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DEVELOPMENT OF A MECHANIZED BATH SAMPLING METHOD

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Abstract

The injection and the dissolution of alumina in the molten cryolite are crucial steps of the Hall-Héroult process because of their impact on the cell efficiency and stability. A better understanding of the dissolution can support the scientists to optimize the energy consumption of the electrolysis process. This requires the study of the dissolution kinetics of alumina experimentally. In order to follow the evolution of the alumina concentration with good precision after its injection, a semi-automatic mechanical sampling system has been developed. The computer controlled system is able to take molten bath samples at around 1000°C for later chemical and microstructural analysis. The appropriate operation of the sampling system required the resolution of several problems, like the choice of appropriate dimensions and material suitable for a very destructive environment. In the present paper, the design process, including problems and solutions, of a semi-automatic molten cryolite sampling system is presented.

Introduction

One of the most common method used to determine the alumina concentration in industrial cells is based on the comparison of temperature histories obtained during the cooling of bath sample and reference after being removed from the electrolysis cell (STARprobe™ [1,2]). The major advantage of this method is the short time needed to obtain the concentration of alumina, which is very important for an industrial usage. However, this equipment is not available for common university laboratories.

Voltammetry is another possible technique to follow variation of alumina concentration [3-5]. However, it is hard apply in molten cryolite bath due to impurities, grounding problems, thermal effect, etc. For this reason, validation with mechanical sampling for chemical analysis is necessary. Techniques such as XRD, XRF and carbothermic reduction of alumina (LECO method) can be used [3,6,7]. Even if those techniques do not give immediate results, they are effective for research purposes. The public literature does not provide any examples of mechanical bath sampling techniques at large laboratory scales.

This paper presents a mechanical molten bath sampling system, designed to be used in a unique large-scale laboratory cell. The system assures a spatial and temporal repeatability.

Methodology

A mechanical molten bath sampling system was designed for an experimental project. It provides samples of approximately 100 grams of molten bath in order to determine the concentration of alumina later in laboratory. The device is able to pull out samples from an experimental oven following a semi-automatic procedure. The oven used for this experiment was custom built for this project and has a big capacity. In order to reproduce as accurately as possible the conditions of an industrial electrolytic cell, the oven can reach temperatures above 1000°C.

Samples are extracted from the bath at a predetermined frequency immediately after an injection of alumina. The samples are pulled out at the same position inside the bath at a fixed distance from the alumina injection. The later analysis of the sample will determine the dissolution kinetic of alumina in the electrolytic bath.

Previous designs

Mechanical sampling systems have been used since the beginning of this project but several major changes were made since the original concept was designed. Three complete systems have been developed and tested. The system originally designed was rejected because of its complexity and its sensibility to repeated thermal shocks. In addition, the first system did not allow the visualization from above the furnace during a sampling sequence. In a second, simplified system, the bath was sampled with a series of experimental stainless steel cups. However, it turned out that the system agitated strongly the bath close to the surface when it was inserted, thus disturbing significantly the temporal variation of the alumina concentration. A visualization experiment was conducted at room temperature in a see-through water tank in order to see the impact of the insertion of the sampler on the liquid surface (Figure 1). For this experiment, the stainless steel cup was also kept at room temperature. It was observed that the air contained inside the metallic cup generated a strong agitation on the liquid surface. The system presented in this paper has been designed to solve the problems encountered with two previous concepts.

