

THE LIQUIDUS ENIGMA

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Abstract

If one calculates the liquidus temperature of Hall-Héroult bath using its chemical analysis and almost any of the liquidus correlations found in the literature, one finds that some cells operate successfully for extended periods at temperatures below the calculated liquidus. There are several possible explanations for this enigma: 1. Impurities not included in the chemical analysis may be lowering the true liquidus. 2. Liquidus correlations have been based upon measurements made on baths synthesized from pure chemicals rather than baths taken from industrial cells and chemically analyzed. There may be an analytical bias. 3. There may be a measurement bias in determining bath temperature in the cell. 4. Bath may be able to remain for long periods in a supersaturated state. 5. Industrial cells may be operating with suspended precipitate. Bath samples taken under these conditions would contain particulate while the assumption is made that the sample contained only liquid. The true explanation appears to include all of the above with 1, 3 and 5 playing the major roles.

Importance of liquidus temperature

The liquidus temperature is the temperature at which freezing starts. It sets the lowest temperature at which a Hall-Héroult cell may be operated without a precipitate forming. Bath needs to be kept sufficiently above the liquidus temperature, i.e., have sufficient superheat or ΔT , to provide the heat of solution for alumina additions. A low liquidus temperature permits a low operating temperature. This is desirable because, all else being equal, lowering the operating temperature by 1°C improves current efficiency by about 0.18% (1).

Superheat controls the formation of side ledge and bottom freeze. The carbon sides of the cell must be protected by a layer of frozen bath to prevent erosion. To maintain a frozen ledge, sufficient heat, Q , must be extracted through the wall to drop the temperature (across the boundary lay-

er at the liquid-frozen bath interface) from that of the adjacent liquid to the liquidus temperature. (2) The resulting ledge will have a thickness, X .

$$Q = h \cdot A \cdot \Delta T \quad (1)$$

$$X = K \cdot A \cdot (T_L - T_S - Q \cdot R_W) / Q \quad (2)$$

Where:

Q = heat flow

h = heat transfer coefficient, in consistent units

A = interface area

ΔT = temperature drop across the boundary layer

≈ bath temperature – liquidus temperature (under steady state conditions)

K = thermal conductivity of frozen bath, in consistent units.

T_L = liquidus temperature

T_S = shell temperature

R_W = thermal resistance of the wall, in consistent units.

Of equal importance, bath creeps under the metal pad by capillary action and will freeze there where ever the temperature is below the liquidus. Frozen bath on the bottom increases the cathode voltage by constricting current flow. On the other hand, to minimize flow of horizontal electric currents in the metal pad, it is desirable for the freeze to extend to but not past the “shadow” of the anodes. Horizontal currents are bad because they interact with the cell’s magnetic field to produce metal pad movement and instability.

Equations giving liquidus temperatures

The literature is replete with measurements of liquidus temperature (3,4). The most recent and probably the most

accurate are those of Sterten and his students (5,6). They correlated their determinations of the cryolite-precipitating liquidus, T_{LC} in °C, by equation 3.

$$T_{LC} = 1011 - 0.072(\%AlF_3)^{2.5} + 0.0051(\%AlF_3)^3 + 0.14(\%AlF_3) - 10(\%LiF) + 0.736(\%LiF)^{1.3} + 0.063[(\%LiF)(\%AlF_3)]^{1.1} - 3.19(\%CaF_2) + 0.03(\%CaF_2)^2 + 0.27[(\%CaF_2)(\%AlF_3)]^{0.7} - 12.2(\%Al_2O_3) + 4.75(\%Al_2O_3)^{1.2} \quad (3)$$

Where:

$\%AlF_3$ = Wt $\%AlF_3$ excess over cryolite, Na_3AlF_6 .
 $\%LiF$, $\%CaF_2$, $\%Al_2O_3$ are Wt% of respective components.

