Technical Report

Non-invasive estimation of dissolved alumina concentration in Hall - Heroult reduction cells

Prepared for
United States Department of Energy
Golden Field Office

I & I Solicitation DE-PS36-02GO90014
I & I Grant No. DE-FG36-02GO12047
David G Bell, Principal Investigator

16 February 2004

Contract Manager
James P Damm

Project Manager
Steve Sargent

Executive Summary

The present best practice for the preparation of primary aluminum is by electrolysis of alumina in the traditional Hall-Heroult reduction cell. The process conditions in the electrolyte of this cell required for the reduction to proceed are sufficiently harsh to have precluded the implementation of in situ sensing of the electrolyte composition, specifically the concentration of the ionized alumina.

This report reveals the theoretical basis for a non-invasive method for estimation of the ionized alumina concentration which does not require the use of any sensor in direct contact with the cell electrolyte. The proposed method can in principle be applied with equal efficacy to the so-called drained cathode cell designs and to cells having any anode composition, because only knowledge of the electrolyte conduction behavior is required a priori. For an operating cell, the proposed method requires only readily available electrical measurements and the facilities to process the acquired signals. The proposed method rests on the ability to identify certain characteristics of the transients in the reduction cell terminal voltages caused by the quasiperiodic introduction of alumina. It will be shown that these voltage transients manifest measureable properties, in a statistical sense, that should permit estimation of the ionized alumina concentration with a delay of one alumina feed cycle.

The next logical step following the present work, consistent with the Aluminum Technology Roadmap [1], is to experimentally verify the predictions made here; no doubt practical refinements to the proposed approach will evolve during the course of experimentation. Successful verification of the proposed estimation method will permit the design of reduction cell control algorithms based directly on the mass balance of alumina in the electrolyte.

This report assumes that the reader understands certain basic concepts important to the operation of electrolytic cells, and the Hall-Heroult cell in particular. References [2,3] provide such concepts in a manner accessible to the technically educated reader; reference [6] is a more thorough treatment.

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1. Introduction

The practical prediction of the performance of industrial scale carbon anode Hall-Heroult reduction cells from the first principles of electrochemistry is a very complex undertaking, resulting in mathematical models that require measurements unobtainable in industrial practice. Researchers in this field have conducted many experiments, guided by these principles, with the aim of developing computationally simple empirical models. Such models still incorporate the concentration of dissolved alumina in the electrolyte as a measured variable, limiting the predictive utility of these models for the practicing process engineer or chemist tasked with optimizing the performance of industrial reduction cells. It is just such a model from which the present investigation proceeds.

Consider the well known exemplary curve in Figure 1, depicting the dependence of the reduction cell observed terminal voltage, at equilibrium, on the concentration of dissolved (ionized) alumina.

Figure 1

The indicated range of alumina concentration in Figure 1 is typical of the limits encountered in industrial practice. This example was computed using the cell voltage model described in Section 4 of this report, based on published work by Huglen, Lillebuen, and Mellerud[2], for a nominal cell current of 125 kAmperes and assumed typical values for other key parameters such as the electrode separation ("anode-cathode distance") and the electrolyte temperature. The principal feature of interest here is that the observed resistance exhibits a local minimum within the typical operating range of the alumina concentration. Such non-monotonic behavior complicates the application of ordinary controller algorithms, including for example the well known Proportional-Integral-Derivative algorithm or the lead-lag algorithm. The controls engineer will recognize that the transfer function of the resistance vs. alumina 'process' possesses zeros (not poles) in the right half plane of the Laplace domain, or, alternatively, zeros outside the unit circle in the Z plane when modeling the process in discrete time. Since the alumina concentration is unknown to the controls practitioner in industrial cells, other schemes have been applied to 'locate' the alumina concentration operating point. Typically such schemes deliberately apply a macro disturbance to the cell alumina feed cycle in an effort to create an identifiable response in the cell terminal resistance; in one common example, alumina feed is inhibited so that the cell controller can observe the resistance response when the alumina concentration is known to be approximately linearly decreasing with time. Alumina feed is restarted depending on some measurement derived from the cell resistance. Starvation schemes are at some risk for causing anode effect events; cells operating at high anode current densities are at greater risk for anode effects.