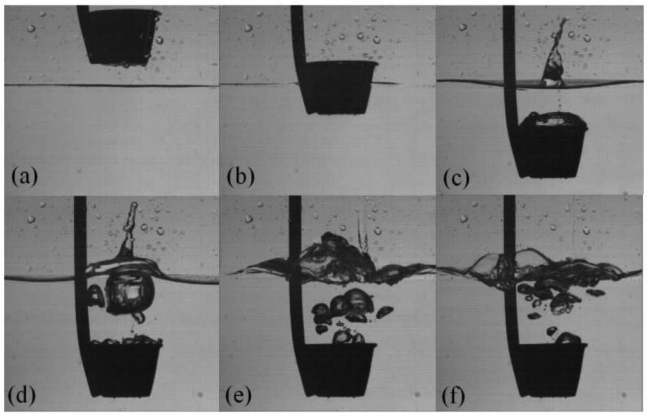
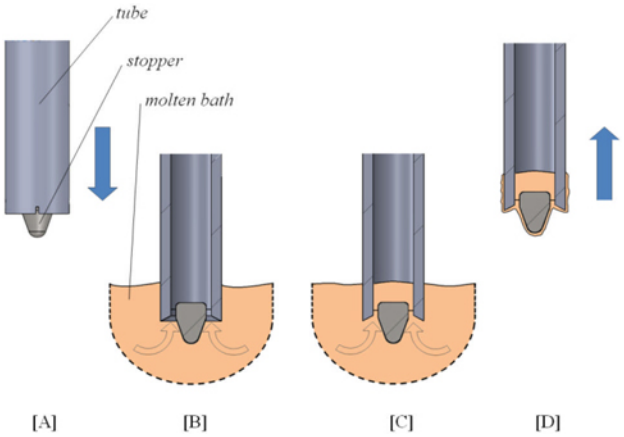


Figure 1. Agitation of the previous system in the liquid

New design

The system consists of a series of 24 inches long stainless steel tubes with 1½ and 1 inch outside and inside diameters. These tubes are immersed one by one in the bath of molten cryolite at a predetermined position and depth in the experimental oven. The molten bath that makes contact with the inner and outer surfaces of the stainless steel tube solidifies because of the much lower temperature of the tube. The tubes are pre-heated to 120°C before the sequence starts and the bath is approximately at 975°C. Once the bath is solidified on the stainless steel tube, it is removed from the cryolite bath and the sample is recovered after it has been is cooled. In order to accelerate the solidification process to assure that the cryolite contained within the tube does not escape when extracted from the bath, a metal stopper is placed at the lower end of the stainless steel tube. The stopper reduces the gap that needs to be sealed by the crust formation on the lower end of the tube to capture the sample. Figure 2 shows the schematic representation of the stainless steel tube, the position of the stopper and the stages of the sampling sequence.



[A] *The tube of stainless steel with the stopper is ready to be inserted into the liquid cryolite bath.*
[B] *The sampling tube is inserted into the molten cryolite.*
[C] *Instantaneously, cryolite penetrates inside the tube and a cryolite starts to solidify on all metal surfaces*
[D] *The crust formation seals the gab between the tube and the stopper and the tube is extracted*

Figure 2. Sampling tube and sequence

The sample is captured inside the tube and can be extracted when it is cooled down. It is essential to cool down the sample as quickly as possible in order to stop the dissolution of alumina in the bath. For this reason, an air stream is sent on the tubes after their extraction from the bath.

Due to the impurities on the metal surfaces, the samples are sanded with an abrasive paper before being sent to the laboratory for the analysis. When the size of the sample recovered inside the tube is sufficient, only this part is sent to the laboratory. In this case, the crust that formed on the external surfaces of the tube is not analyzed because its alumina concentration can differ from the actual sample. Picture of the sampling tube after an immersion and the internal part of the sample are presented in figure 3.

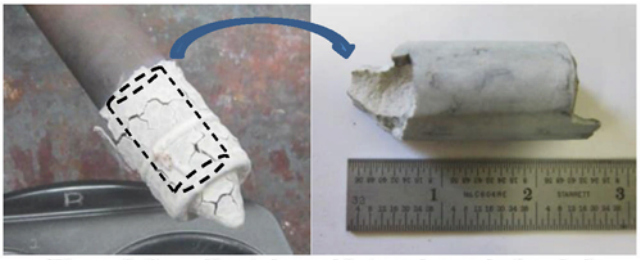


Figure 3. Sampling tube and internal sample (sanded)

In order to visualize in real time the crust formation on a sampling tube, a visualization experience was prepared with in a see-through water tank. The stainless steel tube was inserted in liquid nitrogen for 5 minutes and then plunged the water. Ice formed on the external surfaces of the tube, simulating the crust formation in a cryolite bath. The pictures of this experiment are presented in figure 4.

