

INTERPRETING THE COMPONENTS OF CELL VOLTAGE

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Abstract

Several misconceptions are prevalent concerning the components of cell voltage. The equilibrium potential, also known as the decomposition potential or reversible potential frequently is confused with the voltage equivalent of the total energy required by the cell to reduce alumina. The voltage intercept of cell volts vs. current extrapolated to zero current is sometimes mistakenly taken to be the back emf or counter electromotive force of the cell. The value is consistently lower than the true back emf. Pseudo resistance, the slope of cell volts vs. current, is frequently confused with the true ohmic resistance of the cell. This paper will define the various components of cell voltage, discuss how they can be determined and describe their use in cell control and diagnosis of operating problems.

List of Symbols

A_b	Effective area of bath, sq cm	ΔH	Overall enthalpy of cell reaction, j
$a_{Al_2O_3}$	Activity of alumina	h	Anode immersion depth, cm
A_{an}	Cross sectional area of a single anode, sq cm	I	Total current, amps
$AeOr$	% alumina at anode effect	i	Current density, I / A_b , amps / sq cm
$Bemf$	Back emf (counter electromotive force), volts	i_c	Concentration limited current density, amps / sq cm
CE	Current efficiency as a fraction. %CE as a %	i_r	Reaction limited current density, amps / sq cm
D_{sn}	Cell design factor. Compensates for different cells at the same current density having anode effects at different alumina concentrations.	l	Liquid phase
D_{ac}	Anode to cathode distance, cm	L_A	Ave. of new and spent anode length, cm
d_b	Bubble layer thickness (under anode), cm	n	Number of electrons involved in reaction
E°	Standard potential, volts	p	Reaction order, or charge transfer coef.
E_{Al}	Voltage equivalent of energy to reduce alumina	R	Gas constant, 8.3144 j / k mol
E_{bub}	Bubble overvoltage, IR_{bub} , volts	R_{an}	Anode resistance, ohms
E_{cell}	Total cell voltage	R_{ca}	Cathode resistance, ohms
E_E	Equilibrium potential, volts	R_b	NaF / AlF ₃ weight ratio
E_{pc}	Polarized cell potential, volts	R_{ba}	Effective resistance of bath, ohms
F	Faraday constant, 96,485 j /voltage equivalent	R_{bub}	Extra bath resistance caused by bubbles, ohms
F_i	Current fanning from anode in direction, i	ROS	Relative saturation of bath with alumina
ΔG	Free energy of cell reaction, j	R_{pseudo}	Slope of volt amp curve, ohms
G	Carbon consumption (electrolytic + Boudouard)/ theoretical	R_x	Bus resistance, external to cell, ohms
g	Gas phase	ΔS	Cell reaction entropy change, j/K
		S_i	Distance to adjacent anode or twice the distance to an insulating wall, cm
		T	Bath temperature, Kelvin
		T_{AnBk} ..	Anode bake finishing temperature, °C
		T_b	Bath temperature, °C
		T_r	Temp. material entering bath, °C
		V_{ext}	Voltage, extrapolated to zero amps
		W_A	Ave. of new and spent anode width, cm
		%	Mass percent for bath components, volume percent for cell gas components
		α	Alpha phase of alumina, corundum
		γ	Gamma phase of alumina
		Φ	Bubble coverage (fraction of anode)
		η_{ca}	Concentration overvoltage at anode, volts
		η_{sa}	Surface overvoltage at anode, volts
		η_{cc}	Concentration overvoltage at cathode, volts

Components of Cell Voltage

The voltage in a cell is the sum of the back emf (counter electromotive force), the bath's ohmic voltage, the additional ohmic voltage caused by bubbles, the voltage drops through the anode and cathode and voltage drops external to the cell.

$$E_{cell} = E_{emf} + IR_{ba} + IR_{bub} + IR_{an} + IR_{ca} + IR_x \quad 1.$$

The E_{emf} is made up of the equilibrium potential plus overvoltages. The equilibrium potential (reversible potential or Nernst potential) is the voltage required to hold the cell in equilibrium. The kinetics of producing products requires additional voltage at both electrodes (overvoltages). These overvoltages result from concentration gradients and surface reactions at the electrodes.

