THE INFLUENCE OF DISSOLVED METALS IN CRYOLITIC MELTS ON HALL CELL CURRENT INEFFICIENCY

Ray D. Peterson and Xiangwen Wang
Manufacturing Technology Laboratory
Reynolds Metals Company
P.O. Box 1200, Sheffield, Alabama, USA

Abstract

Results from a laboratory study of dissolved metals (including aluminum, sodium, and lithium) in cryolitic melts were coupled with the Lillebuen equation for Hall Cell current inefficiency to make predictions for industrial cells. The effects of bath chemistry and operational parameters, such as bath temperature, were considered over a reasonable operating range. Examination of both constant cell temperature and constant cell superheat (the difference between operating temperature and bath freezing point) was made for varying bath compositions.

Results showed that decreasing cryolite ratio increased current efficiency under both conditions, but maintaining a constant superheat resulted in a greater increase in current efficiency. Increasing LiF concentration in the electrolyte did not increase current efficiency when the bath temperature remained constant, but did cause a considerable increase when a constant superheat was maintained.

Introduction

In the accompanying paper,[1] we presented the results of our study to determine the types and amounts of dissolved metals in cryolitic melts. Aside from a purely theoretical interest in knowing the reactions involved in the system, the major driving force for understanding the nature of dissolved metals is to use this knowledge to improve the current efficiency of industrial Hall cells.

Many papers have been written which discuss the effects of various cell operating parameters which influence the current efficiency. These operational properties include: electrolyte temperature and electrolyte composition which encompasses cryolite ratio, % alumina, and concentration of either optional or unintentional additives. These variables not only control chemical and physical properties of the electrolyte, but as the accompanying paper shows, they also directly dictate the amount of dissolved metals in the electrolyte. An excellent review paper has been written on the effect of bath additives and their effect on current efficiency.[2]

Several mathematical models for prediction of current efficiency of aluminum electrolysis are available. These include models by Robl and co-workers,[3] Lillebuen and co-workers,[4] and Evans and co-workers.[5] All of these models involve the process of metal dissolution and subsequent reoxidation by dissolved or partially-dissolved CO_2 bubbles evolved at the anode. These models can give both qualitative and quantitative insight into how the design of cells (such as magnetic field, metal and electrolyte velocities, and metal pad area) and electrolyte chemistry can influence current efficiency. Advantages and shortcomings of these models have been discussed by Grjotheim and co-workers[6] and Haupin.[7]

The Lillebuen Model has been accepted as a reasonable tool in describing the process of metal dissolution and oxidation, as well as a reliable model for estimating the current efficiency if the operational parameters of a specific Hall cell are well characterized. This model was chosen for making predictions of current efficiency by coupling it with our regression equation for solubility of metals as a function of electrolyte chemistry. Chen and Taylor[8] have pointed out that a numerical constant associated with the reaction rate may be in error. However, since the model must be "calibrated" to an existing cell to be an accurate predictor of current efficiency, this restriction is not significant.

The objective of this paper is to relate our metallic solubility data and its derived predictive equation to the current inefficiency of the Hall cell through the use of the Lillebuen current efficiency equation. It must be pointed out that while the model may predict a current efficiency for a given set of conditions, in actual practice these conditions may be unachievable. Such conditions might include a lack of thermal balance in the cell, lack of alumina solubility, poor electrolyte conductivity, crusts which are too hard, etc. Consequently, as with all models, the predictive results must be tempered with a knowledge of what is realistic cell technology and practice.

Current Efficiency Model

The Lillebuen model for current efficiency can be expressed by the following equation:

$$\eta = 100 - 219.3 I^{-1} A_{Al} D_{Al}^{0.67} \mu^{-0.5} V_L^{0.83} d^{-0.17} \rho^{1.5} C_{Al}^*(1-\phi) \quad (1)$$

where

η:	Cell current efficiency (%)
I:	Cell current (kA)
A_{Al}:	Cathodic aluminum surface exposed to electrolyte (m²)
D_{Al}:	Diffusion coefficient of dissolved metals (m²/sec)
μ:	Viscosity of electrolyte (Pa·sec)
V_L:	Average velocity of electrolyte referred to cathodic Al metal (m/sec)
d:	Inter-electrode distance (m)
ρ:	Density of electrolyte (kg/m³)
C_{Al}^*:	Thermodynamic solubility of metals in the electrolyte (apparent Al wt%)
ϕ:	Fraction of metal saturation solubility in bath at the boundary layer/melt interface.

