EXTENDED ENERGY BALANCE FOR HALL-HÉROULT ELECTROLYSIS CELLS

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The energy balance of an electrolysis cell considers as primary reaction the electrolytic decomposition of alumina and the heating of alumina and carbon anodes to the reaction temperature. The extended energy balance takes also secondary reaction into account like the air burn of the anodes, the conversion of γ to α alumina, the reactions of the impurities of alumina as well as of the carbon anodes and heating of the scoop device, etc.

HHCellVolt is a new version of a MS Windows PC programs that investigates the essential parameters of cell operation like the cell voltage, cell layout, operational factors and electrolyte properties. HHCellVolt investigates this extended energy balance in a transparent and didactic way: it shows the theoretical background of the applied relations, the origin of the thermodynamic data and represents finally the results in a graphical way.

Several examples especially applied to high ampere cells with features like slotted anodes or four anode rows show the capability of HHCellVolt.

Introduction

For several years MS Windows PC programs (ElysePrg [1], AlPrg [2]), were used to investigate the essential parameters of cell operation like the cell voltage, cell layout (dimensions of anode table, target current intensity), operational factors (electrolyte composition and mass) and electrolyte properties (temperature, gas bubbles under the anode). These programs let you optimize these parameters, for instance, concerning energy consumption or heat loss.

Haupin Diagram and Basic Energy Balance

Warren Haupin was the first to published diagrams [3] that showed the components of cell voltage and their relation to energy consumption. He used these diagrams [4] to study the influence of replacing the consumable carbon anodes of an electrolysis cell by inert non consumable anodes per example.

HHCellVolt draws similar diagrams (Fig. 1). On the left side you see the main panel with input fields and value sliders. You change the value either by conventional keyboard input into the field or by dragging the thumb of the corresponding value slider.

On the right side you see an example of an Haupin Diagram. It shows the components of the cell voltage and of the energy balance. When you drag the diagram up with the mouse pointer a panel shows the meaning of the symbols and their values. For more information please consult the user's guide of HHCellVolt on the web [5].

