

1. FUNDAMENTALS

The selected papers on aluminum electrolysis fundamentals encompass the early pioneer research work conducted by some of the technological giants in our industry (such as Jomar Thonstad, Warren Haupin, Barry Welch, Ernest Dewing, and Nolan Richards), to the recent new developments and breakthroughs. The foundations for the physicochemical properties of modern bath chemistry, anode polarization studies, alumina dissolution mechanisms, and our understanding of the thermodynamics of the electrochemical processes were developed during the 1960s and 1970s. However, the technological development in the area of fundamentals is ongoing. For example, in 1985 the first current efficiency model was published by Bjorn Lillebuen, but it was not until 20 years later that accurate current efficiency measurements were made in individual industrial electrolysis cells by Gary Tarcy and Knute Torkelp. Perhaps no individual has made a greater contribution to the general understanding of the fundamentals of the aluminum electrolysis process in *Light Metals* than Warren Haupin, and four of his major papers are included in this section.

PRINCIPLES OF ALUMINUM ELECTROLYSIS

WARRENE E. HAUPIN

2820 Seventh Street Road

Lower Burrell, PA 15068

Abstract

For years Hall-Héroult cells have been operated successfully using procedures and recipes based largely upon experience. In today's competitive environment it is valuable to supplement experience with scientific principals. This paper attempts to describe some rather complex concepts in a simplified manner for those who never have had or have forgotten their training in electrochemistry, thermodynamics or kinetics.

Although sodium ions carry the current through the bath, the cathode reaction extracts aluminum and leaves at the interface a melt that is richer in sodium fluoride and therefore has a higher liquidus temperature (melting point) than the bulk. The anode reaction produces aluminum fluoride at the anode-bath interface. Good convection mixes electrolyte, restoring the bulk composition, but this mixing aggravates the reoxidation of dissolved metal by carbon dioxide thereby lowering current efficiency. Kinetics causes the anode reaction to produce carbon dioxide instead of carbon monoxide, the thermodynamically favored product. These kinetic factors increase the cell voltage by about 500 mv. When the oxide dissolved in the electrolyte is nearly depleted, fluorine is codeposited on the anode surface producing a non-wettable fluorocarbon film. Current then flows by arcing, producing an *Anode Effect*. This causes emission of carbon tetrafluoride and increases the cell voltage by over 25 volts.

Introduction

The Electrolytic Cell or Pot

A typical modern aluminum reduction cell, commonly called a pot, Figs. 1a and 1b, begins with a rectangular steel shell, 9–14 m long by 3–4 m wide by 1–1.2 m high, lined with refractory thermal insulation. Within this is an inner lining of carbon to contain the highly corrosive molten fluoride electrolyte (or bath, as it is commonly called) and liquid aluminum. Electric current enters the cell through 18 to 32 prebaked carbon anodes or through a single continuous self-baking Søderberg anode, Fig.2. A crust of frozen bath

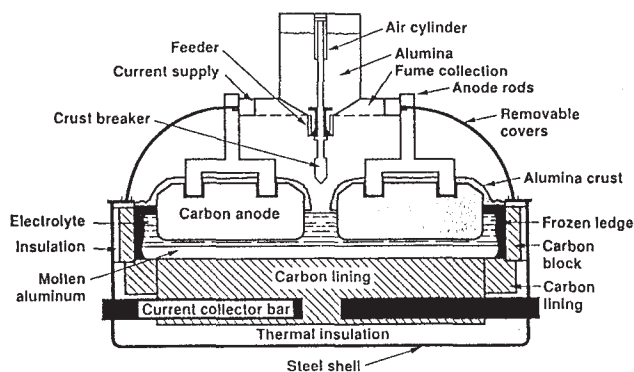


Fig. 1a Hall-Héroult Cell with Prebaked anodes. (cross section)

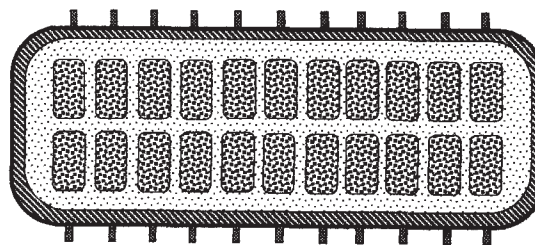


Fig. 1b. Hall-Héroult Cell with Prebaked Anodes. (plan view)

and alumina covers the molten bath. Cells with prebaked anodes are generally fed alumina in frequent small doses by point feeders. Cells with Søderberg anodes are generally fed large doses at the sides of the cell every few hours. Thermal insulation is adjusted to provide sufficient heat loss to maintain a protective ledge of frozen electrolyte on the walls of prebaked anode cells, but not on the bottom under the anodes. This must remain bare to provide electrical contact to the molten aluminum. The frozen ledge thermally and electrically insulates the walls preventing their acting as cathodes and being eroded by formation of aluminum carbide that subsequently would dissolve in the molten electrolyte and be oxidized. The ledge serves

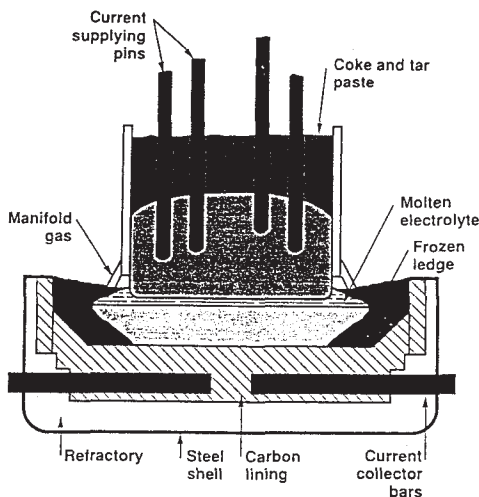


Fig. 2. Aluminum electrolyzing Cell with Soderberg Anode.

also to stabilize the temperature of the bath by freezing to a greater thickness when heat generation is low and thinning when heat generation increases. Unfortunately, either freezing or melting of ledge alters bath composition because cryolite freezes out selectively. In Soderberg cells the ledge is formed by the process of alumina dissolution instead of freezing.

