

## Electromechanical Characterization of the Ramming Paste and the Aging Effect on its Performance

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### Abstract

The ramming paste plays a fundamental role in the life of an electrolysis cell and its energy efficiency. On the one hand, it prevents the infiltration of liquid aluminium into the cell and, on the other hand, it seals the cathode blocks, which protect them from damage and ultimately from failure. The aging of the coal tar pitch based ramming paste, due to the evaporation of the softeners ensuring its malleability at room temperature, is likely to influence its physical properties. Also, during the compaction of the coal tar pitch based ramming paste, the binder present in its composition releases carcinogenic products such as polycyclic aromatic hydrocarbons, which constitutes a real danger for health. To overcome this problem, several eco-friendly ramming pastes have been developed in recent years. However, the physical properties of these new pastes and their effects on the process efficiency are not yet well known. This work aims to study the aging effect on the physical properties of the ramming pastes. In this perspective, a standard coal tar pitch based ramming paste and an eco-friendly one were investigated. The characterization of the aging effect is focused on the measurement of quantities such as apparent density, mass loss, volumetric change, Young's modulus, Poisson's ratio, compressive and tensile strength as well as electrical resistivity. The results of this study reveal that the aging of the ramming pastes mainly affects the mass loss and the Poisson's ratio.

**Keywords:** Aluminium electrolysis, ramming paste, eco-friendly ramming paste, ramming paste aging, physical properties.

### 1. Introduction

In the aluminium electrolysis cells, the cathode blocks are sealed with the ramming paste. The main role of this paste is to prevent electrolyte bath and molten aluminium infiltration into the lining and to absorb the thermal expansion of the cathode blocks. The standard cold ramming paste is a mixture of dry aggregate (mainly calcined anthracite and artificial graphite) and a binder containing coal tar pitch. To lower the softening point of the paste and make it compactable at room temperature, softeners are added to the binder. As these softeners are volatile materials, the paste aging is likely to influence its physical, mechanical and electrical properties. Few papers have been published on the effect of the paste aging. Allard et al. [1]

have investigated the evolution of two properties (the rammability index and the volumetric expansion) versus the months of storage for the eco-friendly paste NeO<sup>2</sup>. The results revealed that after 12 months of storage the rammability index has undergone a slight increase, synonymous with a dry paste, whereas the volumetric expansion has undergone a slight decrease which, nevertheless, remains above the threshold of 1 % recommended by the authors of the study. Therefore, the authors concluded that the ramming paste NeO<sup>2</sup> could be stored for at least 11 months.

The emanations generated by the standard ramming paste have harmful effects on health and the environment. As a result, migration from standard to eco-friendly paste seems inevitable. Therefore, the characterization of the eco-friendly ramming paste becomes a priority. The objective of this work is to evaluate the aging effect on the performance of the ramming paste. To fulfill this objective, a standard and an eco-friendly ramming paste were used. The mechanical and electrical tests undertaken as well as the results obtained are presented in this paper.

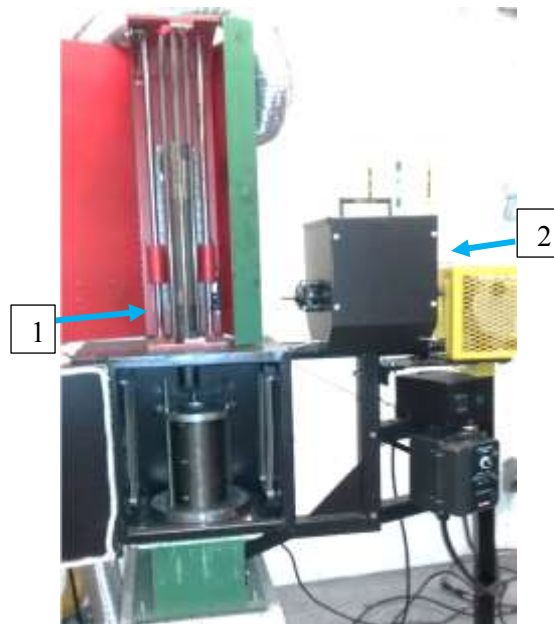
## **2. Experimental Methods**

### **2.1. Materials**

In this work, two ramming pastes have been studied: i) a standard coal tar pitch based ramming paste, used for many years in the industry and ii) an eco-friendly ramming paste of a new generation, recently introduced in Alcoa smelters. Upon receipt of the pastes, they were divided into several sealed containers and stored at room temperature to simulate storage conditions in the factory. The aging of the pastes has been followed during a period of 10 months, between the age of three and twelve months. Each month, one container of each paste was used to fabricate samples and thus to analyze the paste properties.

