EXTENDED ENERGY BALANCE FOR HALL-HÉROULT ELECTROLYSIS CELLS

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Plan of the Presentation

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- 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

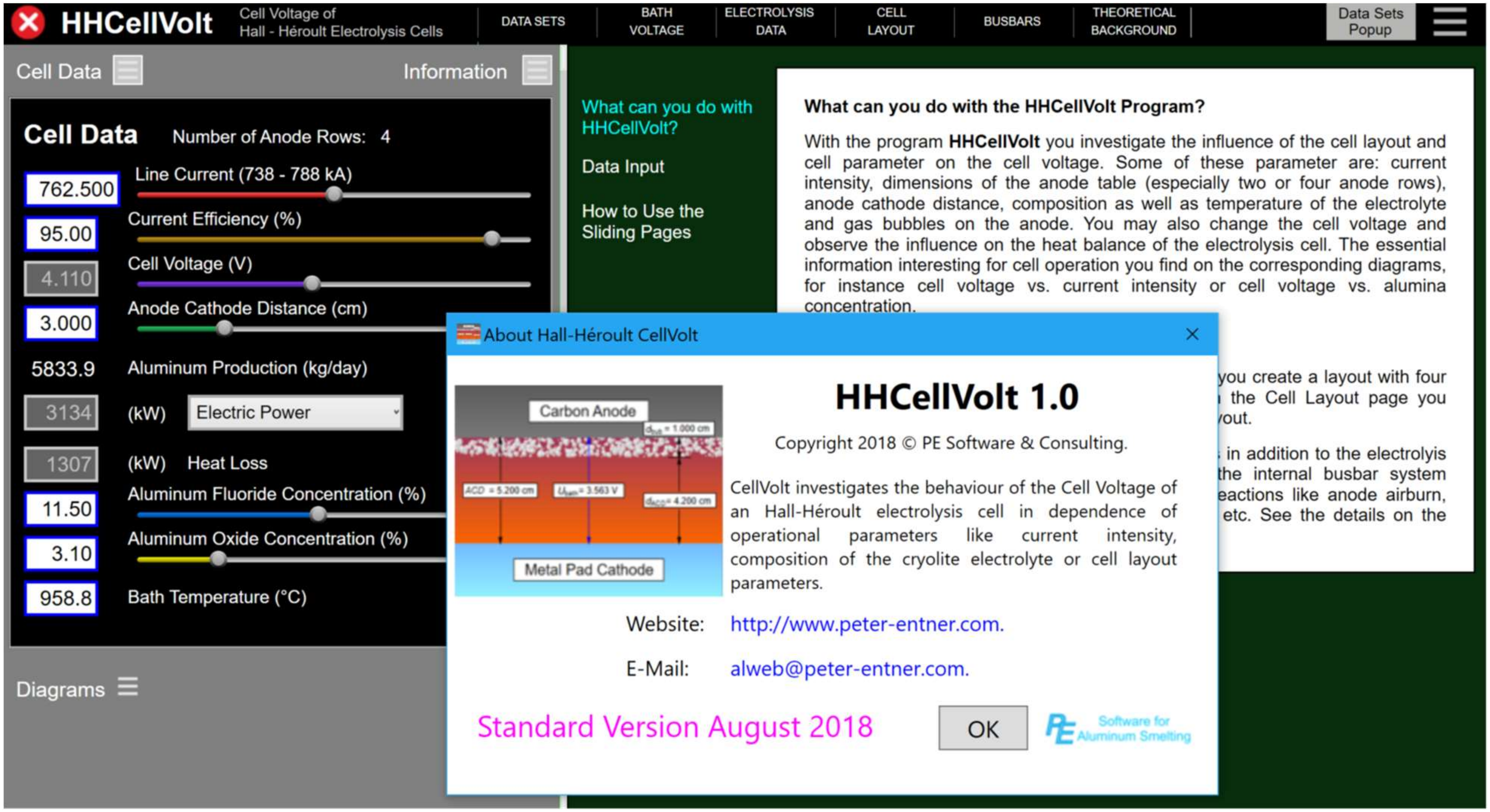
Introduction to Cell Voltage Calculation Software

- 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.

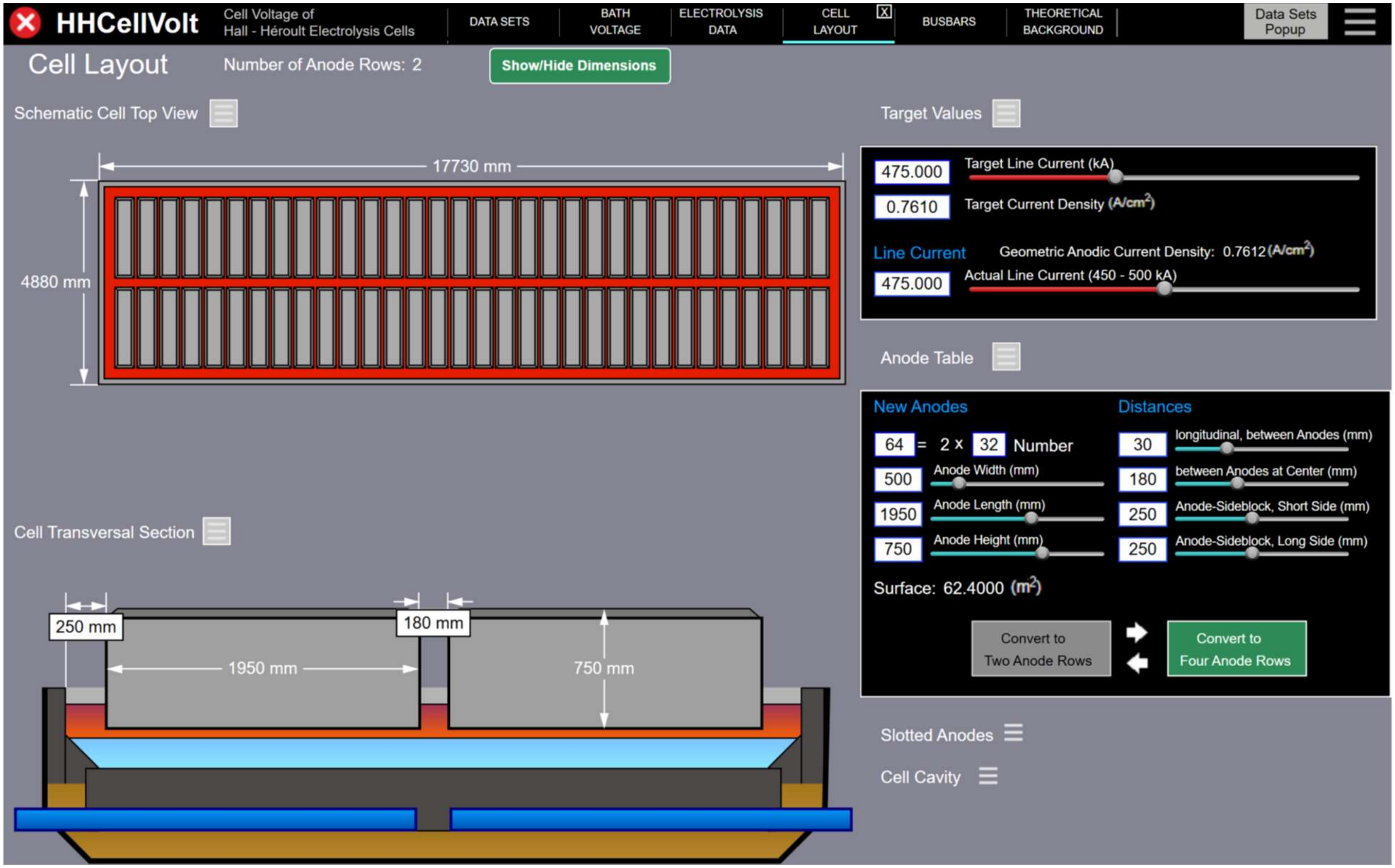
Introduction to Cell Voltage Calculation Software