The anode-to-molten aluminum spacing, anode-cathode distance, ranges from 3–6 cm. Steel current-collector bars, joined into the carbon lining, carry the electric current from the cell. Aluminum is electrochemically deposited from dissolved alumina into the molten aluminum pool. Oxygen of the dissolved alumina is discharged onto and consumes the cell's carbon anodes.

Potline

From 150 to over 200 cells or pots are connected in series, forming a potline, Fig. 3, to allow use of high voltage rectifiers. High voltage rectifiers cost much less and are more efficient than high current rectifiers of the same power rating. Series electrical connection also requires less bus.

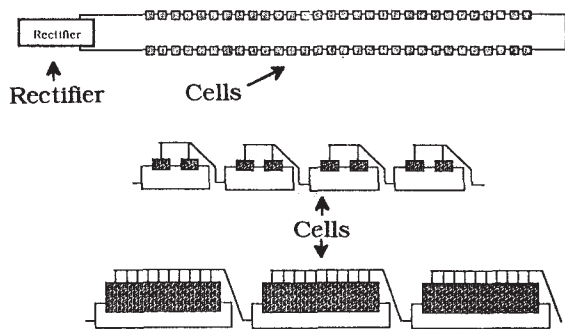


Fig. 3. Potline consists of many cells connected in series

Electrolyte or Bath

Molten cryolite (Na_3AlF_6), having a high solubility for aluminum oxide, is the major component of the Hall-Heroult electrolyte or bath. Low operating temperatures improve efficiencies, hence, the liquidus temperature (where freezing starts) is lowered by various additives from 1011°C (for pure cryolite) to 920 – 970°C. The alumina feed, aluminum fluoride and calcium fluoride are the most common additives. Calcium enters the electrolyte as calcium oxide impurity in the alumina and reacts with aluminum fluoride to attain a steady state concentration of 3 to 10% CaF_2 from which it is co-deposited into the aluminum and lost by other mechanisms at a rate equal to its introduction. In Europe, the concentration of aluminum fluoride is reported and controlled as excess aluminum fluoride, it being the excess over the aluminum fluoride content of cryolite. In the US, the excess aluminum fluoride is usually reported and controlled as the bath ratio, R, the weight ratio of sodium fluoride to aluminum fluoride. Some plants report and control cryolite ratio, CR, the mol ratio of sodium fluoride to aluminum fluoride. CR is numerically twice the weight ratio, R. Table I shows the relationship between excess aluminum fluoride and bath ratio or cryolite ratio. It is not valid for baths containing lithium fluoride or appreciable magnesium fluoride (added at some smelters). Chemists tell us that sodium fluoride and lithium fluoride are strong Lewis bases. Aluminum fluoride is a strong Lewis acid and magnesium fluoride is a weak Lewis acid. Cryolite and calcium fluoride are neutral. Consequently, baths containing excess aluminum fluoride are acid baths. Acid baths suppress the dissolution of sodium metal into the bath and therefore give higher current efficiencies. The effect of additives on the physical and chemical properties of baths was reviewed in *The Influence of Additives on Hall-Heroult Bath Properties* [JOM, Nov 1991]¹. The book, Grjotheim, et al. *Alumintum Electrolysis*², provides detailed properties.

wt% xs-AlF ₃	8		10		12	
	CR	R	CR	R	CR	R
0	3.000	1.500	3.000	1.500	3.000	1.500
1	2.920	1.460	2.918	1.459	2.916	1.458
2	2.842	1.421	2.839	1.419	2.835	1.418
3	2.767	1.383	2.762	1.381	2.757	1.378
4	2.694	1.347	2.688	1.344	2.681	1.340
5	2.623	1.312	2.615	1.308	2.607	1.304
6	2.554	1.277	2.545	1.273	2.536	1.268
7	2.488	1.244	2.478	1.239	2.467	1.234
8	2.423	1.212	2.412	1.206	2.400	1.200
9	2.360	1.180	2.348	1.174	2.335	1.167
10	2.299	1.150	2.286	1.143	2.272	1.136
11	2.240	1.120	2.225	1.113	2.211	1.105
12	2.182	1.091	2.167	1.083	2.151	1.075
13	2.126	1.063	2.110	1.055	2.093	1.047
14	2.071	1.035	2.054	1.027	2.037	1.018
15	2.017	1.009	2.000	1.000	1.982	0.991

Basics

Chemical Notation

An explanation of chemical notation is in order. Take Al₂O₃ as an example. It represents alumina and indicates that each molecule of alumina is composed of 2 atoms of aluminum combined with 3 atoms of oxygen. Al₂O₃ has a molecular weight of 101.96 calculated by multiplying two times 26.98 (the atomic weight of aluminum) plus 3 times 16.00 (the atomic weight of oxygen). Table II lists a number of elements and compounds of interest and their atomic or molecular weights.