### **2.2. Sample Fabrication**

Four-inch laboratory samples are required to obtain a significant radial deformation for the calculation of the Poisson's ratio. St-Arnaud et al. [2, 3] have proposed a compaction method using a Proctor Mechanical Rammer, based on a multilayer approach, to acquire the desired samples. This test method provides samples with a green apparent density comparable to the average density of a representative assembly for the peripheral seam [4]. However, the density distribution within the compacted samples is not uniform. In this work, in order to fabricate samples with homogeneous density distribution, the Proctor was instrumented by a feeding system (Figure 1) presented in Chen et al. [5]. This feeding system introduces the ramming paste continuously into a split cylinder steel mold with an internal diameter of 101.6 mm (4 in). The compaction took place as the rammer, with a diameter of 50.8 mm (2 in) and a weight of 2.49 kg (5.5 lb), falls freely through a distance of 457.2 mm (18 in) over the tamped surface and repeatedly in a circular pattern. After the sample being compacted, its upper surface was trimmed to remove excess material. Finally, the average dimensions of the sample are 101.6 mm (4 in) in diameter and 230 mm (9 in) in height.



**Figure 1. Proctor Mechanical Rammer (1) and the feeding system (2).**

### **2.3. Sample Baking**

The green ramming paste samples were placed in an Inconel<sup>®</sup> container and covered with coke in order to avoid oxidation during the baking process. The samples were then baked at 1000 °C using the heating program specified in ISO 20202:2004 standard [6]. The furnace temperature was kept at 1000 °C for 2 hours to ensure that all specimens reached that temperature. Then, the furnace switched off allowing the samples to cool down to room temperature. Once baked, both extremities of the sample were cut to obtain samples with 101.6 mm (4 in) in diameter and 203.6 mm (8 in) in height. The green and baked apparent densities were calculated by dividing the mass by the apparent volume measured according to ASTM D5502-00 standard [7].

### **2.4. Compression Tests**

The compression tests were carried out at room temperature on the baked samples. An MTS 322 load frame equipped with a 250 kN load cell was used to perform these tests. Before testing, the samples were provided with sulfur capping using ASTM C617 standard [8] to ensure parallelism between both end surfaces. To evaluate Young's modulus and Poisson's ratio, the samples were loaded-unloaded three times up to 20 % of their compressive strength. The loading rate was chosen at 0.15 MPa/s. According to ASTM C469 standard [9], Young's modulus was identified as the average slope of the second and third loading of the stress-strain curve. Poisson's ratio was calculated as the ratio of the axial and radial deformation for the second and third loading [9]. The sample deformations were measured using axial and circumferential extensometers (MTS 632.11 F-90). The compressive strength was determined by loading the sample until failure occurs. The maximum stress value recorded during this latter load was reported as the compressive strength [10]. Each test was repeated on three samples.

### **2.5. Indirect Tensile Tests**

The indirect tensile tests (or Brazilian tests) were performed at room temperature on baked specimens. The test consists of applying a diametric compressive force along the length of the sample until failure occurs. The loading rate was set to 12.8 MPa/s. As indicated in ASTM C469 [34], two bearing strips of 3 mm thick plywood, 25 mm wide and of a length longer than

that of the specimen were placed between the press platens and the sample. These bearing strips were used to distribute the applied load along the length of the sample. Since the sample size exceeded that of the press platens, additional steel bars were used to ensure that the load was applied to the entire sample. Finally, a custom-made jig was used to align the sample, the plywood strips and the steel bars. Each month, the indirect tensile strength was measured on three samples. The tensile strength was evaluated using the following Equation:

$$T = \frac{2P}{\pi ld} \quad (1)$$

where  $P$  denotes the maximum applied load indicated by the testing machine,  $l$  and  $d$  are the length and the diameter of the sample, respectively.

## 2.6. Electrical Resistivity

The electrical resistivity of the baked samples was measured using a four-point probe device based on the ISO 11713 standard [11]. The current is injected through the sample via two steel plates connected to a DC Power Supply HP/Agilent 6031A. To ensure optimum distribution of the current, the external load applied to the top of the sample corresponds to 20 % of its compressive strength, i.e. 36 kN for the standard paste and 11 kN for the eco-friendly paste. Voltage drop has been measured at a 90° interval over the circumference of the sample for a total of four measures per sample. An Agilent 34 461A digital multimeter was used to measure the voltage drop. Each month, the electrical resistivity was measured on three samples. The electrical resistivity was defined as:

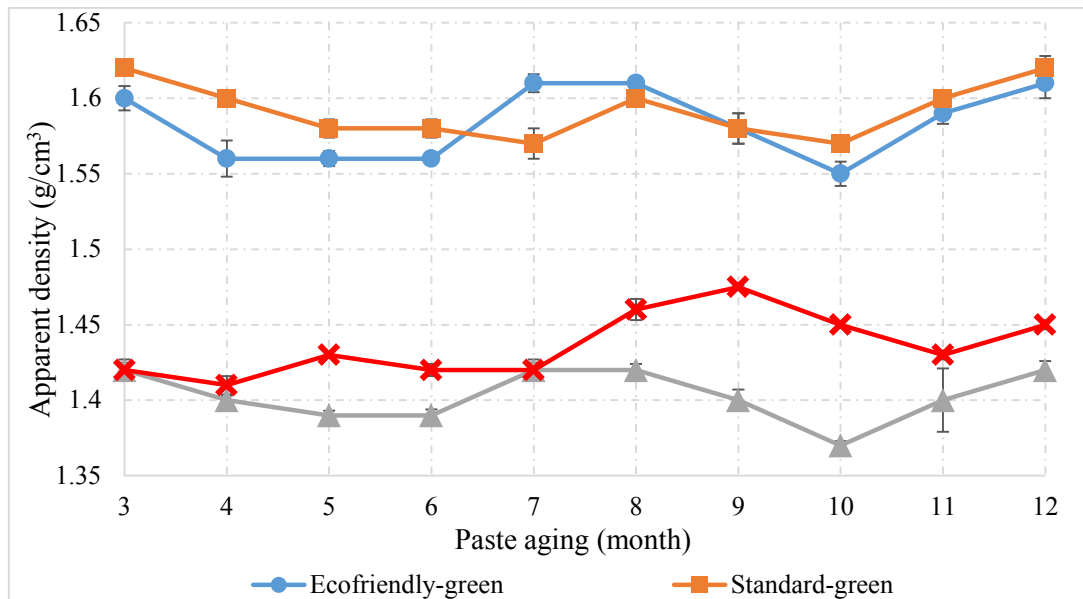
$$\rho = \frac{UA}{Il} \quad (2)$$

where:  $\rho$  Electrical resistivity ( $\Omega m$ )  
 $U$  Mean voltage drop (V)  
 $A$  Cross-section of the sample ( $m^2$ )  
 $l$  Distance between electrodes (m)  
 $I$  Electrical current through the sample (A)

## 3. Results and Discussion

### 3.1. Apparent Density

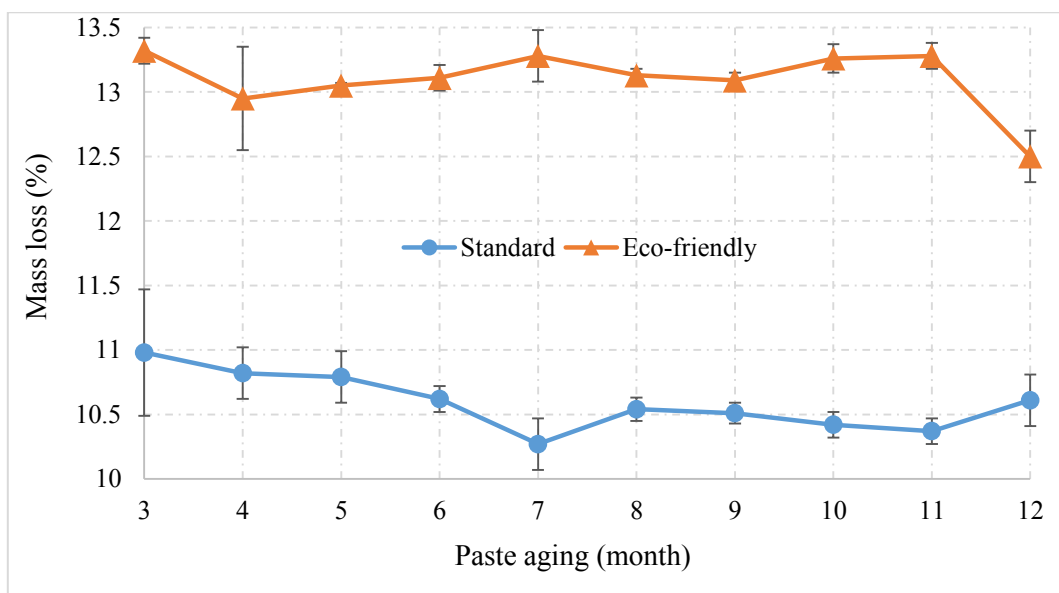
The effect of paste aging on its green and baked apparent density is shown in Figure 2, for standard and eco-friendly ramming paste. The apparent densities present fluctuations that do not exceed  $0.06 \text{ g/cm}^3$ . These fluctuations could be explained by the inhomogeneity of the ramming paste, i.e. distribution of the particle size in a sample. Moreover, no consistent trends toward increasing or decreasing apparent density over paste aging could be observed. Therefore, it can be concluded that the aging of the standard and the eco-friendly ramming pastes does not affect their green and baked densities.



**Figure 2. Evolution of the green and baked apparent densities versus the paste aging for standard and eco-friendly ramming pastes.**