Since the equation was derived from the convective mass transfer of dissolved metals at the metal/electrolyte interface

(dissolved metals are then oxidized by CO_2), the current efficiency, η, is mathematically expressed as a function of cathodic aluminum surface exposed to bath electrolyte, diffusivity of dissolved metals in the bath electrolyte, viscosity and density of bath electrolyte (related to fluid hydrodynamics), bath velocity, anode-cathode distance, and metallic solubility in the bath electrolyte. Consequently, knowledge of these parameters is essential in deriving the current efficiency. Unfortunately, some parameters are difficult to obtain and only their approximate values are available.

The parameters which appear in the Lillebuen equation, are discussed in more detail in the following sections:

I, A_{Al}, d, V_L, and ϕ: These parameters are directly related to the cell size, design structure, and operational conditions.

The cell current, I, can be accurately obtained from the industrial cell operation.

Anode-cathode distance (or ACD), d, is difficult to measure accurately and varies from time to time, as well as from anode to anode. Therefore, only a measured average value can be used on a specific cell.

The cathodic aluminum surface exposed to bath electrolyte, A_{Al}, depends upon not only the cell size, structure, and size of the side ledge freeze, but also on the surface roughness caused by the magnetic field. However, since A_{Al} usually has a relatively-large value (when not considering the roughness), minor changes of A_{Al} will not result in a large variation of the current efficiency (for example, $A_{Al} \approx 33$ m^2 for a 150 kA industrial cell).

The velocity of bath electrolyte, V_L, may be the most difficult cell parameter to obtain or assign. It can be affected by the metal pad motion caused by the cell magnetic field, by the gas evolution from the anode, and by thermal and mass gradients within the cell. The electrolyte velocity is not uniformly distributed within the bath between the anode and the cathode. Any errors in the estimate may substantially affect the calculation of current efficiency. No measured values have been reported in the literature for industrial cells. A value equal to or larger than the velocity of the metal pad is usually selected. Grjotheim and Welch[9] suggest 0.05 to 0.25 m/sec as a possible range for 150 kA cells. An average value can be derived by solving for velocity as the only unknown in a well-characterized cell.

The fraction of metal saturation solubility in the bath at the metal/melt interface, ϕ, is a fixed value once the type of cells is selected. It may also be considered as one of the parameters used to analyze the cell performance. The larger the ϕ value, the better the cell performance (lower oxidation rate of dissolved metals). This is probably one of the least-defined parameters.

D_{Al}, μ, d and C_{Al}^*: Selection of these physicochemical properties is discussed below:

Diffusion coefficients of dissolved metals in the cryolite melts, D_{Al}, have been reported by a number of researchers including Ødegård,[10] Feng and co-workers,[11] and Dewing and Yoshida[12] to name a few. The diffusion

coefficients were all reported for apparent Al metallic species even though we now know that metallic Na plays an important role. No diffusion coefficients for metallic Na and Li in fluoride melts are available and, therefore, we must assume that all species have a similar value. The magnitude of 10^{-8} m^2/sec is the generally-accepted range for these diffusion coefficients. However, the reported results are not consistent with one another, and there is not enough reliable data available to obtain a correlation equation for D_{Al} as a function of melt composition and temperature. A value of 3×10^{-8} m^2/sec is selected for all of the calculations.

Viscosity of bath electrolyte, μ, is calculated using a regression equation as outlined in the final project report[13] covering the solubility work.

Density of bath electrolyte, ρ, is calculated according to internal RMC/MTL equations derived from literature values. This term and the previous term are functions of bath chemistry, but they do not vary greatly. They are a second-order effect and could possibly be held constant.

The metallic solubility in the cryolite melts, C_{Al}^*, is calculated using the regression equations obtained from the work reported in the companion paper[1] and which will be reported later.[14]

For general industrial cells without previous knowledge of cell scale, equation (1) can also be modified to:

$$\eta = 100 - 21.93 i^{-1} D_{Al}^{0.67} \mu^{-0.5} V_L^{0.83} d^{-0.17} \rho^{1.5} C_{Al}^* (1-\phi) \qquad (2)$$

where   i is cathodic current density in A/cm^2, and is not a fixed value since the cathodic Al surface varies with the time. It also depends on the type of cell being analyzed.

Current Efficiency Predictions

As stated above, to predict a particular cell's current efficiency, the cell's physical characteristics must be known and put into the Lillebuen equation. Where certain values are not known, they must be estimated and then calibrated to a well-defined cell. Two types of cells will be examined in this section: a detailed look at a center-break feed prebake cell and a few selected cases for a point-feed prebake cell.