Electrical energy and alumina are the principal contributors to the total cost of reduction of primary aluminum. Since minimum cost is the objective in the industrial setting, the process engineer must find and maintain the operating conditions which minimize the overall cost. For a given cell cathode and structural design, the minimum electrical energy input clearly should occur when the terminal resistance is minimized, assuming that the cell design maintains an electrolyte temperature suitable for its composition. For a typical electrolyte, the optimum current efficiency is found at very low alumina concentrations, so low that the theoretical current efficiency cannot be sustained whilst avoiding the anode effect. Reference [2] page 144 presents some graphical illustrations

of the variation of current efficiency with alumina concentration; it is clear from these graphs that the optimum current efficiency is achieved for (weight) alumina concentrations of one percent or less. Depending on the relative costs for alumina and energy for a particular smelter, the minimum-cost operating point is likely located between those that define the optimum current efficiency and the minimum energy consumption, representing a range of alumina concentrations of approximately 1% to 3%.

2. *Proposal objectives*

The practicing reduction process engineer has long known that the pulsed feeding of alumina causes momentary disturbances to the electrolyte chemistry and therefore to the observed electrical conductivity of the electrolyte. This deliberately qualitative characterization of this knowledge reflects the lack of precise application of this phenomenon in the traditional operation of industrial scale Hall-Heroult reduction cells. The present industrial practice of reduction cell control involves a variety of schemes for inference of cell operating states from the macro behavior of the cell resistance; reference [10] chapter 9 provides a good survey of typical practice. The key point here is that cell resistance behavior is the controlled variable, inferring the electrolyte state from the curve in Figure 1.

The motivation for inferential methods of course evolves from the practical difficulties associated with in-situ electrolyte sensors. The method proposed herein involves inference as well, taking advantage of relatively inexpensive instrumentation and signal processing electronics to achieve a near real time estimate of the electrolyte state.

The stated objectives of the present effort, in summary, are first to predict the characteristics of the feed transient as manifested in the cell potential signals, second to introduce practical methods for the detection and measurement of these transient signals, and third to estimate the electrolyte alumina concentration from the feed transient characteristics. These are the objectives identified in the "Technical hurdles..." paragraph in the project proposal. This report will address these objectives in the proposed sequence.

The cell considered in this report is the conventional Hall-Heroult reduction cell with pre-baked carbon anodes, conventional cryolite electrolyte, metal-pool cathode. The technique revealed here is not limited to this case; it is readily applied to other cell designs utilizing periodic feeding strategies, as long as the steady-state cell voltage dependence on alumina concentration can be measured on an experimental scale.

3. *The Feed Process*

The mechanics of alumina feed in the pre-bake anode reduction cell design are conceptually quite simple. A crust breaking device, typically operated pneumatically, penetrates the solidified electrolyte 'crust' vertically from above the electrolyte. Within a few seconds of this breaking operation, alumina powder is discharged into the opening in the crust.

Let us not be deceived by the simplicity of this mechanism. A practical description of the alumina feed process must consider, at a minimum, these physical processes:

- > diffusion of the unreacted alumina powder into liquid electrolyte;
- > ionization of alumina taking place at the surfaces of the powder grains;
- > diffusion of the ionized alumina into the electrolyte;
- > distortion of the expected diffusion concentration profiles by convection processes in the electrolyte, resulting either from gas bubble agitation or magnetohydrodynamic stirring processes;
- > consumption of ionized species by electrochemical reactions.

For the present purpose, in which we seek to describe the differential conductivity of the bulk electrolyte caused by the introduction of alumina, we will choose to abandon the analysis of those phenomena that may contribute to the spatial distortion of concentration profiles in diffusion processes. Thus the quantitative analysis of MHD convection and bubble agitation will not be considered here. However, it is worth noting that wave motion in the cell electrolyte and the metal pool induced by MHD is known to exhibit periods on the order of minutes, which is of course similar to the periods associated with alumina feeding. This can influence the observation of the alumina feeding transient voltage signals and thus cannot be ignored in practice; a possible scheme to facilitate the identification of this wave motion is discussed in section 6 of this report.