### 3.2. Mass Loss

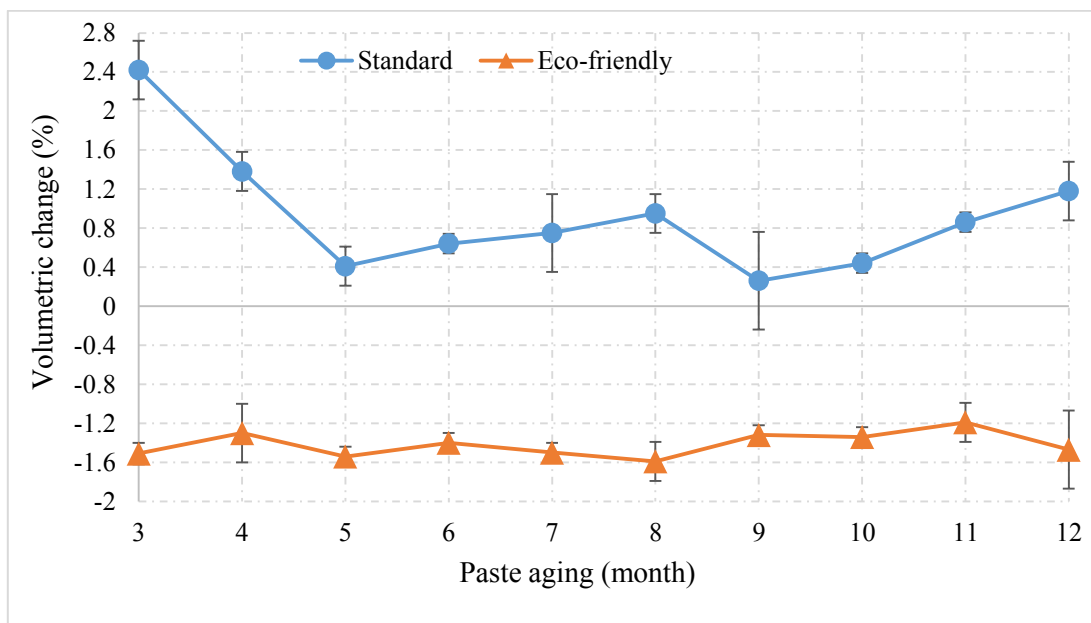
Figure 3 shows the evolution of the mass loss versus paste aging, for standard and eco-friendly ramming pastes. The mass loss was calculated according to ISO 20202:20 standard. For the eco-friendly ramming paste, the mass loss fluctuates around 13.2 % during the first nine months. Afterward, the mass loss decreases to 12.5 % in the last month. In the case of the standard ramming paste, its mass loss decreases during the first five months before stabilizing around 10.5 %. Hence, the aging of the standard and the eco-friendly ramming pastes decreases marginally their mass loss. The mass loss values of the standard paste samples are consistent with those obtained by St-Arnaud et al. [2, 3] and Orangi et al. [12]. It is also observed that the mass loss of the eco-friendly paste is higher than that of the standard paste. This would be related to the difference of the binder used in each paste.



**Figure 3. Evolution of the mass loss versus paste aging for standard and eco-friendly ramming pastes.**

### 3.3. Volumetric Change

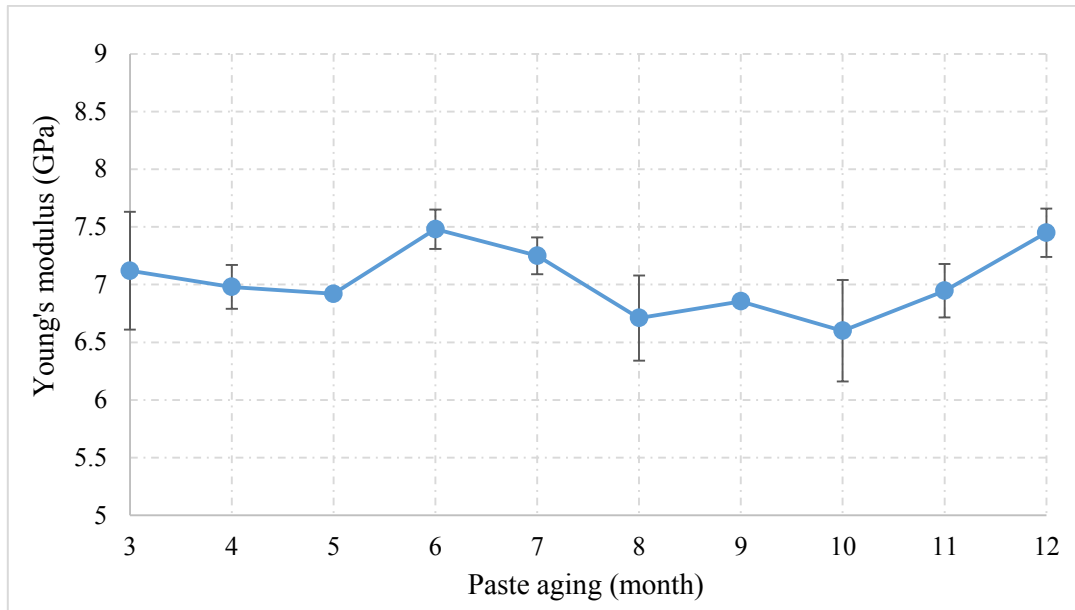
The volumetric change is calculated by dividing the difference of volume between the baked state and the green stage by the volume of the green state. The results of volumetric change value versus paste aging are presented in Figure 4, for standard and eco-friendly ramming paste. As seen in this graphic, the volumetric change of the standard paste decreases from 2.4 % to 0.4 % during the first two months of the study. Although the fluctuation of the volumetric change after the age of five months, it remains lower than that experienced during the first two months of the study. Thus, the aging of the standard paste decreases its volumetric change. In regards to the eco-friendly ramming paste, its volumetric change is nearly constant from the age of three months to that of twelve months. Hence, the eco-friendly paste aging does not influence its volumetric change. Nevertheless, these results reveal a crucial point, which is the shrinkage of the eco-friendly paste after baking (negative volumetric change). Such shrinkage could increase the risk of metal infiltration in the pot, which could be detrimental for the performance of the pot.