Current Efficiency of Center-Break Cell

Operational characteristics and common electrolyte composition of a conventional center-break cell are shown in Table I.

A conventional electrolyte (MCR=2.60) with alumina and calcium fluoride as additives and minor impurities of 0.5% LiF and 0.5% MgF_2 is presented as the base condition. The freezing points for this electrolyte and several others are shown in Table II. The last column presents the calculated total metallic solubility (as % aluminum). The regression equation derived in the metal solubility work[1] did not include terms for the presence of CaF_2 or MgF_2. However, work with real and synthetic industrial baths has shown that very little dissolved calcium or magnesium metal is found in electrolyte. Additionally, cryolite ratio and temperature are the dominant factors influencing dissolved metal content. Exclusion of CaF_2 or MgF_2 effects should not significantly bias the results.

Two values which are unique to the cell and must be estimated or calibrated are the electrolyte velocity and the fraction of

metal saturation solubility in the interfacial electrolyte. According to Lillebuen, ϕ, the fraction of metallic saturation solubility in the electrolyte interfacial boundary layer, lies in the range of 0.01 to 0.1 for most operational cells. The value was set at 0.05 for this study. By calibration against a known plant metal production current efficiency (88.5% with the conventional electrolyte), the electrolyte velocity is estimated to be 0.242 m/sec for the center-break cell. This "apparent" electrolyte velocity is almost four times the metal velocity, but may be in a reasonable range when we consider that the electrolyte will be "pumped" by the evolution of bubbles released at the anode in addition to being moved by the metal. The velocity does fall into the upper end of the range suggested by Grjotheim and Welch.[9] This estimated value is not unique; if a different value for the fraction of metallic saturation solubility in the electrolyte interfacial boundary layer had been chosen, a different electrolyte velocity would have been calculated.

Table I. Operational Characteristics and Electrolyte Composition of a Center-Break Prebake Cell	
Amperage, kA	160
Current Efficiency, %	88.5
Surface Area of Aluminum Pad, m^2	32.0
Average Metal Velocity, cm/sec	6.2
ACD, cm	5.08
Operating Temperature (°C)	970
Molar Cryolite Ratio	2.60
% Al_2O_3	3.5
% CaF_2	6.0
% MgF_2	0.5
% LiF	0.5

Now that all variables are defined, it is possible to estimate the effect of changing bath chemistry on the current efficiency of a center-break cell. Three general cases of varying electrolyte are presented below: varying cryolite ratio, varying alumina concentration, and varying LiF concentration.

Cryolite Ratio

The effect of varying molar cryolite ratio was examined for three cases:

a. isothermal operation at 980°C,
b. isothermal operation at 970°C, and
c. operation with constant 15°C superheat over the electrolyte freezing point.

All other process and electrolyte variables were held constant. Figure 1a presents the total metal solubility (in Al wt %) for the three cases. Both isothermal cases show an increase in total dissolved metals as the cryolite ratio increases. In all cases, the metal solubility is higher for the 980°C case than for the 970°C case. The 970°C case covers only a portion of the cryolite ratio range since at the higher cryolite ratio values the melt would not be molten or have enough superheat to allow normal operation. For the case of the constant 15°C superheat operation, the increase in metal solubility with increasing

cryolite ratio is greater since both increasing temperature and cryolite ratio are involved. For every increase of 0.1 in molar cryolite ratio, an increase of approximately 0.0067 wt % Al will result for the constant superheat case while an increase of only 0.0015 wt % Al will result for the isothermal cases.
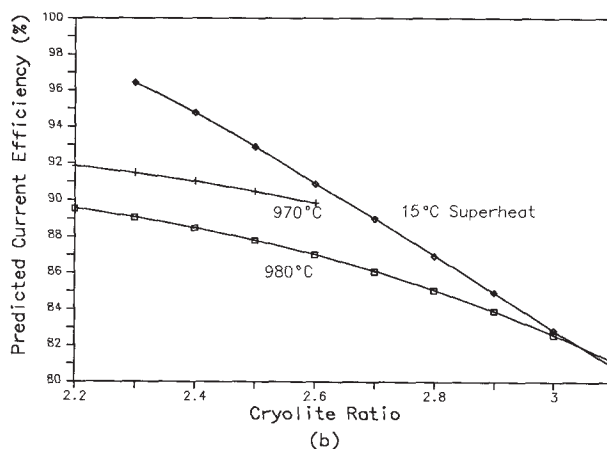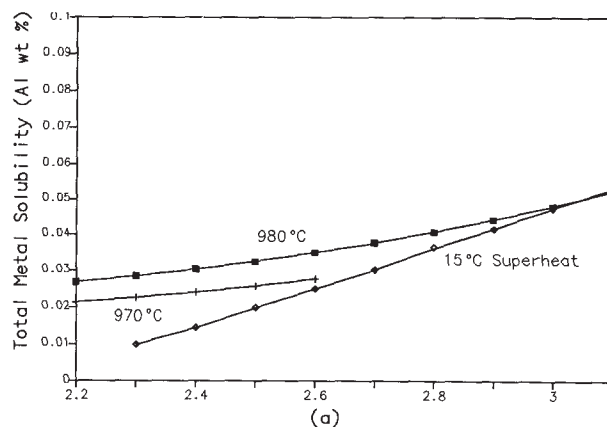

