CB01 - Thermo-Mechanical Characterization of Multilayer Clean Ramming Paste Joint

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Abstract

The main carbon components of the Hall-Héroult electrolysis cell are cathodes and anodes. Cathode blocks are arranged so that a gap is left between them to allow their expansion at high temperature. These gaps are filled by ramming paste to prevent infiltration of the liquid metal during cell operation. The ramming paste is a carbonaceous material, which is mainly composed of anthracite and graphite, and a coal tar pitch (CTP) binder. More precisely the binder is obtained by distillation of coal tar, which is a by-product of the cokefaction of coal. CTP contains Polycyclic Aromatic Hydrocarbons (PAH), being potentially carcinogenic. For the health and safety reasons, new generation of ramming pastes, denoted as clean ramming pastes, are developed without the use of coal-tar-pitch.

Properties of ramming paste such as mechanical strength, rammability and density determine if they are acceptable for cell construction. For instance, the density after compaction can greatly influence the baked density and the thermomechanical properties of the ramming paste in the cell. To reveal the relationship between density and other properties such as the compressive strength, volume change and mass loss, an experimental investigation was performed at both industrial and laboratory scales. Different levels of compaction were used to obtain targeted densities. The samples were characterized during and after baking by thermogravimetric analysis and mechanical tests.

Keywords: Hall-Héroult process, clean ramming paste, thermomechanical characterisation.

1. Introduction

The Hall-Héroult cell consists of a metallic shell, refractory lining and a significant proportion of carbonaceous materials, such as graphitized cathodes. The graphitized cathodes constitute the top layer of the bottom of the cell which is directly in contact with molten metal and contains it. The cathode blocks are arranged so that a gap of a certain thickness is intentionally left between them to accommodate cathode expansion during cell operation. The gaps are located between the cathodes themselves and between the cathodes and the inner wall of the electrolysis cell [1]. These gaps must be filled with a carbonaceous material, called the ramming paste. The role of the ramming paste is to prevent the infiltration of liquid metal or cryolite into the cell lining and to absorb the expansion of the cathodes during the heat-up of the electrolysis cell [1].

For many years, the conventional ramming paste, with CTP binder, has been used in cell construction and exhibited suitable mechanical and physical properties [2]. Polycyclic Aromatic Hydrocarbons (PAH) can be found in big proportion in the conventional ramming paste, basically due to the presence of CTP [3]. The PAHs are known to be harmful for health, having also an

important noxious impact on the environment [2]. To mitigate these negative effects, Eco-Friendly or Clean ramming pastes have been developed and used in cell construction for a while. [3]. The binder in the Clean ramming pastes is basically biomass-based [2]. Although different types of Clean ramming pastes are available on the market and are being used in industrial scale [3], little information can be found in the literature on their exact chemical composition and production process. Even less information is found in the literature regarding the performance of Clean ramming pastes in electrolysis cell and this aspect is still at an investigation stage [3]. Seemingly, the physical and mechanical behavior of Clean ramming pastes in electrolysis cells and their impact on the lifetime of the cells is not well known. A failure, caused by an improper ramming paste, may cause premature loss of the electrolysis cell, resulting in significant economic loss [1]. Thus, generation of knowledge aiming at better understanding of thermomechanical and physical properties of the Clean ramming paste is of great interest for the industry.

In addition to the chemical composition, the ramming process of the paste can also influence the thermo-mechanical behavior of the ramming paste in the joints between cathode blocks [4]. The long experience of using conventional paste has made it possible to develop techniques and standard methods for quality control of the ramming paste, allowing viable performance of the cells [5]. As the type and the nature of the Clean ramming paste is quite different from those of the conventional ones, further investigations are required to establish best practice to achieve suitable results in the cell with high level of confidence.

The laying of the ramming paste is performed, according to the design of the cell, by depositing multiple layers of paste which are compacted successively [1]. The amount of the paste deposited for each layer depends on the size of the gap to seal. The compaction of each layer is controlled by several parameters which depend on the type of ramming equipment [6]. For instance, for the machines using vibration compaction the parameters such as frequency, applied load or the number of passages could be considered as important parameters to control the process. The compaction is carried out until a desired green density is obtained. The density is usually characterized by coring a sample from the compacted joint or by using non-destructive techniques to assess its hardness. The ultimate objective is to provide adequate mechanical resistance and good adhesion between the paste and gap walls while allowing the paste to accommodate the expansion of the cathode blocks [1]. Indeed, through different compaction sequences, a homogeneous density is also sought.

Due to the relatively new usage of the Clean ramming pastes in the cell construction, it could take years before revealing their long-term performance in the cell. However, laboratory tests combined with the knowledge acquired on the conventional pastes may help setting the right parameters to achieve the best performance. Indeed, these parameters could certainly be adjusted as the field data will be generated in the coming years. In the meantime, the laboratory tests can generate insights for better understanding the behaviour of the Clean ramming pastes, namely their rammability, density gradient and mechanical strength. For instance, the smelters adjust the ramming process to meet the density recommended by the suppliers to meet the QC requirements. In this paper, we present the experimental results encountered with characterization of a commercial Clean ramming paste obtained by industrial compaction process. Density distribution of the compacted sample was revealed and a series of laboratory samples, exhibiting the same density range, were prepared for further characterization.