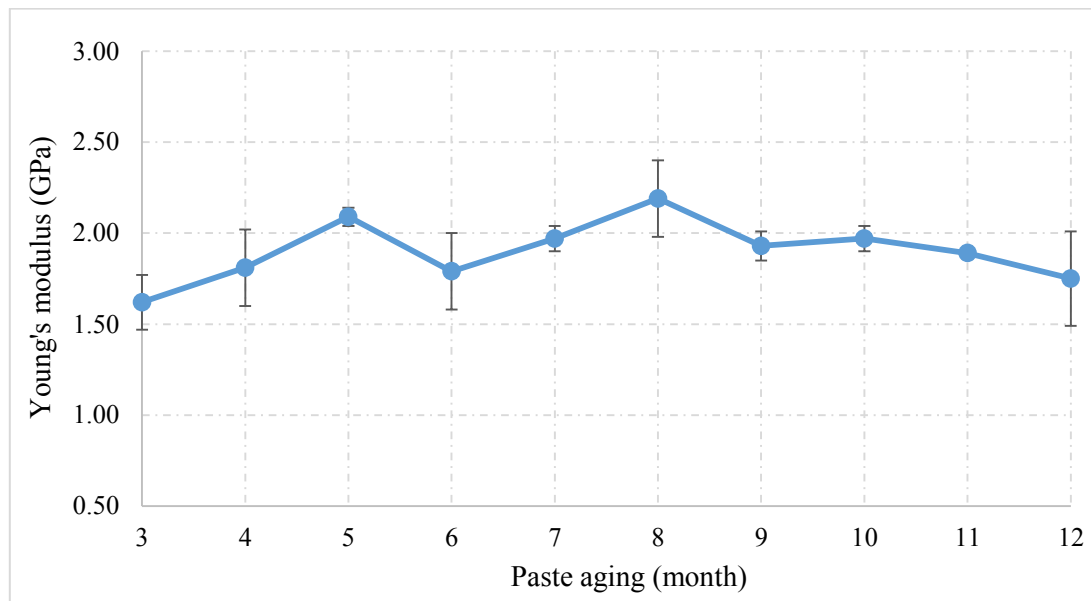
**Figure 4. Evolution of the volumetric change versus paste aging for standard and eco-friendly ramming paste.**

### 3.4. Young's Modulus

The evolution of Young's modulus versus the paste aging for standard and eco-friendly paste are given respectively in Figures 5 and 6. The Young's modulus of the standard paste samples fluctuates between 6.5 GPa and 7.5 GPa, whereas that of the eco-friendly paste varies between 1.6 GPa and 2.3 GPa during the ten months of the study. These fluctuations could be attributed, among others, to a slight misalignment of extensometers or the heterogeneous structure of the material. Thereby, it may be concluded that the aging of the standard and the eco-friendly ramming pastes has no effect on their Young's modulus. On the other hand, Young's modulus values of the standard paste are higher than those obtained by St-Arnaud et al. [2, 3]. This would be explained by the difference of the method used to compact the samples.



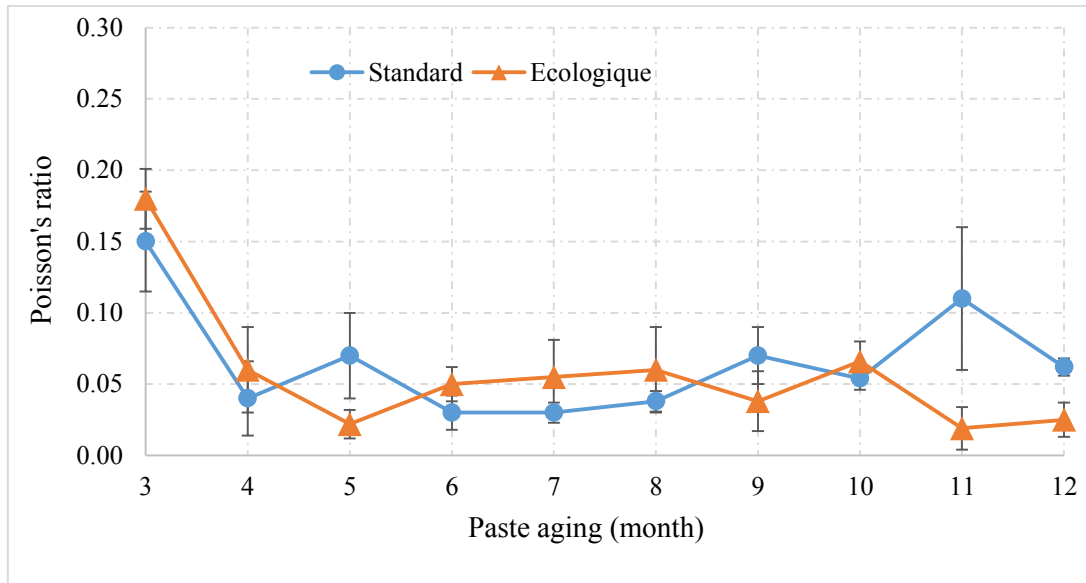
**Figure 5. Evolution of Young's modulus versus paste aging for the standard ramming paste.**



