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## Why data-density method is better than step-cooling method to identify Liquidus temperature

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# Why data-density method is better than step-cooling method to identify Liquidus temperature

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**Abstract.** This paper advances an alternative data-density method, which provides a more accurately and reliably identify on-line liquidus temperature ( $T_L$ ) of molten aluminium electrolyte. An in-house computer program of data-density algorithm was developed for a complete investigates and analysis the relationship between data-density and temperature curve of molten aluminium electrolyte. Traditional step-cooling algorithm detects  $T_L$  largely depending only on temperature curve geometry, such as inflection point is obvious or obscure and imperceptible. When there is not inflection point on temperature curve, in such case, traditional step-cooling algorithm is unable to firm clarify there exists  $T_L$  or not, not mention to identify  $T_L$ . Experiments and tests show that even slight or nearly no nuance of inflection point presented on the temperature curve, but there exists a little different data-density on the temperature curve, which can be captured and identified by data-density algorithm. Direct measurements in industrial cells by data-density algorithm is clearly outperforms conventional step-cooling first derivatives and step-cooling second derivatives methods for determining the  $T_L$  of molten aluminium electrolyte.

## 1. Introduction

The temperature of reduction cells ( $T_B$ ) normally should be higher than Liquidus temperature ( $T_L$ ) in aluminum production. Superheat value ( $\Delta T$ ) is the difference between  $T_B$  and  $T_L$ , which can be drown by the following equation:  $\Delta T = T_B - T_L$ .  $\Delta T$  around or slight below 10°C is to be considered a desired value. So,  $T_L$  is one of the key parameters in the production of primary aluminum in the Hall-Héroult bath. If we can pick up  $T_L$  and get  $\Delta T$  on spot, that means we can reduce energy consumption by  $\Delta T$  and improve energy efficiency.

Data-density analysis focus on the thermal events about phase transformation interval of molten aluminum electrolyte and monitor temperature changes of temperature cooling curve of molten aluminum electrolyte. Data-density analysis is also a powerful tool for evaluating and comparing feature representations of temperature curve of molten aluminium electrolyte. By the actual test experiment and analysis of the results, feasible and effective of data-density method for identifying the  $T_L$  in molten aluminum electrolyte are confirmed.

## 2. Literature review

Regression analysis, step-cooling analysis and differential thermal analysis(DTA) are all belong to thermal analysis, which is a powerful method to describe the crystallization behavior of molten aluminum electrolyte. Mr. Wang jiawei has clearly classified the test methods to  $T_L$  of aluminum electrolyte, which can be divided into static test and field dynamic test by setup.



### 2.1 Detection liquidus by off-line analysis

There are two typical off-line (static) analysis methods to identifying the  $T_L$ . One is called regression analysis, which established on a few cell parameters which may require numerous physical measurements and chemical analyses and largely dependents on some key chemical compositions of aluminum electrolyte to be carefully analyzed. Another is a compromise method to measure  $T_L$  by off-line way in laboratory “furnaces”. The procedure include: put finely ground sample (taken from potroom) into a dedicated electric furnace to reheat up again by temperature elevation control system and cool normally at the rate below 0.45 °C/min in order to avoid undercooling. As cooling speed can be regulated, the aluminum electrolyte will have plenty time to cooling and show their physics characteristics of inflection point when sample change from molten state into solid state.

### 2.2 Detection liquidus with step cooling algorithm on-line

Field dynamic test by setup based upon traditional step-cooling algorithm from literature is not too much. P. Verstreken et al. constructed a probe for measuring  $T_L$ , which is based on the principle: when a cold object immersed into molten aluminium electrolyte that result in unsteady heat transfer process and transfer among solidification layers. The process effected by a various of factors and no more reported about this instrument to be applied in real production.

Cry-O-Therm superheat sensor developed by Heraeus Electro-Nite provides the potline with intuitively reading of  $T_L$  with step-cooling algorithm for determining  $T_L$  at industrial production, the main shortcomings of the sensor is with an expendable disposable measuring probe, as a matter of fact, which heavy hinder their probe to be applied in mass aluminium reduction cell.