$$E_{emf} = E_E + \eta_{sa} + \eta_{ca} + \eta_{cc} \quad 2.$$

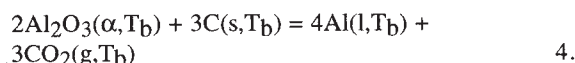
Determination of the Components of Cell Voltage

Knowing the cell reaction, the equilibrium potential can be calculated from thermodynamics. Overvoltages must be measured. We will consider first the values that can be calculated.

Equilibrium Potential

The standard potential, E° , is calculated from ΔG , the standard free energy change for reaction 4 with all reactants and products at unit activities:

$$E^\circ = \Delta G / (nF) \quad 3.$$



By thermodynamic convention, ΔG in equation 3 should have a negative sign. This would make E° negative, as is required by thermodynamic convention. By this convention the cell voltage and all components of it are negative because energy is consumed rather than produced. However, engineers and pot operators consider the cell voltage positive, hence the sign of all cell voltage components has been made positive. Alpha alumina was used in reaction 4 because gamma and other non- alpha aluminas convert to alpha as they go into solution.

Substituting $n = 12$, $F = 96,485 \text{ j /volt equiv.}$ and numerical values for ΔG as a function of T :

$$E^\circ = 1.896 - 0.000572 T \quad 5.$$

The Nernst equation corrects the standard potential for the actual activities to give the equilibrium potential, E_E :

$$E_E = E^\circ - \frac{RT}{12F} \ln \frac{a_{Al}^4 a_{CO_2}^3}{a_{Al_2O_3}^2 a_C^3} \quad 6.$$

Al, CO_2 , and C are close enough to their standard states that they can be assigned unit activities. The activity of alumina must be obtained from measurements.

Activity of alumina

Activities are thermodynamic concentrations. For many years equation 7 has been used to calculate the activity of alumina. It was based upon data that Rolin¹ and Vetyukov and N. Van Ban² obtained from measurement of cell potential vs. alumina concentration in cryolite.

$$a_{Al_2O_3} = ROS^{2.77} \quad 7.$$

$$ROS = \%Al_2O_3 / (\%Al_2O_3 \text{ at saturation}) \quad 8.$$

A recent analysis by Dewing and Thonstad³ of cryoscopic data, showed that the above data^{1, 2} was inaccurate. The slope of $\log(a_{Al_2O_3})$ vs. $\log(\%Al_2O_3)$ was 3 in dilute solutions and 1.5 in concentrated solutions corresponding to species containing, respectively, 1 and 2 atoms of oxygen. Extrapolating their data to saturation, one obtains an alumina saturation value of 13.8% for cryolite at 1027°C rather than the commonly accepted value of 13.1% determined by Solheim, et al⁴ indicating Solheim's value may be a bit low. Using 13.8 for saturation, good agreement with Dewing and Thonstad's activity data is obtained with equation 9 down to $ROS = 0.5$. Accuracy deteriorates at lower concentrations where the exponent of ROS approaches 3 as ROS approaches 0. However, a 4th degree polynomial, equation 10, provides nearly a perfect fit of the data as shown in Figure 1.