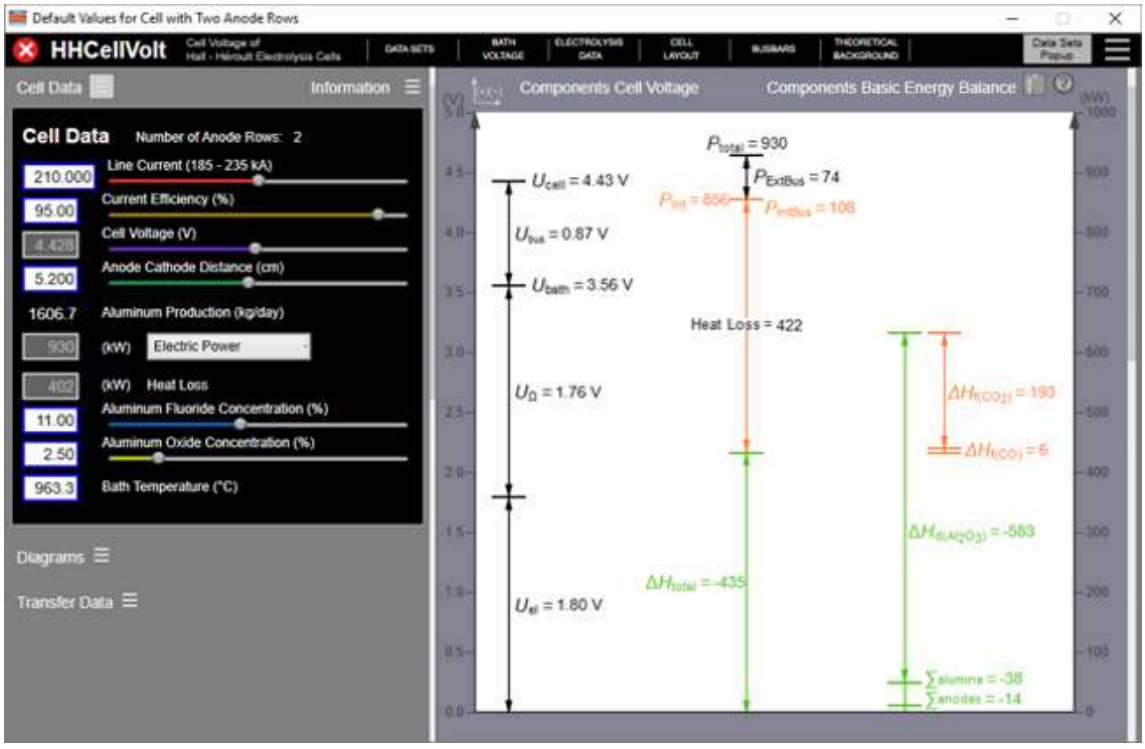

Fig. 1: The main page of HHCellVolt with Haupin Diagram: on the left you see the main input panel. The panel contains input field with values sliders. You change the values with the keyboard, the mouse wheel or by dragging the thumb of the value slider.

As already mentioned the **Basic Energy Balance** was used to investigate the effects when replacing the consumable carbon anodes by inert non consumable anodes. This balance considers only the electrolysis reaction (Equ.1, η: fractional current efficiency), the heating of alumina and the heating of the anodes as well as the heat production by Joule heat inside the cell.

$$\frac{1}{2}\mathrm{Al_2O_3} + \frac{3}{4\eta}\mathrm{C} = \mathrm{Al} + \frac{3}{4}\left(2 - \frac{1}{\eta}\right)\mathrm{CO_2} + \frac{3}{2}\left(\frac{1}{\eta} - 1\right)\mathrm{CO} \qquad \text{Equ.1}$$

Extended Energy Balance

This balance considers in addition to the Basic Energy Balance more events and chemical reaction that happen in the electrolysis cell. These processes produce either energy (exothermic reactions, heat sources) or consume energy (endothermic reaction, heat sinks).

In the literature and on the Internet, you find several publications that report about applications and programs that treat the behavior of an Hall-Héroult electrolysis cell ([6] – [12]). Some of them ([7] - [9]) examine especially the extended energy balance of an electrolysis cell.

HHCellVolt divides the chemical reactions and events that are relevant for the energy balance in the following way: alumina, anode carbon and other processes. The contribution of processes at the cathode (aluminum carbide formation or reaction of sodium with the bottom carbon blocks, for instance) are considered to be too small for the energy balance.

HHCellVolt shows on the THEORETICAL BACKGROUND sliding page the reactions and how it determines the components of the energy balance (Fig. 2).