## 3. Why introduction data-density algorithm to identify liquidus temperature

### 3.1 Molten aluminum electrolyte is a complex impurities and multi-component system

Since  $T_L$  reflects bath composition, aluminum electrolysis always appears as binary systems of  $Na_3AlF_6$ - $AlF_3$  or  $NaF$ - $AlF_3$ , ternary system of  $NaF$ - $KF$ - $AlF_3$ , nevertheless, barely exhibition as single system. In addition, aluminum occurs naturally as the mineral bauxite (primarily is  $Al_2O_3$  alumina) and is dissolved into molten cryolite ( $Na_3AlF_6$ ). In order to increase electrical conductivity and solubility property and decrease temperature of primary crystallization, small additive such as  $LiF$ ,  $NaCl$ ,  $CaF_2$ ,  $MgF_2$  or compound addition of  $NaCl$  and  $LiF$  sometimes are added into molten cryolite-based aluminum electrolyte, in the actually occurring cases various quantities of them may be introduced. This implies the system of molten aluminum electrolyte is a complex impurities system and multi-component system.

### 3.2 complex impurities and multi-component system with small or no inflection point

According to open authority literatures report: the quantity of precipitation phase of ternary system and binary system are inconspicuous or small and even without comparing with pure system, because the heat of transformation of precipitation phase is so small that temperature of primary crystallization could not be reflected on time-temperature curves obviously, not to mention distinct inflection point appearing in the time-temperature traces. That means the latent heat of crystallization process in the impurities system of molten aluminum electrolyte is lower than in pure materials and the temperature plateau is not obvious and small or no.

### 3.3 low molecular ratio of $NaF/AlF_3$ (CR) of electrolyte with small or no inflection point

Low molecular ratio of  $NaF/AlF_3$  (CR) is another vital factor to influence the transition of  $T_L$  goes to dissipation or is a little. Consequently, in most cases, multi-component system and small molecular ratio of  $NaF/AlF_3$  (CR) of molten aluminum electrolyte exhibit no inflection point or very slightly sign on time-temperature curves.

### 3.4 first derivatives to identify the arrest point and second derivatives to the inflection point

As we know, both the arrest point of first derivatives and inflection point of second derivatives on the temperature curve can be taken as the  $T_L$  at normally condition. Whether it is stationary point or point of horizontal inflection, as soon as  $T_L$  is concerned, the mentioned points both have the same mean and always regards these points as temperature value of primary crystallization of molten aluminum electrolyte. That means, if there exist certainly both the inflection point and the arrest point on the temperature curve, the  $T_L$  can be identified by traditional step-cooling algorithm of both first derivatives and second derivatives.

All in all, whether it is pure substance or multi-component system or small molecular ratio of  $NaF/AlF_3$  ( $CR$ ), when both the arrest point and inflection point on cooling temperature curve is obscured or inconspicuous, the  $T_L$  identified by first derivatives and second derivatives of step-cooling algorithm is very difficult and nearly impossible. This situation is most in aluminium production, which calls us to explore a new way to pick up  $T_L$  of arbitrary system.

## 4. Data picked up by our setup

### 4.1 Method of data capture

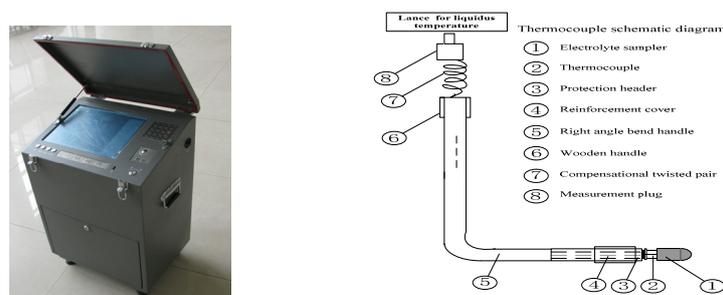


Figure 1 Equipment with an embedded system (left) and a handheld lance (right)

Our equipment mainly consists of an embedded system ( $470*380*800mm$ ) (left) and a handheld lance (right) shown at Figure 1. Measurement at potroom is covered two stages. Firstly, the crucible (namely metal cup) of sensor is slowly immersed into aluminum reduction cells with about 100mm deep and stay within a period of 30 seconds until a peak or a stable temperature plateau is obtained. Secondly, after temperature curve drops-off or buzzer on lance makes alarm and *LED* on lance produces flicker, the crucible should be drawn out slowly and smoothly avoid cutting off heavy electromagnetic to cause unexpected impact on embedded system and suspended with 200 mm high up at the bore of furnace in order to make the crucible gradually cooling. At the same time, temperature signal is picked-up at the rate of interval of 10ms by sensor and immediately converted into digital signal. The information of digital signal is stored on memory and at the same time the temperature-time curve trace is on-line produced and displayed on the screen by our embedded system, and the  $T_L$  of temperature curve also can be counted and identified by data-density algorithm.