Table II

Element or Molecule	Name	Atomic or Molecular Weight	Normal Valence
Al	Aluminum	26.982	+3
O	Oxygen	15.999	-2
C	Carbon	12.011	+/-2,4
Ca	Calcium	40.08	+2
K	Potassium	39.102	+1
F	Fluorine	18.998	-1
Li	Lithium	6.939	+1
Mg	Magnesium	24.312	+2
Na	Sodium	22.990	+1
S	Sulfur	32.064	+/-2,4,6
Al ₂ O ₃	Alumina	101.961	
CO	Carbon monoxide	28.011	
CO ₂	Carbon dioxide	44.010	
CF ₄	Carbon tetrafluoride	88.005	
CaF ₂	Calcium fluoride	78.08	
LiF	Lithium fluoride	25.937	
MgF ₂	Magnesium fluoride	62.309	
NaF	Sodium fluoride	41.988	
SO ₂	Sulfur dioxide	64.063	

Now examine the chemical reaction:



The phase (solid, liquid, gas or solution) is given in parentheses after each item. If the phase is a solution, such as bath, it is helpful to name the solution rather than just indicate "sol." Reaction (1) states that a gram mol of alumina dissolved in bath reacts with 1.5 gram mols of solid carbon to form 2 gram mols of aluminum liquid and 1.5 gram mols of carbon dioxide gas. A gram mol is the number of grams of the substance equal to its molecular weight.

Decomposition or deposition potential

Equation (1) allows one to calculate the electrochemical decomposition potential of alumina electrolyzed with carbon anodes. From thermodynamics we know that the equilibrium or decomposition potential can be calculated by the following equation when all

reactants and products are in their standard states, that is, pure or saturated:

$$E^{\circ} = -\Delta G^{\circ} / (nF) \quad (2)$$

ΔG° is the standard Gibbs free energy change for the reaction. This is calculated by summing the free energies of formation (from the elements) of the products and subtracting the free energies of formation of the reactants. Gibbs free energies of formation are tabulated for the relevant compounds in the JANAF Tables³. For reaction (1):

$$\Delta G^{\circ}_{(1)} = 1.5 \Delta G^{\circ}_f(\text{CO}_2) - \Delta G^{\circ}_f(\text{Al}_2\text{O}_3) \quad (3)$$

Numerically $\Delta G^{\circ}_{(1)} = 688,108 \text{ J}$ at 1240 Kelvin. The free energies of formation for Al and C are zero because they are pure elements.

n is the number of electrons exchanged in the equation as written, in this case 6.

F is the Faraday constant, 96,485 J/(g•eq volt) g•eq. is gram equivalents, see Faraday Law.

$$E^{\circ} = 1.189 \text{ v at } 1240 \text{ K or } 967^{\circ}\text{C for reaction 1.}$$

Carbon, aluminum and carbon dioxide are nearly pure phases and can therefore be assumed to be in their standard states, but alumina is in its standard state only when it is at saturation. The Nernst equation gives the decomposition potential when some or all components are not in their standard state:

$$E_d = E^{\circ} - [RT / (nF)] \ln (K_e) \quad (4)$$

R is the gas constant, 8.3144 J/(K,mol)

T is temperature in Kelvin,

\ln is the natural logarithm.

K_e is the equilibrium constant. For the generic equilibrium: $bB + cC \leftrightarrow gG + hH$, $K_e = (a_G^g a_H^h) / (a_B^b a_C^c)$ Where: a_G, a_H, a_B, a_C represent the activity of species G, H, B, and C. **Activities** are thermodynamic concentrations and must be determined experimentally – often by electrochemical or vapor pressure measurements.

For reaction (1):

$$K_e = [a^2(\text{Al}) \cdot p^{1.5}(\text{CO}_2)] / [a(\text{Al}_2\text{O}_3) \cdot a^{1.5}(\text{C})] \quad (5)$$

However, **Al, C, and CO₂** have activities = 1.

$$a(\text{Al}_2\text{O}_3) = [\%(\text{Al}_2\text{O}_3) / \%(\text{Al}_2\text{O}_3)^*]^{2.77}$$

Where $\%(\text{Al}_2\text{O}_3)^*$ is the $\%(\text{Al}_2\text{O}_3)$ at saturation.

The exponent 2.77 came from an analysis by Dewing⁴ of alumina activity data.

Hence the decomposition potential for reaction (1) is:

$$E_d = E^{\circ} + [T / (25136)] \ln [\%(\text{Al}_2\text{O}_3) / \%(\text{Al}_2\text{O}_3)^*] \quad (6)$$

At 1240 K and half saturation with alumina:

$$E_d = -1.189 - 0.034 = -1.223 \text{ volts}$$

Note that the decomposition voltage, E_d , represents Gibbs free energy, not the total energy to make aluminum. Extra energy is supplied by heat. Note also that E_d is only slightly greater than E^0 at half saturation, but at lower alumina concentrations E_d becomes appreciable and triggers the anode effect. E_d is negative because thermodynamic convention considers the voltage negative when power is required rather than being produced.