- **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 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 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.**

Introduction to HHCellVolt



Introduction to HHCellVolt



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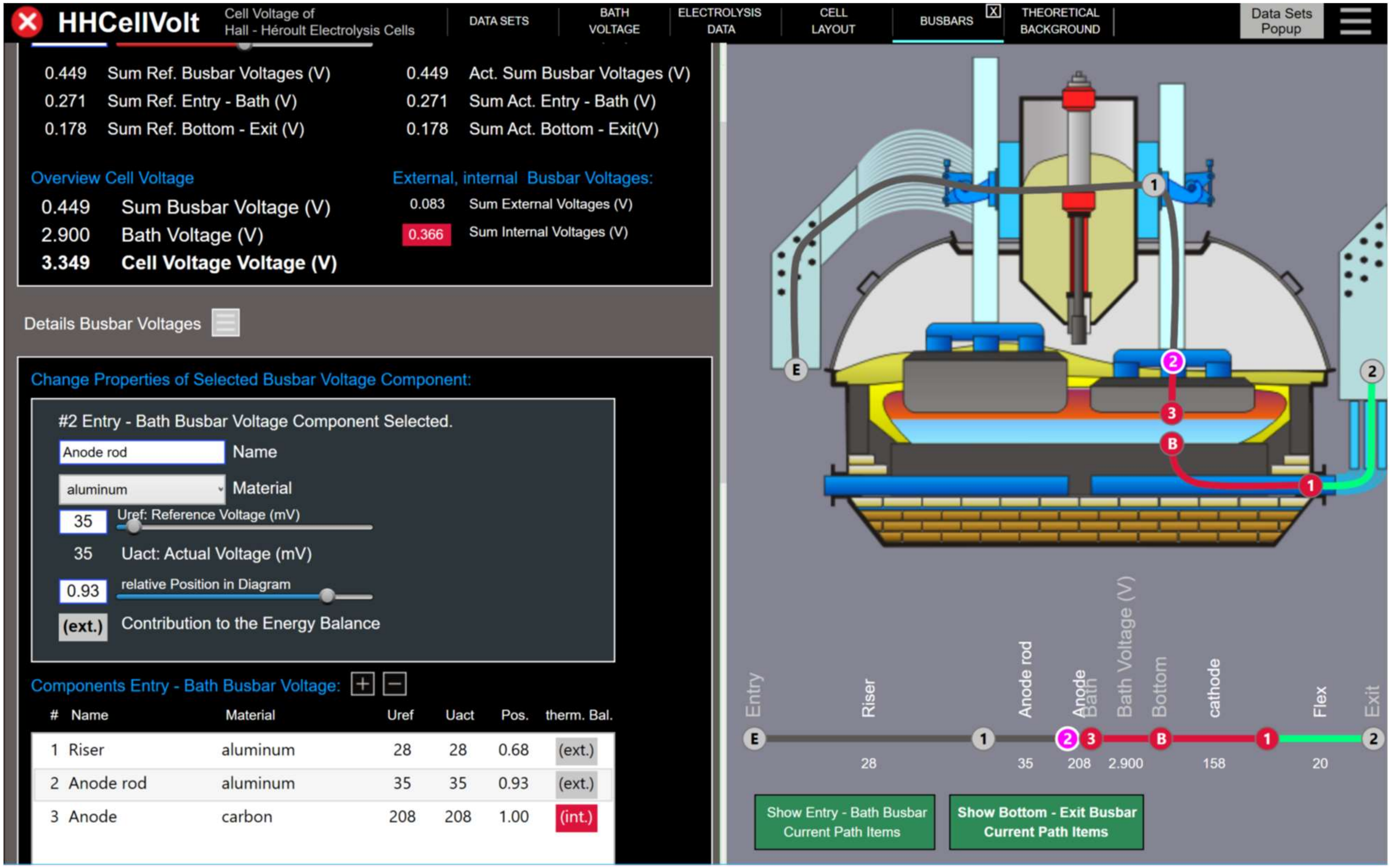

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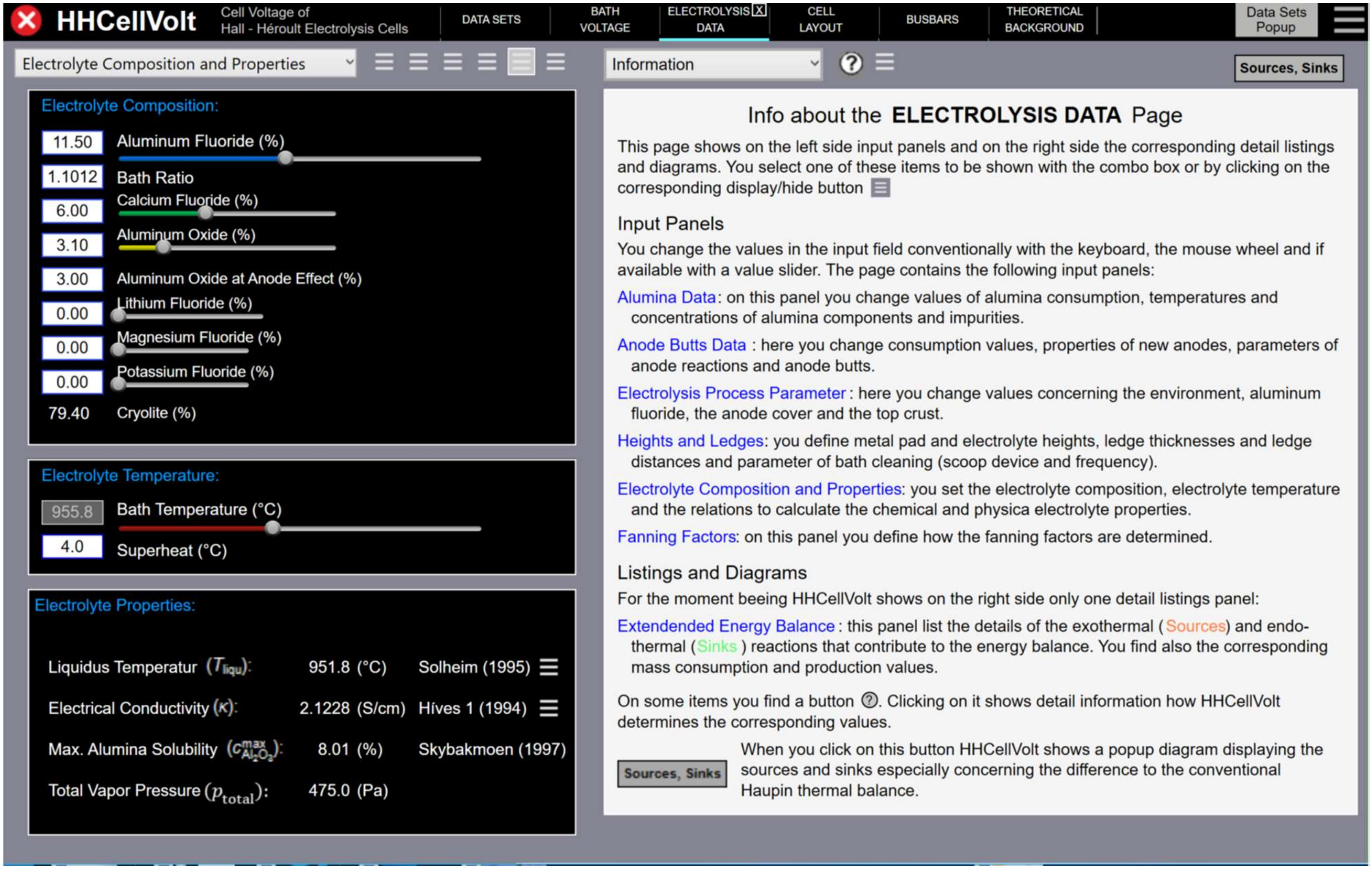