### 4.2 Data processing with data-density

Data-density is simply defined as the value in the given series or numerical set which appears with the highest frequency. For example, supposed there exist ten raw data, such as 2.3, 2.1, 1.1, 0.8, 2.2, 1.7, 2.4, 3.8, 3.3 and 4.2; rounded to decimal places and construct new data of 2, 2, 1, 1, 2, 2, 2, 4, 3 and 4 respectively. After rounding, the identical data distributed at different area will be rearranged at different group, only the identical data near to each other can be rearranged at the same group, that means the data-density of the above dataset is three about 2 at the fifth position, but not five about 2 at the first position, which is shown at figure 2.

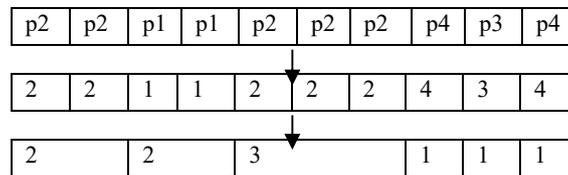


Figure 2. Identical data are grouped

### 4.3 The principle of $T_L$ identified by data-density

When we investigate carefully temperature curve of aluminum electrolyte occurring over the temperature range, there is actually a little or more a difference in data-density on curve, even the curve is smooth curve. The situation of free distribution of temperature data on temperature curve actually interprets the facts about of data-density on temperature curve is random. On the other hand, a slight variation of temperature in aluminum electrolyte cell (reflected on the temperature curve) directly result the change in distribution of data-density.

In view of the physical characteristics of different data-density with certain probability fall into the temperature curve, the temperature curve reflects and expresses the distribution condition of data-density, a lot of different widths histogram with different number of the same identical data appeared on the temperature curve. The random distribution of data-density can visualize on-line and better reflect the possibility position of  $T_L$  on cooling temperature curve. The biggest widths histogram is the biggest data-density and also is just the  $T_L$  corresponding.

### 4.4 The $T_L$ identified by data-density algorithm and first derivative step-cooling method

To verify the accuracy of data-density algorithm, we take the first derivative step-cooling algorithm as reference to comparing the results of  $T_L$  identified by the two algorithms. When there is a distinct arrest point on temperature curve, there is reasonable and a good agreement between the two algorithms to identity  $T_L$ . At left of figure 3,  $T_L$  identified by first derivative step-cooling and at middle by data-density algorithm. At right of figure 3 presents the  $T_L$  caught by data-density with the most numbers of 176 among the histograms, that means, the data-density is then the value where the histogram reaches its peak.

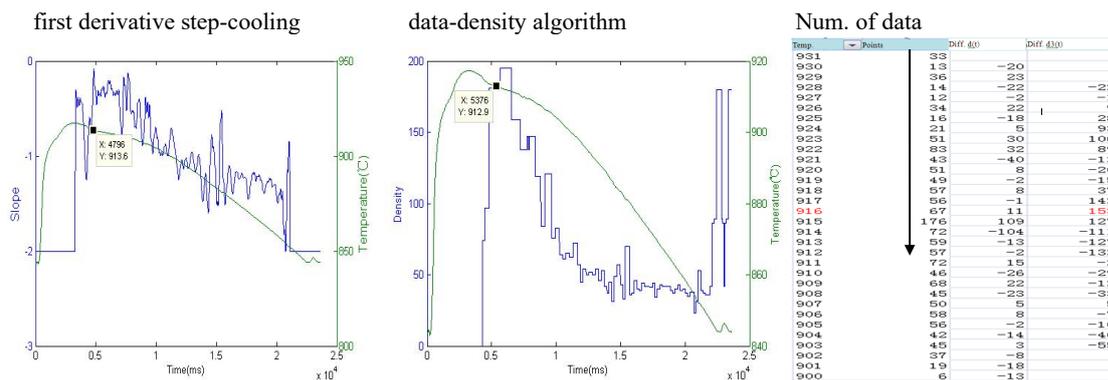


Figure 3. liquids identified by step cooling algorithm and data density algorithm

Around the place of the biggest data-density always presents the slop rate of temperature curve decrease or near to zero. This suggests some extent correlation between the temperature curve and data-density, and the phenomenon is inherence feature of temperature curve of aluminium electrolyte, which led to  $T_L$  can be estimated by different aggregate amount of temperature data.