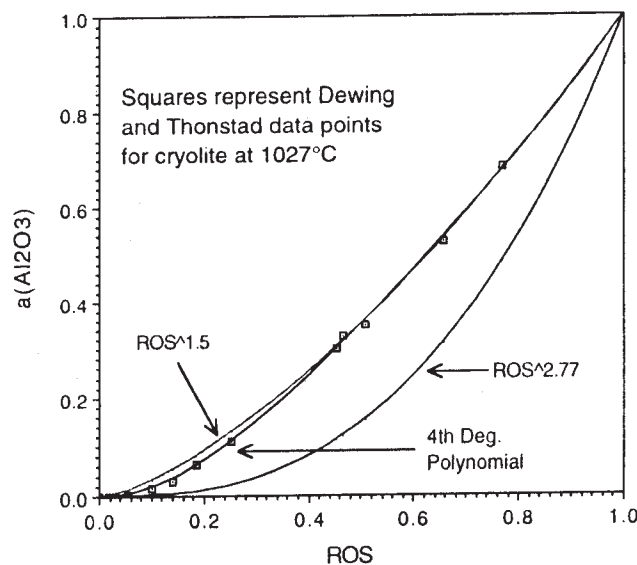


Figure 1. Comparison of equations for alumina activity

$$a_{Al_2O_3} = ROS^{1.5} \quad 9.$$

$$a_{Al_2O_3} = - 0.03791 ROS + 2.364 ROS^2 - 2.194 ROS^3 + 0.8686 ROS^4 \quad 10.$$

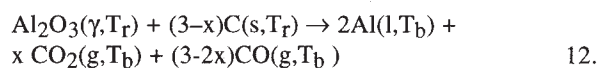
Equation 10 makes the assumption that the equilibrium between one oxygen and two oxygen species is entirely a function of relative saturation. This may not be strictly true. Bath acidity may have more influence on alumina activity than is reflected by the saturation value. Equation 10, however, is probably the best we can do until new measurements of alumina activity are obtained for a range of industrial baths.

Voltage Equivalent of Energy to Make Aluminum

The equilibrium potential, E_E , is sometimes confused with E_{Al} , the voltage equivalent of the total reaction enthalpy required to make aluminum. Indeed IE_E does represent the electrochemical energy, but additional heat energy, I^2R , is required to raise the alumina and carbon to temperature and supply the thermodynamic quantity $T\Delta S$. The voltage equivalent of the total energy to make aluminum, which the author calls E_{Al} , can be calculated:

$$E_{Al} = \Delta H (CE) / (nF) \quad 11.$$

ΔH is the enthalpy for reaction 12.



$$x = 0.03 \% \text{CO}_2 / (1. + 0.01 \% \text{CO}_2) \quad 13.$$

Current efficiency enters Equation 11 because only the aluminum actually made requires energy. Calculation requires knowing %CO and %CO₂ (normalized to 100%). These values can be calculated from the current efficiency using Beck's⁵ equation.

$$\% \text{CO} = [200G - 2(\% \text{CE}) - 8] / G \quad 14.$$

$$\% \text{CO}_2 = 100 - \% \text{CO} \quad 15.$$

$$G \approx 1.05 \text{ for prebaked anodes}$$

$$G \approx 1.19 \text{ for Soderberg anodes}$$

This allows us to calculate E_{Al} :

$$E_{Al} = [\% \text{CE}/100] [\% \text{CO}_2 (3.7000 + 0.0005099 T_b) + \% \text{CO} (2.300 + 0.0002847 T_b)] / (\% \text{CO} + 2 \% \text{CO}_2) \quad 16.$$

Equation 16 is valid for steady state operations. In the dynamic state, the heating of carbon, the heating and dissolution of alumina and electrochemical reduction must be treated separately as functions of time.

Overvoltages

Overvoltages must be measured. The data can then be fitted to equation 17 or 18, depending upon whether the overvoltage is caused by concentration gradients or by either a slow chemical reaction or slow charge transfer. Equation 17 is for concentration overvoltage. Equation 18 is for reaction or charge transfer overvoltage. Since both charge transfer and reaction overvoltages

have the same mathematical form it is convenient to lump them together as surface overvoltage.

$$\eta_c = \frac{RT}{nF} \ln \frac{i_c}{i_c - i} \quad 17.$$

$$\eta_s = \frac{RT}{npF} \ln \frac{i}{i_r} \quad 18.$$

Measurement of Overvoltages

One way to measure overvoltages is to place a reference electrode close to the electrode under study and measure the difference in potential between the two (Welch and Richards⁶). Care must be taken to avoid (or to measure and subtract out) the ohmic voltage drops in the electrode under study and in the electrolyte between the electrode under study and reference electrode.