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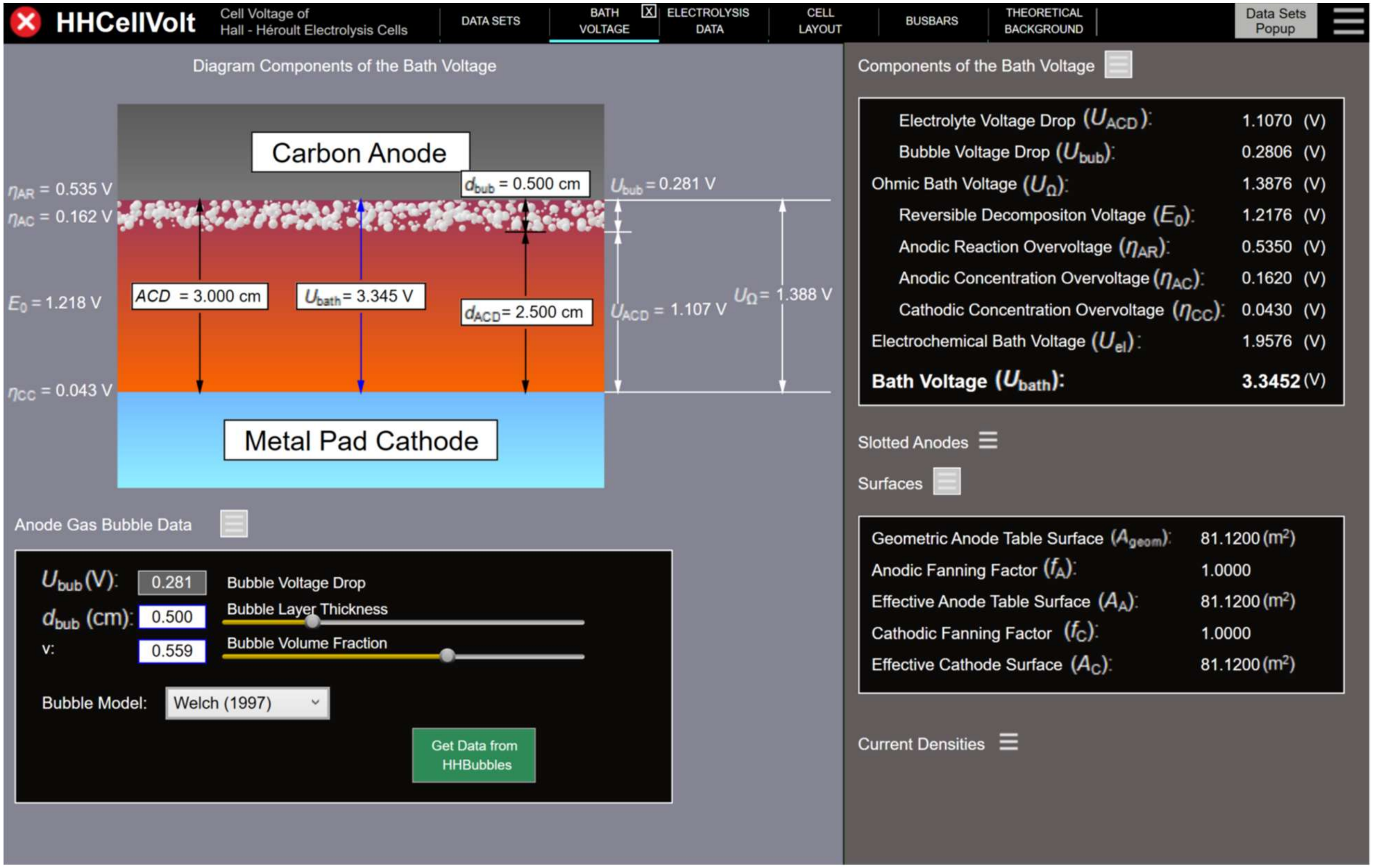

