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EVOLUTION OF THE THERMO-MECHANICAL PROPERTIES OF RAMMING PASTE FROM AMBIENT TO OPERATING TEMPERATURE IN A HALL-HEROULT CELL

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Abstract

The ramming paste behavior is a key parameter in the cell performance used for the aluminum electrolysis. This anthracite and coal tar pitch mixture bakes during the cell start-up and chemical transformations in the ramming paste are observed. The mechanical properties of the paste are related to these transformations and change with time and temperature during the cell start-up. This paper presents the methodology used to determine the evolution of the mechanical properties of ramming paste, using experimental conditions representative of a cell start-up. Experimental results for temperatures from ambient to 960°C are presented and the effects of the test conditions are discussed.

Introduction

In the aluminum industry, electrolysis cells are used to produce aluminum. During aluminum electrolysis, a large amount of electrical energy is consumed. In addition to the costs associated to this energy consumption, the electrolysis cells must be replaced after a limited period of time. To increase cell life and performance, the behavior of its components must be well known.

The electrolysis cell is made of a steel shell where refractory materials are added. The refractory materials are used to protect the metallic surface from the electrolytic bath and to minimize the heat losses. Figure 1 illustrates the structure of a complete aluminum electrolysis cell. The bottom surface of the cell, mainly made of prebaked carbon blocks, forms the cathode (or the cathodic plan).

The electric current needed for the aluminum electrolysis is provided to the cell via a bus bar and collector bar system. To seal the voids between the cathodes and between the cathodes and sidewall, a carbon paste is used. This paste consists of anthracite filler (aggregate particles) and a coal tar based binder and is rammed in the joints. This paste, also called ramming paste, is viscous and easily deformable [1].

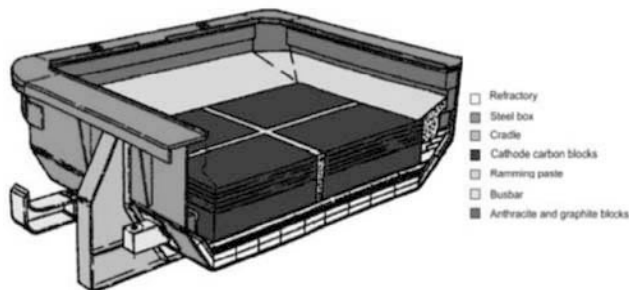


Figure 1: Typical structure of an aluminum electrolysis cell

During the electrolysis cell start-up, the cell is heated from ambient temperature to 600°C to 900°C (depending of the cell

technology), this reduces the thermal shock at bath addition. During this period, the paste initially green and highly deformable absorbs the thermal expansion of carbon blocks. As the paste bakes, chemical reactions occur and the paste becomes less deformable. The solidification of the binder occurs at temperatures above 500°C. When completely baked, the mechanical behavior of the paste is similar to the one of a carbon block.

As liquid bath and aluminum are above the cathode surface, the joints formed by the ramming paste are critical for the cell. Past experience has showed that bath or metal penetration in joints could be the origin of early cells failures. The evolution of the thermo-mechanical properties of the ramming paste during baking are consequently of practical importance to avoid early cell failures. These properties are influenced by the paste composition, apparent density and by the temperature and the heating rate. Finally, the confinement of the paste during lining preparation has also an important impact on the paste dilatation [2].

Many ISO standards have been developed to qualify the ramming paste [3]. These tests methods have been developed for green paste, completely baked paste and to determine the expansion/shrinkage upon baking. To avoid joint and cell failures, specific tests must be developed to quantify the evolution of the thermo mechanical properties of the paste during baking, using test conditions similar to those joints undergo during cell preheating. This paper presents the experimental approach used to study the evolution of the thermo mechanical properties of the ramming paste during cell startup.

Results and Discussion

Expansion/ shrinkage

A good ramming paste should have a net positive expansion to avoid the formation of a gap between the cathode blocks. If a gap occurs, the cathodic plan could be damaged by bath or metal infiltration. ISO methods [4,6] have been developed to determine the expansion / shrinkage of the paste. These methods are quite useful to qualify the ramming paste but the test conditions do not represent the ones met during the electrolysis cell start-up.