Another technique is to record potential vs. position of a reference electrode probe scanned between the anode and cathode (Haupin⁷). This technique provides data from which anode overvoltage, cathode overvoltage and effective current density in the bath can be determined. The probe has been simplified and improved over that described in the reference. The present probe uses 18 ga tungsten wire threaded through 8 mm OD quartz capillary tubing. The lower end is sealed by fusing the quartz to the tungsten. About 2 mm of wire should extend past the seal. This is plated with aluminum, as described in the reference to become an aluminum reference electrode. A glassblower can heat and bend the probe to the required shape to make measurements under an anode. Quartz will hold its shape at bath temperature and dissolve slowly enough that duplicate scans can be made before the probe fails. A rugged, accurate positioning device as described in the reference is needed or better yet, one like that described by Torklep⁸.

Current interruption provides yet another technique to measure overvoltages. Upon current interruption, all ohmic voltages disappear and the E_{mf} is observed. The reading must be made within 0.01 sec because overvoltages decay rapidly. In principle, the various overvoltages can be determined by their differing rates of decay. Some problems are: 1. interrupting the circuit very quickly with no arcing, 2. suppressing ringing (voltage oscillations) that obscure the beginning of the voltage decay curve, 3. interpreting overvoltages on electrodes having a distribution of current densities and hence a distribution of overvoltages. A commercial current interrupter⁹ is available that works with laboratory cells up to 100 amps. It is much more difficult to make these measurements on plant cells. Many years ago the author connected an oscilloscope across a plant cell (using long shielded leads to get outside the magnetic field) and followed the voltage trace when a line had to be shut down. It was 0.5 sec before the ringing disappeared. This made it difficult to extrapolate back to the moment of current interruption. The voltage decay appeared to combine two time constants, one of about 1 sec and another of 15 sec. In about a minute the voltage had decayed to E_E where it held for many minutes.

Concentration overvoltage at the anode

Concentration gradients in the bath close to the anode produce concentration overvoltage. Concentration overvoltage is normally small but at low alumina content, concentration overvoltage increases to the point where fluoride ions discharge

centration, bath temperature and anode size was derived from the early work of Piontelli et al.¹⁰ augmented with later laboratory and plant data⁷.

$$i_c = [0.00464 T_b - 3.454] [C_a (\%Al_2O_3) + C_b (\%Al_2O_3)^2] A_{an}^{-0.1} D_{sn} \quad 19.$$

$$C_a = 1.443 - 1.985 R_b + 1.131 R_b^2 \quad 20.$$

$$C_b = 0.4122 - 0.2037 R_b \quad 21.$$

$$D_{sn} = i / \{ [0.00464 T_b - 3.4544] [C_a (AeOr) + C_b (AeOr)^2] A_{an}^{-0.1} \} \quad 22.$$

This gives the working equation:

$$\eta_{ca} = [T / 23210] \ln [i_c / (i_c - i)] \quad 23.$$

Surface overvoltage at anode

The measured anode overvoltages^{6, 7, 10, 11} combine both concentration and surface overvoltage. Therefore, before analyzing the data, it was necessary to subtract out concentration overvoltage using Equation 23. Then the data was fitted to Equation 18 providing values for p and i_r . Values of p correlated with anode baking finishing temperature.

$$p = 3.773 / \ln (T_{AnBk} + 273) \quad 24.$$

Values obtained for i_r were fitted to the expression:

$$i_r = \text{Exp} [0.560 \ln (\%Al_2O_3 + \%LiF/4) + 0.276 (R_b - 1.5) - 5.849] \quad 25.$$

Combining Equations 18 and 24, and evaluating constants gives:

$$\eta_{sa} = 1.142e-5 \ln (T_{AnBk} + 273)(T) \ln (i / i_r) \quad 26.$$

Equation 26 is inaccurate below 0.01 amp/cm². This generally presents no problem, but if required, as in Figure 3, Equation 27 can be substituted below 0.01 amp/cm². This is much easier than using the Butler, Volmer, Erdey, Gruz equation generally recommended¹² in this range of overvoltage.

