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.

Composition	Units	Typical values	Standards
Al ₂ O ₃	% wt	46 to 54	
Fe ₂ O ₃	% wt	< 1.5	NF EN ISO
CaO + MgO	% wt	< 0.6	12677
$Na_2O + K_2O$	% wt	< 0.6	

Table 1. Chemical composition requested.

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 SiO₂.

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

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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