For the expansion / shrinkage test, the ISO method recommends to compact cylindrical samples of paste in a cylindrical steel crucible with repeated impacts made by a 6.35 kg cylindrical mass; 100 strokes / impacts are recommended at a rate of 1 impact/second. The sample size is 50 mm dia x 50 mm long and during the expansion / shrinkage test, the samples must be heated up to 980°C at a rate of 180°C/h [4].

The heating rate and the compaction level have an influence on the volumetric deformation of the paste. A well compacted ramming paste has a reduced amount of voids and less

gas can be trapped inside the material. In industry, the paste is rammed mechanically until a target density is reached. As the joints are relatively deep, the paste has to be rammed or compacted in many layers. If the paste is over-rammed, damage may be caused by a degradation of the aggregate particles. Consequently, a specific density must be reached in opposition to a specified number of strokes. On the other end, the heating rate is not constant in the cell over the entire cathodic plan and a single heating rate of 180 °C/h cannot describe adequately the thermo-mechanical behavior of the paste. The heating rate used during the tests must take different values to be representative of different joints inside the cell.

In this investigation, the compaction level and the heating rate were modified from the ISO standards to represent the conditions met during an electrolysis cell start-up and to determine the thermo-physical behavior of the paste in these conditions. For the tests, the paste was rammed with a device similar to the one prescribed in the ISO standard but the number of strokes was adjusted to meet the density measured in a real cell. The target density is between 1.627 to 1.630 g/cm³. Figure 2 plots the density as a function of the number of strokes for 170g of ramming paste.

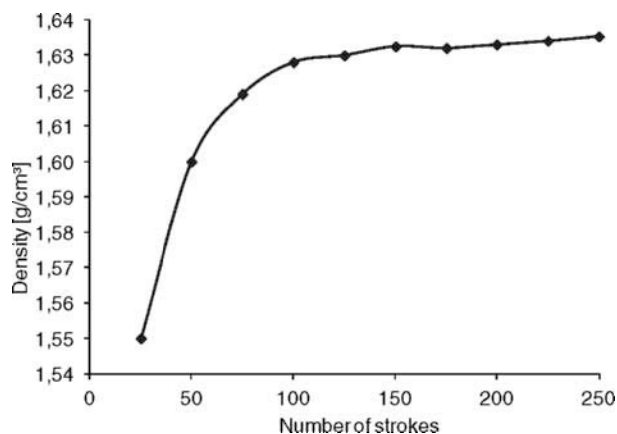


Figure 2: Paste density as a function of the number of strokes for 170g of ramming paste

For the expansion/shrinkage tests, a RDC-195 Shrinkage device available at Arvide Research and Development Centre (ARDC) and illustrated in Figure 3 was used. In this device, during the expansion / shrinkage experiments, the samples are confined laterally with graphite particles in a quartz crucible to maintain the cylindrical shape of the sample when the paste softens. This confinement imitates the paste dilatation in the narrow joints between the blocks during cell preheating. To measure the linear thermal expansion, a quartz disc free to move vertically is placed on the top of the sample. The expansion is measured using a LVDT connected to vertical alumina-pushrod in contact with the disc. The ramming paste expansion / shrinkage is measured parallel to the compaction axis.

Thermal expansion tests were performed in inert gas over a temperature range from room temperature to 1000 °C. During the tests, the heating rate was adjusted to correspond with values measured in real electrolytic cells.