Thus we will model the conductivity disturbance by describing the diffusion and kinetic processes. The deposition and subsequent diffusion of unreacted alumina powder was approximated as follows: an initial mass M of alumina powder is introduced at time $t=0$ into the cell electrolyte such that the

alumina is uniformly distributed in a sphere of radius R embedded in the liquid electrolyte. Thus the incremental concentration ΔC of unreacted alumina in the electrolyte at a distance r from the point of introduction of the alumina powder at time t can be found by solving the diffusion equation in one dimension by further assuming the extent of the electrolyte to be infinite to simplify the boundary conditions. Alumina thus dispersed into the electrolyte will ionize into electrically charged species (ions) approximately as a first order rate process with rate constant k . Thus we are solving the diffusion equation with irreversible first order chemical reaction of the diffusing species:

$$\frac{\partial \Delta C}{\partial t} = D \frac{\partial^2 \Delta C}{\partial r^2} - k \Delta C, \quad ,$$

where D is the diffusion coefficient for alumina powder in molten cryolite, and is assumed to be constant.

Thus, for homogeneous electrolyte, we have

$$\Delta C = \frac{3M}{8\pi R^3} e^{-kt} \left[\operatorname{erf} \left(\frac{R-r}{2\sqrt{Dt}} \right) + \operatorname{erf} \left(\frac{R+r}{2\sqrt{Dt}} \right) \right] + \frac{1}{R} \sqrt{\frac{Dt}{\pi}} e^{-\frac{(R-r)^2}{4Dt}} - e^{-\frac{(R+r)^2}{4Dt}} .$$

For the present problem, we are interested in the variation of concentration with time; by numerically integrating the incremental concentration $\Delta C(r,t)$ over the sphere r , we obtain the incremental concentration as a function of time. Note that the formulation so far only accounts for diffusion and ionization of the alumina powder; the consumption of the ionized species by the electrolysis process has not yet been considered.

Figure 2 depicts a typical normalized diffusion profile, obtained using the above formulation and a nominal value for the diffusion coefficient. Reference [3] cites numerous laboratory results for the diffusivity of alumina in cryolite melts, obtained over a range of cryolite compositions and temperatures. For the purposes of this investigation, in which the goal is to identify a signal processing method for concentration estimation, a typical value supported by experiment may be chosen; a value of $D = 2.0 \text{ cm}^2/\text{sec}$ will be used here.

Figure 2

In order to use the diffusion result to estimate the shape and magnitude of the alumina concentration disturbance that follows the feed event, some operating parameters of the nominal reduction cell must be assumed; values that are representative of present industrial practice will of course be used. To quantify a concentration disturbance, one will also require:

- structural data - total electrolyte weight, alumina feed weight;
- operational data - cell current and current efficiency.

In this case, some estimate of the dependence of current efficiency on alumina concentration, neglecting other factors, will be needed. In reference [2], chapter 5, as well as in work by G P Tarcy that this author is aware of, support for a simple linear dependence would be suitable for the present work; a penalty of 2% current efficiency for each 1% (by weight) increase in the alumina concentration will be assumed. Figure 3 depicts a typical concentration disturbance in which the starting concentration at the time of the feed event is 1.9 % alumina by weight.

Figure 3

This curve is representative of the typical expected concentration disturbance. For leaner starting concentrations, the current efficiency tends to be higher, so the rate of consumption is greater, and conversely. In actual practice, the shape of the observed concentration disturbances may deviate from this simplified model; the simplified pulse shapes will be used to illustrate the estimation concepts to follow and to demonstrate their application. Specifically, these disturbances will be used as inputs to the reduction cell voltage model to generate the corresponding expected voltage pulses.