Chemical Equilibrium



The \leftrightarrow indicates equilibrium. The reaction goes in either direction. The equation states liquid aluminum reacts with sodium fluoride in the bath to maintain a sodium concentration in the bath consistent with the activities of sodium fluoride and aluminum fluoride in the bath. The equilibrium constant K_e is given by:

$$\ln K_e = -\Delta G^0 / (RT) \quad (8)$$

$$K_e = \{a^3(\text{Na}) \cdot a(\text{AlF}_3)\} / \{a(\text{Al}) \cdot a^3(\text{NaF})\} \quad (9)$$

But $a(\text{Al}) \approx 1$ because the aluminum is a nearly pure phase. Solving for $a(\text{Na})$ one gets:

$$a(\text{Na}) = [\text{Exp}(-\Delta G^0 / 8.3144T) \cdot a(\text{AlF}_3) / a^3(\text{NaF})]^{1/3} \quad (10)$$

$\ln(x)$ = natural logarithm of x .

$\text{Exp}(x)$ = e^x , the inverse of $\ln(x)$

Data for ΔG^0 can be obtained from JANAF Tables³.

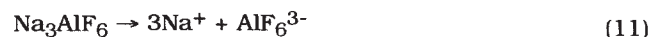
Activity data for sodium fluoride and aluminum fluoride can be obtained from Sterten et al.⁵.

Knowing the activity of sodium metal in the bath is important because sodium dissolved in the bath is the major source of current inefficiency.

Thermodynamics tells us that at equilibrium, the activities are the same in all contacting phases. Hence, even though the concentrations of sodium will be different in the bath and in the aluminum, their sodium activities will be the same.

Ionic Structure of Bath

Many molten salts ionize, that is, components break into positive and negative particles called ions. Movement of ions, because of their electrical charge, provides electrical conductivity. Molten cryolite ionizes forming sodium and hexafluoroaluminate ions⁶:



The hexafluoroaluminate ions, AlF_6^{3-} , dissociate further,^{7,8,9} predominately:



Some AlF_6^{3-} dissociates^{8,9}:



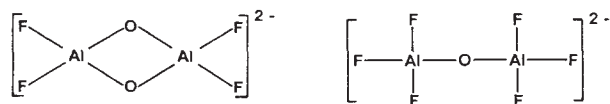
The degree of AlF_6^{3-} dissociation varies with the ratio

of sodium fluoride to aluminum fluoride⁹:

<u>NaF/AlF₃ Ratio</u>		<u>AlF₆³⁻</u>
<u>Molar</u>	<u>Weight</u>	<u>Dissociates</u>
3	1.5	25%
2	1.0	55%
1	0.5	100%

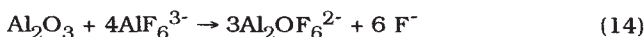
Dissolution of Alumina

Molten cryolite is a very good solvent for aluminum oxide. Raman spectrographic studies¹⁰ indicate that when alumina dissolves, only oxygen species with bridging Al-O-Al bonds are formed. This information, vapor pressure, density and heat of solution leads to the most probable species having the following structure:



These species can be formed by AlF_6^{3-} reacting with alumina.

Low alumina concentration and low bath ratio favor¹¹:



High alumina concentration and high bath ratio favor¹²:



The differing reactions lead to different heats of dissolution¹³. At low concentrations it takes 280 kJ/mol while at high concentrations it takes only 84 kJ/mol to dissolve alumina. This leads to the anomaly that alumina additions will have a greater cooling effect at low alumina concentrations and possibly be more difficult to dissolve.

Ions with a positive charge are attracted to the cathode and are called cations. Ions with a negative charge are attracted to the anode and are called anions. The following ions are present:



Also Li^+ , $\text{Al}_2\text{O}_2\text{F}_6^{4-}$ and $\text{Al}_2\text{O}_2\text{F}_{10}^{6-}$ may be present

The sodium ion, Na^+ , carries 95% to 99% of the electric current and F^- carries essentially all the rest¹⁴.

Electrode Reactions

Faraday Law

Electric current flows through metallic conductors by movement of electrons. This is called electronic conduction. Current flows through an electrolyte by

movement of ions and is called ionic conduction. The change from electronic conduction in the bus and electrodes to ionic conduction in the bath requires chemical reactions to take place at the electrodes. At the cathode, electrons react to discharge positive ions and produce a reduced product or to form negative ions. At the anode electrons are extracted either by discharging negative ions to form an oxidized product or by forming positive ions. Some ions, depending upon the elements involved, have charges greater than one and therefore require a number of electrons to discharge them. To account for this, the gram equivalent weight, $g \cdot eq$, (the number of grams equal to the molecular weight divided by the valence or number of electrons transferred) is used rather than the $g \cdot mol$ (the number of grams equal to the molecular weight) when calculating the theoretical amount deposited or consumed.

Michael Faraday determined that the amount of material deposited or dissolved in the absence of parasitic reactions was proportional to the quantity of electric current passed and to the equivalent weight of the material. Avogadro determined that one gram mol of any substance always contained the same number of atoms ($N_A = 6.0220 \times 10^{23}$). The charge on an electron, e , is 1.6022×10^{-19} coulombs (amp seconds). Multiplying these two figures together gives the Faraday constant, $F = N_A e = 96485$ amp sec./ $g \cdot eq$. Converting to aluminum this gives a theoretical production of 8.0538 kg/k ampere day or 17.756 lbs/(k ampere day).

Boundary Layer

There is a very thin stagnant layer of bath (boundary layer) at the surface of each electrode. Convection does not function in this layer. Ions must diffuse through it. This creates concentration gradients. Gas bubbling makes the layer much thinner at the anode than at the cathode.