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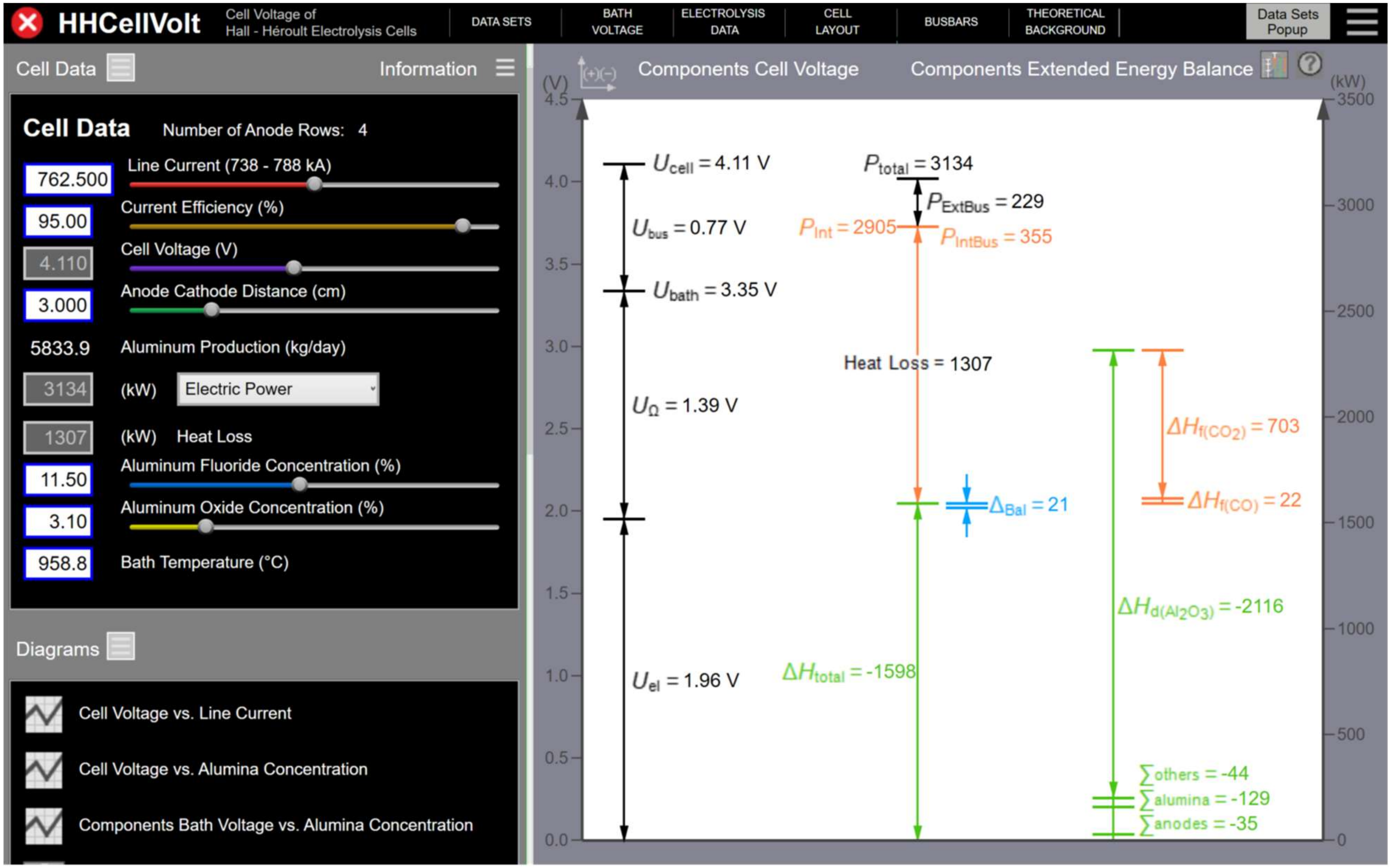
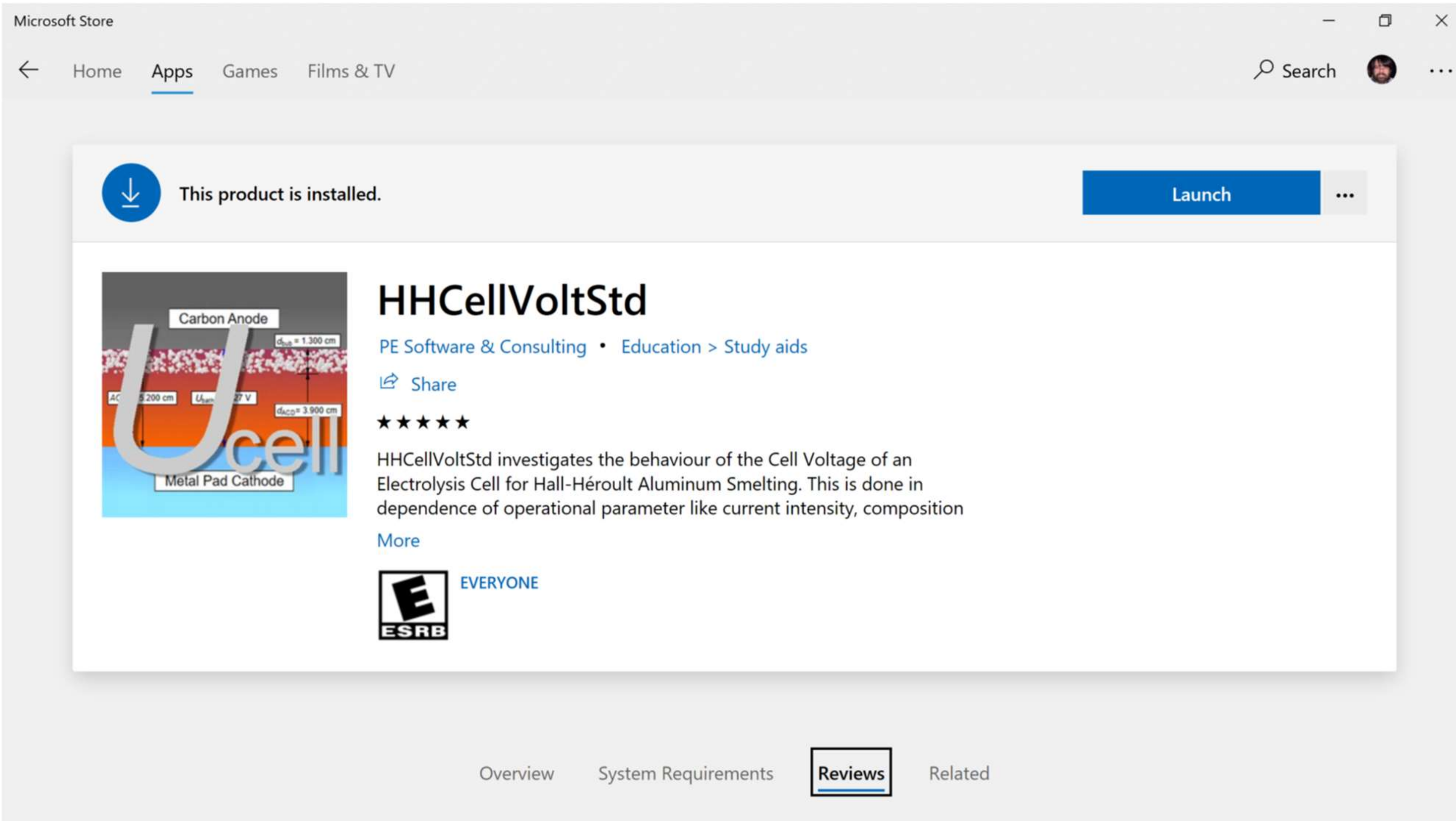