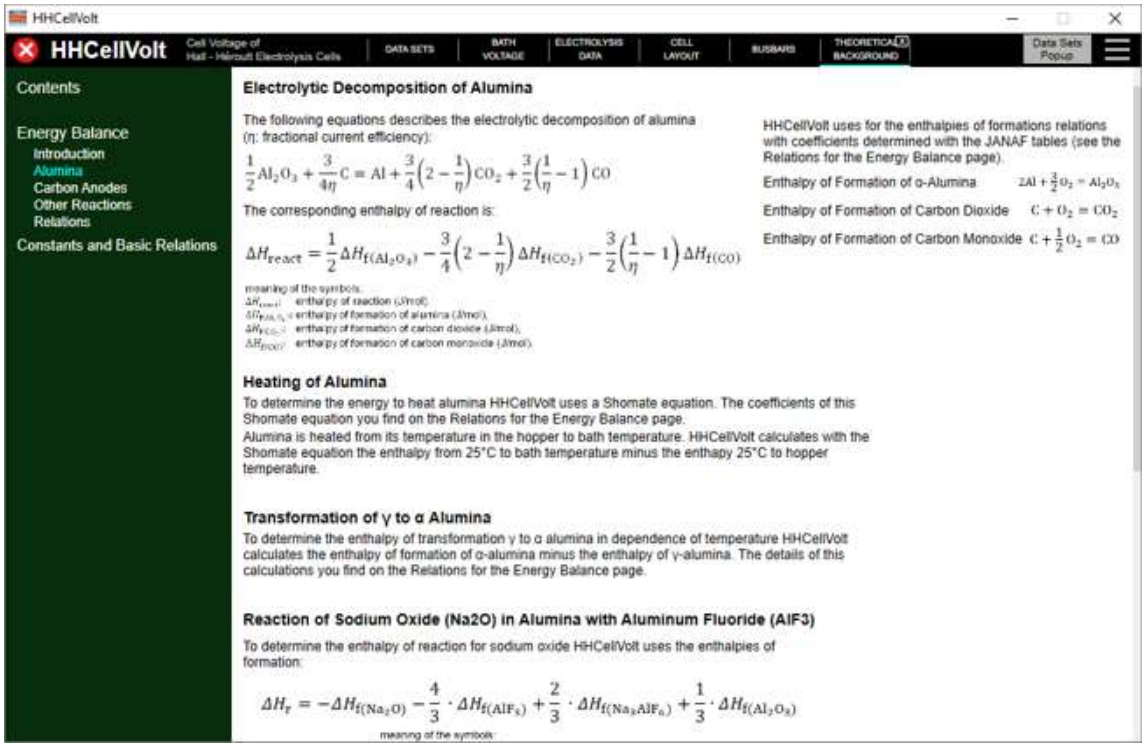

Fig. 2: THEORETICAL BACKGROUND, Alumina Panel: this panel shows the details of alumina reaction concerning the energy balance: among others the γ to α phase transformation or reaction of impurities like sodium oxide, for instance.

The Relations for the Energy Balance panel shows the details how HHCellVolt determines the thermodynamic values. Linear interpolation or Shomate relations are applied using the JANAF tables (Fig. 3).

The user of HHCellVolt defines on the Electrolysis Data Page the extend of these processes, for instance, how much the entire air burn of the carbon anodes contributes to the energy balance. Figure 4 shows an overview diagram of all the exothermic and endothermic processes that HHCellVolt considers for the extended energy balance. It indicates also the difference Extended minus Basic Energy Balance. That difference can be positive or negative depending on the user selection. Similar to the Haupin Diagram HHCellVolt displays also a diagram of the Extended Energy Balance (Fig. 5).

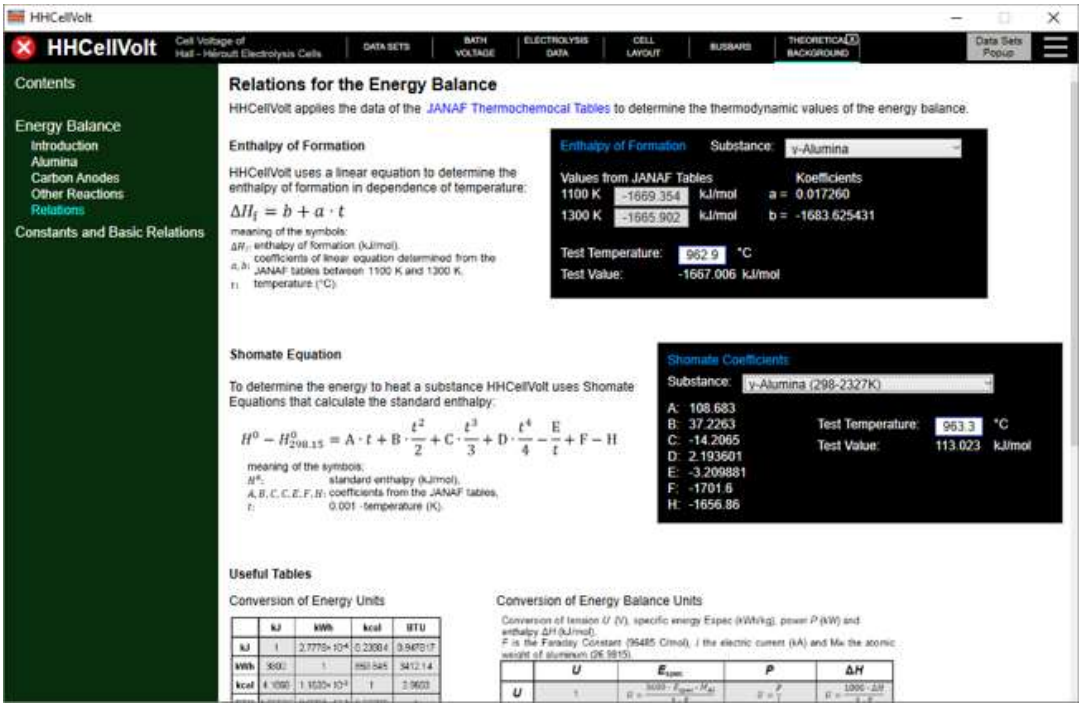

Fig. 3: THEORETICAL BACKGROUND, Relations for the Energy Balance Panel: HHCellVolt uses linear interpolation or Shomate relation to calculate the temperature dependent thermodynamic values. This panel lists the coefficients and calculates example values.