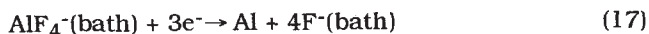
Cathode Reaction

Although neither the anode nor the cathode reaction is fully understood, enough is known to form a reasonably consistent picture. While the carbon lining of the cell is often called the cathode, the true cathode is the surface of the molten aluminum. The cathode reaction is often expressed simplistically as:

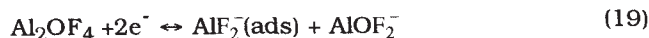
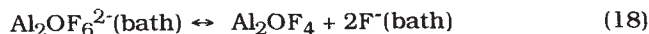


However, no Al^{3+} cations are present in the electrolyte. Instead, aluminum is found in anion complexes such as AlF_4^- , AlF_6^{3-} , $Al_2OF_6^{2-}$ and $Al_2O_2F_4^{2-}$. The fact that the Na^+ ion is the principal current carrier led some early investigators to assume that Na was the primary product discharged at the cathode and that aluminum was produced by a secondary reaction. However, the voltage required to deposit aluminum is about 0.22 volt lower than that required to produce

sodium, hence aluminum should be the primary product. The reaction is often written:



Recent work by Thonstad¹⁴, however, indicated that aluminum is discharged from oxyfluoroaluminate ions by a three-step process with charge transfer taking place in two steps:



The notation, (ads) is used to indicate that this species is adsorbed on the surface of the cathode. Sodium ion, Na^+ , carries the current and is transported to the cathode interface. $Al_2OF_6^{2-}$ must diffuse to the interface and, to maintain charge neutrality, 2 Na^+ ions accompany it. The stepwise discharge of one $Al_2OF_6^{2-}$ ion produces one atom of liquid aluminum, one $AlOF_2^-$ ion and 4 F^- ions. The 4 F^- and one $AlOF_2^-$ set free are just sufficient to neutralize the space charge of the 5 Na^+ , three transported by the current and two that accompanied the $Al_2OF_6^{2-}$. The $AlOF_2^-$ ion produced at the cathode can react with AlF_4^- to produce more $Al_2OF_6^{2-}$ ion.

Either mechanism, that in reaction (17) or that of Thonstad et al., result in a high concentration of NaF at the cathode interface. This raises the liquidus temperature (the temperature at which freezing starts) and can cause a solid layer to form on the metal pad. This effect has been observed when operating at low superheat (i.e. close to the liquidus temperature) and low bath ratio (where there is a large increase in liquidus temperature with a small increase in sodium fluoride concentration). When the solid forms, it raises the voltage causing the layer to melt. Then the sequence repeats. The fluctuating voltage can be quite puzzling until the cause is discovered. The remedy is to raise the superheat.

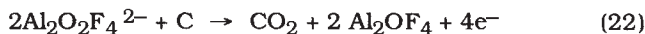
The sodium concentration of the aluminum always reflects the NaF/ AlF_3 ratio of the bath in contact with it, reaction (7). High sodium in the aluminum once was considered an indication of low current efficiency, but no longer. The shift in bath ratio at the cathode causes the aluminum to contain more sodium than would be predicted from the bulk concentration. Modern, very quiet cells have less metal pad movement, hence a higher concentration gradient across the boundary layer. This results in higher current efficiency but also higher sodium concentrations in the aluminum than that from older cells.

Anode Reaction

The anode reaction can be written:



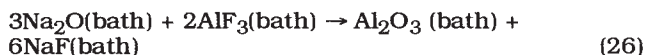
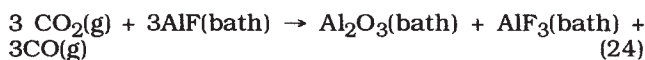
But uncomplexed oxide ions do not exist in the electrolyte. Sterten¹⁵ calculated from bond energies that the first oxygen can be removed from $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ much easier than the second or the one oxygen from $\text{Al}_2\text{OF}_6^{2-}$. This suggests that the anode reaction is:



Equilibrium between $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ and $\text{Al}_2\text{OF}_6^{2-}$ would be restored by:



Thermodynamic calculations indicate that the equilibrium composition of anode gas at bath temperature would be about 99% CO and 1% CO_2 . However, based on the volume of gas produced or net carbon consumed (with dusting subtracted out) the primary product formed at the anode is essentially all CO_2 . Anodic formation of CO_2 requires four electrons per molecule while formation of CO requires only two; hence, the volume of gas produced per ampere hour gives the primary CO/CO_2 ratio of the gas formed at the anode. Subsequent reduction of CO_2 to CO by aluminum monofluoride or sodium dissolved in the electrolyte does not change the gas volume (equations 24 & 25). For gases at the same temperature and pressure, equals mols represent equal volumes.



It is surprising but fortunate that the anode gas composition is displaced so far from thermodynamic equilibrium; otherwise carbon consumption would be nearly twice as great as it is.

A simple explanation for this displacement from equilibrium is that oxygen is being supplied electrochemically at a higher rate than CO can be formed. Nature adjusts by attaching two oxygens to each carbon atom instead of one, but this requires additional energy, which appears as overvoltage.