Figure 1. Effect of varying molar cryolitic ratio on (a) total metal solubility and (b) predicted current efficiency.

The current efficiencies corresponding to the predicted metal solubilities are presented in Figure 1b. All three cases show decreasing current efficiency with increasing cryolite ratio. The current efficiency values for the 980°C case are lower over the entire cryolite ratio range than the 970°C case. The isothermal cases show a drop of approximately 0.6% per 0.1 molar cryolite ratio unit. The change in current efficiency with cryolite ratio is greatest for the constant superheat case. A drop of approximately 2.32% per 0.1 cryolite unit is observed for this condition.

For this cell at a molar cryolite ratio of 2.6, the 10°C difference in operating temperature results in a 2.86 percentage difference in current efficiency or 0.29% increase in current efficiency with each 1°C drop in operating temperature. This value is somewhat higher than the value of 0.16% increase per 1°C reported by Alcorn and coworkers[15] for a similar style of cell, but closer to an industrial average of 0.19% per 1°C reported by Kvande.[2]

It must be remembered that the above current efficiency predictions are based on holding all conditions constant. If the cryolite ratio of a cell was to be lowered in order to increase the

current efficiency, the anode - cathode distance may also have to be lowered to adjust for the change in electrolyte conductivity in order to maintain cell thermal equilibrium. The decrease in ACD would be detrimental to current efficiency, and the total predicted increase in current efficiency may not be achieved.

Alumina Concentration

The effect of alumina concentration on current efficiency was evaluated in the same three cases as previously outlined. The predicted metallic solubility is shown in Figure 2a. The total metallic solubility is not a very strong function of alumina content. For the isothermal cases, a slight decrease in solubility occurs as the alumina content increases. The trend is stronger for the case of constant superheat. The addition of alumina decreases the freezing point of the electrolyte, and, consequently, the operating temperature for a constant superheat cell decreases. This decrease in temperature yields a greater decrease in metal solubility.
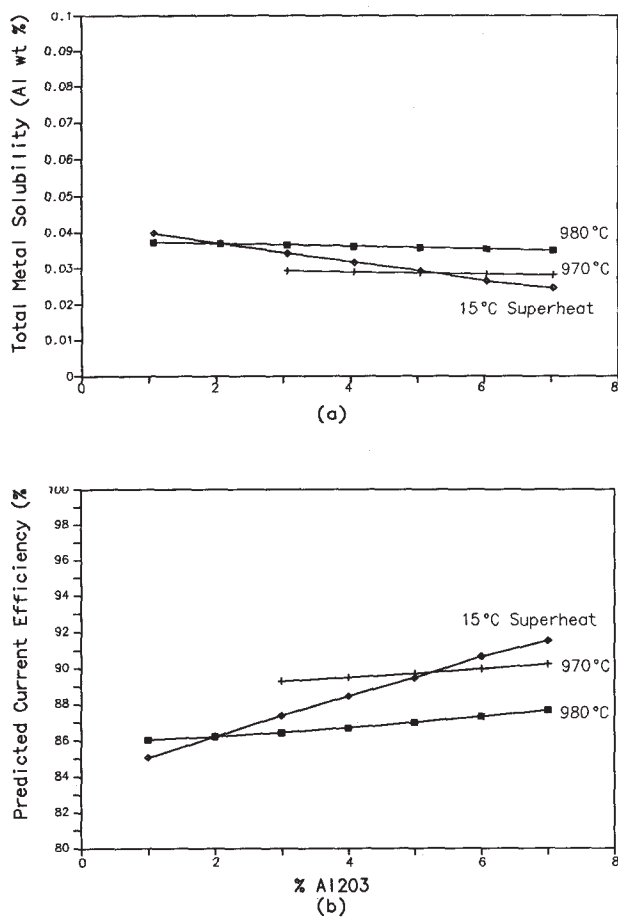

(a)

% Al2O3
(b)

Figure 2.   Effect of alumina content on (a) total metal solubility and (b) predicted current efficiency.