**Figure 6. Evolution of Young's modulus versus paste aging for the eco-friendly ramming paste.**

### 3.5. Poisson's Ratio

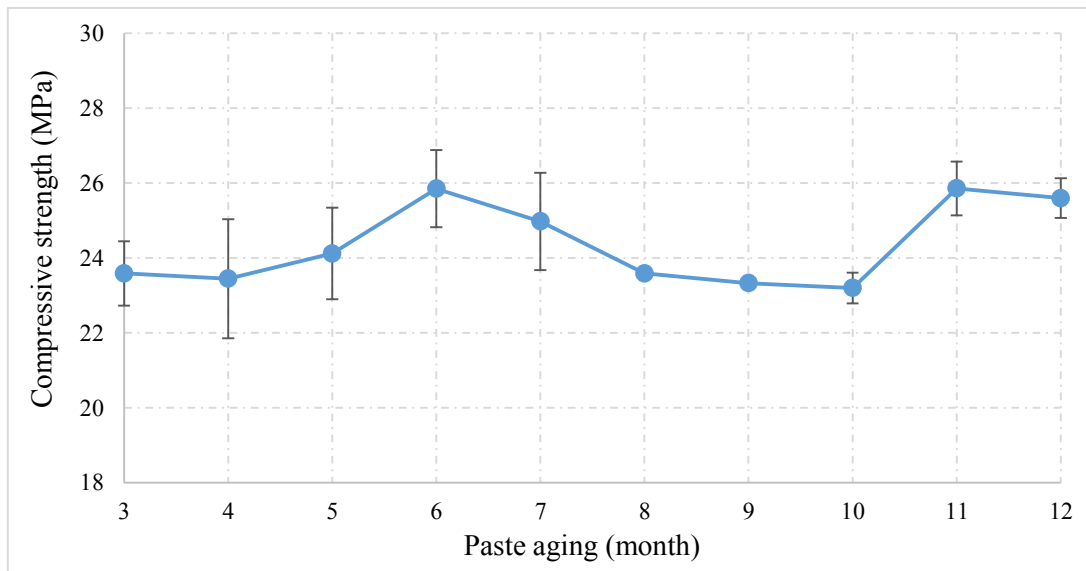
Poisson's ratio for both pastes, shown in Figure 7, decreases of around 67 % from the age of three months to that of four months. During the following nine months, this coefficient fluctuates between 0.02 and 0.06 for both pastes, except for the value obtained in the 11<sup>th</sup> month of the standard paste. Based on these results, it may be concluded that the aging of the standard and the eco-friendly ramming paste decreases their Poisson's ratio.



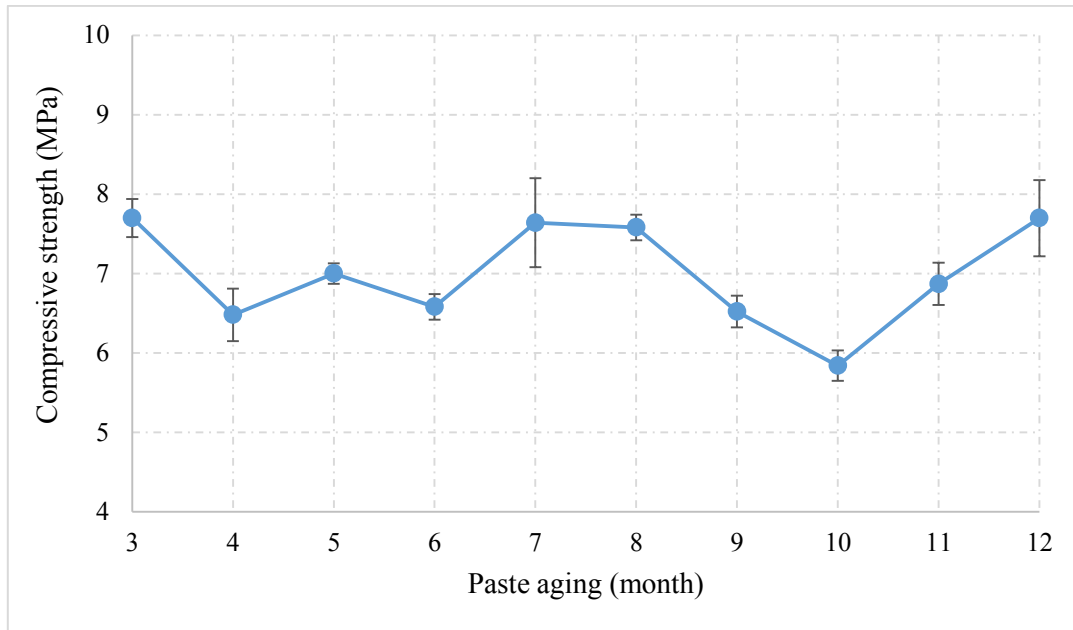
**Figure 7. Evolution of Poisson's ratio versus paste aging for standard and eco-friendly ramming paste.**

### 3.6. Compressive Strength

The aging effect on the compressive strength for standard and eco-friendly ramming pastes are presented respectively in Figures 8 and 9. It seems that the compressive strength, of both pastes, is not affected by their aging since the curves do not present any trends toward increasing or decreasing over the paste aging. As shown, the compressive strength values of the standard paste are three times higher than those of the eco-friendly one. This relatively low compressive strength of the eco-friendly ramming paste could lead to the initiation of cracks at the peripheral seam, which could in turn lead to the infiltration of liquid aluminium into the lining.