2. Methodology

2.1. Industrial Scale Samples

To examine the density distribution obtained by industrial compaction of the Clean ramming paste, a representative mold for the peripheral seal of the cell was designed. The dimensions of the mold, as approximately shown in Figure 1, was chosen in a way that the mold could fit in the peripheral joint of the cell. Once the mold was fitted in the joint, the paste compaction was performed using the same equipment as used in cell construction and according to the normal practice; i.e. the same load, compaction frequency and vibration time. The mold was made so that it could be removed from the location where it was compacted. As shown in Figure 1, the width of the mold is of the same width as the space between the cathode block and refractory wall. The mold was made of aluminium to allow scanning the whole sample by X-ray tomography, without removing the compacted paste from the mold.

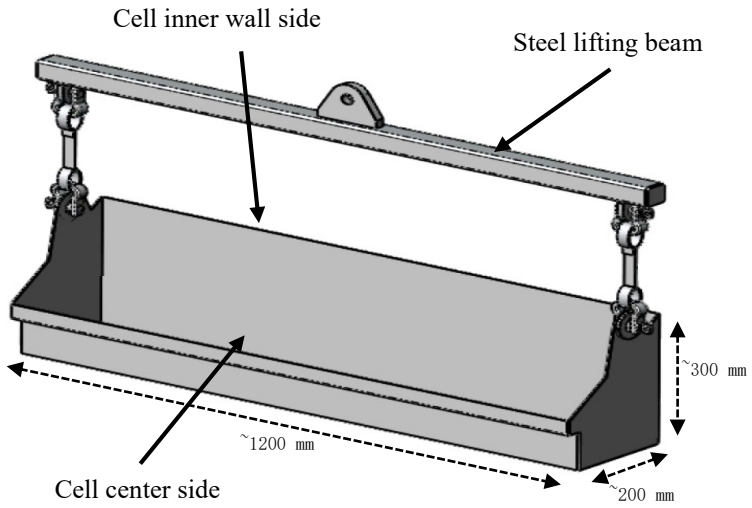


Figure 1. Schematic representation of the mold used for compaction in industrial scale.

During the sample production, the mold was placed in the peripheral joints. Then, it was filled with clean ramming paste for a first layer, and it was compacted using the industrial compactor. In the same way, the second layer was compacted. Figure 2 shows the compacted sample once the mold was removed from the cell. The sample was scanned with X-ray by the CT-scan equipment (Figure 3). The scan of this sample allowed the observation of the density variation within the sample.

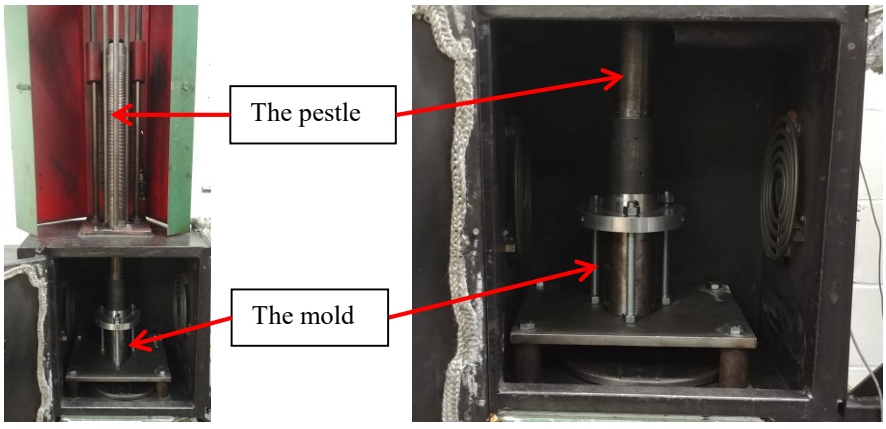
Figure 2. The industrial scale sample of the peripheral joints.

Figure 3. The sample in the CT-scan.

2.2. Laboratory-Scale Samples

To investigate the effect of density on the properties of the compacted paste, we produced samples in laboratory scale with different densities. The range of the density in the lab-scale samples was chosen based on the range of the density observed in the industrial-scale sample; i.e. (1.50-1.53) g/cm^3, (1.60-1.63) g/cm^3 and (1.70-1.73) g/cm^3.

The lab-scale samples were manufactured with a compactor adapted to NF P 94-093 standard [7]. Compaction was carried out using a cylindrical hammer, with a diameter of 50 mm and a weight of 6.30 kg. The hammer is lifted by an automated mechanical system to a height of 50 mm, and released on the paste in the cylindrical mold. Figure 4 shows the compactor: (a) is an overview of the compactor and (b) is the cylindrical mold used to make the samples. The impact of the hammer causes the densification of the paste in the mold. The samples obtained by this method have a diameter and a height of 50 mm. The variation in density depends on the number of the hammer hits on the sample. We adjusted the number of hits to obtain the targeted densities. The different target densities of (1.50-1.53) g/cm^3, (1.60-1.63) g/cm^3 and (1.70-1.73) g/cm^3 were achieved by 15, 40 and 200 hits, respectively referred to compaction 1, compaction 2 and compaction 3. It is worth mentioning that the weight of the samples was different for different compaction modes since we tried to keep height of the sample's constant.