The associated current efficiencies for the varying alumina concentration are shown in Figure 2b. The isothermal cases show a slight increase in current efficiency as alumina concentration increases. For the isothermal cases, the current efficiency increases 0.23 percentage points per 1% alumina increase. This compares favorably with the results of Alcorn and coworkers[15] who report 0.38 percentage points per 1% alumina increase. The case of constant superheat has a much

stronger increase due to alumina additions--approximately 1% current efficiency increase per 1% alumina.

As outlined in Kvande's paper,[2] the effect of alumina concentration on current efficiency has been a controversial subject.   Lillebuen and Mellerud[16] contend that current efficiency passes through a minimum at approximately 4%. Our model does not show this trend, but changes in bubble formation and wetting due to alumina variation are not included.   Our model predictions are in contradiction to the work of Leroy and coworkers[17] who reported an increase in current efficiency with decreasing alumina.

LiF Concentration

The three previously-used example conditions for cell operation were applied to the case of varying LiF content. The effect of varying LiF concentration on metal solubility is shown in Figure 3a. For the two isothermal cases, the total metal solubility is nearly independent of the LiF content. The constant superheat case shows a marked decrease in total metal solubility as LiF content increases.   This decrease is due to the substantial lowering of the bath operating temperature with increasing amounts of LiF.
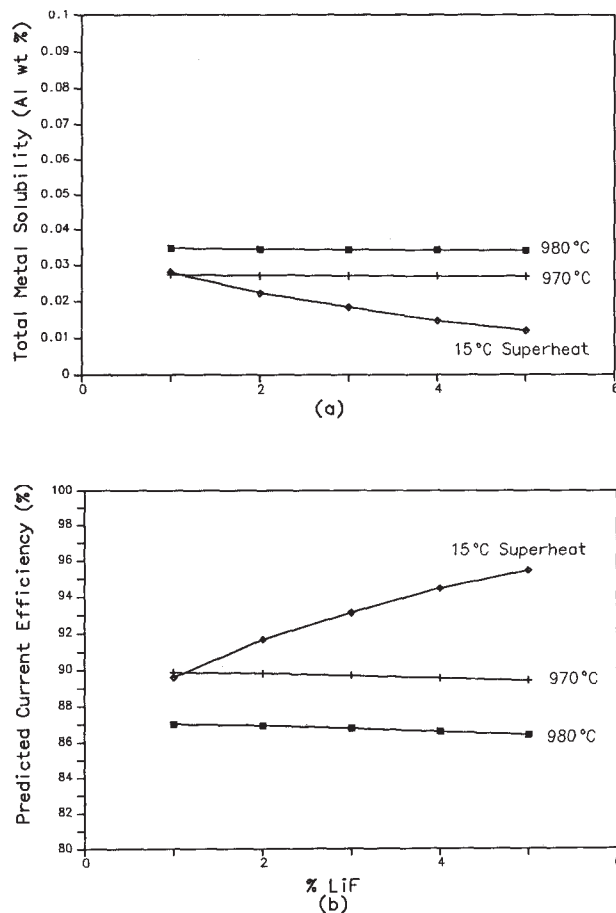

(a)

% LiF
(b)

Figure 3.   Effect of LiF content on (a) total metal solubility and (b) predicted current efficiency.

The corresponding current efficiency predictions are shown in Figure 3b. When the bath temperature is held constant, there is no change in current efficiency with increasing concentrations of LiF in the melt. This observation has been confirmed in laboratory studies by Fellner and coworkers[18,19] and Müftüoglu

and coworkers[20] in which they reported that the addition of LiF to the bath had little or no influence on the current efficiency when the bath temperature was held constant.

For this cell, a current efficiency increase of 3% is predicted from the change of operating temperature from 980°C to 970°C. For the case of the cell operating with a constant superheat of 15°C, the increase in current efficiency with increasing LiF content is quite strong. An increase of 1% LiF in the electrolyte corresponds to a 1.4 percentage point increase in current efficiency. However, it should be pointed out that the current efficiency predictions for the higher concentrations of LiF will probably not be achievable in an actual practice due to thermal restrictions or alumina sludging problems in the reduction cells.

