### EXTENDED ENERGY BALANCE FOR HALL-HÉROULT ELECTROLYSIS CELLS

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#### **Presented by: Marc Dupuis**



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#### **Plan of the Presentation**

- Introduction to Cell Voltage Calculation Software
- Introduction to HHCellVolt
- HHCellVolt on the Microsoft Store
- Haupin Diagram and Basic Energy Balance
- Extended Energy Balance
- Electrolysis Cells with Four Anode Rows
- Example of the Calculation of Impact of the Extended Reactions on the Cell Operating Conditions
- Conclusions





#### Introduction to Cell Voltage Calculation Software

- The classical Hall-Héroult process produces aluminum by electrolysis using carbon block anodes and a liquid aluminum cathode.
- For several years, MS Windows PC programs (ElysePrg [1], AlPrg [2]), were used to investigate the essential parameters to operate such an electrolysis cell like the cell voltage, cell layout, operational factors and electrolyte properties.
- HHCellVolt is an enhanced version of this software that contains new features. This publication describes these extensions and improvements.





#### Introduction to Cell Voltage Calculation Software

- 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  $\gamma$  to  $\alpha$  alumina, the reactions of the impurities of alumina as well as of the carbon anodes and heating of the scoop device, etc.
- 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.

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Cell Layout	Number of Anode Rows: 2	Show/Hide Dimensions					
Schematic Cell Top View				٦	Target Values		
4880 mm		7730 mm			475.000 Target 0.7610 Target ine Current O 475.000 Actual Anode Table	Line Current (kA) Current Density (A/cm Geometric Anodic Curre Line Current (450 - 50	<sup>2</sup> ) ent Density: 0.7612(A/cm <sup>2</sup> ) 0 kA)
Cell Transversal Section	 	<mark>∖m</mark> 750 mm		1 S	64     =     2 x     32       500     Anode Width       1950     Anode Length       750     Anode Height       urface:     62.4000	Number 3 (mm) 18 th (mm) 25 nt (mm) 25 (m <sup>2</sup> ) Convert to o Anode Rows	Image: Convert to Four Anode Rows
					Slotted Anodes Cell Cavity 📃	≡	



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#### **HHCellVolt on the Microsoft Store**





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#### Haupin Diagram and Basic Energy Balance

- Warren Haupin was the first to published diagrams that showed the components of cell voltage and their relation to energy consumption.
- HHCellVolt draws similar diagrams. 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. HHCellVolt draws a Haupin diagram showing the components of the cell voltage and of the energy balance.





### Haupin Diagram and Basic Energy Balance



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#### Haupin Diagram and Basic Energy Balance

- The Haupin or Basic Energy Balance considers the electrolysis reactions, heating of alumina as well of the anodes and the heat production of the internal cell conductors.
- This balance considers only the electrolysis reaction (Eq.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.

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

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- The Extended Energy 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).
- To make the determination of the Extended Energy Balance transparent as possible HHCellVolt shows on the THEORETICAL BACKGROUND sliding page the reactions and how it determines the components of the energy balance.