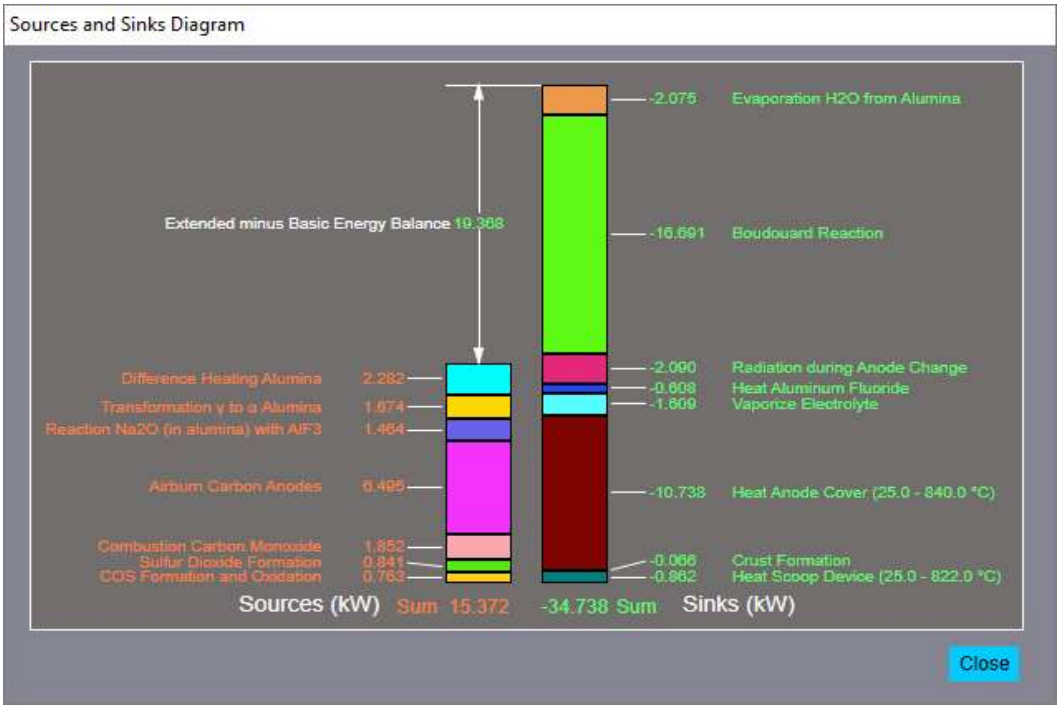

Fig. 4: Diagram of Energy Sources and Sinks: HHCellVolt shows the processes and their values that take part in the extended energy balance. The difference of the Extended minus Basic Energy Balance is indicated.

