all samples characterized after 30 thermal cycles by a slight increase of the Young's modulus and a significant increase of the shear modulus. The decrease in Poisson's ratio is mainly a consequence of the decrease of the shear modulus. These observations are different than the ones observed for proper thermal shocks where the decrease in Poisson's ratio is more driven by a decrease on E modulus. This leads to the conclusion that traditional thermal shocks methods, i.e. quenching with air or water and high temperature gradients, cannot directly be used to evaluate refractory bricks resistance to thermal cycling for an anode baking furnace usage.

Test results also reveals discrepancies between the sources of bricks tested. On one hand, bricks from supplier #4 have better pure mechanical resistance properties with higher density and mechanical resistance properties (higher Young's modulus, shear modulus and HMOR). This is probably obtained with a high forming force during production. On the other hand, supplier #3 bricks have better thermal stresses resistance properties. Although the mechanical properties seem lower than supplier #4, it is interesting to know that these bricks show good performance on anode baking furnaces.

The introduction of ratio $\sigma_r\,(1-\upsilon)$ / E calculation based on the thermoelastic approach of Kingery seems to be a good indicator to assess the possible resistance and performance of refractory bricks for anode baking furnace environment and specific constraints. There is probably a limitation in terms of mechanical strength with the density as well as a limitation with the thermal conductivity (link with anode baking furnace energy consumption).

This study can further be improved by:

- ✓ Having additional discussions with suppliers to understand which part of the process is relevant i.e. raw material selection, recipe, forming and sintering process (temps/temperature),
- ✓ Extending the number of thermal cycling used during this test campaign to 80 or 100 thermal cycles to visualize the final evolution of parameters until an age similar to that of the end of fluewall lifetime,
- ✓ Measuring additional properties for all materials as thermal conductivity “k” and coefficient of thermal expansion "α" as to be able to calculate the Kingery factor.

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