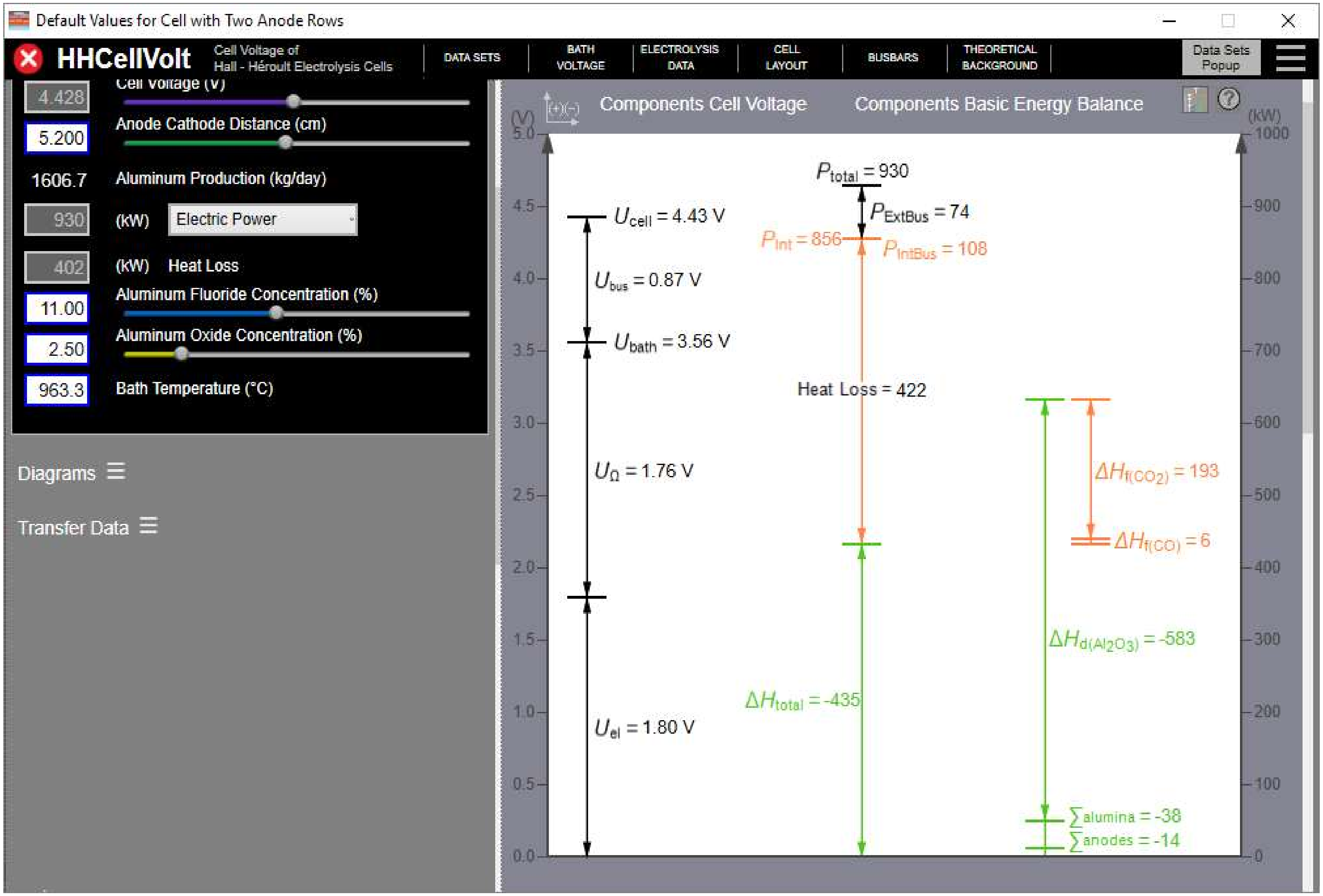
HHCellVolt on the Microsoft Store



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



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.**

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

Extended Energy Balance

- 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.

Extended Energy Balance

HHCellVolt | Cell Voltage of Hall - Héroult Electrolysis Cells | DATA SETS | BATH VOLTAGE | ELECTROLYSIS DATA | CELL LAYOUT | BUSBARS | THEORETICAL BACKGROUND | Data Sets Popup

Contents

Relations for the Energy Balance

HHCellVolt applies the data of the JANAF Thermochemocal Tables to determine the thermodynamic values of the energy balance.

Enthalpy of Formation

HHCellVolt uses a linear equation to determine the enthalpy of formation in dependence of temperature:

$$\Delta H_f = b + a \cdot t$$

meaning of the symbols:
- ΔH_f: enthalpy of formation (kJ/mol).
- a, b: coefficients of linear equation determined from the JANAF tables between 1100 K and 1300 K.
- t: temperature (°C).

Enthalpy of Formation — Substance: α-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 uses Shomate Equations that calculate the standard enthalpy:

$$H^0 - H^0_{298.15} = A \cdot t + B \cdot \frac{t^2}{2} + C \cdot \frac{t^3}{3} + D \cdot \frac{t^4}{4} - \frac{E}{t} + F - H$$

meaning of the symbols:
- H^0: standard enthalpy (kJ/mol),
- A, B, C, C, E, F, H: coefficients from the JANAF tables,
- t: 0.001 · temperature (K).

Shomate Coefficients — Substance: α-Alumina (298-2327K)

- A: 102.429
- B: 38.7498
- C: -15.9101
- D: 2.628181
- E: -3.007551
- F: -1717.93
- H: -1675.69

Test Temperature: 963.3 °C
Test Value: 107.972 kJ/mol

Useful Tables

Conversion of Energy Units

	kJ	kWh	kcal	BTU
kJ	1	2.7778×10^{-4}	0.23884	0.947817
kWh	3600	1	859.845	3412.14
kcal	4.1868	1.1630×10^{-3}	1	3.9683

Conversion of Energy Balance Units

Conversion of tension U (V), specific energy Espec (kWh/kg), power P (kW) and enthalpy ΔH (kJ/mol).
F is the Faraday Constant (96485 C/mol), I the electric current (kA) and M_{Al} the atomic weight of aluminum (26.9815).

	U	E_{spec}	P	ΔH
U	1	[illegible]	[illegible]	[illegible]

Extended Energy Balance

HHCellVolt | Cell Voltage of Hall - Héroult Electrolysis Cells | DATA SETS | BATH VOLTAGE | ELECTROLYSIS DATA | CELL LAYOUT | BUSBARS | THEORETICAL BACKGROUND | Data Sets Popup

Heat Carbon Anodes

No coefficients of the Shomate relation for carbon were found in the literature. HHCellvolt uses a linear relation determined with the values from the JANAF tables between 1100 and 1300K.

You find the corresponding Shomate coefficients on the Relations for the Energy Balance page.

Airburn Carbon Anodes

Dealing with the reaction of oxygen with carbon the heating of air (i.e. nitrogen) according to AlZharouni (Web-Lit.Equ. 4, p.5) has to be taken into account.

$$(C + O_2 + 3.8N_2)_{T_a} = (CO_2 + 3.8N_2)_{T_r}$$

T_a: ambient temperature (°C),
T_r: reaction temperature (°C).

You find the Shomate coefficients for heating of nitrogen on the Relations for the Energy Balance page.

Combustion Carbon Monoxide

HHCellVolt determines the combustion of carbon monoxide as AlZharouni (Web-Lit.Equ. 5, p.5):

$$(2CO)_{T_r} + (O_2 + 3.8N_2)_{T_a} = (2CO_2 + 3.8N_2)_{T_r}$$

T_a: ambient temperature (°C),
T_r: reaction temperature (°C).

Enthalpy of formation of carbon dioxide minus enthalpy of Formation of carbon monoxide minus heating of nitrogen.