One further set of examples are presented for a center-break prebake cell to demonstrate the impact for different bath compositions on current efficiency. The base case operating and bath conditions will be used to compare several potential bath chemistry conditions. The base conditions of MCR=2.60 with alumina and calcium fluoride as additives and minor impurities of 0.5% LiF and 0.5% MgF_2 are shown in Table II. Additionally, a lithium-modified version of the same electrolyte is shown for two operating temperatures. The freezing points for the electrolytes are also tabulated.[21] The last column presents the calculated total metallic solubility (as wt % aluminum). For the case of the lithium-modified electrolyte, metal solubility is shown for the same operational temperature as the unmodified electrolyte and for an electrolyte at 15°C superheat above the new freezing point. Finally, a case for a lithium-modified bath with an increased cryolite ratio (1.40) is presented. This increase in ratio is often made to industrial cells when lithium is added to the electrolyte.

Table II. Electrolytes for a Center-Break Prebake Cell

Molar Cryolite Ratio	% Al_2O_3	% CaF_2	% MgF_2	% LiF	Freezing Point (°C)	Operating Temperature (°C)	Metal Solubility (%)
2.60	3.5	6.0	0.5	0.5	960	975	0.0311
2.60	3.5	6.0	0.5	3.0	939	975	0.0305
2.60	3.5	6.0	0.5	3.0	939	954	0.0184
2.80	3.5	6.0	0.5	3.0	943	958	0.0243

As already stated, the base case had a current efficiency of 88.5% when operating at 975°C. For the case of the lithium-modified bath with no reduction in operating temperature, the new calculated current efficiency drops to 88.3%. When the cell operating temperature is decreased to 15°C superheat above the new freezing point, the new calculated current efficiency increases to 93.1%. The last case for the electrolyte with lithium and an increased cryolite ratio had a current efficiency of 91.0%. This value is in agreement with observations made in plants converting to lithium-modified electrolytes with increased ratio.

Changes in current efficiency for the different operational cases are shown graphically in Figure 4. With the presence of 3% lithium fluoride in the electrolyte and no decrease in temperature, the current efficiency actually decreases by 0.2 percentage points. However, when the electrolyte operating temperature is decreased by 21°C to take advantage of the lower electrolyte melting point, the current efficiency can be increased by 4.6 percentage points. This difference in current efficiency once again illustrates the critical nature of taking advantage of lithium fluoride's ability to decrease operating temperature. The final case of modifying the electrolyte with

lithium and increasing the ratio shows a decrease in current efficiency of 2.1 percentage points from the previous case. Even though the operating temperature is very close to the previous case, the increased ratio causes a significant increase in dissolved metal and a decrease in current efficiency, but when compared to the base case, the current efficiency has been increased by 2.5 percentage points.
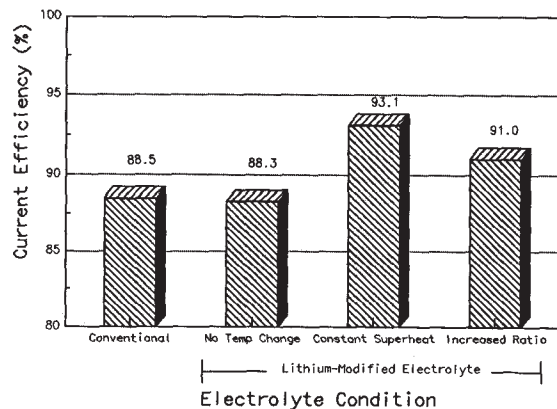

Figure 4.   Current efficiency predictions for a center-break prebake cell with various electrolyte compositions.

Current Efficiency of Point-Feed Cell

Operational characteristics of a conventional point-feed cell are shown in Table III.

Table III. Operational Characteristics of a Point-Feed Prebake Cell

Amperage, kA	180
Current Efficiency, %	94.5
Surface Area of Aluminum Pad, m^2	31.0
Average Metal Velocity, cm/sec	5.75
ACD, cm	3.68

Possible cell bath chemistries for a conventional point-feed cell are shown in Table IV. A conventional low-ratio electrolyte (MCR=2.32) with only alumina and calcium fluoride as additives and minor impurities of 0.5% LiF and 0.5% MgF_2 impurities is shown along with a lithium-modified version of the same electrolyte. The freezing points for the electrolytes are also tabulated.[21] The last column presents the calculated total metallic solubility (as wt % aluminum) for each operational case. For the case of the lithium-modified electrolyte, metal solubility is shown for the same operational temperature as the unmodified electrolyte and for an electrolyte at 10°C superheat above the new freezing point. As in the previous example, a fourth case with increased ratio is presented.