Kell Volta	age of BATH ELECT roult Electrolysis Cells DATA SETS VOLTAGE D	ROLYSIS CELL BUSBARS THEORETICAL Data Sets Popup
Contents	Relations for the Energy Balance	
Energy Balance Introduction Alumina Carbon Anodes Other Reactions Relations Constants and Basic Relations	HHCellVolt applies the data of the JANAF Thermochemodeneous Enthalpy of Formation HHCellVolt uses a linear equation to determine the enthalpy of formation in dependence of temperature: $\Delta H_{\rm f} = b + a \cdot t$ meaning of the symbols: $\Delta H_{\rm f}:$ enthalpy of formation (kJ/mol). coefficients of linear equation determined from the <i>a</i> , <i>b</i> : JANAF tables between 1100 K and 1300 K. <i>t</i> : temperature (°C).	Cal Tables to determine the thermodynamic values of the energy balance.         Enthalpy of Formation       Substance:         \u03c4_Alumina       \u03c4_Alumina         Values from JANAF Tables       Koefficients         1100 K       -1692.437       kJ/mol       a = 0.011235         1300 K       -1690.19       kJ/mol       b = -1701.726660         Test Temperature:       962.9       °C         Test Value:       -1690.909       kJ/mol
	Shomate Equation To determine the energy to heat a substance HHCellVolt Equations that calculate the standard enthalpy: $H^{0} - H^{0}_{298,15} = A \cdot t + B \cdot \frac{t^{2}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{4}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{3}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} - \frac{t^{6}}{2} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} + C \cdot \frac{t^{6}}{3} + C \cdot \frac{t^{6}}{3} + D \cdot \frac{t^{6}}{4} + C \cdot \frac{t^{6}}{3} + C \cdot t^{6$	uses Shomate       Substance: $\alpha$ -Alumina (298-2327K)         E       + F - H         E       t + F - H         E       - 102.429         B:       38.7498         Test Temperature:       963.3         °C       C:         C:       -15.9101         D:       2.628181         E:       -3.007551         F:       -1717.93         H:       -1675.69
	Useful Tables           Conversion of Energy Units         Conversion           kJ         kWh         kcal         BTU         Conversion         enthalpy Δ           kJ         1         2.7778×10 <sup>-4</sup> 0.23884         0.947817         F is the F.         weight of a           kWh         3600         1         859.845         3412.14         Image: Conversion           kcal         4         1968         1         1630×10 <sup>-3</sup> 1         3 9683         Image: Conversion	on of Energy Balance Units I of tension <i>U</i> (V), specific energy Espec (kWh/kg), power <i>P</i> (kW) and <i>H</i> (kJ/mol). araday Constant (96485 C/mol), <i>I</i> the electric current (kA) and Mai the atomic luminum (26.9815). <i>U</i> <u><b>E</b><sub>spec</sub> <b>P</b> ΔH 3600 F v Mai P</u>

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😢 HHCellVolt	Cell Voltage of Hall - Héroult Electrolysis Cells	DATA SETS VOL	ATH ELECTROLYSIS TAGE DATA	CELL LAYOUT	BUSBARS	THEORETICAL	Data Sets Popup
Contents Energy Balance Introduction Alumina Carbon Anodes Other Reactions Relations Constants and Basic Rela	Heat Carbon An No coefficients of t HHCellvolt uses a between 1100 and You find the corres Balance page. Airburn Carbor Dealing with the re according to AlZha $(C + O_2 + 3.81)$ $T_a$ : ambient tempe $T_r$ : reaction tempe You find the Shoma Balance page. Combustion Ca HHCellVolt determ $(2CO)_{T_r} + (O_2 - T_a)$ : ambient temper $T_r$ : reaction temper $T_r$ : reaction temper Enthalpy of formati minus heating of ni Boudouard Rea $CO_2 + C = 2CO$ HHCellVolt calcula formation of carbor	nodes he Shomate relation for linear relation determine 1300K. ponding Shomate coeffic <b>n Anodes</b> action of oxygen with ca rouni (Web-Lit.Equ. 4, p $N_2)_{T_a} = (CO_2 + 3.81)$ rature (°C), rature (°C). ate coefficients for heatin <b>arbon Monoxide</b> ines the combustion of c $+ 3.8N_2)_{T_a} = (2CO_2)^2$ rature (°C). ion of carbon dioxide mini- itrogen. <b>action</b> ) tes the enthalpy of react n dioxide minus twice the <b>ulfur Dioxide</b>	carbon were found in the divit the values from cients on the Relations of the heating of air $_{0.5}$ ) has to be taken into $N_2$ ) $_{T_r}$ and of nitrogen on the Relations arbon monoxide as Al2 $_2$ + $3.8N_2$ ) $_{T_r}$ hus enthalpy of Format cient for the Boudouard for the Boudo	he literature. the JANAF tabl for the Energy (i.e. nitrogen) account. elations for the Zharouni (Web- tion of carbon m reaction with: en of carbon mono	es Energy Lit.Equ. 5, p.5) nonoxide nthalpy of oxide.	);	
	The coefficients of $S + 2CO_2 = S$	the relation for the enthance $0_2 + 2CO$	alpy of reaction of:				