(a) (b)

Figure 4. The compactor used for making the samples.

The samples were baked according to ISO 20202: 2004 standard method [8]. This baking method provides the heating conditions comparable to the heating of cathodes and rammed joints during electrolysis cell start. The baking conditions were also chosen such that the carbon samples are not exposed to oxidizing environment. A heating rate of 35 °C/h was used to heat the sample from 20 °C to 500 °C and then the heating rate was increased to 100 °C/h for the temperature range of 500 °C to 1000 °C. When the temperature reached 1000 °C, a soaking time of 2 h was imposed. Figure 5 represents the heating cycle of the samples.

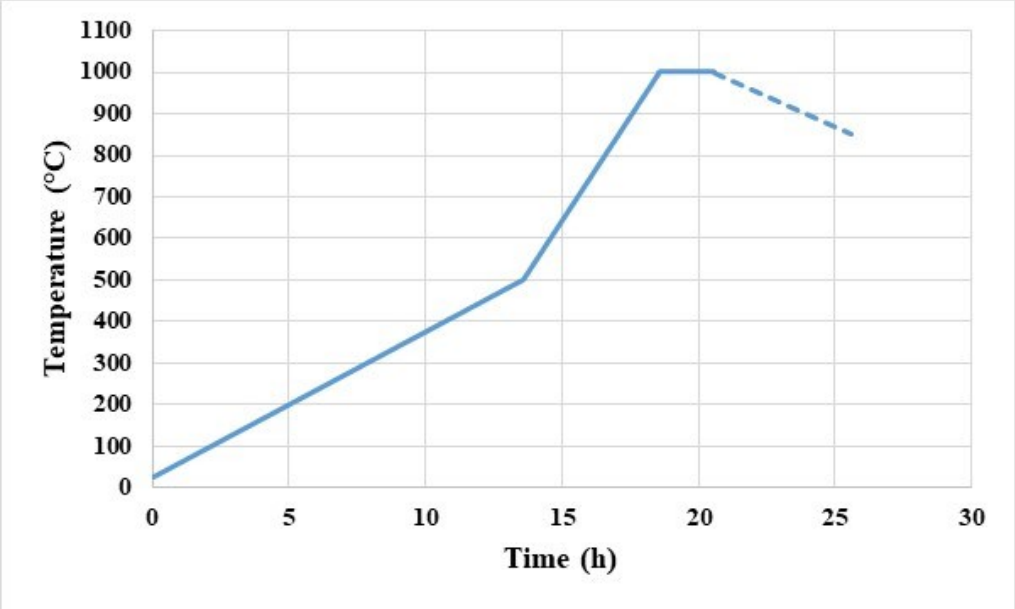


Figure 5. Baking curve.

The apparent density of each sample was measured according to the ASTM D5502-00 standard method [9]. The geometric measurements of the samples were taken before and after baking to calculate their volume change. Measurements were taken using a caliper. Four measurements of heights and eight measurements of diameters were performed and the average value of each was considered for the density calculations. The samples were then weighted, and their apparent density was calculated.

After baking, the ramming paste samples might shrink or expand in different heating stages. However, in this work, only the final volume was considered and an attempt to corelate it with mechanical properties was made. The percentage of volume change was obtained by dividing the value of the volume change to the initial volume, according to the Equation 1. This parameter is referred as “shrinkage”.

$$\Delta V\% = \frac{V_{baked} - V_{green}}{V_{green}} \times 100 \quad (1)$$

Where:

V_{green} Volume of the green sample (cm^3)

V_{baked} Volume of the baked sample (cm^3).

The thermogravimetry analysis allowed continuous recording of the mass loss as a function of temperature. The tests were carried out based on the ISO 12988-2: 2004 standard method [10]. The sample was kept under an inert nitrogen atmosphere to prevent oxidation. The sample was connected to a balance and a thermocouple was placed over the sample to monitor the temperature. The weight and temperature were recorded with data logging software (Figure 6).

The compressive tests were carried out at room temperature using a hydraulic press model MTS 32, according to the standard method ASTM C695-91 [12], and using a loading rate of 1 kN/s.