Using the same calibration procedure as outlined in the last section, the "apparent" electrolyte velocity is calculated to be 0.18 m/sec. This lower velocity value may be due to the fact that this cell has better magnetic compensation and slightly less movement of the electrolyte by the metal pad.

Table IV. Electrolytes for a Point-Feed Prebake Cell

Molar Cryolite Ratio	% Al₂O₃	% CaF₂	% MgF₂	% LiF	Melting Point (°C)	Operating Temperature (°C)	Metal Solubility (%)
2.32	2.5	4.0	0.5	0.5	957	967	0.0204
2.32	2.5	4.0	0.5	2.0	945	967	0.0207
2.32	2.5	4.0	0.5	2.0	945	955	0.0155
2.40	2.5	4.0	0.5	2.0	956	966	0.0215

Once again, it is possible to estimate the impact of changing bath chemistry for the current efficiency of the point-feed cell. For the case of the lithium-modified bath with no reduction in operating temperature, the new calculated current efficiency is nearly unchanged at 94.3%. When the cell operating temperature is decreased to 10°C superheat above the new freezing point, the new calculated current efficiency is 95.8%. The fourth case of raising the molar cryolite ratio from 2.32 to 2.40 while maintaining 2% LiF results in a current efficiency of 94.2%.

The changes in current efficiency are shown graphically in Figure 5. Once again the effect of operating temperature on cell current efficiency is observed. The 12°C decrease in operating temperature made possible by the addition of 2% LiF has increased the current efficiency by 1.3 percentage points. For the last case with lithium-modified electrolyte and increased cryolite ratio, the operating temperature is raised by 11°C. This fact, when coupled with the increased ratio, leads to a significant increase in dissolved metals and decreased current efficiency from the previous case as well as the base case.
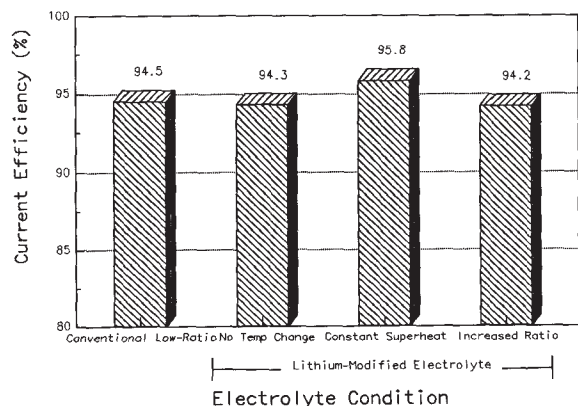

Figure 5.   Current efficiency predictions for a point-feed prebake cell with various electrolyte compositions.

Conclusions

This study has shown that cryolite ratio and bath temperature are the major factors of electrolyte variables influencing cell current efficiency. The effect of alumina content on current efficiency is marginal according to the model. The presence of lithium fluoride in the cell electrolyte can have a significant positive impact on current efficiency if the cell operating temperature is decreased to reflect the change in the electrolyte freezing point. The previous examples have shown marked increases in current efficiency result when the LiF content is increased. However, if the bath temperature is not lowered as the electrolyte chemistry is modified, no significant change in

current efficiency will be observed. Increasing the cryolite ratio after increasing the LiF content of the electrolytes decreases the overall effectiveness of the lithium addition on current efficiency. However, it must be remembered that while changes to the electrolyte may increase current efficiency, other factors must be considered. Other important cell parameters such as cell voltage, thermal balance, or alumina solubility may be adversely affected by electrolyte changes which can lead to adverse cell operating conditions.

References

1. X. Wang, R. D. Peterson, and N. E. Richards, "Dissolved Metals in Cryolitic Melts," Light Metals, 1991, The Metallurgical Society, Warrendale, PA, 1991.

2. H. Kvande, "Current Efficiency of Alumina Reduction Cells," Light Metals, 1989, P. G. Campbell, ed., The Metallurgical Society, Warrendale, PA, 1989, pp. 261 - 268.