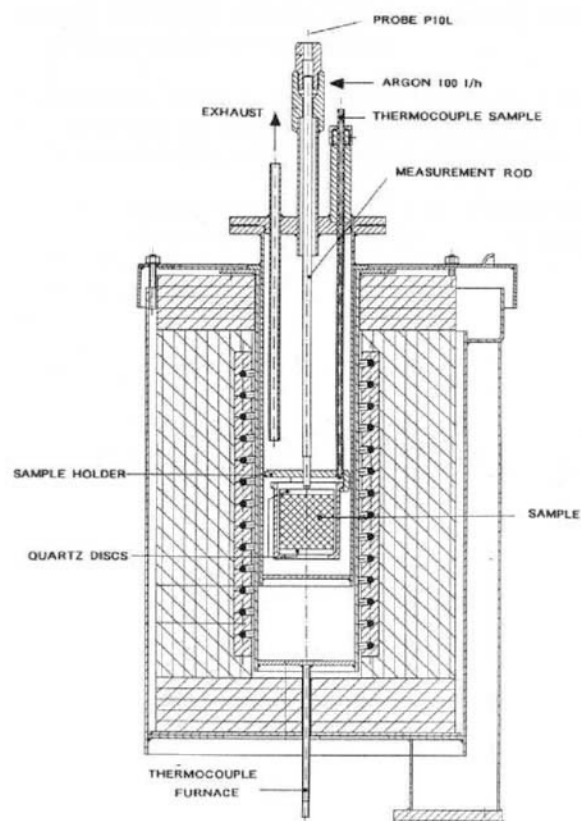


Figure 3: RDC-195 Shrinkage device

Typical expansion and shrinkage curves obtained for three different heating rates are presented in Figure 4. The maximum expansion observed around 100-150 °C is caused by the thermal dilatation and the pressure build-up by gases; pyrolysis products and binder vapors trapped within the paste. Between ~100 °C and 200 °C, the coal tar binder in the paste softens and the paste cannot sustain load or pressure. The binder behaves like a viscous liquid and gases may be released from the paste. At higher temperature, the binder in the paste becomes rigid and less deformable. The volume of the paste becomes relatively constant when the temperature reaches 300 °C.

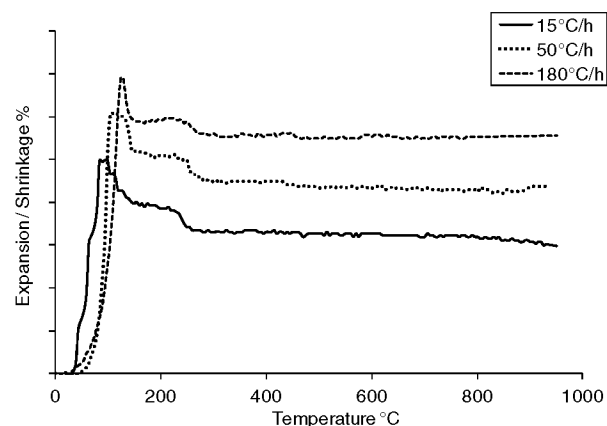


Figure 4: Ramming paste expansion / shrinkage curves for different heating rates

As illustrated in Figure 4, the expansion of the paste begins at lower temperature as the heating rate decreases. The shrinkage of the ramming paste is linked to the softening point of the binder and to the volatiles release. The time and the temperature control this transformation reaction. To take place, the paste must be heated sufficiently and for a certain amount time. At a low heating rate, an increased period of time elapses before the same final temperature is reached and the transformation reactions may begin at a lower temperature.

It is important to notice that during the expansion tests, the temperatures were measured with a thermocouple placed at the top of the crucible and may not represent the temperature inside the ramming paste during baking. However, the test results show the heating rate influence on the volumetric expansion / shrinkage.

Considering the ramming procedure and the viscosity of the paste, the microstructure of the compacted samples is probably not isotropic. In the test proposed, the free surfaces are perpendicular to the compaction axis, i.e. the expansion / shrinkage is measured in the axis parallel to the compaction axis. In a real cell, the most relevant expansion/shrinkage is in the one perpendicular to the compaction axis (for the side of the cell, the compaction is made vertically and the most relevant expansion / shrinkage occurs on the horizontal plane, between carbon blocks and side lining). This discrepancy has not been largely discussed in past works, is not considered in the ISO standard and should be investigated in future works.