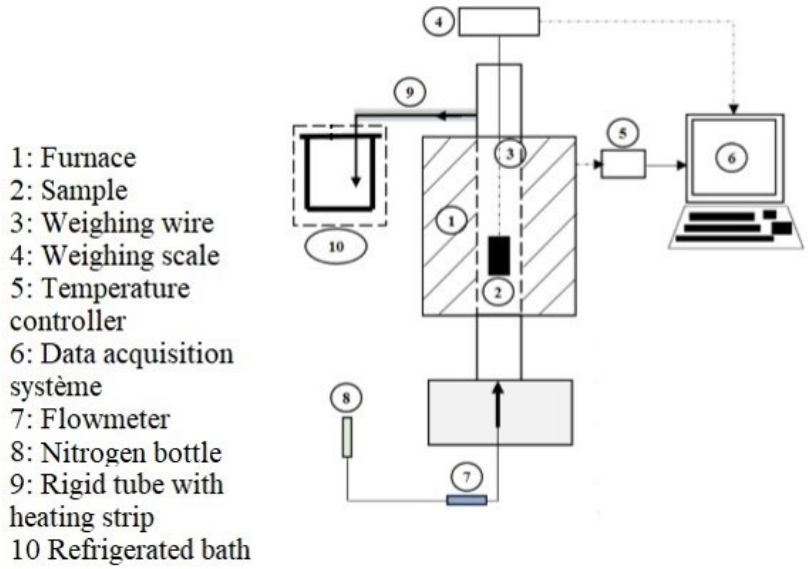


Figure 6. Schematic representation of thermogravimetry equipment [11].

3. Results and Discussion

3.1 Sample Scan

First, the representative industrial-scale sample of the peripheral joint was scanned lengthwise in the CT-scan. The aluminium mold prevented any deformation or disintegration of the sample during handling. Due to the limited length of the sample, some edge side effects were also observed. Thus, the sample could be divided into three parts, as it is presented in Figure 7. The central part was considered as the representative sample without edge effects.

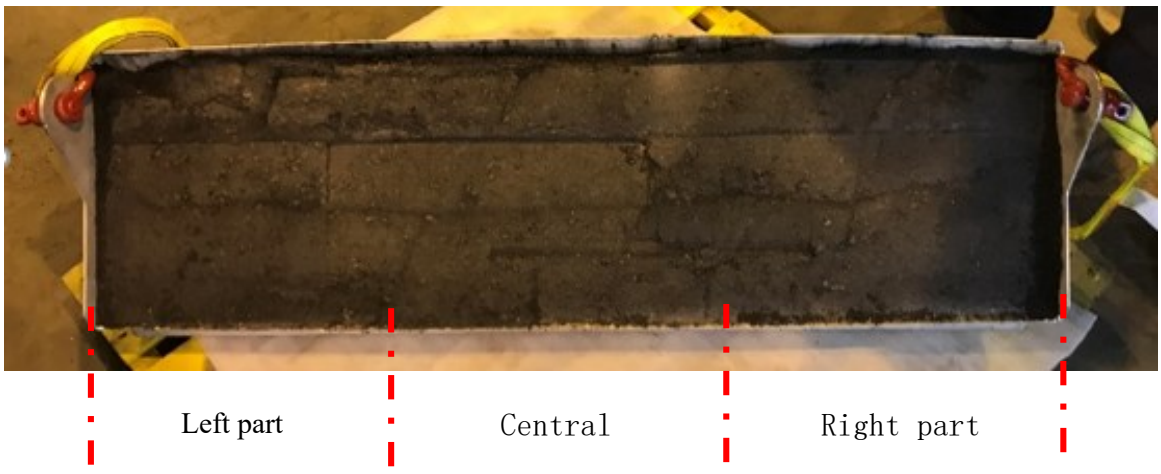


Figure 7. The different parts of the sample.

Figure 8 presents the cross-section images obtained by the CT-scan of the three different parts of the sample. Images (a), (b) and (c) correspond respectively to the left side, the center, and the right side of the sample. The gray scale corresponds to the CT numbers; black areas indicating voids, dark grey areas indicating low density and pale grey areas indicating high density regions.

We can easily observe, on the images (a) and (c), the boundary between the first layer and the second layer, as it is indicated by the red arrows. In the image (b) the boundary line between the two layers is almost invisible. Furthermore, the top layer seems to be less dense than the bottom layer and this difference is much more evident for the left and right parts of the sample. This difference in density is most likely due to the attenuation of the edge effect in the central part. In other words, the compaction is less effective at the vicinity of the mold walls. We focused our further investigation on the central part of the sample, since there was no edge effect.

The area designated by the yellow arrows is the low-density area, as characterized by the CT numbers. This zone can be seen in all three parts, but it is denser in the central part, compared to the side parts. The presence of this low-density zone is most likely due to the effect of the vertical mold wall, attenuating the compaction process. It is worth mentioning that such a difference of density could also be present in the cell joint since the cathode could have the same effect as the mold wall. However, this aspect has not been investigated yet and it remains as a hypothesis which deserves more investigation in the future.