Sterten correlated the alumina precipitating liquidus, T_{LA} in °C, by equation 4 and alumina solubility in weight % by equation 5.

$$T_{LA} = 1000.0 * B / [\ln (\%Al_2O_3) - A + B] \quad (4)$$

$$(\%Al_2O_3)_{Sat} = \exp \{ A + B [(1000 / T) - 1] \} \quad (5)$$

Where:

T = Bath Temperature, °C
 $(\%XXXX)$ = wt% of the component XXXX

$$A = 2.464 - 0.007(\%AlF_3) - 1.13 \times 10^{-5} (\%AlF_3)^3 - 0.0385(\%Li_3AlF_6)^{0.74} - 0.032(\%CaF_2) - 0.040(\%MgF_2) + 0.0046\%[(\%AlF_3)(\%Li_3AlF_6)]^{0.5} \quad (6)$$

$$B = -5.01 + 0.11(\%AlF_3) - 4.0 \times 10^{-5} (\%AlF_3)^3 - 0.732(\%Li_3AlF_6)^{0.4} + 0.085[(\%AlF_3)(\%Li_3AlF_6)]^{0.5} \quad (7)$$

The Enigma

The above equations agree within a few degrees with most of the earlier data. This leaves unanswered a long-standing puzzle. If one calculates the nominal liquidus from the chemical analysis of the bath and the above equations (or by almost any of the liquidus correlations found in the literature) one finds that many cells operate successfully for extended periods at temperatures below this liquidus. This is analogous to water remaining liquid

below its freezing point for several hours in a stirred vessel. It seems impossible. Moreover conventional wisdom requires that the bath be 10 to 15 °C above the liquidus to provide sufficient heat content to dissolve alumina additions. In fact it requires about 8.5 °C superheat to handle a 1% addition. Breaking this down, heating the alumina to temperature will produce a temperature drop in the bath of 5.4 °C. Dissolving the alumina will drop the temperature another 8 °C. A 4.9 °C lower liquidus, resulting from the extra percent alumina, only partially compensates for the temperature drop. How then are these cells able to operate at or below the calculated liquidus temperature? It seemed until now that the calculated liquidus temperatures were simply too high. Many investigators have made new measurements using various techniques to improve accuracy and remove the discrepancy, but they continued to find essentially the same liquidus temperatures.

How can it be explained?

Probably we should accept the measured liquidus values and look for other explanations of this enigma. Some possible explanations are: 1. Impurities not included in the bath analysis may be lowering the true liquidus. 2. Liquidus measurements were made on baths synthesized from pure chemicals rather than bath compositions determined by chemical analyses. There may be an analytical bias. 3. There may be a bias in how bath temperature is measured in the cell. 4. Bath may be able to remain in a supersaturated state for long periods. 5. Industrial cells may be operating with suspended precipitate. The sampled and analyzed bath would include these suspended particles but the liquidus equation assumes the bath to be completely liquid.

Let us examine the validity of each suggested explanation.

Explanation #1

There indeed are impurities present that generally are not determined by the bath analysis. Being at very low concentrations, their freezing point lowering, ΔT in °C, can be estimated by using the cryoscopic equation derived from thermodynamics.

$$\Delta T = (n * R * T^2 / \Delta H_f) * X_i \quad (8)$$

Where:

n = number of foreign entities formed when a molecule of impurity 'i' dissolves.

R = the gas constant.

T = melting point of solvent, degrees Kelvin.

ΔH = the heat of fusion of the solvent (cryolite in this case).

X_i = the mol fraction of impurity added.

This equation can be simplified to equation 9, specific for cryolite.

$$\Delta T = 240 \cdot n \cdot (\% 'i') / MW_i \quad (9)$$

Where:

$\% 'i'$ = weight percent of impurity.

MW_i = molecular weight of the impurity.

Probable values for n would be 1 for metallic sodium, 1 for FeF_3 (F is present in cryolite) and 5 for Fe_2O_3 . Individually the effect of each impurity is small, but taken together they may, depending upon amounts present, lower the liquidus 1 to 3 °C.

Explanation #2

The rapid techniques used for bath analysis (X-Ray diffraction, X-Ray fluorescence, Lewis acid and other pH methods for bath ratio) all depend upon reference standards. Since there is no industry wide set of standard samples, a possibility of analytical bias exists. Moreover, the analytical results by X-Ray diffraction and the aluminum chloride leach determination of alumina depend upon the rate of quench of the sample. X-Ray gives better results with a rapidly quenched sample while the aluminum chloride method for alumina gives better results with a slowly cooled sample. Analytical problems, however, seem to be under control. Bath samples have been exchanged between plants and companies and analyzed using different techniques. Where significant deviations occurred between methods or plants, the causes were found and corrected.

Explanation #3

Bath temperature generally is measured at the end of the pot about midway between the frozen ledge and the anode. Mathematical modeling indicates that the temperature here may be as much as 15°C lower than under the anodes. Actual temperature measurements, however, indicated a temperature gradient of only 2 to 7 °C. It would be desirable to make temperature measurements under the anodes on a routine basis, but this

is too difficult.