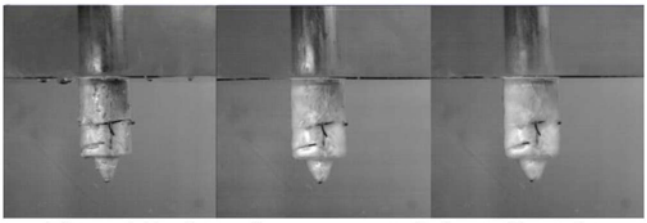


Figure 4. Ice formation on a pre-cooled sampling tube

Optimization of the sampler design

The conception of the mechanical sampler required the analysis of various design parameters. The main objectives were to maximize the sample size and to accelerate the sampling sequence.

In order to analyze the sample in the laboratory, a minimum of 60 grams are required. The analysis included different designs of tubes in an experimental cryolite bath. After samplings, the solidified cryolite formed on the stopper and on the outer wall of the tube was measured and the amount of crust collected inside and outside of the tube was weighed.

The second parameter to be optimized is the sampling speed. It has been observed that the dissolution phenomenon occurs quite rapidly in the bath [8-13]. It is important to have samples as quickly as possible after the injection of alumina to draw an accurate picture of the dissolution kinetic. Considering this fact, the insertion time had to be reduced to its minimum, which is the time needed for the crust to fill completely the gap between the stopper and the tube in order to trap the rest of the sample inside the tube.

In order to analyze the impact of the sampler design on the two conditions, four parameters have been studied: the material and the diameter of the stopper, as well as the insertion time and depth.

Stopper material

Two materials were tested for the stopper, namely stainless steel and copper. The theory suggested that the crust formation would be faster on the copper because of its higher thermal conductivity. After the experiment, no significant difference was noted between the use of a stopper made of copper or stainless steel. The thickness of the crust that formed on the stainless and copper stopper were 2,34 and 2,41 mm respectively. This is probably due to the high temperature difference between the stopper and the bath, especially compared to the superheat. With this information, it was already possible to say that the choice of material for the final system will be of stainless steel for its cheaper and because it is easier to work with. Additionally, the red coloration of the samples along the contact surface between the copper and the cryolite suggests the possibility of a chemical reaction that can modify the composition of the samples (Figure 5).

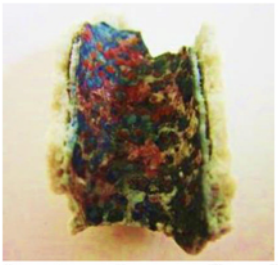


Figure 5. Sample surface reaction with copper

Stopper diameter

The second parameter that was examined is the diameter of the stopper. Four different stopper diameters were chosen: 1/2, 5/8 3/4 and 7/8 inch. The results of this study are shown in figure 6.

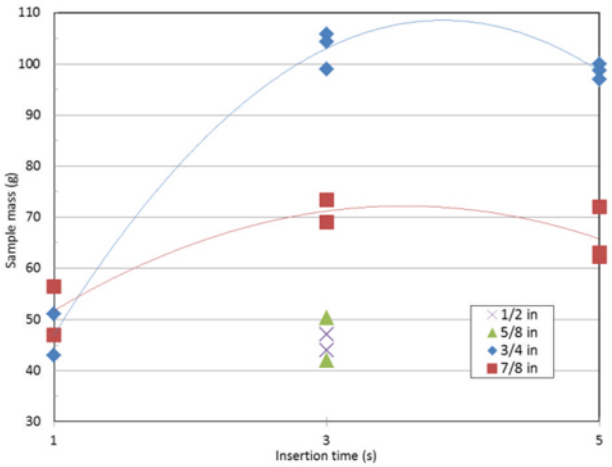


Figure 6. Stopper size and insertion time analysis

The results show that the two smallest stoppers (1/2 and 5/8 inch) were too small. The crust formation was not fast enough to seal the gap between the stopper and the tube. The molten bath was not retained in the tube and thus the sample was not big enough. On the other hand, the tube with the 3/4 inch stopper gave the maximal sample weight. The reason is that the gap between the 7/8 inch stopper and the 1 inch tube is too small. The cryolite didn't have the time to penetrate inside the tube before the gap was closed by the crust formation.