Boudouard Reaction

$$CO_2 + C = 2CO$$

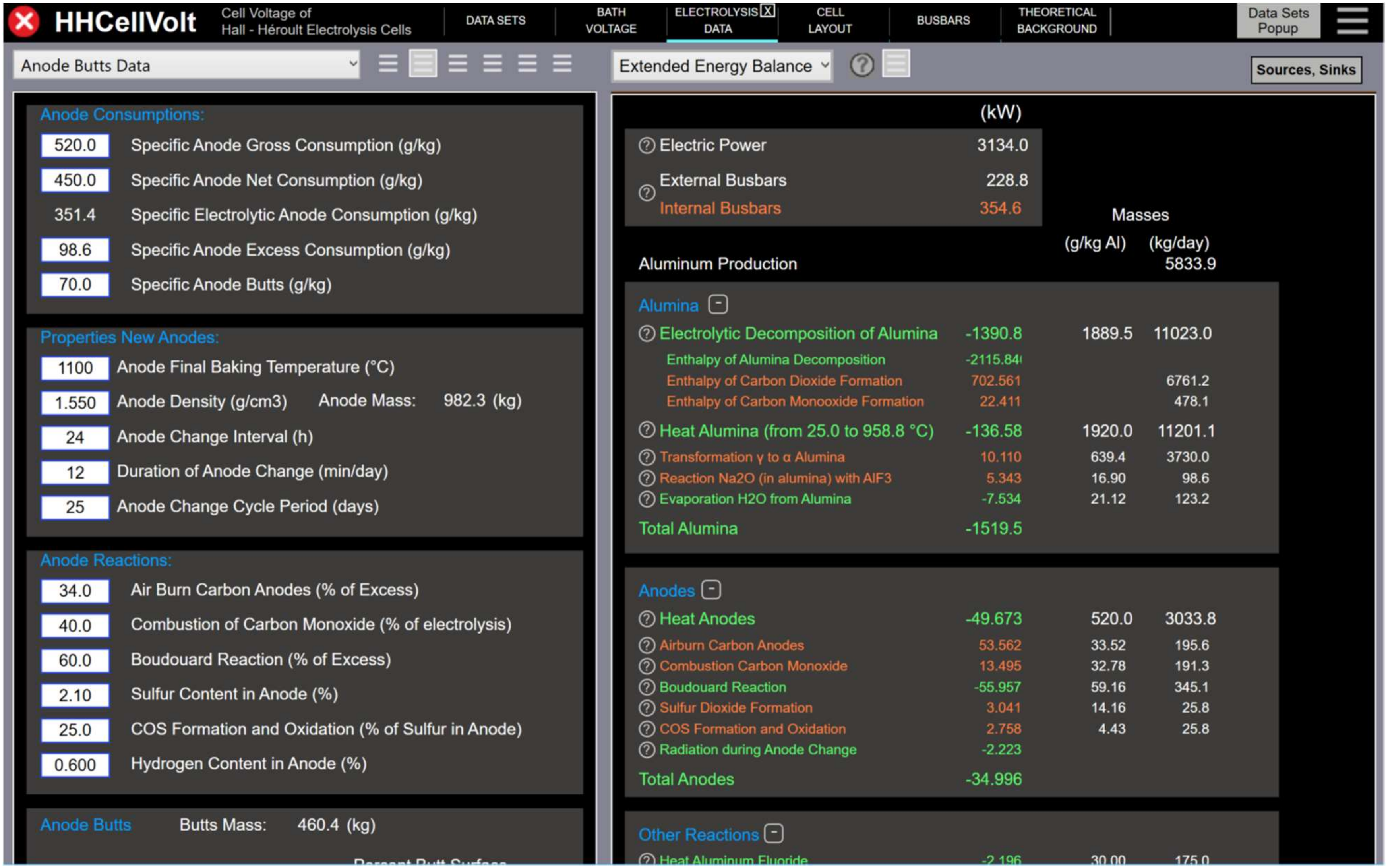
HHCellVolt calculates the enthalpy of reaction for the Boudouard reaction with: enthalpy of formation of carbon dioxide minus twice the enthalpy of formation of carbon monoxide.

Formation of Sulfur Dioxide

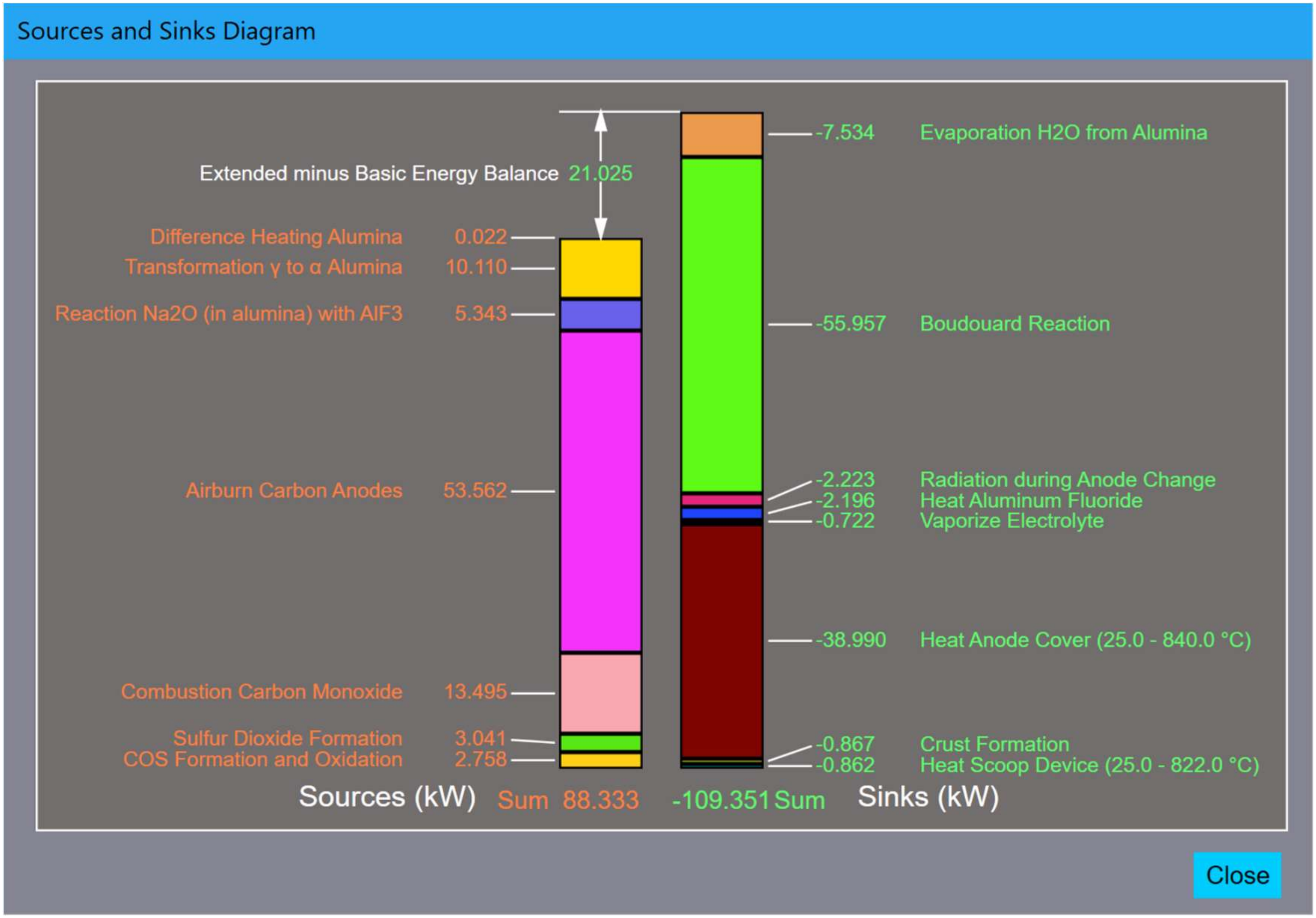
The coefficients of the relation for the enthalpy of reaction of:

$$S + 2CO_2 = SO_2 + 2CO$$

Extended Energy Balance



Extended Energy Balance



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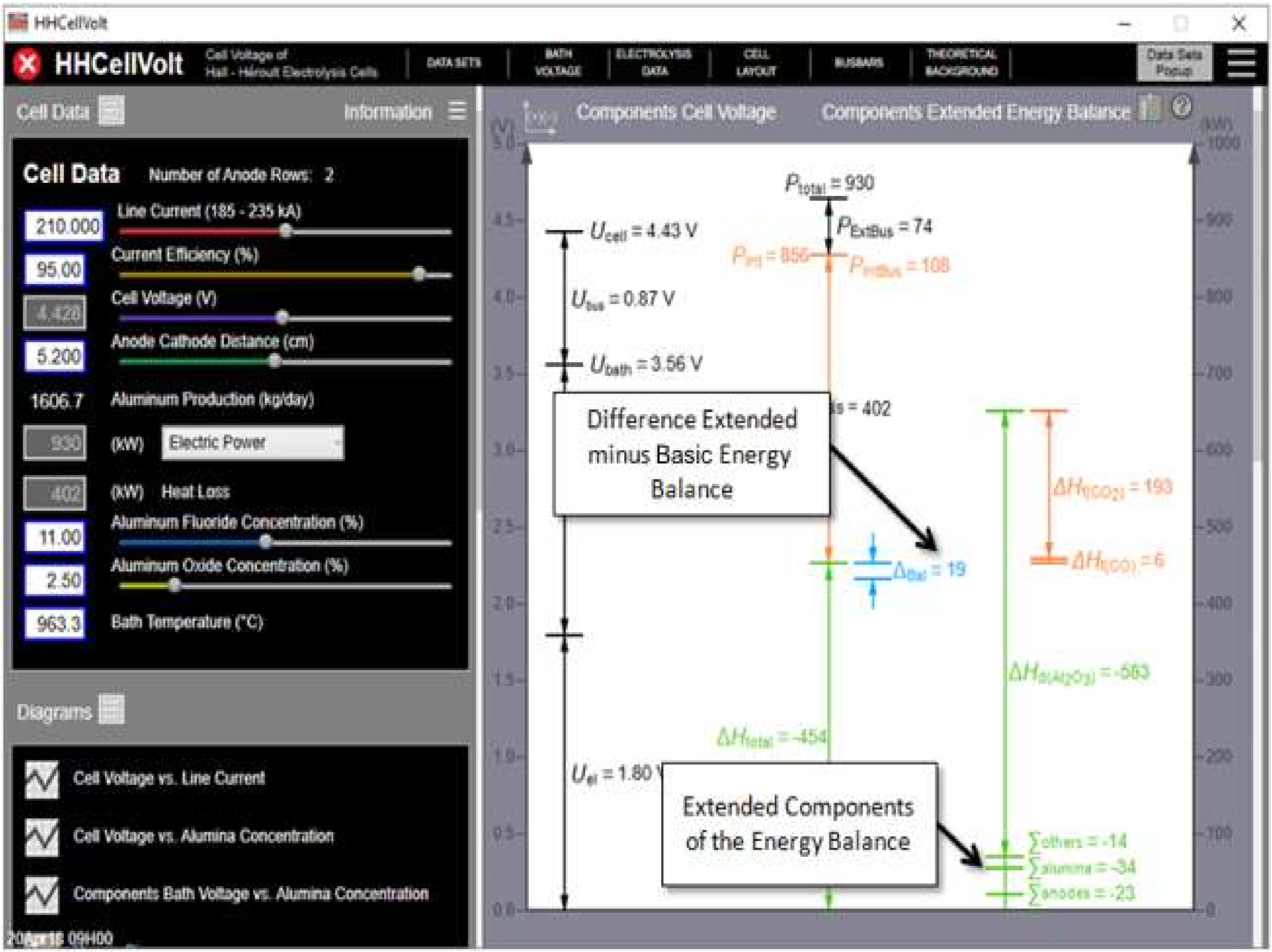
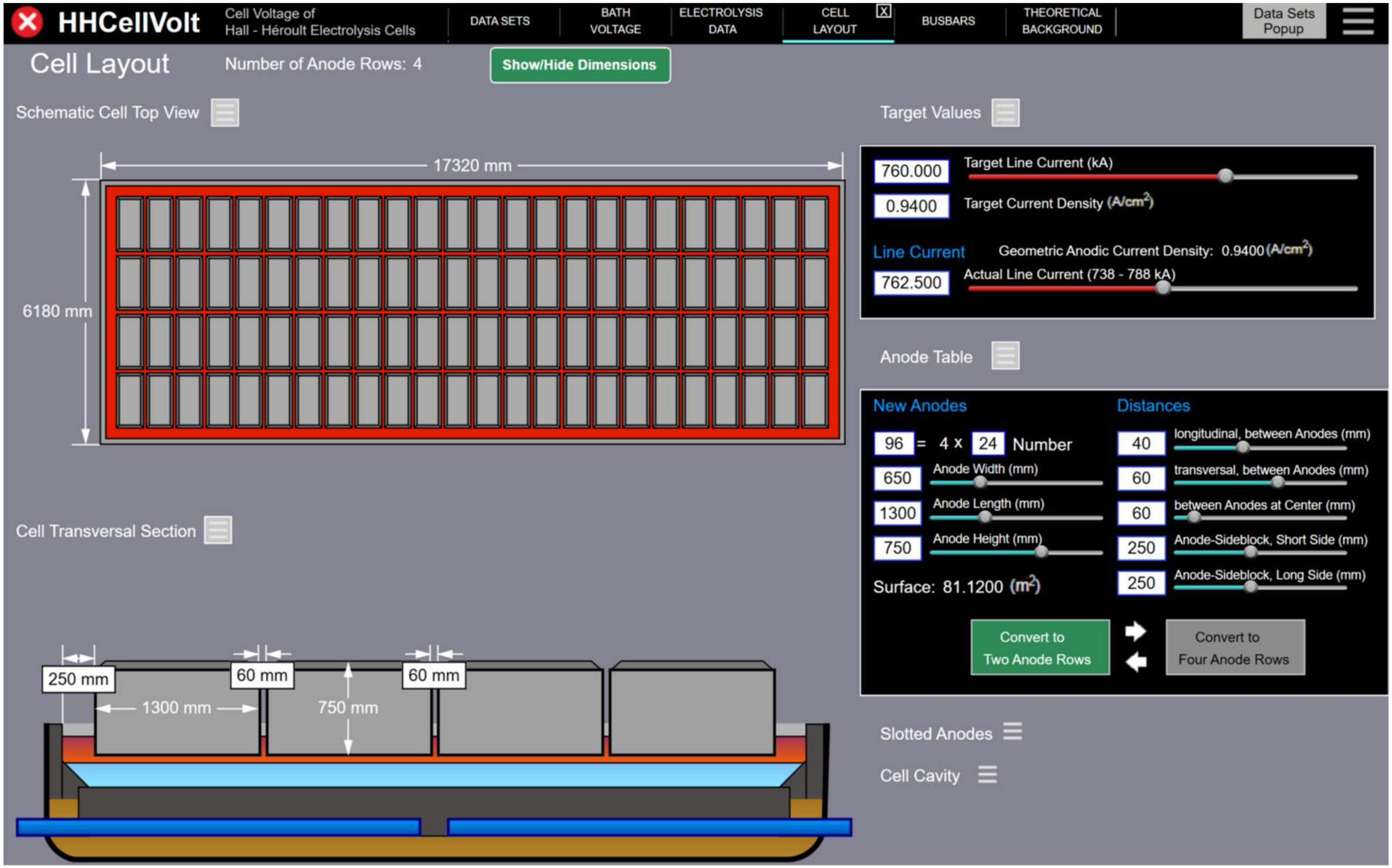