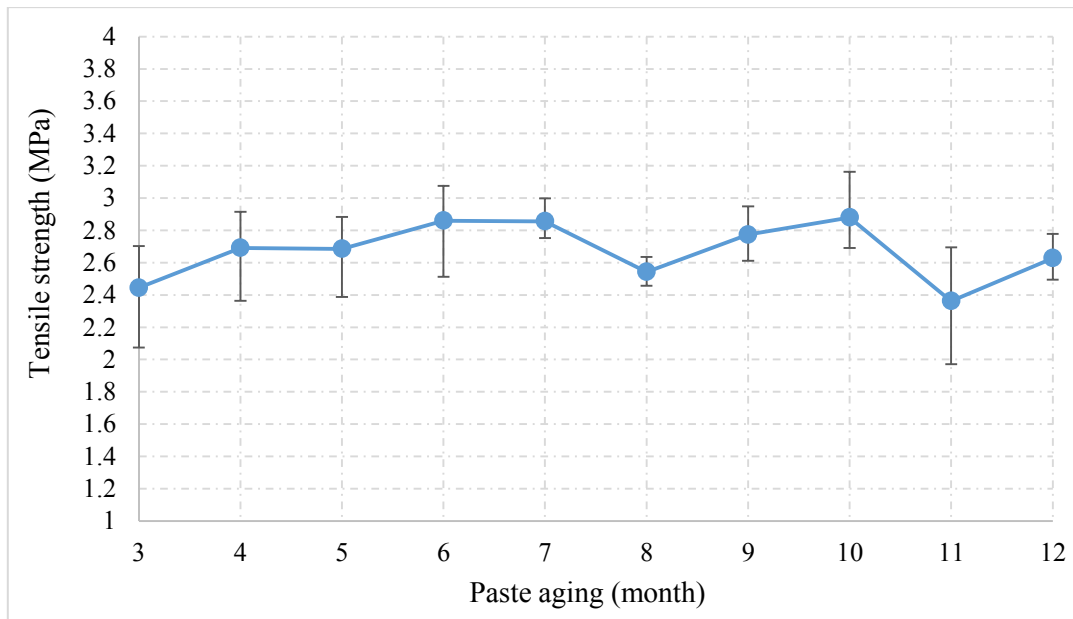
**Figure 8: Evolution of the compressive strength versus paste aging for the standard ramming paste.**



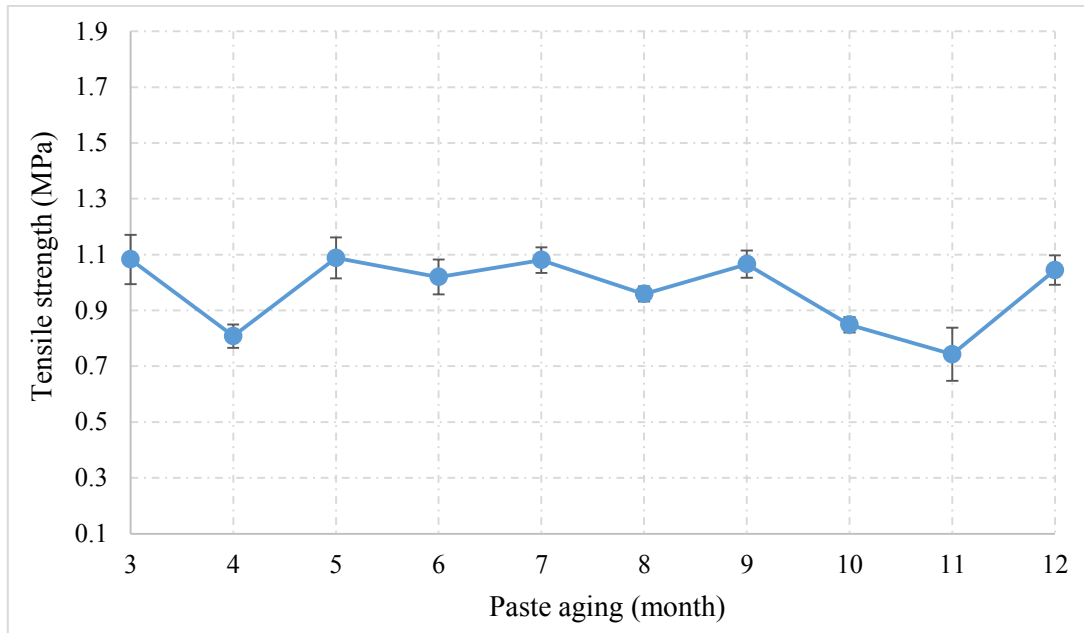
**Figure 9: Evolution of the compressive strength versus paste aging for the eco-friendly ramming paste.**

### 3.7. Tensile Strength

The evolution of tensile strength versus paste aging for standard and eco-friendly ramming paste is presented in Figures 10 and 11, respectively. As observed, the tensile strength values of the standard paste fluctuate between 2.4 MPa and 2.8 MPa, whereas those of the eco-friendly paste vary between 0.7 MPa and 1.1 MPa. Such low variations combined with the absence of a clear trend in the evolution of the tensile strength of both pastes suggest that pastes aging does not affect their tensile strength.