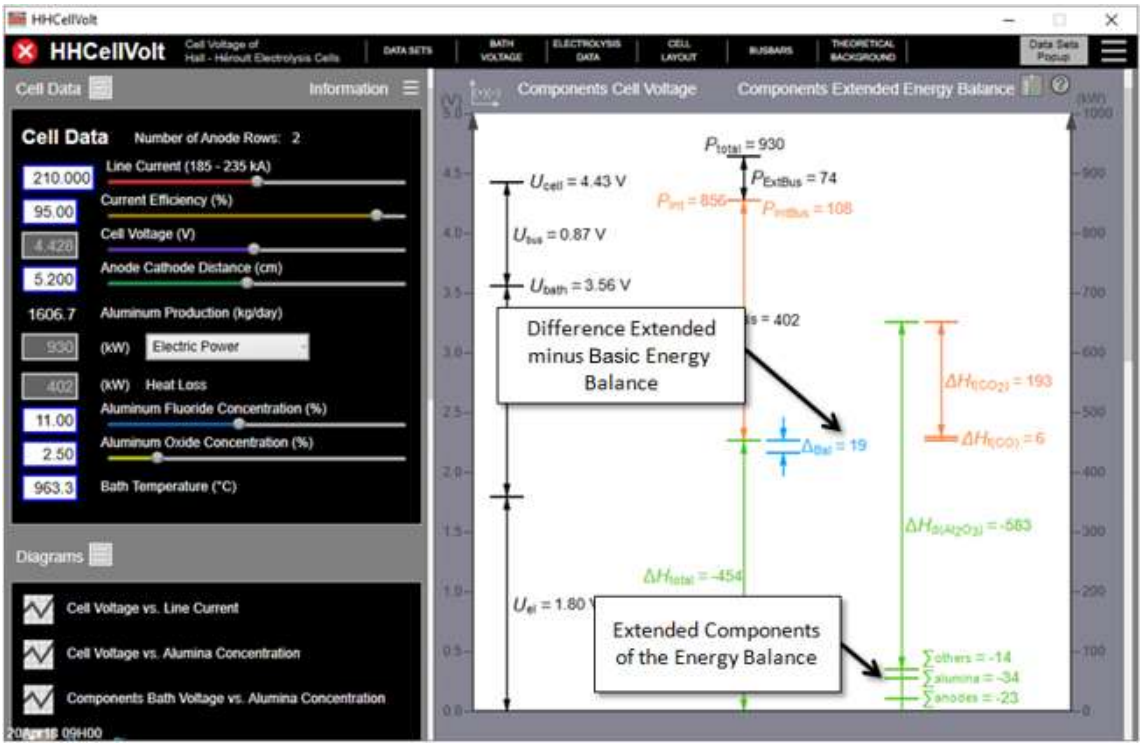

Fig. 5:Extended Energy Balance Diagram: Compared to the Haupin Diagram (Fig. 1) this figure shows in addition the components of the extended balance and indicates also the difference between the two balances.

Electrolysis Cells with Four Anode Rows

A recent publication [13] considers the idea to construct electrolysis cells with four anode rows (see also [14]). With HHCellVolt you may investigate the design options and corresponding cell voltage of such an electrolysis cell.

HHCellVolt contains adapted panels and diagrams to handle this extended anode table layout. Also the algorithms, calculating the anodic fanning factors or bubble voltage, for instance, are adapted to this new anode panel layout.

Example of the calculation of impact of the extended reactions on the cell operating conditions

In [13], a wide cell using four anode rows operating at 762.5 kA was presented. As proposed by Barry Welch, one of the co-author, the equivalent energy to make metal was specified to be 6.6 kWh/kg instead of Haupin's suggested value of 6.34 kWh/kg. For an operation at 95% of current efficiency, this corresponds to an equivalent voltage to make the metal of 2.104 V instead of 2.021 V. In turn, for an operation at 762.5 kA that represents 1604.3 kW instead of 1541.0 kW of power requirement to continually produce the metal and carry on the extended reactions. For an assumed cell operation at 4.1 V and an external busbar drop of 300 mV, this represents a calculated cell internal heat of 1293.2 kW instead of 1356.5 kW.