The expansion / shrinkage tests were performed on samples from the same batch. However, a relatively large differences were observed in results, which may be due to the heterogeneous feature of the paste..

Chemical transformation

The binder used to make the ramming paste is usually an organic mixture. As it bakes, some hydrocarbon vapors are released from the binder and the mass of the ramming paste decreases. To study the evolution of these reactions that involve a weight loss and their impact on the thermo-mechanical behavior of the paste, thermogravimetric tests were also performed with different heating rates.

The tests were done with one type of ramming paste, using three different heating rates. An electrically heated furnace equipped with a high-precision balance was used to heat and bake 250 g of ramming paste (maximum capacity of the crucible) from ambient temperature up to 900 °C. During the test, thermocouples were placed in the sample to accurately measure the temperature. The sample was compacted using the procedure described before and placed in the crucible. No additional confinement or packing material was put between the sample and the crucible used to limit the mass loss to the paste. The atmosphere inside the furnace was also purged with argon to prevent oxidation or other undesired reactions.

The weight changes in the ramming as a function of temperature are presented in Figure 5 for different heat rates. For the range of heating rates used, no relevant difference was observed. From 15 °C/h to 100 °C/h, the chemical reactions that involve a weight loss are mainly a function of the temperature. From 200-225 °C, the mass lost becomes important.

If we compare the expansion / shrinkage curve with the mass loss, we observe that the major variations are not obtained for the same range of temperature. The ramming paste expansion / shrinkage is mainly completed at 300 °C while the mass loss is

almost maximum for this temperature. A relationship between these results was expected. However, many effects could explain these discrepancies. The most obvious are:

- Effect of thermocouple localization on the temperature measured (inside or outside the paste);
- Effect of paste confinement (with or without packing material inside the crucible to imitate paste confinement between carbon blocks).

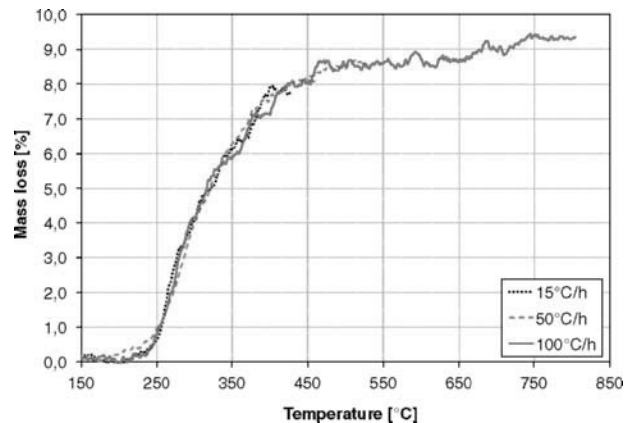


Figure 5: Mass loss in the ramming as a function of temperature for different heating rates

Mechanical behavior

The chemical transformations and the volumetric expansion / shrinkage of the ramming paste during baking modify its mechanical properties. No specific standard or test has been developed to characterize this evolution. Based on previous investigations, it has been observed that the mechanical properties are influenced by the paste compaction (density - over ramming may produce a degradation of the aggregate in the paste and consequently may modify the mechanical properties), the temperature and the time at elevated temperature (or heating rate).

To reproduce the effect of the thermal dilatation of the carbon blocks on the paste during cell pre-heating, compression tests were performed on paste samples. To make good correlations with other experimental data, the test samples were prepared using the procedure described above for the expansion / shrinkage tests with one difference, the samples were 100mm length (50 mm dia). This ratio length : diameter of 2 has been chosen to be in accordance with the standards used for concrete, even though for ramming paste the usual ISO standard for compressive strength is a ratio length : diameter of 1. To compact this amount of ramming paste, an increase in the number of strokes was needed.