### 4.5 $T_L$ identified by data-density algorithm not by first derivative step-cooling algorithm

At top of the figures 4 is a typical example about  $T_L$  can't be identified by step-cooling first derivative

algorithm, as there is not arrest point or not inflection point on the temperature curve. In other words, the precondition of using step-cooling first derivative algorithm to determine the  $T_L$  is that the temperature curve must present arrest point, otherwise, the  $T_L$  cannot be determined. At the bottom of the figures 4, the  $T_L$  correctly identified by data-density algorithm, even temperature curve presents barely certain trend and no evident arrest point.

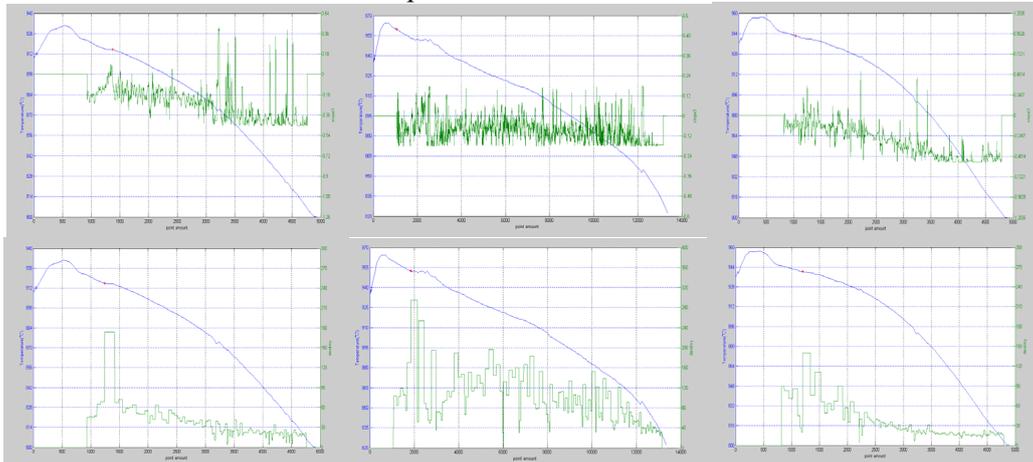


Figure 4. liquids identified by data-density algorithm but not by step-cooling algorithm

#### 4.6 $T_L$ identified by data-density algorithm at potroom

A real on-site snapshot at Hall-Héroult cells with 160KA for measuring  $T_L$  by method of data-density algorithm is shown at Figure 5. The experiments indicate some extent correlation between the temperature curve and data-density, which led to  $T_L$  can be estimated by statistical analysis of different aggregate amount of temperature data. There are all not obvious or not desired inflection point characteristics on the three temperature curves of figure 5, but the  $T_L$  are still correctly estimated and identified by data-density algorithm. The results demonstrate that the data-density analysis algorithm is a feasible method to determine the  $T_L$ .

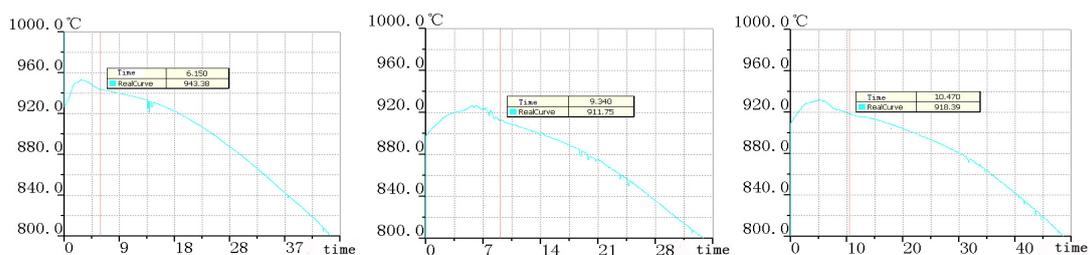


Figure 5. The  $T_L$  direct identified in industrial cells by data-density algorithm

## 5. Conclusions

After many years of computer simulation on the original temperature data collected from each potrooms and a varied of strictly experiments at aluminum reduction cells, it is reasonable to conclude that: based on the principle of probability, the characteristics of temperature curve can be clearly revealed by data-density algorithm. In addition, data-density algorithm can make up for the defect of conventional step-cooling algorithms and improve the accuracy of identifying the  $T_L$ , data-density algorithm has a large potential of wide application.

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