$$\eta_{sa} = [1.142e-3 \ln (T_{AnBk} + 273)(T) \ln (0.01 / i_r)] i \quad 27.$$

Concentration overvoltage at the cathode

Laboratory¹³ and scanning reference electrode data⁷ led to the following equation for cathode overvoltage. Thonstad and Rolseth¹³ explained why the mathematical relationship looks like reaction overvoltage although it is actually concentration overvoltage.

$$\eta_{cc} = [(2.73 - 0.5 R_b) T / 75000] \ln (i / 0.283) \quad 28.$$

Bubble Overvoltage

The extra voltage drop in the bath caused by bubbles is sometimes called bubble overvoltage even though it is ohmic, not electrochemical. It does, however, have some of the characteristics of an overvoltage. Because the resistance is a function of current, the voltage drop is not linear with current. Since the bubbles act like capacitors, bubble overvoltage has a time constant albeit minute. I have never seen any measurements of this time constant, but it can be calculated from gas coverage and bubble thickness to be between 10⁻¹³ and 10⁻¹⁴ seconds—far too small to be observed by current interruption or to be considered part of the Bemf. However, since it is nonlinear with current, I include E_{bub} in the polarized cell potential.

$$E_{pc} = \text{Bemf} + E_{bub} \quad 29.$$

Hyde & Welch¹⁴ and Aaberg, Ranum, Williamson and Welch¹⁵ present an excellent analysis and equations for calculating the extra resistance caused by bubbles under the anode. Their data gives an average layer bubble thickness:

$$d_b = (0.5517 + i) / (1. + 2.167 i) \quad 30.$$

Data by Aaberg, et al¹⁵ on gas coverage under the anode was supplemented with data by Haupin⁷ and fitted to equation 31.

$$\Phi = 0.5090 + 0.1823 i - 0.1723 i^2 + 0.05504 i^3 + (0.4322 - 0.3781 R_b) / (1. + 1.637 R_b) + [0.431 - 0.1437 (\%Al_2O_3 - AeOr)] / [1. + 7.353 (\%Al_2O_3 - AeOr)] \quad 31.$$

The extra voltage caused by bubbles becomes:

$$E_{bub} = i / k [d_b / (1 - \Phi) - d_b] \quad 32.$$

Effective Areas for Voltage Calculations

When current leaves the anodes, it fans out from the sides of the anode increasing the effective bath area. Under the central portion of the anode, current flows vertically, but the current density is lowered by the current leaving from the sides of the anode. Current leaving the sides of the anode experiences lower anode overvoltage (because of lower current density), higher bath voltage (because of the greater distance) and lower cathode overvoltage (because of the lower current density). The total voltage drop, however, is the same as under the center of the anode.

Voltage calculations in this paper are based upon current densities under the center of the anode. This simplifies calculations because here anode, bath and cathode all have the same current density. This current density can be determined with a finite element or finite difference computer model. A more simple method is to use fanning factors to calculate the effective bath area. These fanning factors are hypothetical extensions of the anode dimensions that produce an area that when summed for all anodes in the cell and divided into the cell current gives the current density under the anode. The fanning factor relationship was derived from data by Haupin⁷ and Welch¹⁶.

$$A_b = \Sigma(L_A + F_1 + F_2) (W_A + F_3 + F_4) \quad 33.$$

$$F_i = [0.1656 D_{ac} - 0.0043 D_{ac}^3 + 0.1270 S_i - 0.0034 S_i^2 + 0.0394 D_{ac} S_i] [0.3844 + 0.06166 h + 0.001822 (L_A + W_A) - 0.000178 h (L_A + W_A)] \quad 34.$$

$$i = I / A_b \quad 35.$$

Difference between Vext and Bemf

The back emf, Bemf, or counter emf of a cell is the equilibrium potential plus all overvoltages. It is the voltage that remains when one subtracts out all ohmic voltages, as by interrupting the current.