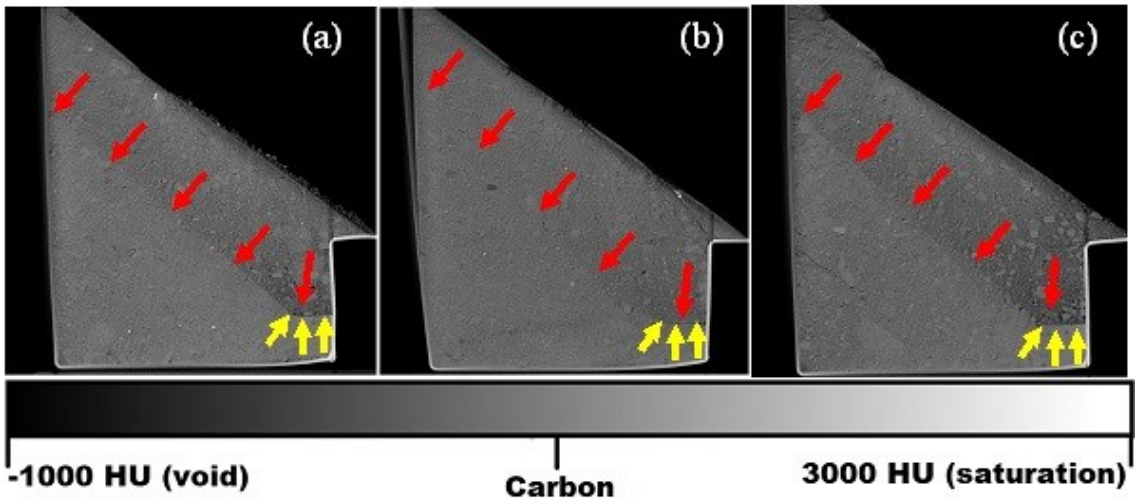


Figure 8. Scan images for visual inspection: (a) left side, (b) center side and (c) the right side of the sample.

The density distribution in the central part of the sample was quantified, based on the CT-scan results. The detailed process for analyzing CT-scan data have been presented elsewhere [13]. The density mapping throughout the central part of the sample revealed four different areas, as represented in Figure 9. The calculated densities are 1.68 g/cm^3, 1.65 g/cm^3, 1.62 g/cm^3 and finally 1.51 g/cm^3 corresponding to the zones 1, 2, 3 and 4, respectively. As it can be seen, the Zone 4 exhibits the lowest density, compared to the other zones, and the highest density was observed for zone 1.

3.2 Sample Characterization

During baking, the ramming paste undergoes physical changes due to different physico-chemical phenomena, resulting in density, volume and structural changes [5]. The volumetric change is due to the release of volatiles of the binder and due to the phase change of the paste [5]. The volume change is an important physical property of the ramming paste for the proper functioning of the electrolysis cell. Significant shrinkage can create a void between the paste and the cathode blocks, leading to metal and electrolyte infiltration and causing the premature stop of the electrolysis cell [1].

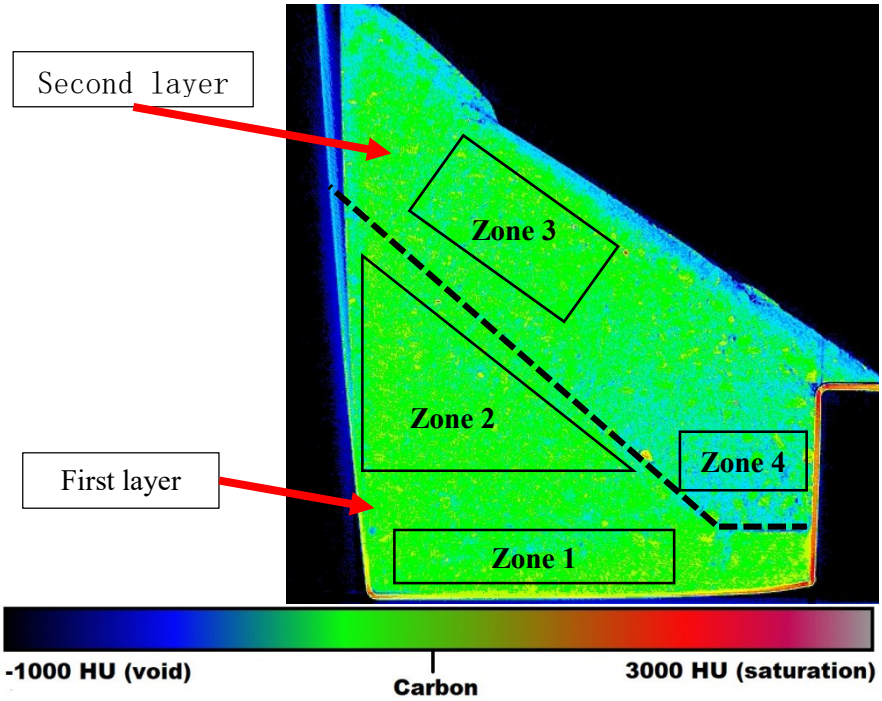


Figure 9. Different area of density in RGB.

Laboratory-scale samples were prepared with three compaction levels, as described in section 2.2. Figure 10 compares the average weight, volume and density for each series of samples. Figure 10 (a) shows the green and baked weight of the samples with different compaction levels. It is worth mentioning that the difference between the mass of the samples is due to the quantity of paste used to have the same target height. The mass loss for all samples was in the same range (12,3 % to 12,7 %), suggesting the mass loss is basically due to the thermal effect rather than to the compaction level.

Figure 10 (b) shows the average volume of the samples before and after baking. All samples shrunk after baking. For compaction 1 (low density) the shrinkage is 1.19 % and for the compaction 3 (high density), the shrinkage is 0.56 %. In other words, the higher compaction level results in a lower shrinkage.