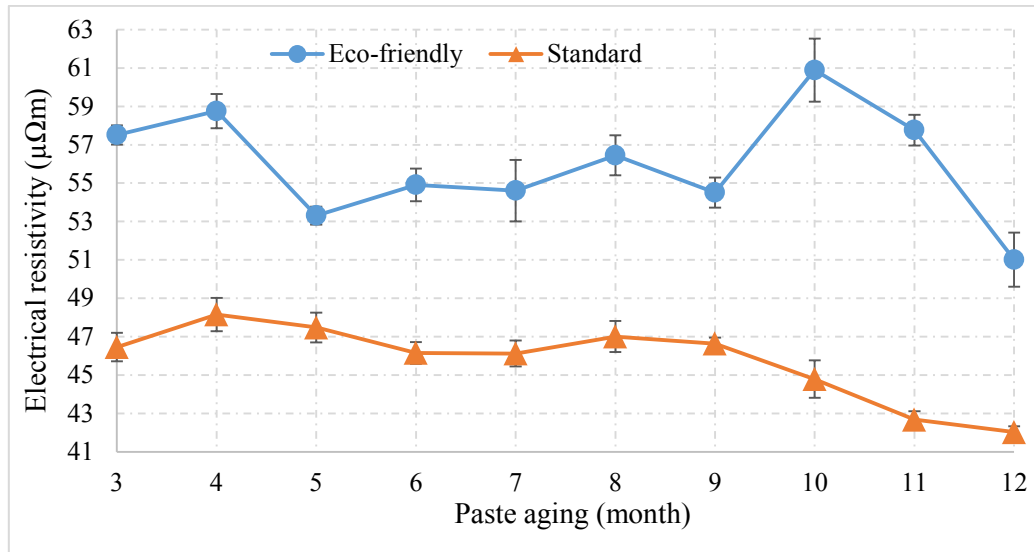
**Figure 10. Evolution of the tensile strength versus paste aging for the standard ramming paste.**



**Figure 11. Evolution of the tensile strength versus paste aging for the eco-friendly ramming paste.**

### 3.8. Electrical Resistivity

The results of electrical resistivity values versus paste aging are shown in Figure 12, for standard and eco-friendly ramming paste. Regarding the eco-friendly paste, the electrical resistivity values fluctuate between  $61 \mu\Omega.m$  and  $51 \mu\Omega.m$  during the ten months of the study. These fluctuations were found to be associated with the variations of the samples' density. Thus, the aging of the eco-friendly paste does not influence its electrical resistivity. For the standard ramming paste, its electrical resistivity decreases from the age of 4 months to that of 12 months, from roughly  $48 \mu\Omega.m$  down to  $42 \mu\Omega.m$ . Comparing the evolution of the electrical resistivity to that of the density, shows no accordance between those two properties. Hence, it could be concluded that the aging of the standard ramming paste decreases its electrical resistivity.



**Figure 12. Evolution of the electrical resistivity versus paste aging for the standard and the eco-friendly ramming pastes.**

#### 4. Conclusions

The main objective of this work was to study the effect of the paste aging on its physical, mechanical and electrical properties. For this purpose, two pastes were used: a standard and an eco-friendly ramming paste. During a period of 10 months, ranging between the third and the twelfth month of the paste aging, samples were fabricated using a new continuous compaction method developed within the MACE<sup>3</sup> Research Chair at Laval University. Density, mass loss, volumetric change and electrical resistivity of these specimens were measured. Compression and Brazilian tensile tests were carried out on the samples in order to assess their Young's modulus, Poisson's ratios, compressive and tensile strengths. The results showed that the aging of the standard paste decreases its mass loss, volumetric change, Poisson's ratio and electrical resistivity. However, the age of this paste does not seem to influence its green and baked density, Young's modulus, compressive and tensile strength. Concerning the eco-friendly paste, it was shown that the aging decreases its mass loss and Poisson's ratio. Whereas, the green and baked density, volumetric change, electrical resistivity and mechanical properties (Young's modulus, compressive and tensile strength) do not seem to be affected by the paste aging.

The results also suggest that the use of the eco-friendly ramming paste, studied in this work, could increase the risk of liquid infiltration into the lining. This is related to its shrinkage after baking (high mass loss and negative volumetric change) as well as its lower mechanical properties (Young's modulus, compressive and tensile strength) compared to standard ramming paste.

#### 5. Acknowledgments

Authors gratefully acknowledge the financial support of Alcoa Inc., the Natural Sciences and Engineering Research Council of Canada. A part of the research presented in this paper was financed by Fonds de Recherche du Québec-Nature et Technologies (FRQNT) by the intermediary of the Aluminium Research Centre-REGAL. The authors would also like to extend their appreciation to Guillaume Gauvin and Hugues Ferland for their technical support.

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