$$Bemf = E_{cell} - I (R_{ba} + R_{bub} + R_{an} + R_{ca} + R_x) \quad 36.$$

Vext, on the other hand, is the voltage intercept of cell volts vs. current extrapolated from a small change in current to zero current. The slope of this extrapolation is the pseudo resistance used in cell control. Pseudo resistance is frequently confused with the true ohmic resistance of the cell.

$$Vext = E_{cell} - I R_{pseudo} \quad 37.$$

$$R_{pseudo} = R_{ba} + R_{bub} + R_{an} + R_{ca} + R_x + \Delta E_{bub} / \Delta I + \Delta \eta_{sa} / \Delta I + \Delta \eta_{ca} / \Delta I + \Delta \eta_{cc} / \Delta I \quad 38.$$

When one compares the components of R_{pseudo}, equation 38, with the sum of ohmic resistance in equation 36, it is clear why Vext and Bemf are different. Pseudo resistance contains the true ohmic resistance plus a good bit more. A comparison of Vext and Bemf as functions of alumina concentration is shown in Figure 2.

Application to Cell Control

Subtracting an average value of Vext from the cell voltage before dividing by current takes out scatter (noise) caused by line current variations when calculating pseudo resistance. The same is true for the normalized voltage calculated by multiplying the pseudo resistance by a standard current.

Determining Vext whenever there is a line current variation of adequate magnitude gives a check on the resistance control of alumina. If the cell is operating well, and not too close to anode effect, the value of Vext correlates with alumina concentration and can be used to control the alumina feed rate. Perhaps an even more valuable benefit of determining Vext routinely, is that when the correlation disappears it signals either an anode problem or operation too close to anode effect. Operation close to anode effect will produce very low or negative values of Vext. Moreover there will be hysteresis, i.e. Vext calculated for a fall in current will be different from the value calculated when the current is restored.

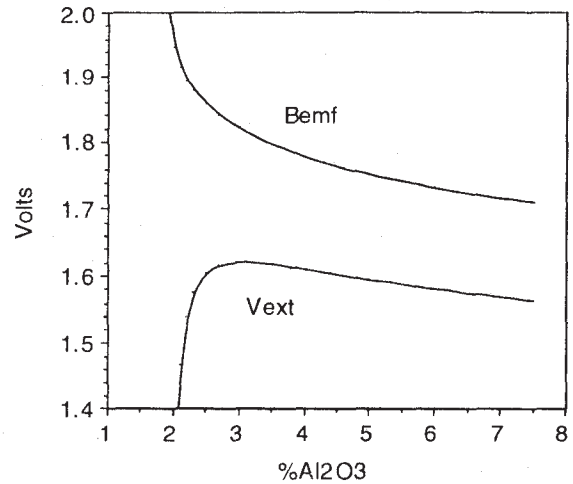


Figure 2. Cemf and Vext compared for 10% AlF₃, 6.5% CaF₂, 0.3% MgF₂, 10°C superheat. The rise in E_{cell} at low alumina produces a steep slope of E_{cell} vs i, as shown in Figure 3. Here extrapolation for Vext gives low values.

Figure 3 shows the calculated cell voltage as a function of current density. A low alumina concentration of 2.6% was chosen to show the cause of very low or negative Vext values.