4. *The Cell Voltage Model*

The observed terminal voltage of the reduction cell can be estimated by a combination of theoretical results and some empirical adaptations where the theory is incomplete. The model used here is presented by Huglen, Lillebuen, and Mellerud in [2], page 131. This model incorporates terms for the principal physical phenomena consistent with the generally accepted theory of operation of the Hall-Heroult reduction cell. Specifically, the additive terms for the cell terminal voltage comprise the following physical contributions:

- > reversible reaction potential;
- > cathode overvoltage due to alumina concentration;
- > anode overvoltage due to reaction;
- > anode overvoltage due to alumina concentration;
- > time-averaged voltage drop due to gas bubbles under the anodes;
- > ohmic voltage drop due to electrolyte conductivity;
- > cell structural ohmic voltage drops.

Each of these terms, excluding structure conductivity, depends on the alumina concentration in the electrolyte. This model does not consider inductive or capacitive phenomena, which cannot be neglected in actual practice, since the cell current is not constant in industrial scale cells. The industrial cell current will contain time varying components due to, for example, harmonics of the AC power system frequency introduced by the rectifier system, wave motion in both the metal pool and electrolyte of the subject cell and its neighbors, and disturbances caused by non-steady-state behavior of any other cell in the circuit (anode effects, for example). Also, the stochastic component of real cell voltage observations, mainly due to gas bubble formation and release under the anodes, must be considered in practice as well. The effects of these phenomena on the observed cell voltage can in practice be suitably attenuated by sampling diversity schemes and by the application of combined continuous- and discrete-time filters to the cell voltage and current signals.

This model, with a nominal cell current of 125 kiloAmperes at a current density of 1.0 Amperes/cm², was used to produce the cell steady-state terminal resistance curve presented in Figure 1.

5. *Dynamic behavior of the cell voltage*

The diffusion and ionization results of Section 3 and the cell voltage model of Section 4 will now be used to simulate the cell voltage transients that result from the pulsed addition of alumina powder to the electrolyte.

The salient parameters of a hypothetical reduction cell and its operating conditions that were used in the simulations that follow are summarized below. The assumed alumina feeder calibration was based on a feeding interval of 200 seconds at a mean current efficiency of 94%.

> anode effective electrical area	12.5 m ²
> cathode effective electrical area	14.0 m ²
> total structural resistance	2.50 Ω
> anode effective current density	1.00 A/cm ²
> electrolyte Cryolite ratio	2.41
> mean interpolar distance	6.00 cm
> electrolyte temperature	960 °C

Simulated cell voltage responses were computed for starting alumina concentrations over the range of 1% to 6% by weight in 0.1% increments.

Following a feed event, a transient in the cell voltage is observed. The characteristics of this voltage transient depend principally on two key factors: first, the amplitude and time-domain shape of the alumina concentration pulse, which depends on the diffusion profile and ionization kinetics; second, the derivatives of the cell terminal resistance with respect to alumina concentration. Simply put, the voltage transient due to an alumina feed event can be viewed as a projection of the alumina concentration transient. Thus, at very low initial concentrations, a relatively large negative amplitude voltage transient would be observed, and conversely at high initial concentrations, a positive amplitude voltage transient would be observed. In the region near about 2.5% alumina, the terminal resistance curve is near a minimum, so the first derivative tends to zero and the voltage transient observed is very small.

These observations are illustrated in Figure 4, depicting voltage transients at initial alumina concentrations of 1.5 wt%, 2.5 wt%, and 4.5 wt% , each with the mean voltage removed.

Figure 4

The shapes of the alumina feed voltage transients are uniquely characterized by the operating conditions in the cell electrolyte which govern the behavior of the cell's terminal voltage. In the absence of noise, distortions, and voltage signals generated by phenomena other than concentration transients, the identification of the transients depicted in figure 4 would be a simple matter indeed. In actual practice the observable voltage signal at the cell's terminals will manifest numerous other components; in the present case, some of these components can complicate the transient identification problem. Of specific concern here are two general classes: signals of a stochastic nature with amplitudes similar to the subject transients (such as those due to gas bubble mechanics under the anodes),