Cell Voltage

Mechanisms have been discussed: (1) how electrons from the cathode discharge aluminum-containing ions to form aluminum at the cathode and (2) how electrons enter into the anode, from oxygen-containing ions in the bath discharging oxygen on the anode to form carbon dioxide. There exist, however, barriers to the transport of electrons. They can be thought of simplistically as walls over which the electrons must pass. This is illustrated in Figs. 5a,b and c. Fig. 4a shows the distribution of electrons due to thermal excitation with no potential applied to the cell. Fig. 4b shows a potential equal to the decomposition

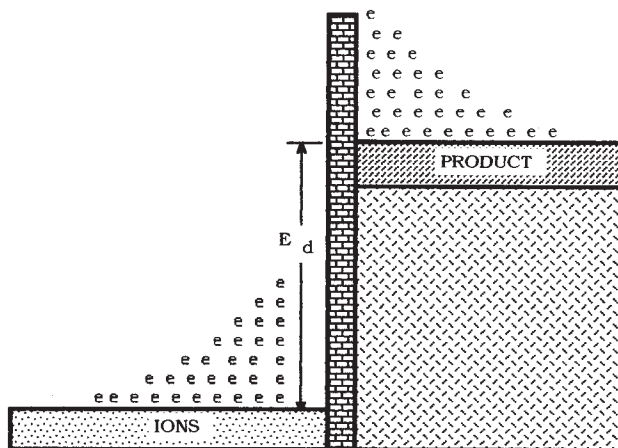


Fig. 4a. Potential Barrier. No voltage applied, no current flow.

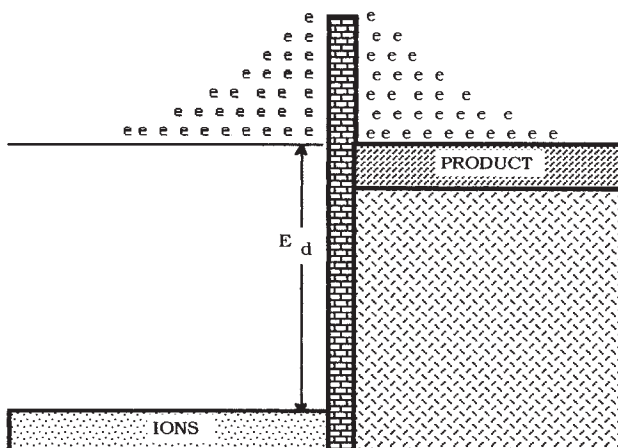


Fig 4b $E = E_d$ applied, No net current flow.

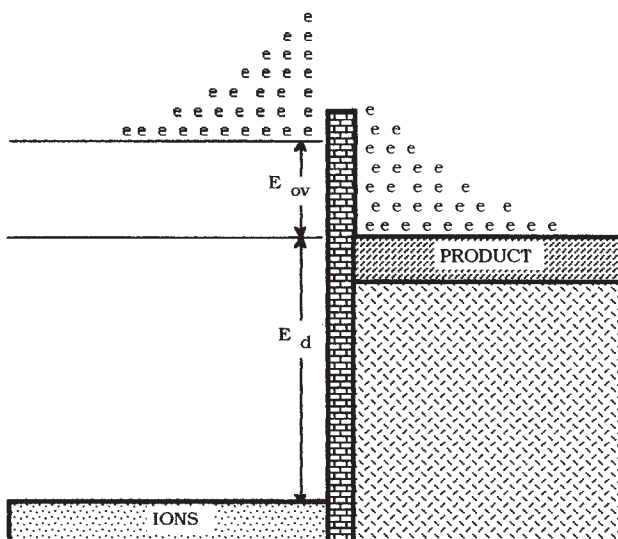


Fig. 4c. $E = E_d + E_{ov}$ applied. Appreciable current flows making product.

potential applied. Electrons will hop over the barrier and hop back. This results in a small forward current with an equal reverse current producing no overall effect. Electrochemists call this the exchange current. If an appreciable current is to flow to produce appreciable product, a potential greater than the equilibrium decomposition potential must be applied as shown in Fig. 5c. Now there is a great excess of electrons to spill over the barrier and appreciable current flows. The potential across the electrode interface in excess of the equilibrium decomposition or deposition potential is called overvoltage.

In addition to this reaction overvoltage, a further increase of voltage is needed because the concentration of reacting ions is lowered at the electrode-bath interface. Owing to the lower concentration of reacting ions, the decomposition potential will be higher than that calculated for the bulk concentration. This extra voltage is called concentration overvoltage.

The total cell voltage will include the decomposition potential, all overvoltages, the ohmic voltage drops through the bath, the anode and the cathode plus external ohmic voltage drops. The voltage drop through the bath is increased 0.15 to 0.25 volts by gas bubbles at the anode. Carbon dust and/or undissolved alumina suspended in the bath also lowers the electrical conductivity of the bath. A typical distribution of voltages and energy requirements is shown in Fig. 5. Note that the energy to make aluminum exceeds the decomposition potential plus overvoltages. Some ohmic heating is used in making aluminum. The calculated cell voltage as a function of alumina concentration and anode-to-cathode distance, Fig. 6, is useful in cell control.

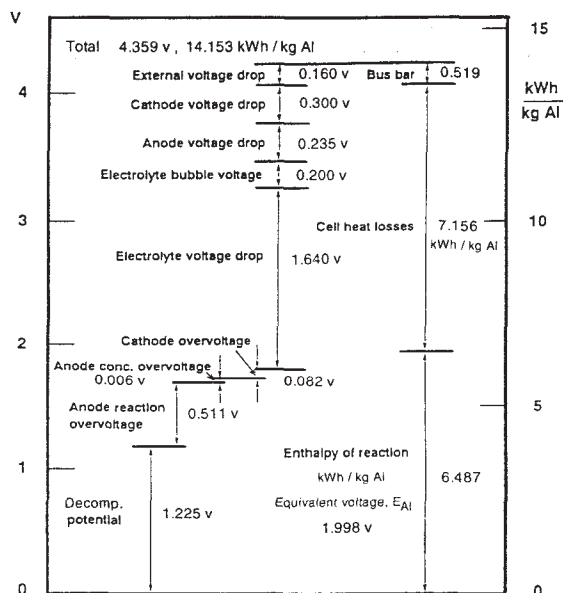


Fig. 5. Typical distribution of voltages and energy in cells. Volts scale (left) and kWh/kg Al (right) correspond at 92% current efficiency.