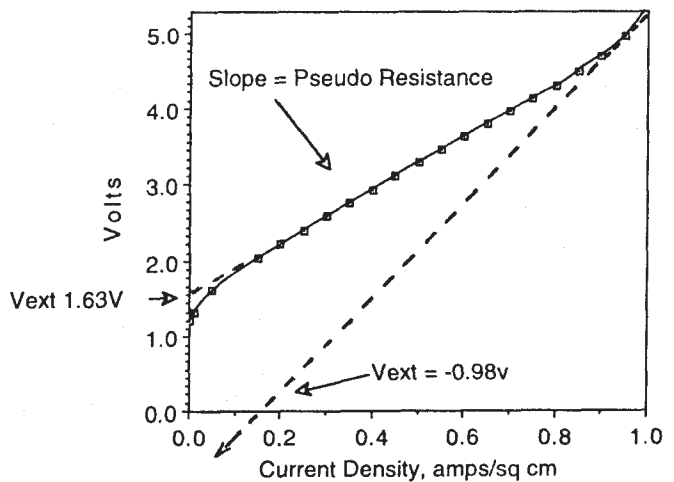


Figure 3. Cell voltage vs Current density. Calculated for 2.6% alumina, 10% AlF₃, 6.5%CaF₂, 0.3% MgF₂ and 10°C superheat. Above 0.8 amps/cm², E_{pc} increased rapidly causing the slope, ΔE/Δi, to increase. Here, extrapolation to zero current produced a negative value for Vext.

Curves 4 and 5 show the components of cell voltage and how they vary with alumina concentration, anode-to-cathode spacing and current density.

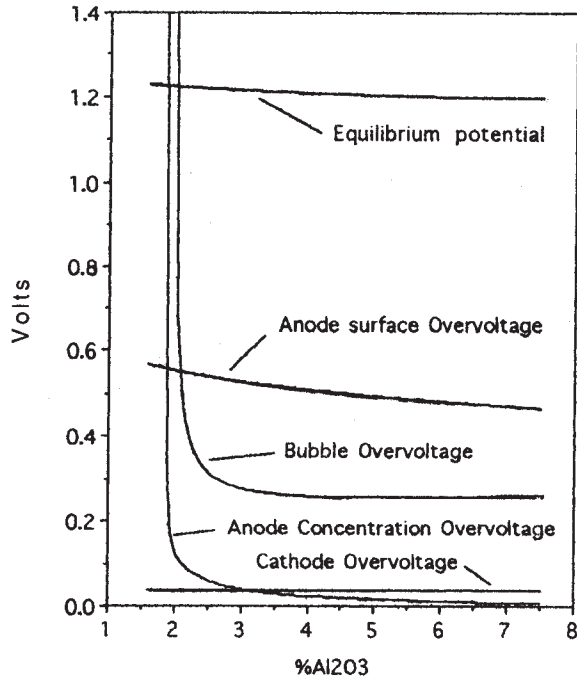


Figure 4. Components of polarized cell potential, calculated for 10% AlF₃, 6.5%CaF₂, 0.3% MgF₂, 10°C superheat and 0.8 amps / cm²

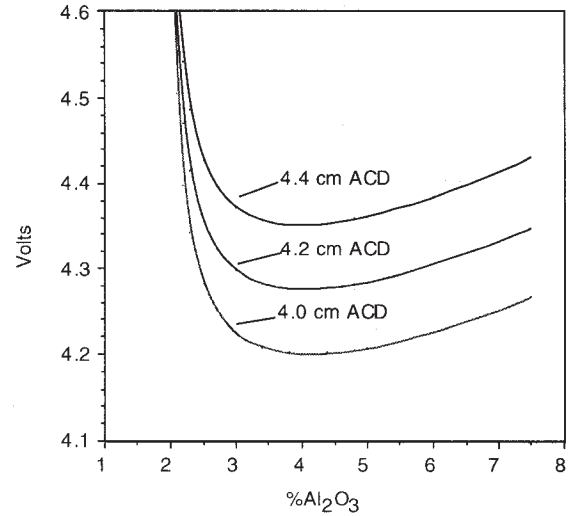


Figure 6 Cell voltage vs. % alumina at several anode-to-cathode spacings. These curves were obtained by summing all the components shown in Figures 4 and 5.