Insertion time

Figure 6 also gives information on the optimal insertion time. The stoppers were tested at three different insertion times (1, 3, 5 seconds). It is possible to see that the sample masses are approximately equivalent for 3 and 5 seconds. This shows that after 3 seconds, the crust formation has enough time to completely fill the gap between the stopper and the tube and that no bath is lost when the tube is extracted from the cryolite. In order to confirm this observation, the crust thickness was measured on the external surface of the stainless steel tube. The results are shown in figure 7.

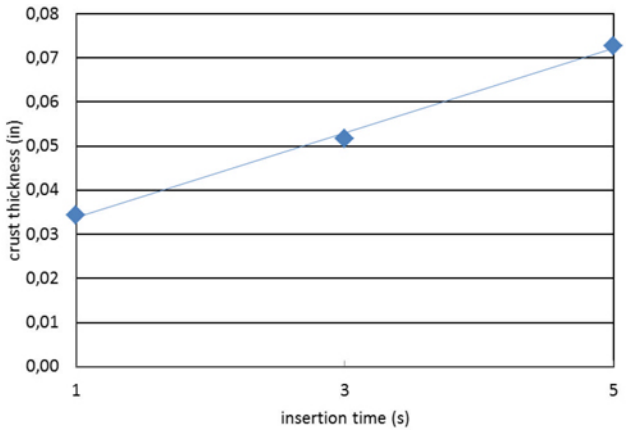


Figure 7. Crust thickness

This graph confirms that the crust formation is fast enough to fill the gap in three seconds. The gap between the stopper and the tube is 1/16 inch (0,0625 inch). The crust formation starts simultaneously on the internal part of the tube and on the surface of the stopper. After three seconds, a crust of approximately 0,1 inch can be formed with these conditions. This is more than the 0,0625 inch gap that needs to be filled by the crust. This gives a security factor to make sure that the sample is perfectly confined in the tube.

Insertion depth

The last parameter that has been studied for the design of the mechanical sampler was the insertion depth. Three primary values were tested: 1¼, 2½ and 3¾ inches. The internal sample mass were weighted for the three insertion depths with the two biggest diameter stopper (3/4 and 7/8 inch). The results are shown in figure 8.

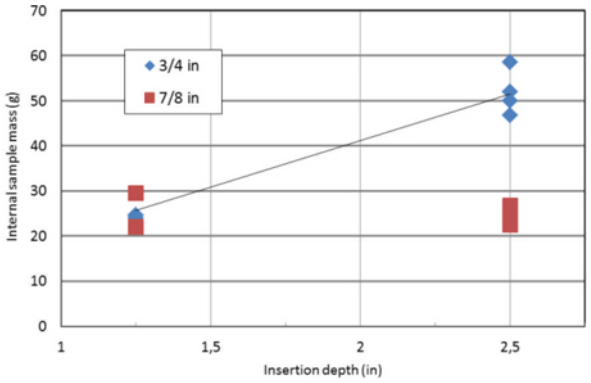


Figure 8. Insertion depth analysis

The graph shows that for the 3/4 inch stopper, the internal sample is proportional to the insertion depth. This is logical because more cryolite can enter the tube before it is extracted for the cryolite. The internal quantity recovered with the 7/8 inch stopper does not seem to be affected by the insertion depth. This proves the earlier assumption that the gap is filled too rapidly by the crust formation. This prevents the liquid to bath enter the internal cavity of the tube.

Conclusions of design analysis

The parametric analysis showed that the optimal design includes the use of a 3/4 inch stainless steel stopper, with an insertion time of 3 seconds and a minimal insertion depth of 2½ inches or more.

In order to confirm the advantages of the new sampling method, the perturbation of the liquid by the sampling tube and cup were compared using a high-speed camera. To simplify the experience and increase transparency, the visualization was made in a water tank at room temperature. The sampling tube and cup were also kept at room temperature for this experiment. The analysis of the videos showed that the liquid was not agitated by the insertion of the tube. Figure 9 shows the comparison between the two sampling systems, immediately after their insertion into the water tank.