3. R. F. Robl, W. E. Haupin, and D. Sharma, "Estimation of Current Efficiency by a Mathematical Model Including Hydrodynamic Parameters," Light Metals, 1977, K. B. Higbie, ed., The Metallurgical Society of AIME, New York, 1977, pp. 185 - 202.

4. B. Lillebuen, S. A. Ytterdahl, R. Huglen, and K. A. Paulsen, "Current Efficiency and Back Reaction in Aluminum Electrolysis," Electrochimica Acta, Vol. 25, (1980) pp. 131 - 137.

5. J. W. Evans, Y. Zundelevich, and D. Sharma, "A Mathematical Model for Predictions of Currents, Magnetic Fields, Melt Velocities, Melt Topography, and Current Efficiency in Hall-Heroult Cells," Metallurgical Transactions, B, Vol. 12B (1981), pp. 353 - 360.

6. K. Grjotheim, W. E. Haupin, and B. J. Welch, "Current Efficiency - Relating Fundamental Studies to Practice," Light Metals, 1985, H. O. Bohner, ed., The Metallurgical Society, Warrendale, PA, 1985, pp. 679 - 694.

7. W. E. Haupin, Production of Aluminum and Alumina, John Wiley & Sons, Inc., New York, 1987, pp. 134 - 149.

8. J. J. J. Chen and M. P. Taylor, "The Current Efficiency Model of Lillebuen, et al., for Aluminum Electrolysis," Electrochimica Acta, Vol. 35, (1990), pp. 109 - 110.

9. K. Grjotheim and B. J. Welch, Aluminum Smelter Technology, Aluminum-Verlag, Dusseldorf, 1988, p. 173.

10. R. Ødegård, "On the Electrochemistry of Dissolved Aluminum in Cryolitic Melts," Electrochimica Acta, Vol. 33, (1988), pp. 527 - 535.

11. N. X. Feng, K. Grjotheim, and H. Kvande, "Current Efficiency Measurements in Laboratory Aluminum Cells - VIII. Current, Temperature, and Cathode Alloy Composition, Al-Diffusivity," Canadian Metallurgical Quarterly, Vol. 25, (1986), pp. 287 - 291.

12. E. W. Dewing and K. Yoshida, "Electronic Conductivity in Cryolite-Alumina Melts," Canadian Metallurgical Quarterly, Vol. 15, (1976), pp. 299 - 303.

13. X. Wang and R. D. Peterson, Dissolved Metals in Cryolitic Melts, Manufacturing Technology Laboratory Report 1030, 1990.

14. X. Wang and R. D. Peterson, "Dissolved Metals in Cryolitic Melts," to be published.

15. T. R. Alcorn, C. J. McMinn, and A. T. Tabereaux, "Current Efficiency in Aluminum Electrolysis by Gas Analysis," Light Metals, 1988, L. G. Boxall, ed., The Metallurgical Society, Warrendale, PA, 1988, pp. 683 - 695.

16. B. Lillebuen and T. Mellerud, "Current Efficiency and Alumina Concentration," Light Metals, 1985, H. O. Bohner, ed., The Metallurgical Society, Warrendale, PA, 1985, pp. 637 - 645.

17. M. J. Leroy, T. Pelekis, and J. M. Jolas, "Continuous Measurement of Current Efficiency, by Mass Spectrometry, on a 280 KA Cell," Light Metals, 1987, R. D. Zebreznik, ed., The Metallurgical Society, Warrendale, PA, 1987, pp. 291 - 294.

18. P. Fellner, K. Grjotheim, K. Matiasovsky, and J. Thonstad, "Current Efficiency Measurements in Laboratory Aluminum Cells," Canadian Metallurgical Quarterly, Vol. 8, (1969), pp. 245 - 248.

19. P. Fellner, K. Grjotheim, and H. Kvande, "Current Efficiency Measurements in Laboratory Aluminum Cells, VI - Back Reactions," Canadian Metallurgical Quarterly, Vol. 23, (1984), pp. 421 - 425.

20. T. Müftüoglu, D. Bratland, C. Castellano, K. Grjotheim, and J. Thonstad, "Current Efficiency Measurements in Laboratory Aluminum Cells, IV - The Influence of Stirring and LiF Additions," Canadian Metallurgical Quarterly, Vol. 18, (1979), pp. 19 - 22.

21. A. T. Tabereaux, "Phase and Chemical Relationships of Electrolytes," Light Metals, 1985, H. O. Bohner, ed., The Metallurgical Society, Warrendale, PA, 1985, pp. 751 - 761.