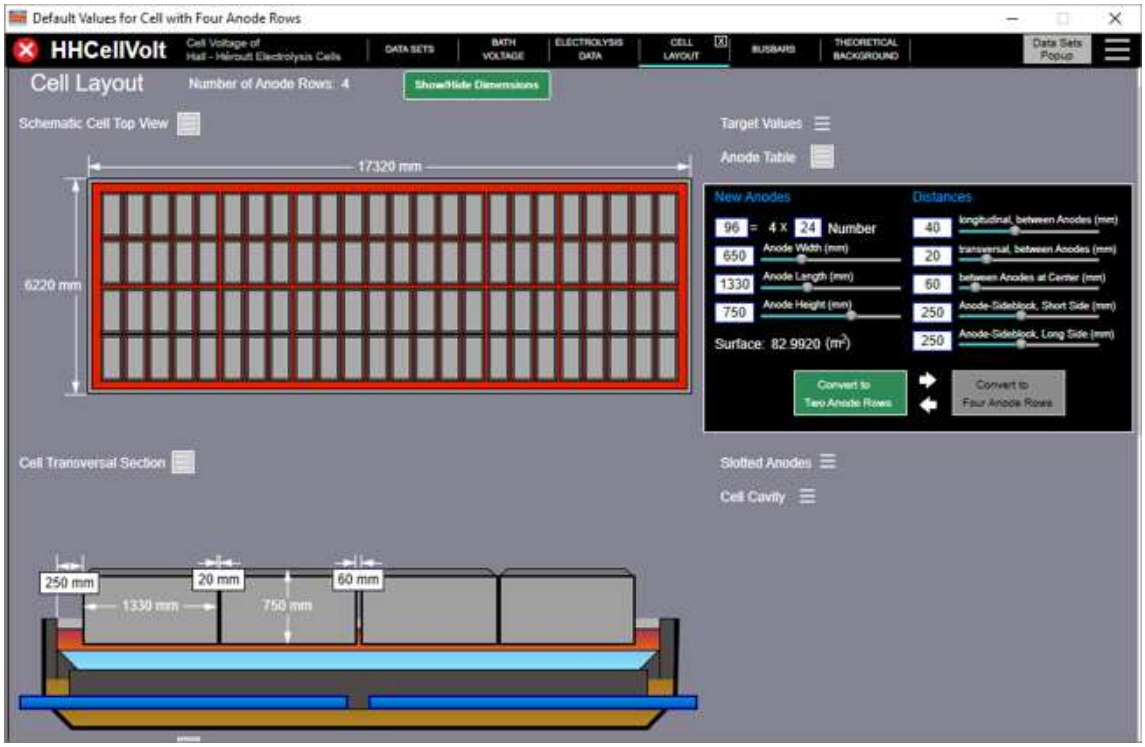

Fig. 6: Electrolysis Cell with Four Anode Rows: the figure shows the adapted panels and diagrams to handle a cell layout with four anode rows. Activating the corresponding button, you may switch between the conventional and extended anode panel layout.

So, for a cell operation at 762.5 kA and 95% current efficient, this 0.26 kWh/kg extra energy requirement to carry-on the extended reactions represent 63.2 kW less of heat dissipation. HHCellVolt will calculate that for us, but it will not tell us what the impact of that difference of cell heat loss on the cell operating conditions will be. For that, we have to use another mathematical model, in the present case, Dyna/Marc 14 [15] was used.

Since Dyna/Marc 14 uses Haupin's equation to calculate the equivalent voltage to make the metal and hence doesn't support the calculation of the impact of the extended reactions on the cell internal heat calculations, that impact will be assess indirectly by increasing the external busbar drop by 83 mV from 300 mV to 383 mV and by reducing accordingly the ACD in order to maintain the same cell voltage. Those 2 adjustments produce the same change of cell internal heat and hence have the same thermal impact on the cell operation than the addition of energy required to carry-on the extended reactions.

Table 1 presents the comparison of the cell operating conditions prediction using on the left Haupin recommended 6.34 kWh/kg energy requirement to produce the metal and on the right using Welch recommended 6.6 kWh/kg energy requirement to carry-on both the metal production and the extended reactions.

Table I: Comparison of predicted operational data

Amperage	762.5 kA	762.5 kA
Nb. of anodes	48	48
Anode size	2.6m X .65m	2.6m X .65m
Nb. of anode studs	4 per anode	4 per anode
Anode stud diameter	21.0 cm	21.0 cm
Anode cover thickness	15 cm	15 cm
Nb. of cathode blocks	24	24
Cathode block length	5.37 m	5.37 m
Type of cathode block	HC10	HC10
Collector bar size	20 cm X 12 cm	20 cm X 12 cm
Type of side block	HC3	HC3
Side block thickness	7 cm	7 cm
ASD	25 cm	25 cm
Calcium silicate thickness	3.5 cm	3.5 cm
Inside potshell size	17.02 X 5.88 m	17.02 X 5.88 m
ACD	3.0 cm	2.8 cm
Excess AlF_3	11.50%	11.50%
Anode drop (A)	347 mV	347 mV
Cathode drop (A)	118 mV	118 mV
Busbar drop (A)	300 mV	383 mV
Operating temperature (D/M)	968.9 °C	967.5 °C
Liquidus superheat (D/M)	10.0 °C	8.6 °C
Bath ledge thickness (D/M)	4.51 cm	6.04 cm
Metal ledge thickness (D/M)	0.54 cm	2.08 cm
Current efficiency (D/M)	95.00%	95.00%
Cell Voltage (D/M)	4.10 V	4.10 V
Internal heat (D/M)	1330 kW	1267 kW
Energy consumption	12.87 kWh/kg	12.87 kWh/kg