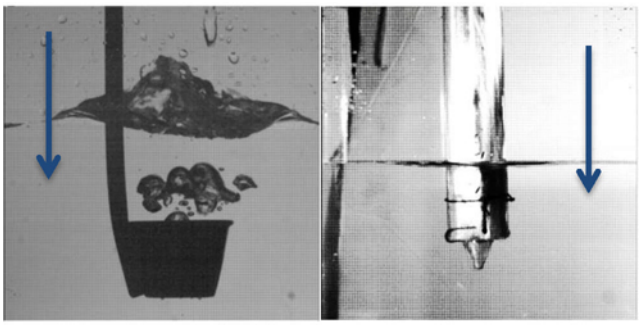


Figure 9. Impact of the sampler insertion in a liquid

This analysis shows that the tube sampler is able to give more reliable data than the previous design because it causes less turbulence in the liquid.

Mechanized sequence

Another feature of the sampling system is to be operated semi-automatically. For this reason, the steel tubes are attached to a sampling robot. The robot consists of two rails (horizontal and vertical) that are connected to actuators controlled by an automated system connected to a control computer. The two rails deliver a vertical and horizontal movement. Figure 10 shows the main elements of the experimental setup including the experimental oven and the sampling robot. An automated sequence was programmed with Matlab Simulink tool. This tool is a block diagram environment for multi domain simulation and Model-Based Design Approach. Using a sampling robot also ensures greater safety during handling. The sampling sequence is automated, but requires manual intervention of an operator to install and remove the stainless steel tubes after each immersion. The use of a sampling robot also ensures that the position and the insertion depth remain constant during all the sampling sequence. The programming of the sequence also determines a sampling frequency. Since the dissolution of the alumina is rather rapid, it is advantageous to minimize the time between two samplings. The first sample can be collected six seconds after the injection of the alumina and the following samples are collected at an interval of fifteen seconds.

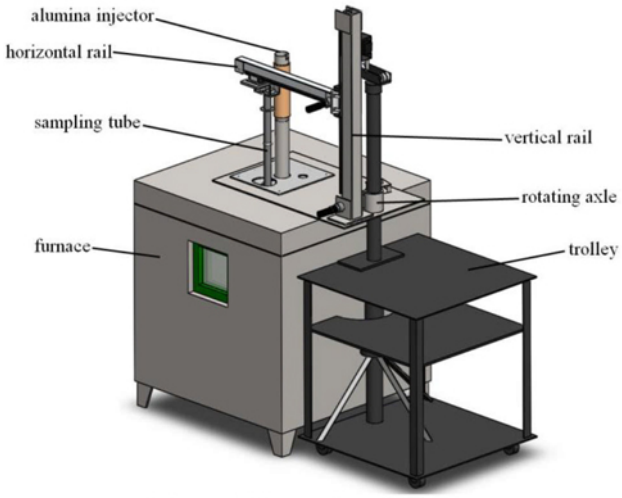


Figure 10. Experimental setup

The mechanized sampler is placed on a trolley and can be approched next to the experimental furnace when the cryolite is liquefied. The main platform can be rotated on the cover of the oven. At least two operators are needed to perform an sampling sequence. A first operetor handles the sampling tubes and the other activates the sequence from the control panel.

Sample analysis methods

During a standard injection/sampling sequence, seven samples are taken. A first sample is extracted before the injection of alumina (t_0), followed by six other samples right after the alumina addition. The chemical composition of those samples is determined using three different analytical techniques, described

in table 1. The combined results of LECO and XRD analysis give the evolution of the alumina concentration in the bath.

Table 1. Sample analysis methods

Method	Properties measured
XRD	Percentage of crystalized phase present (ex.: % Na_3AlF_6, %CaF_2, % Al_2O_3 α, % Al_2O_3 γ).
XRF	Elementary composition (mass concentrations of elements)
LECO	Total concentration of all alumina phases (Al_2O_3 (total) = α + γ + amorphous).

Conclusion

A mechanized cryolite bath sampling system has been developed to study experimentally the kinetics of alumina dissolution in cryolite bath. The sampler is able to provide series of samples at a predetermined depth and position in a molten cryolite bath. The samples are used to carry out chemical analysis in order to determine the evolution of the alumina concentration after an injection. The system presented in this paper is the result of the development of the design of the sampler. This last version can provide sufficient mass of the samples without disturbing the molten cryolite. Additionally, the design of the sampler allows the visualization of the sampling sequence form an overhead view.

Acknowledgements

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