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Cell Voltage of Hall - Héroult Electrolysis Cells DATA SETS	BATH ELECTROLYSIS CELL BUSBA VOLTAGE DATA LAYOUT BUSBA	ARS THEO BACK	GROUND		Data Sets Popup
Anode Butts Data $\checkmark$ $\equiv$ $\equiv$ $\equiv$ $\equiv$ $\equiv$	Extended Energy Balance Y				Sources, Sinks
Anode Consumptions:		(kW)			
520.0 Specific Anode Gross Consumption (g/kg)	⑦ Electric Power	3134.0			
450.0 Specific Anode Net Consumption (g/kg)	External Busbars	228.8			
351.4 Specific Electrolytic Anode Consumption (g/kg)	Internal Busbars	354.6	Mas	sses	
98.6 Specific Anode Excess Consumption (g/kg)	Aluminum Production		(g/kg Al)	(kg/day) 5833.9	
70.0 Specific Anode Buills (g/kg)	Alumina 🕒				
Properties New Anodes:	⑦ Electrolytic Decomposition of Alumina Enthalpy of Alumina Decomposition	-1390.8 -2115.84(	1889.5	11023.0	
1.550       Anode Density (g/cm3)       Anode Mass:       982.3 (kg)	Enthalpy of Carbon Dioxide Formation Enthalpy of Carbon Monooxide Formation	702.561 22.411		6761.2 478.1	
24 Anode Change Interval (h)	⑦ Heat Alumina (from 25.0 to 958.8 °C)	-136.58	1920.0	11201.1	
12 Duration of Anode Change (min/day)	(2) Transformation $\gamma$ to $\alpha$ Alumina (2) Reaction Na2O (in alumina) with AIE3	10.110	639.4 16.90	3730.0 98.6	
25 Anode Change Cycle Period (days)	<ul> <li>② Evaporation H2O from Alumina</li> </ul>	-7.534	21.12	123.2	
	Total Alumina	-1519.5			
Anode Reactions:					
34.0 Air Burn Carbon Anodes (% of Excess)	Anodes -	40 673	520.0	3033.8	
40.0 Combustion of Carbon Monoxide (% of electrolysis)	Airburn Carbon Anodes	-49.073	33.52	195.6	
60.0 Boudouard Reaction (% of Excess)	<ul> <li>O Combustion Carbon Monoxide</li> </ul>	13.495	32.78	191.3	
2.10 Sulfur Content in Anode (%)	Boudouard Reaction     Sulfur Disvide Formation	-55.957	59.16	345.1	
25.0 COS Formation and Oxidation (% of Sulfur in Anode)	<ul> <li>OS Formation and Oxidation</li> </ul>	2.758	4.43	25.8	
0.600 Hydrogen Content in Anode (%)	⑦ Radiation during Anode Change	-2.223			
	Total Anodes	-34.996			
Anode Butts Butts Mass: 460.4 (kg)	Other Reactions				
Dereent Dutt Curfeee	Heat Aluminum Eluoride	-2 196	30.00	175.0	

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- 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.





😣 HHCellVolt	Cell Voltage of Hall - Héroult Electrolysis Cells	DATA SETS	BATH VOLTAGE	ELECTROLYSIS DATA	CELL LAYOUT	X	BUSBARS	THEORETICAL BACKGROUND	Data Sets Popup
Cell Layout	Number of Anode Rows: 4	Show/H	ide Dimensions						
Schematic Cell Top View						Tar	get Values		
		7320 mm				760 0.9 Line 762	0.000 Target 0400 Target Current (0 2.500 Actual	t Line Current (kA t Current Density Geometric Anodic I Line Current (73	) (A/cm <sup>2</sup> ) : Current Density: 0.9400 (A/cm <sup>2</sup> ) 8 - 788 kA)
6180 mm					Ħ	And	ode Table		
						New 96	$= 4 \times 24$	Number	Longitudinal, between Anodes (mm)
Cell Transversal Section						650 130 750 Surf	Anode Width Anode Leng Anode Heigh ace: 81.1200	n (mm) th (mm) nt (mm)	<ul> <li>transversal, between Anodes (mm)</li> <li>between Anodes at Center (mm)</li> <li>Anode-Sideblock, Short Side (mm)</li> <li>Anode-Sideblock, Long Side (mm)</li> </ul>
250 mm 	-> ->-> - 60 mm 0> 750 mm	m				Slo	tted Anodes	Convert to o Anode Rows	Convert to Four Anode Rows