Figure 10 (c) shows the green and baked density of the samples prepared at different compaction levels. The density of the samples increases from compaction 1 to compaction 3. However, the density ratio, defied as the change of density divided by the initial green density, was observed to be almost the same for all samples. For the three compaction levels, the density ratio was 11.71 %, 11.61 % and 12.24 %, respectively. The results show that the final baked density is directly related to the green density of the ramming paste, while the compaction level has not significant effect on the density ratio. This means that the baking process results in the same densification level on the samples, regardless of their initial green density (in the range of the densities studied on this work). Thus, the samples with higher green density result in higher baked density and the difference between the green density of the samples are not be mitigated by baking process.

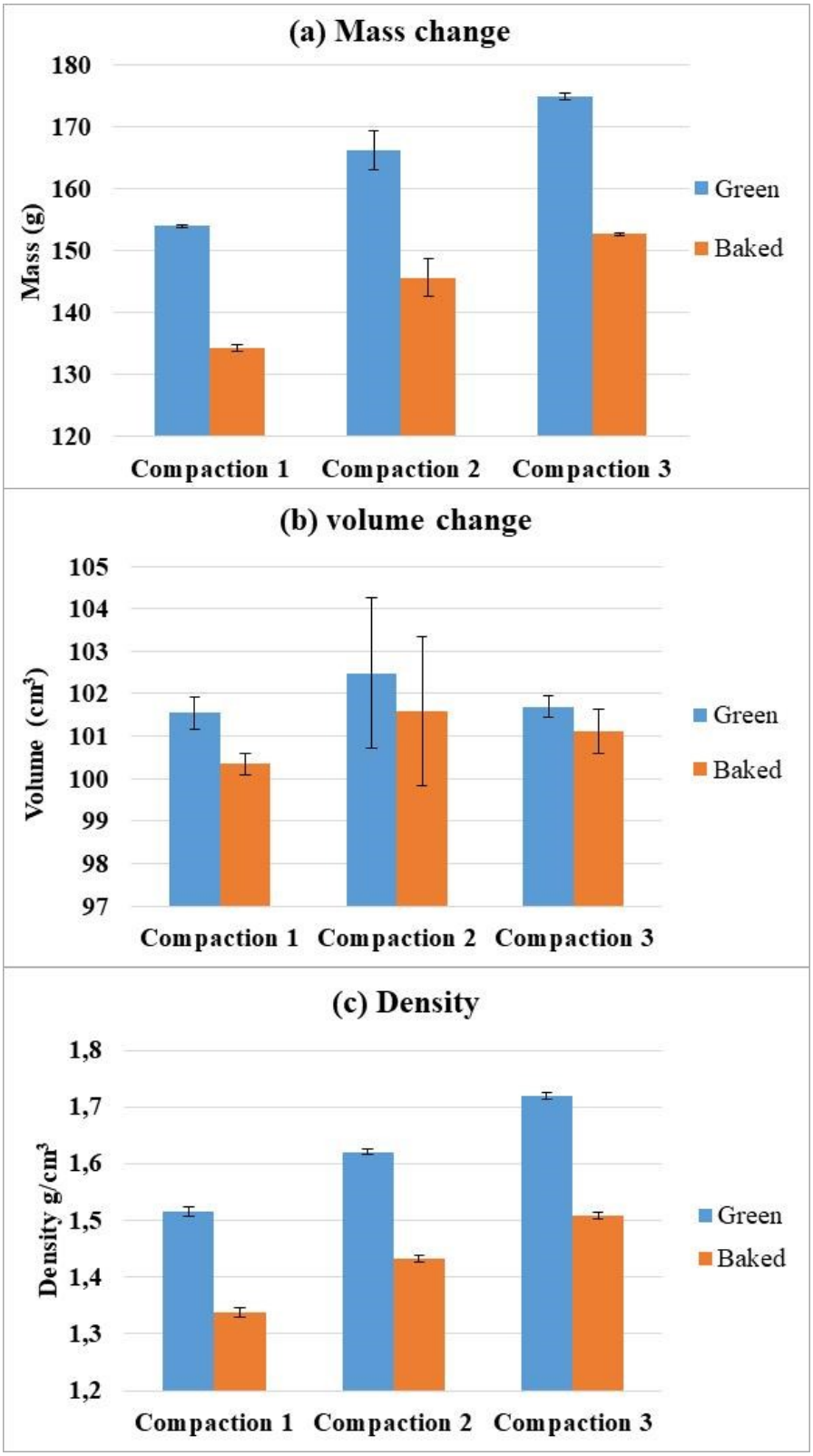


Figure 10. Clean ramming paste physical properties before and after baking: (a) green and baked weight, (b) volume after and before baking and (c) green and baked density.

The volume change as a function of density of the samples is shown in Figure 11. For each density range, four samples were prepared. It is observed that all samples underwent shrinkage in all density ranges. To verify if the difference between the three compactions is statistically significant, the student's statistical test was carried out. The difference between compaction 1 and 3 is significant with a P_{value} of 0.038. This means that the shrinkage of the ramming paste after baking would depend on its green density. So that the green density of the ramming paste could be considered as an effective parameter to achieve a desired level of shrinkage. Indeed, this data is a general observation related to the behaviour of the ramming paste which was baked without being confined. It is not possible to compare the volumetric change of the samples to that being occurred in the electrolysis cell, because the paste in the cell is confined and is exposed to external forces resulting from the expansion of cathodes.