and signals whose power spectra share components with the subject transients (such as those due to MHD-induced waves in the metal pool and in the electrolyte). Since the goal here is the identification of the alumina feed voltage transients, leading by inference to the alumina concentration, then any proposed algorithms must of course be tested on realistically corrupted signals. For this initial effort we will consider the case of the anode bubble 'noise' signal added to the desired feed voltage transient signal, since a realistic simulation is easily achieved. Based on the author's experience, the anode bubbles are known to produce a stochastic constant mean signal having approximately gaussian density. Figure 5 depicts the 1.5 wt% voltage transient as it might be observed in the industrial setting, with the 'noise' signal due to anode bubbles present. This simulated observation was generated with zero-order hold sampling at 100 Hz and added gaussian noise with a peak to peak amplitude of 30 mV. The peak amplitude of the feed transient is about 3 mV; the signal to noise ratio here is about -20 dB (that is, noise energy is about 20dB greater than the signal energy), which is one of the challenging features of this problem.

Figure 5

6. *Identification of the voltage transient*

The discussion now turns to the problem of transient signal detection in uncorrelated gaussian noise. The theoretical features of this problem are reviewed in detail in the references [8,11]; only the essential concepts which establish the suitability of the proposed approach will be discussed.

The essential features of this problem are:

- > alumina concentration is analytically related to an observable voltage transient signal;
- > the 'shape' of the transient signals is known a priori, and can be generated for any arbitrary alumina concentration;
- > the voltage transients have negligible energy beyond 0.1 Hz;
- > the signal to noise ratio is unfavorable;
- > the noise may be considered to be gaussian to a good approximation;
- > the transient signal is characterized in the time domain.

These features capture both the constraints and the useful leverage applicable to this detection problem, which leads us to the project objective.

It is now proposed that the voltage transients caused by the periodic pulsed introduction of alumina powder into the cell electrolyte can be detected and identified using the third-order cumulant of the convolution of the subject measured voltage transient and matched filters derived from the simulated concentration-dependent transients. A test statistic derived from the third-order cumulant sequence selects the matched filter with the best fit, thus identifying the electrolyte alumina concentration at the start of the feed event. This procedure thus estimates alumina concentration with a delay of one feed event.

This approach is principally motivated by three of the features listed above:
precise prior knowledge of the subject signals,
the noise amplitude is larger than the subject signal,
voltage noise at the reduction cell terminals is a gaussian process.

The detection algorithm comprises the following major steps:

1. acquire the cell voltage signal following an alumina feed event
2. pre-process the voltage signal (low-pass filter, remove mean)
3. convolve the processed voltage with matched filters
4. estimate unbiased third-order cumulants of convolution results
5. compute test statistics from the cumulant sequences
6. select sequence with best value of the test statistic, which then associates the alumina concentration to the corresponding filter.

There are some signal processing related constraints that should be observed in each of these six steps in order to attain good performance from this algorithm, which are reviewed below.

Preliminaries: compute the reference voltage transients, matched filters, reference cumulant sequences.

Compute the expected voltage transients for a suitable range of alumina concentrations, say 0.5 % to 6.0 % in 0.05 % steps, at a sampling frequency that will avoid aliasing the third order statistics of the signals, subtract the unbiased mean values.

Compute the matched filter for each of these voltage transients simply as the time-reverse of the voltage signal.

Choose a reference value for the scalar test statistic, say 1.0 .

Compute the scaling factor for each matched filter, so that the magnitude of the zero-lag third-order cumulant of the convolution of the matched filter with its corresponding voltage transient equals the test statistic.

Step 1: acquire the cell voltage signal following an alumina feed event.

The proposed detection procedure requires the cell voltage signal as a uniformly sampled time series, acquired under specific yet easily implemented conditions:

- > the analog voltage signal must be low-pass filtered prior to sampling;
- > the continuous time filter must conform to a constant group delay characteristic (linear phase) in the passband;
- > the filter attenuation should be at least 70dB at $0.3F_s$, where F_s is the digitizer sampling frequency;
- > zero-order hold sampling is required for $F_s \sim 100\text{Hz}$;
- > the captured signal must begin at the alumina feed event and end at the following feed event.