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E Default Values for Cell with Four Anode Rows	– 🗆 🗙
S HHCellVolt Cell Voltage of Hall - Héroult Electrolysis Cells DATA SETS BATH ELECTROLYSIS CELL BUSBARS THEORETICAL BUSBARS BACKGROUND	Data Sets Popup
Cell Layout Number of Anode Rows: 4 Show/Hide Dimensions	
Schematic Cell Top View 📃 Target Values 🚍	
0.9200 Target Current Density (A/cm <sup>2</sup> )	
Line Current Geometric Anodic Current	ensity: 0.9158 (A/cm <sup>2</sup> )
6220 mm	<u>)</u>
Slot Type: No Slots Longitudinal	Transverse
Cell Transversal Section	
225 Slot Height (mm) 30.0	Slot Height (% of anode height)
250 mm 60 mm	
Cell Longitudinal Section =	



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Cell Voltage of HHCellVolt Cell Voltage of Hall - Héroult Electrolysis (	Cells DATA SETS BATH VOLTAGE	ELECTROLYSIS DATA	CELL	BUSBARS	THEORETICAL BACKGROUND		Data Sets Popup	
Overview Busbar Voltages 🧮	·	0						
Reference Values:762.500Ref. Line Current (kA)0.765Sum Ref. Busbar Voltages (V)0.485Sum Ref. Entry - Bath (V)0.280Sum Ref. Bottom - Exit (V)0.280Sum Ref. Bottom - Exit (V)Overview Cell Voltage0.765Sum Busbar Voltage (V)3.345Bath Voltage (V)4.110Cell Voltage Voltage (V)	Actual Values: 762.500 Act. Line Current (kA) 0.765 Act. Sum Busbar Voltages 0.485 Sum Act. Entry - Bath (V) 0.280 Sum Act. Bottom - Exit(V) External, internal Busbar Voltages: 0.300 Sum External Voltages (V) 0.465 Sum Internal Voltages (V)	(V)						2
Details Busbar Voltages Change Properties of Selected Busbar Voltage Component cathode Name aluminum Material 120 Uref: Reference Voltage (mV) 120 Uact: Actual Voltage (mV) 0.74 relative Position in Diagram Castribution to the Energy Belance	Component: Selected.	Entry	Riser		Anode Bath	Bath Voltage (V) Bottom	cathode	Buspar Exit
Components Entry - Bath Busbar Voltage: +	Uref Uact Pos. therm. Bal.	s	120 Show Entry - Bath Bus Current Path Items	sbar Show Bot Curren	0 345 tom - Exit Bus nt Path Items	3.345 sbar	120 1	60

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- In [13] a wide cell using four anode rows operating at 762.5 kA were 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.
- 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.
- Table II 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: Description of the Cell Design and Operating Conditions

Amperage	762.5 kA
Nb. of anodes	48
Anode size	2.6m X .65m
Nb. of anode studs	4 per anode
Anode stud diameter	21.0 cm
Anode cover thickness	15 cm
Nb. of cathode blocks	24
Cathode block length	5.37 m
Type of cathode block	HC10
Collector bar size	20 cm X 12 cm
Type of side block	HC3
Side block thickness	7 cm
ASD	25 cm
Calcium silicate thickness	3.5 cm
Inside potshell size	17.02 X 5.88 m
ACD	3.0 cm
Excess AIF <sub>3</sub>	11.50%





#### Table II: Comparison of predicted operational data

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



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- As it can be seen in Table II, even is the extra 63 kW required only represents about 4% of the 1450 kW required 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%.

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





#### Conclusions

- 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].
- Clearly, this kind of thermal impact need to be considered when designing high amperage and/or low energy consumption cells.