Figure 7 shows graphically the components of cell voltage and their relationship to energy consumption. Voltages in the cell are related to energy by equation 39.

$$\text{kWh / kg Al} = 298 E / \%CE$$

39

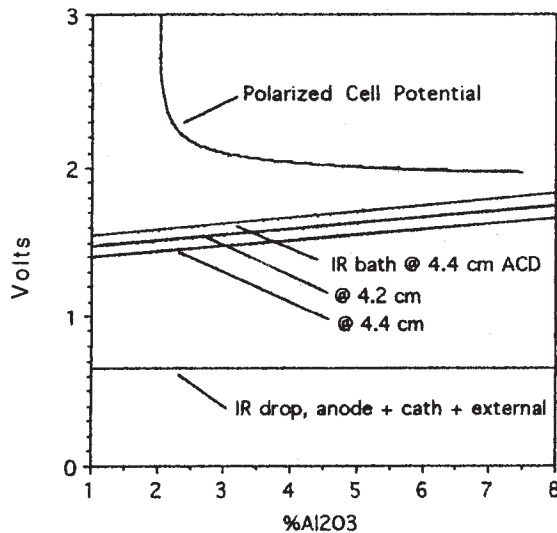


Figure 5. Components of cell voltage for the same bath and conditions as Figure 4.

Figure 6 shows the calculated cell voltage as a function of alumina concentration and anode-to-cathode separation. Curves like these are the basis of most computerized cell control. While the cell is underfed, alumina concentration will fall. When the rate of rise of voltage exceeds a set value, the control will switch to fast feed for a set period. The magnitude of the voltage at this point is an indication of anode-to-cathode distance and can be used to adjust the anodes.

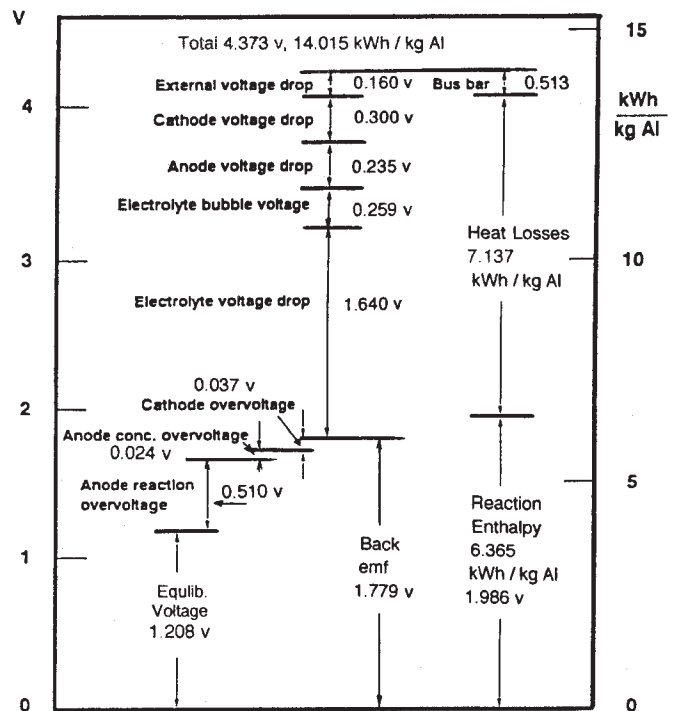


Figure 7. Typical distribution of voltages and energy in a cell. Bath and operational conditions are those of Figures 4 and 5 at 3% alumina. The volts scale (left) and the kWh / kg Al (right) correspond at 93% current efficiency.

Caveats

Cell design, as it influences bath flow and metal pad flow, is known qualitatively to influence overvoltages and bubble voltage. Higher cathode overvoltages have been observed in very stable cells¹⁷. However, no quantitative data was available to incorporate cell stability into the equations for overvoltages or the gas bubble effect.

Conclusion

The components of cell voltage have been dissected and fitted to mathematical functions. The difference between cell resistance and pseudo resistance, between back emf and V_{ext} , between the equilibrium potential and E_{Al} – all terms frequently misunderstood – have been explained. New data is needed on the activity of alumina in industrial baths. Data is needed on the effect of cell design upon bubble retention and overvoltages. Use of V_{ext} measurements to find problem pots was recommended.

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