The compression tests were performed on free standing samples on a mechanical compression testing machine equipped with a three zone split furnace. The complete setup is illustrated in Figure 6. The furnace is equipped with a programmable three zone controller. Constant temperature and temperature ramp can be programmed. During a test, the temperature is measured directly at the surface of the sample, using a thermocouple. Prior to performing the tests, numerical simulations were realized to estimate the temperature difference between the surface and the center of the paste sample. For the heating rate used, the temperature inside the paste was found to be uniform; the maximum variation of temperature was lower than 10 °C.



Figure 6: Compression testing machine

In the test setup, the sample is located between two flat horizontal surfaces made of steel. To minimize the impact of the friction between the sample and the test surfaces on the test results, the aspect ratio for the sample was selected in accordance with ASTM compressive test for concrete (2:1). A deformation rate of 1×10^{-3} /s was imposed on the samples during the tests. LVDTs located outside the furnace are used to measure the relative displacement between the two extremities of the sample.

When the temperature in the paste reaches ~ 150 °C, chemical transformations occur and pyrolysis products evolve from the material. In the experimental setup presented, these products are collected and condensed in an appropriate hood. To protect the furnaces from the condensation of binder vapors, a stainless steel shield was installed on the inner surface of the furnace.

For the compression tests at elevated temperature, the split furnace was flushed with argon to minimize oxidation of the sample. This procedure was acceptable to protect the sample from ambient temperature up to 500 °C. At higher temperature, this procedure was not sufficient to limit the oxidation of the samples. As the temperature increases, the oxygen initially adsorbed by the porous surface of the carbon paste samples evolves and the oxidation cannot be prevented without a complete desorption of the surface.

At the end of the tests performed at elevated temperature, a friable layer with a negligible resistance was found at the surface of the specimen. For these tests, an apparent effective diameter was measured on the test sample, after the completion of the test. This effective diameter was measured at the apparent periphery of the material not affected by the oxidation. This diameter is assumed to be the best approximation of the effective compressive test section and was used to calculate the Young's modulus and the mechanical strength.

As discussed earlier for the expansion / shrinkage, the evolution of the mechanical properties is also highly dependent of the heating rate due to the variation of the density. The experimental setup was equipped with two LVDTs to measure the lateral deformation of the samples during the test. The addition of

two alumina-pushrod inside the furnace was however an additional source of air inlet inside the surface and, consequently, of oxidation. Moreover, due to the rough surface of the unbaked specimen, no consistent data was obtained also at ambient temperature. For all these reasons, the lateral deformation of the test sample was not measured during the test.

To maintain the cylindrical shape of the test specimens, the samples were pre baked from ambient up to 265 °C in a special enclosure placed in a separate furnace. In this enclosure illustrated in Figure 7, the samples were confined laterally with graphite particles, protected from oxidation with an argon injection and cooled down slowly. The tests were then performed from ambient temperature up to 900 °C, using temperature steps of 100 °C. For each test condition, a sample was heated from ambient to a predetermined test temperature in the experimental setup, using a constant heating rate. The compression test was then performed at the test temperature. To evaluate the effect of the test temperature, to minimize the exposition at elevated temperature and consequently, the effect of oxidation, tests were also performed on pre baked samples cooled down at ambient temperature.



a) Enclosure placed in the furnace

b) Paste samples, before addition of graphite particles

Figure 7: Enclosure used to prebake test specimens from ambient temperature up to 200 °C

The Young's modulus and the compressive strength of paste samples were obtained from the compression tests performed. The results obtained are presented in Figures 8 and 9. For each test condition, a minimum of three samples were tested. The results are presented for samples heated and tested at a predetermined temperature (results identified as "Hot tested") and for samples pre baked to a certain temperature and tested at ambient temperature (results identified as "Cold tested").

For the tested paste and test temperature under 200 °C, the Young's modulus of the unbaked paste was low (the binder is highly deformable). When the temperature increases, the binder becomes less deformable and the rigidity of the paste begins to increase linearly as long as the paste is not completely baked. A similar trend is observed for the mechanical strength of the paste as shown in Figure 9. For elevated temperature, the mechanical strength becomes almost equal to the one of the baked product.