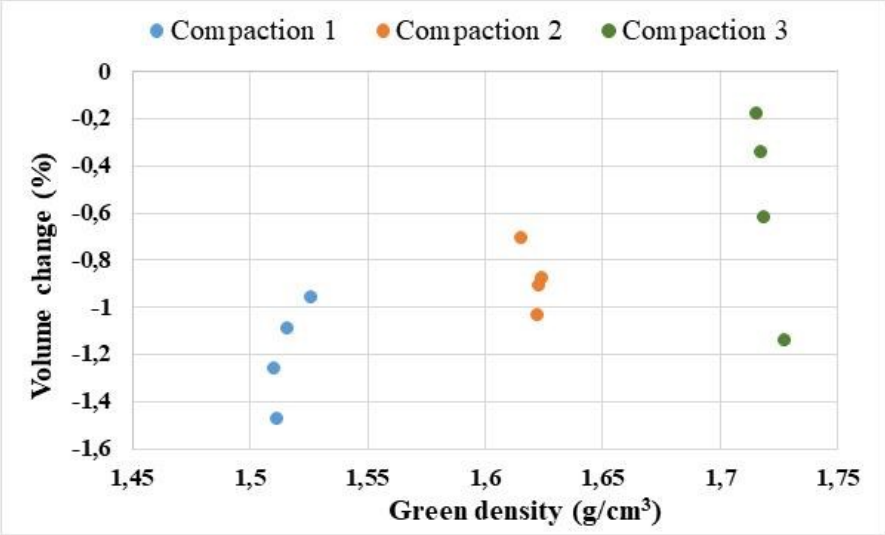


Figure 11. Volume change of the samples after baking.

3.3 Mass Loss

The mass loss of the ramming paste is primarily due to the volatiles coming out of the binder during baking. The anthracite/graphite aggregates do not undergo any loss since they were calcined before being used in the paste. To analyze the correlation between density and mass loss of the Clean ramming paste, two tests were performed. The first test is the measurement of the mass loss after baking, according to the ISO 20202: 20 standard method [8]. The second test consists on thermo-gravimetric analysis (TGA), based on ISO 12988 2: 2004 standard method [10]. The objective of the TGA was to observe the continuous mass loss of the sample as a function of temperature.

Figure 12 shows the mass loss of the samples after baking as a function of the density. The mass loss of samples with green density in the range of (1.50-1.53) g/cm^3 is between 12.5 % and 13.2 %, and those with a density in the range of (1.60-1.63) g/cm^3 exhibit a mass loss between 12 % and 12.6 % and finally samples with density in the range of (1.70-1.73) g/cm^3 showed a mass loss between 12.4% and 13.1 %. According to the student's statistical test there is no significant correlation between the mass loss and the density. The P_{value} between the compactions 1 and 2 was found to be 0.07 while that between compactions 2 and 3 was 0.89 and, finally, the one between compactions 1 and 3 was 0.88.

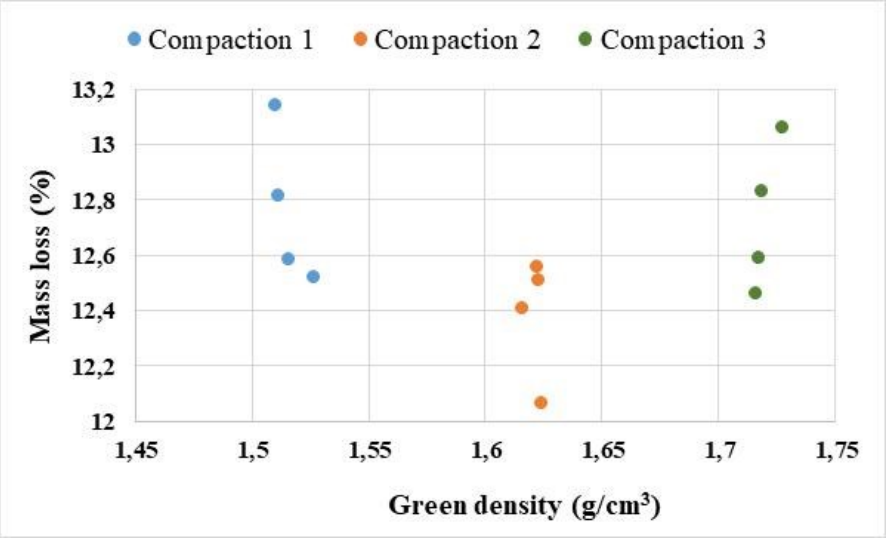


Figure 12. Mass loss after baking.

Figure 13 shows the TGA profiles for three lab-scale samples. The three curves give an idea about the kinetics of volatilization of additives and softeners which constitute the binder in the Clean ramming paste. The volatilization rate could be estimated from the local slope of each curve at different temperatures, which are very close to each other for all three samples. The mass loss of all samples starts at around 180 °C and stops at approximately 700 °C. Between 180 °C and 700 °C the trend of the three curves is quite similar. The slight differences might be due to the different proportions of aggregates and the binder in the samples. The rate of mass loss is maximum in the temperature range of (200 and 300) °C. It is significantly decreased beyond 300 °C and eventually vanishes beyond 800 °C. According to the TGA curves, the results show that the compaction level has no significant effect on the rate of mass loss.