Electrolysis Cells with Four Anode Rows

- **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.**

Electrolysis Cells with Four Anode Rows



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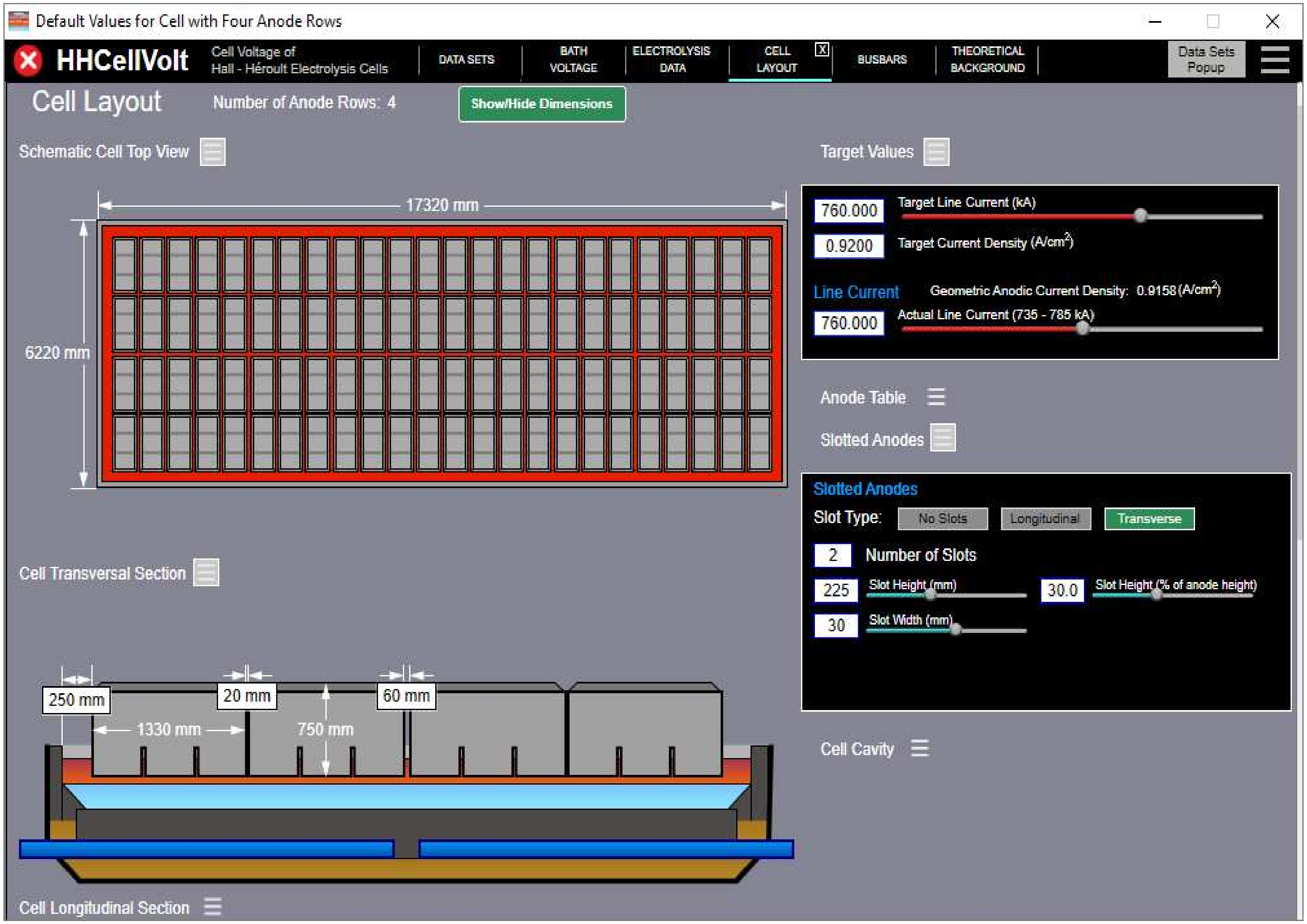

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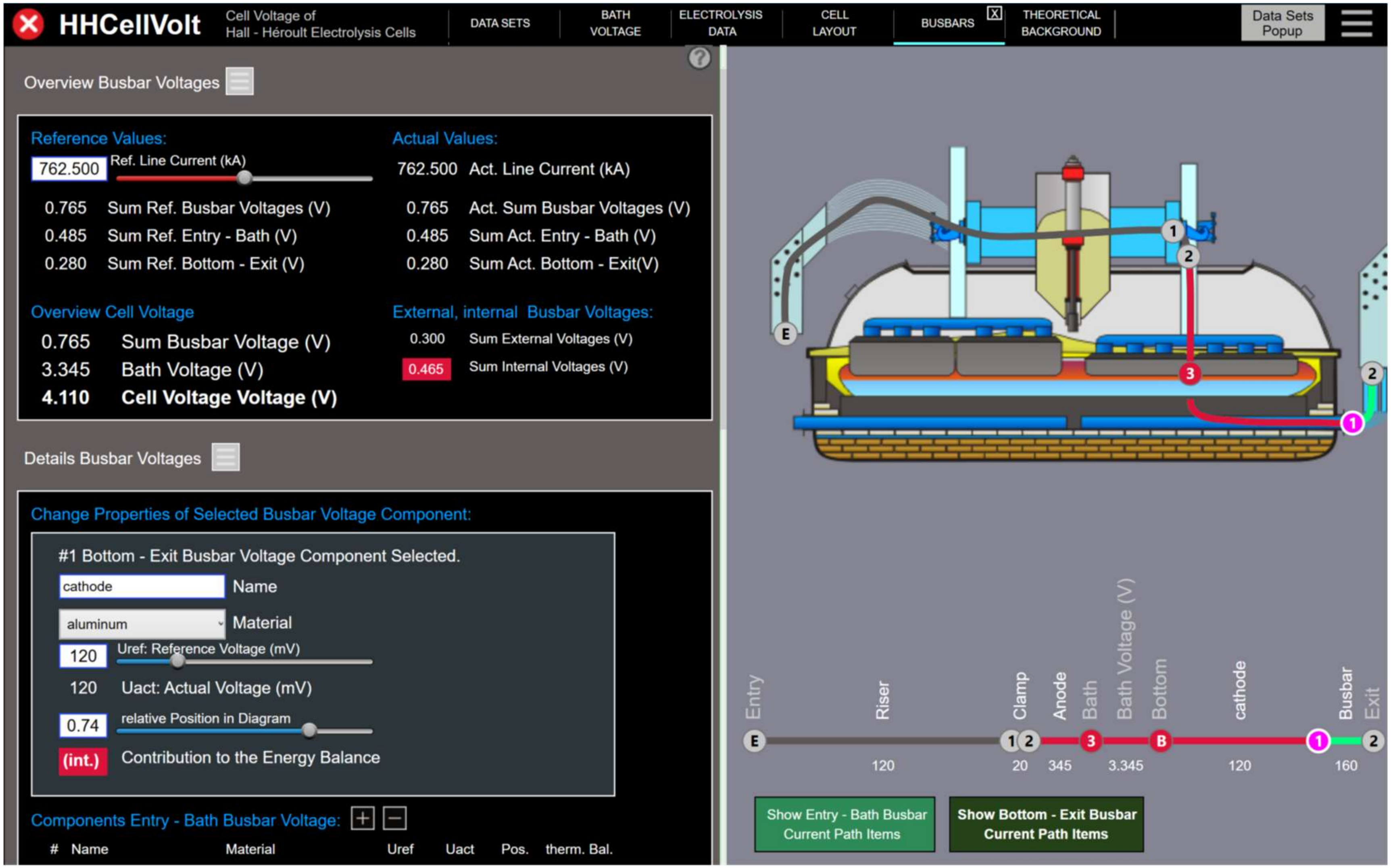

Example of the Calculation of Impact of the Extended Reactions on the Cell Operating

- **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.**

Example of the Calculation of Impact of the Extended Reactions on the Cell Operating

- 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.

Example of the Calculation of Impact of the Extended Reactions on the Cell Operating

- **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.**

Example of the Calculation of Impact of the Extended Reactions on the Cell Operating

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 AlF_3	11.50%

Example of the Calculation of Impact of the Extended Reactions on the Cell Operating

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

Example of the Calculation of Impact of the Extended Reactions on the Cell Operating

- 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%.

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.