As it can be seen in Table I, even if the extra 63 kW required only represents about 4% of the 1450 kW needed to carry-on the metal production, it represents about 5% of the about 1300 kW cell internal heat for a cell operating at 12.9 kWh/kg. That percentage of the cell internal heat will increase further for very low energy consumption cells. Furthermore, since the cell only accommodate the difference by adjusting its cell superheat, that extra 63 kW of energy requirement reduced the cell superheat by about 1.4 °C or 14%. Clearly, this kind of thermal impact been to be accounted for when designing high amperage and/or low energy consumption cells.

Conclusions

In recent years, work has been done to refine the calculation of the energy required to carry-on all the reactions taking place in an aluminium reduction cell ([7] - [9]). This kind of cumbersome enthalpy calculation has been streamlined in a very powerful and user-friendly MS Windows PC program called HHCellVolt.

This make HHCellVolt the perfect tool to make preliminary cell design studies on the impact of the choice of anode panel layout, anode current density, ACD, bath chemistry, anode, cathode and busbar voltage drop etc. on the resulting cell voltage and hence the cell power consumption.

The importance of considering the impact of the energy required to carry-on the extended reactions taking place in a cell has been demonstrated on the example of a wide cell operating at 762.5 kA published recently [13].

References

[1] P. M. Entner, New Feature of ElyseSem/ElysePrg, *Aluminium 75* 1999 12, 1064-1072.

[2] P. M. Entner, AlPrg: a software tool for aluminium smelting, *Aluminium 83* 2007 1/2, 32-35.

[3] W. Haupin, Interpreting the Components of Cell Voltage, *Light Metals* 1998, 531-537.

[4] W. Haupin, H. Kvande, Thermodynamics of Electrochemical Reduction of Alumina, *Light Metals* 2000, 379-384.

[5] User's guide of HHCellVolt: http://www.peter-entner.com/ug/windows/hhcellvolt/toc.aspx

[6] J. Antille, R. von Kaenel, L. Bugnion, Hall-Héroult Cell Simulator: a Tool for the Operation and Process Control, *Light Metals* 2016, 617-622.

[7] A. Al Zarouni, L. Mishra, N. Ahli, M. Bastaki, A. Al Jasmi, A. Arkhopov, V. Potocnik, Energy and Mass Balance in DX+ Cells during Ampere Increase, *Proceedings of XXXI International Conference ICSOBA, XIX International Conference Aluminium of Siberia,* Sept. 4-5, 2013, Krasnoyarsk, Russia p.494-499.

[8] V. Gusberti, D. D. Severo, B. J. Welch, M. Skyllas-Kazaros, Modeling the Mass and Energy Balance of Different Aluminium Smelting Cell Technologies, *Light Metals* 2012, 929-934.

[9] B. Welch, Cell Energy Input - Part2: Its Utilization, *TMS2012 Course Industrial Aluminum Electrolysis*, Sep. 19-14, 2012 Chicoutimi, Quebec, Canada, p84-97.

[10] S. W. Jessen, Mathematical Modeling of a Hall-Héroult Reduction Cell, *Thesis Sep. 2008, Electrical Engineering*, Technical University of Denmark, Lyngby, Denmark.

[11] J. N. Bruggeman, Pot Heat Balance Fundamentals, *Proceedings 6th Australasian Aluminium Smelting Technology Conference and Workshp. Queenstown New Zealand,* Nov. 22-27, 1998 p.167-190.

[12] I. Tabsh, M. Dupuis, A. Gomes, Process Simulation of Aluminum Reduction Cells", *Light Metals* 1996, 451-457.

[13] M. Dupuis, B. Welch, Designing cells for the future - Wider and/or even higher amperage?, *Aluminium* 2017, *Vol. 93 1/2*, 45-49.

[14] Meijia Sun, Baokuan Li, Linmin Li, Jianping Peng, Effect of Steel Multi-Collector Bars on Current Density and Magnetohydrodynamic Stability in an Aluminum Reduction Cell, *Light Metals* 2018, 565-572.

[15] M. Dupuis and H. Côté, 2012. Dyna/Marc Version 14 User's Guide.