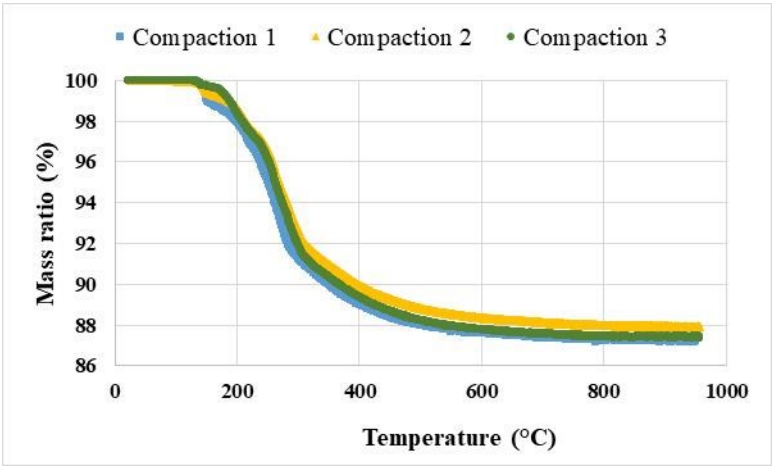


Figure 13. Thermogravimetry analysis.

3.4 Compressive Strength

During the cell heat up, cathode blocks undergo an expansion and apply a considerable force on the ramming paste. That is why it is important to characterize the mechanical strength of the ramming paste and to reveal any correlation between compaction level (density) and the mechanical strength. The compressive strength of the baked samples as a function of density is shown in Figure 14. The samples with highest density (compaction 3) exhibit compression strength twice as high as do the ones with lowest density. We should emphasize here that the

mechanical tests were performed on the cylindrical samples and the applied load was in the same direction as that of the ramming load. In the real pot situation, the load excreted by the cathode on the ramming paste is perpendicular to the direction of the ramming load. In order to get more representative data in future, a Brazilian mechanical test might be more appropriate where a diametric compressive force is applied along the length of the sample until failure occurs [14].

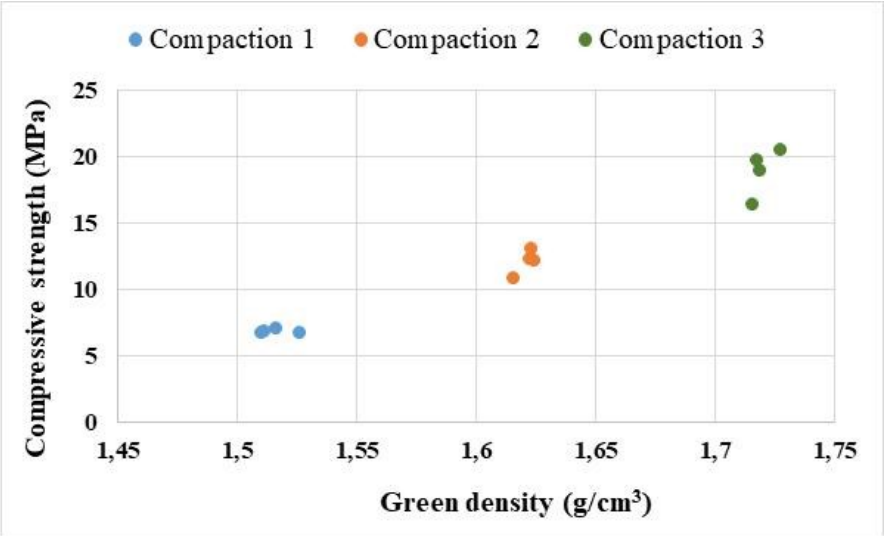


Figure 14. Compressive strength.

4. Conclusions

In this work we prepared a cell peripherical joint using a commercial Clean ramming paste and characterized its density gradient. A representative sample of the peripheral seam was compacted using an industrial compactor. The samples were then removed and characterized using X-ray CT-Scan and the density of the compacted paste was revealed in different zones of the joint. A range of density was observed at different locations of the joint.

The laboratory-scale samples were prepared by using three different compaction protocols to obtain different densities, all in the range of the densities observed at different zones of the industrial-scale sample. The laboratory samples were then baked and characterized to obtain their volume change and mass loss after baking as well as their mechanical strength. The results revealed that the mass loss is not affected by the green density and all samples exhibited the same mass loss ratio. The thermogravimetric analysis of the samples at different density ranges also showed that all samples, regardless of their green density level, exhibit similar mass loss ratio. The green density, however, was shown to significantly affect the volume change. Higher green density resulted in lower volume change. Surprisingly, the green density was shown to have no significant effect on the density change during baking, suggesting that the samples exhibit a same rate of densification for different green densities. The compressive strength of the studied Clean ramming paste was shown to increase significantly with increasing density.

5. Acknowledgment

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