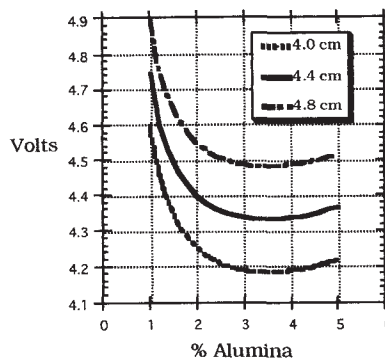


Fig. 6. Calculated cell volts Vs. alumina at various anode-cathode spacings, useful in cell control.

Current Efficiency

The amount of aluminum predicted by Faraday's law is never obtained. The principal loss mechanism is by aluminum reacting with sodium fluoride in the bath to form sodium that dissolves in the bath [reaction 7]. It is subsequently reoxidized by CO₂ [reactions 25 & 26]. The Pearson-Waddington equation:

$$\%CE = 100 - \%CO / 2(\%CO + \%CO_2) \tag{27}$$

is based upon metal being reoxidized by CO₂ forming CO. The fact that the equation agrees well with actual aluminum production supports the contention that metal reoxidation by CO₂ is the major loss mechanism. Dissolved sodium must diffuse away from the aluminum interface before it can be oxidized. Cells with good magnetic compensation have less aluminum pad motion. This slows transport of sodium saturated bath from the aluminum interface and thereby slows the loss of aluminum explaining why these cells have higher current efficiency.

There are several minor loss mechanisms. An activity of aluminum monofluoride, AlF, is generated by reaction 28.



The dissolved AlF is reoxidized by CO₂, reaction (24)

Haarberg, et al¹⁶ determined that dissolved Na imparted electronic conductivity to the bath. Electronic conductivity acts like a short circuit and causes between 1 and 3 % loss in current efficiency (the higher figure at high bath ratios). This loss would be greater if the concentration of sodium were not kept low by reoxidation. It is fascinating that the major loss mechanism keeps another loss mechanism from being a major one.

Impurities in the bath, although present at low concentrations, can be reduced at (or near) the cathode and be reoxidized at (or near) the anode, consuming current without producing product. Phosphorus is particularly bad. It can lower current efficiency by 1% for each 100 ppm phosphorus. Sterten¹⁷ believes that

several impurities play significant roles, being reduced by Na in the boundary layer at the cathode and reoxidized by CO₂ near the anode.

Some phenomena can improve current efficiency. Thonstad and Rolseth¹⁸ observed that particulate alumina can collect at the electrolyte-aluminum interface. They found that this coating inhibited the loss of metal from the aluminum pad and should, therefore, improve current efficiency. Even though alumina is more dense than aluminum, alumina does not settle through the aluminum owing to its high surface tension. Presumably other particulates, such as cryolite precipitated from the electrolyte as a result of the shift in bath ratio at the interface, could act in the same manner as alumina. However, this interfacial film would also inhibit the inward diffusion of the aluminum producing ions, while the Na⁺ ion would be electrolytically transported through the barrier. Hence, the production of sodium would be increased. So while the escape of sodium into the electrolyte is hindered by films, the driving force (concentration of sodium in the aluminum) to cause its escape is increased. Further study is needed to ascertain the net effect on current efficiency.

Low bath ratio, low temperature, a stable metal pad, and a constant (low) alumina concentration promote high current efficiency. Some disagree that low alumina concentration is best, but all agree that excessive muck (undissolved alumina) is bad. Lithium (added as carbonate which reacts with aluminum fluoride to form lithium fluoride) is very effective in lowering the liquidus (bath melting point) and increasing the electrical conductivity of the bath. It should give increased current efficiency by lowering the operating temperature and by allowing larger anode-to-cathode spacing without increasing the cell's voltage (particularly valuable in older less stable cells). Higher conductivity also allows increased current for increased production. Lithium also lowers fluoride evolution.

If the calcium content of the alumina is low, magnesium fluoride may be added beneficially. MgF₂ is weakly acidic, hence it lowers sodium production a little. It has also a greater effect than CaF₂ in lowering the bath's liquidus and in expelling carbon dust from the bath.

Magnetics

A magnetic field, or flux, radiates from all current carrying conductors, Fig. 7. The field is directly proportional to the current and inversely proportional to the distance from the conductor. Fields from the various conductors add vectorially, that is fields of the same sense sum while fields of opposite sense tend to cancel. This is the basis of magnetic compensation. Steel concentrates flux within it, creating a shadow of lowered flux. Magnetic fields interact with electric currents creating forces (the motor effect). These forces (proportional to the field strength, the current density and the direction of each) create swirls and

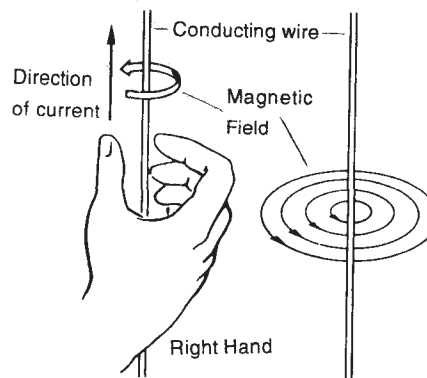


Fig. 7. The direction of the magnetic field depends upon conductor orientation and direction of current flow.

produce an uneven, undulating aluminum surface. Particularly harmful is the interaction between vertical fields and the horizontal current densities in the metal pad. A thick aluminum pad lowers the horizontal current density and, if nothing else changes, improves stability. Magnetic fields cannot be eliminated, just redirected by careful design of steel parts and judicious location of the current conductors.