These requirements are easily met with commercially available components. It is very important to use linear phase filters to minimize distortion of the transient signal of interest; low-pass filters having the Bessel characteristic work best here despite their inferior roll-off slope.

Step 2: Preprocess the acquired cell voltage signal.

Remove the unbiased mean value from the sampled cell voltage signal. Low-pass filter and decimate the zero-mean signal for a new sampling frequency of about 2Hz. The discrete time filters should also have a constant group delay characteristic, which is easily achieved in FIR structures designed with symmetrical windows. Since the entire voltage record is available prior to processing, zero-phase filtering could also be applied.

Figure 6

Step 3: Convolve the processed cell voltage signal with each matched filter. Conventional time-domain convolutions.

Step 4: Estimate the third-order cumulants for each Step 3 sequence. In the simulations generated for the algorithm proposed in this report, only the zero-lag cumulant is required. See reference [8] for cumulant estimation procedures.

Step 5: Compute test statistics from the cumulant sequences. In the present case, only the zero-lag cumulant magnitude is used. Clearly other tests are possible, and would likely be developed as part of a pilot scale test of the methods proposed here.

Step 6: Compare the Step 5 test statistics with the reference test value. The estimated alumina concentration is that which corresponds to the matched filter whose test statistic is closest to the reference value.

The implementation of the proposed algorithm in a practical reduction cell controller will require DSP capability in the controller. The algorithm used for the simulations that follow will certainly not require anything near the state of the art in DSP hardware. A scalar floating point digital signal processor operating at about 50 MHz could complete an estimate in under 10 seconds, well in advance of the next scheduled alumina feed cycle.

7. Simulation Results

The simple algorithm described in the previous section was easily able to establish starting alumina concentration to within 0.20% in the range 0.50% to 6.00% alumina, and remains within 0.05% in the range 0.50% to 4.00% alumina. The latter range covers the operating range of the majority of pre-bake anode reduction cells in the United States and Europe. This performance was achieved with 30 mV peak to peak additive Gaussian noise.

To assist in the visualization of the algorithm, some graphical results are given below. Beginning with the example voltage transients in figure 4 and the anode bubble noise in figure 5, the filters described in Step 2 of the algorithm were applied to produce the signals depicted in Figure 7. Comparing Figure 7 with Figure 4, one might conclude that these signals are still noise contaminated, which indeed has motivated the application of higher-order measures.

Figure 7

To illustrate the discriminating power of the proposed algorithm, we will use the 2.5wt% transient. Figure 8 depicts the convolutions of the noise-contaminated 2.5wt% transient with the (matching) 2.5wt% matched filter and the (unmatched) 2.6wt% matched filter. Figure 9 depicts the third-order cumulants of the signals in Figure 8.

Figure 8

Figure 9

In another example in which signal discrimination is easier, consider the results using the 1.5wt% transient and its neighbor the 1.6wt% transient.

Figure 10

Figure 11

Figure 12

8. Further work

The next sensible step is of course experimental testing of the methods proposed here, comprising at least the activities listed below. Signal recording equipment and chemical analysis facilities would be required at an operating pre-bake aluminum smelter.

- > verify that cell voltage transients are indeed observable;
- > possible further refinements in sampling and processing of the cell voltage signals to exclude contamination by wave phenomena;
- > deliberate operation of the reduction cell in overfed and underfed modes;
- > capture and analysis of electrolyte samples under test conditions.

Assuming that the proposed procedure, perhaps with refinements, yields acceptable results, the next step is to design and commission a prototype device for alumina estimation. This device would estimate the alumina concentration as described above, compute the relationship between the reduction cell's consumption of alumina and prior feeding periods, and provide the existing reduction cell controller with a signal to initiate an alumina feed cycle. At this stage, process engineering personnel at the host aluminum smelter could experiment with cell operations at different alumina concentrations to establish the optimum operating point for their particular cell design and material and energy cost constraints.

The two activities described above probably comprise a three to five year effort. Success of the prototype activity would clearly motivate commercial application. The results of the present simulation study, in which realistic noise magnitudes were considered, suggest that further testing may be justifiable.

9. References

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