Explanation #4

When running cooling curves or differential thermal analyses of Hall Héroult baths in the laboratory, a cooling rate of 0.6 °C per minute or slower is required to prevent under-cooling. Carbon particles in the bath of industrial cells should, however, provide sufficient nuclei to prevent extensive supersaturation. Nevertheless, circulating bath might remain supersaturated long enough to flow up the side of an anode, out to the wall and back down under the anode.

Explanation #5

On the other hand, a precipitate may form and stay in suspension as the bath cools during the flow up the side of an anode, out to the wall and back down under the anode. Suspended particulate would be included in the bath sample and contribute to the chemical analysis in a way identical to supersaturated bath. Using analytical results to calculate the liquidus assumes the sample was entirely liquid and not supersaturated. The calculated liquidus temperature would represent the temperature required to maintain all the particulate in solution.

We can calculate the plausibility of this hypothesis. For the conditions under which most cells operate, the precipitating phase will be cryolite. Subtracting out 5 % cryolite precipitate and recalculating the composition of the liquid phase, we find the new calculated liquidus is lowered about 5 °C for a bath with 12% excess AlF_3 . For a bath with 3% excess AlF_3 , the lowering would be about 1.7 °C. If there were 10% precipitate, the lowering would be about 11 °C at 12% excess AlF_3 or 3.5 °C at 3% excess AlF_3 . The calculation for 10% precipitate gives liquidus values quite in line with industrial experience. It also explains the increasing difference with increasing excess AlF_3 between the calculated liquidus and apparent liquidus based upon pot operation. However, if this explanation is to stand, then 10% solids must not increase excessively the bulk density nor viscosity. No data was found on the effect of suspended particles on these properties; however, its effect can be estimated.

The bulk density of a mixture, δ_{mix} , can be calculated by equation 10.

$$\delta_{mix} = 100 / [(Wt \% \text{ solid}) / \delta_{solid} + (Wt \% \text{ liq}) / \delta_{liq}] \quad (10)$$

Where:

δ = density

Subscript 'solid' represents cryolite particles.

Subscript 'liq' represents the liquid bath.

Equation 10 indicates that even 10% cryolite precipitate would increase the bulk density of the bath only 0.04 g/cc, a minor amount.

The effect upon viscosity can be estimated using the correlation of Mori and Ototake (7), equation 11.

$$\mu_m / \mu_l = 1 + 1.56 \Phi_s / (0.52 - \Phi_s) \quad (11)$$

Where:

μ_m = the viscosity of the mix

μ_l = the viscosity of the liquid, bath in this case

Φ_s = the volume fraction of solids

Equation 11 indicates that 10% solid cryolite precipitate in the bath would increase the viscosity about 37%. This would not significantly affect cell operation. It is about the same change in viscosity as would be produced by increasing the dissolved alumina concentration in a 1.15 ratio bath from 2% alumina to saturation. While this does not prove that baths contain suspended particles it does indicate that we cannot rule out this possibility.

The liquidus discrepancy caused by particulate that dissolves under the anode and reforms at the sampling location is included in the measured temperature gradient between these two locations. To account for the full discrepancy requires that some cryolite particles remain in suspension under the anodes.

For those who operate in the alumina precipitating region of the phase diagram, all that was said about cryolite particles apply also to alumina particles. Here the possibility of supercooling is increased because of the slow kinetics of alumina dissolution and precipitation.

Conclusions

There are numerous mechanisms to account for the apparent liquidus temperature of bath in Hall-Héroult cells being less than the calculated liquidus. Several mechanisms may operate simultaneously, hence it is not necessary for any one of them to account for the full discrepancy. Impurities not included in the chemical analysis will often account for 1 to 3 °C. The location where the bath temperature is measured may be 2 to 7 °C

lower in temperature than the bath under the anodes. Although one can not rule out a systematic error in the chemical analysis of the bath, I believe that most of the remaining 3 to 10 °C discrepancy between the apparent liquidus and the calculated liquidus results from particulate suspended in the bath.

We need physical tests now to confirm or deny the presence of precipitate in the bath, and the kinetics of its formation and dissolution. Much could be learned by taking samples through a preheated vacuum filter using either a porous metal or porous carbon medium.

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