Anode Effect

When the alumina concentration in the bath is nearly depleted, a phenomenon referred to as the *anode effect* takes place. As alumina is depleted, anode overvoltage increases. Surface tension of the melt increases. This, coupled with the electrocapillary effect resulting from the higher anode voltage, reduces wetting of the anode by the bath and causes bubbles to become adherent, grow large, and flatten. Large bubbles increase the local current density on the anode between bubbles, further increasing overvoltage. At an anode overvoltage between 1.1 and 1.6 volts, fluorine-carbon compounds are produced on the anode surface. Fluorocarbon compounds, like Teflon, promote dewetting and growth of a gas film on the anode. Even though the fluorine-carbon surface compounds are unstable at cell temperature, decomposing to carbon tetrafluoride, CF₄, (with trace amounts of C₂F₆), they attain large coverage of the electrode surface when their rate of electrolytic formation exceeds their rate of thermal decomposition. A gas film spreads over the dewetted anode and the only way current can penetrate the film is by electric arcing. Once the cell is on anode effect, electrolysis probably takes place at the gas-electrolyte interface producing oxygen and fluorine, which then react chemically with the anode. The temperature is high in the reaction zone owing to the extremely high energy dissipation at the anode interface. In industrial cells, 25 or more volts develop across this gas film. Even if the alumina concentration is restored, the cell will remain on anode effect until either the current is interrupted for

10 ms or more¹⁹, as by splashing aluminum to short-circuit the cell and allow the gas film to collapse, or by exposing anode area not contaminated with fluorine as by lowering the anodes.

The gas composition changes at anode effect from a normal composition of 80–90% CO₂, 20–10% CO to 2–10% CO₂, 95–70% CO, 3–20 % CF₄. CF₄ is a “greenhouse” gas that, like CO₂ can contribute to global warming. It is important, therefore, to limit the number of anode effects and their duration. With advanced alumina control it may be possible to eliminate most anode effects.

Summary

The discussed fundamentals explained the various components of cell voltage. A family of curves of cell voltage vs alumina concentration at various anode to cathode spacing is useful in cell control. Overvoltages were related to energy barriers that have to be overcome for reactions to proceed at appreciable rates. Electrode reactions result in aluminum fluoride concentrating at the anode surface and sodium fluoride concentrating at the cathode surface altering the local liquidus temperatures. Loss of aluminum by its reacting with the bath to generate sodium, which is subsequently reoxidized by CO₂, was related to bath acidity, temperature and aluminum pad stability.

References

1. W. E. Haupin, *J. of Metals* (Nov. 1991) p28
2. K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky, and J. Thonstad, *Aluminum Electrolysis-Fundamentals of the Hall-Heroult Process* (Dusseldorf: Aluminium Verlag, 1982)
3. JANAF Thermochemical Tables, 3rd. Edition (Washington D.C.: Am. Chem. Soc., 1986)
4. E.W. Dewing, 13 (4) *Canadian Met. Quart* (1974) 607
5. Å. Sterten, K. Hamberg, and I. Mæland, *Acta Chemica Scandinavia* A36 (1982) 392.
6. K. Arndt & W. Kalass, *Z. Elektrochem.* 30 (1924) 12
7. J. Brynstad, K. Grjotheim, and S. Urnes, *Metall.* 52 (1960) 495.
8. E.W. Dewing, “Models of Halo-aluminate Melts” (Paper presented at the Electrochem. Soc. Annual Meeting., Las Vegas, NV. Oct. 1985)
9. B. Gilbert, & T. Manterne, *Appl. Spectroscopy* 44 (1990) 299
10. B. Gilbert, G.M. Begun and G. Mamantov, *Inorg. Nucl. Chem. Letters* 10 (1974) 1123.
11. H. Kvande, *Light Metals 1986* (Warrendale, PA: TMS 1986) 451
12. A. Sterten, *Electrochimica Acta* 25 (1980) 1675
13. J.L. Holm “Thermodynamic Properties of Molten Cryolite and other Fluoride Mixtures” (Dr. techn. Thesis, Univ. of Trondheim, Norway 1971)
14. J. Thonstad, A. Kiswa, J. Kazmierczak “The Kinetics and Mechanism of the Al(III) Electrode Reaction in Cryolite–Alumina Melts” (Norwegian Institute of Technology, to be published)
15. A. Sterten, *Electrochimica Acta* 25 (1980) 1673.
16. G.M. Haarberg, K.S. Osen, J. Thonstad, R.J. Heus, and J.J. Egan, *Light Metals 1991* (Warrendale, PA: TMS 1991) 283
17. Å. Sterten, *J. Appl. Electrochem.* 18 (1988) 473
18. J. Thonstad and S. Rolseth *Light Metals 1976*, V1 (Warrendale, PA: TMS 1976) 171
19. Calandra, A.J., Castellano, C.E., Ferro, C.M., and Cobo, O.: *Light Metals 1982* (Warrendale, PA: TMS 1982). 345