The relatively large standard deviation observed in the results can be related to various sources. At low temperature, when the effect of oxidation is considerably reduced, the deviations can be partially related to the heterogeneous composition of the paste. In the paste, relatively large anthracite particles compared to the size of the test sample can be observed (more than 10 % of the sample diameter). Consequently, the presence of a limited number of large particles aligned or placed relatively close to each other in one sample may modify

considerably the mechanical behavior (Young's modulus and strength) of a test sample.

At higher temperature, the standard deviation in the results increases for the samples tested at elevated temperature. For these temperatures, the oxidation plays a major role. The effective diameter used to determine the effective test section under severe condition of oxidation is certainly a major source of error.

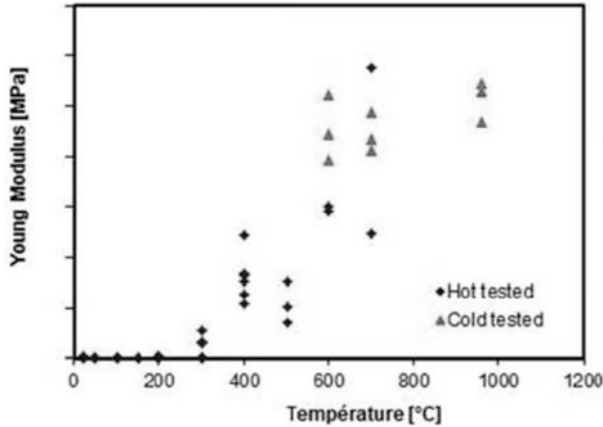


Figure 8: Evolution of the Young's modulus of the ramming paste as function of the test temperature

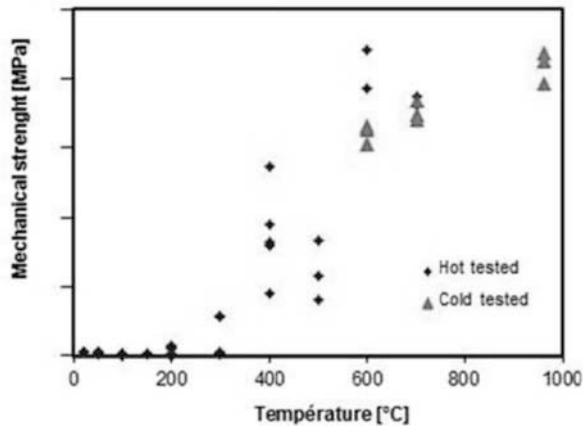


Figure 9: Evolution of the mechanical strength of the ramming paste as function of the test temperature

Conclusion

The evolution of the thermo-mechanical properties of ramming paste has an important impact on the performance of aluminum electrolysis cells. During the heat-up cycle, a proper paste should exhibit a smooth expansion until binder carbonization takes place and should stay dimensionally stable afterwards. A critical situation can occur if the compressive strength of the solidified paste exceeds the compressive strength of the carbon blocks, initially prebaked; occurring stresses may lead to cracking of the carbon blocks. To compensate thermal dilatation in the cell, the rammed paste should remain easily deformable as long as possible. The rammed density, the heating rate and the time have a significant influence on the mechanical and the chemical characteristics of the paste during and after baking.

The influence of the intrinsic paste properties on the behavior of the cell during preheating and start-up is rather difficult to predict, paste seam and cathode blocks having specific thermo-mechanical characteristics. However, by means of computer-aided model calculations, it is possible to get an indication of the performance of different types of paste and consequently, to improve the cell life and performance.

For the test performed on the ramming paste at elevated temperature, the oxidation remains a major problem. The injection of inert gas is not sufficient to prevent oxidation; oxygen is trapped in the porous surface of the samples and evolves when the material is heated. This oxidation reduces the effective test section of the specimen tested. To limit the oxidation, a vacuum furnace should be used to clean oxygen from the porous surface of the test samples.

To get more insight in the cell behavior during cell startup, the data obtained from the experimental procedure described in this paper will be implanted into visco-elasto-plastic model for further analysis by finite element method.

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