Aiming for Zero Anode Effects

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Abstract

The conventional predictor of an incipient anode effect is a high rate of rise of cell voltage. This is used to trigger a fast feed of alumina. Sometimes, however, fast feeding does not start quickly enough to prevent an anode effect. Other indicators can be combined to more accurately trigger the fast feed. These indicators include hysteresis in cell volts vs. current, a rapid fluctuation in anode current distribution, high frequency electrical noise, acoustical noise and pilot anodes. The authors stress the need for a sound, undamaged cathode lining and accurate feeding of high quality alumina. Preemptive anode effect quenches are suggested for cells that do not have automatic feeders.

Introduction

Although it is practically impossible to achieve zero anode effects, an astounding decrease has been achieved over the last decade. The primary reason aluminum smelters are striving to decrease the number and duration of anode effects is to minimize emission of CF_4 and C_2F_6. For many years these gases were considered benign. They did not harm plant or animal life and had no effect upon the ozone layer. However, in 1990, Ellington and Meo [1] implicated these gases as Greenhouse Gases This was confirmed in 1992 by Isaksen et al.[2]. In fact the effect of one ton of CF_4 is equivalent over a 100 year period to approximately 6500 tons of CO_2 and a ton of C_2F_6 is equivalent to approximately 9200 tons of CO_2 [3]. The major primary aluminum producers in the United States entered into a voluntary agreement with the U.S. Environmental Protection Agency (EPA) to lower perfluorocarbon emissions by an aggregate average of 60% by the end of year 2000 based upon the level in 1990. Most producers have achieved better than their agreed reduction and are striving

for still lower levels. The possibility of a tax on greenhouse gases is a concern to the industry.

There are other good reasons to avoid anode effects. They waste energy, tend to overheat the cell, stress the lining by expansion and contraction, melt side ledge causing the electrolyte composition to change and increase anode consumption. Anode effects do, however, have some beneficial effects that must be foregone. They help remove muck (undissolved alumina) from the cell, clean carbon dust from under the anodes and tend to smooth or polish the anode surface. This latter is more important to Söderberg cells.

The Anode Effect Mechanism

An anode effect is a condition where the electrolyte no longer wets the anode and the voltage rises from its normal value to between 20 and 65 volts or more. The mechanism leading to the anode effect is typical of concentration overvoltage[4],

$$\eta_c = \frac{R\,T}{2\,F}\,\ln\left[\frac{i_c}{i_c - i}\right] \qquad (1)$$

where η_c is concentration overvoltage in volts, R is the gas constant, T is the temperature in Kelvin, F is the Faraday constant, i is the maximum current density at any location on any anode, and i_c is the critical current density producing anode effect. Equation 1 simplifies to:

$$\eta_c = 0.00004308\ T\,\ln\left[\frac{i_c}{i_c - i}\right] \qquad (2)$$

The critical current density is primarily a function of the concentration of dissolved alumina. It is, however, influenced

also by electrolyte flow, electrolyte temperature, anode size and spacing, etc. Critical current density decreases as the alumina concentration decreases, causing η_c to rise exponentially as i_c approaches i.

Moreover, with decreasing alumina concentration the surface tension of the electrolyte increases, producing larger gas bubbles on the anode. Hence, the current density on the active parts of the anode increases causing a further increase in overvoltage to the point where fluoride ions, the next most easily oxidized ions, start to discharge. This forms CF_X surface compounds that have very low surface energy and cause complete non-wetting of the anode. With a continuous gas film between the anode and the electrolyte, current now flows by sparking or arcing across this film. Since the cells operate at constant current, this produces a large increase in voltage. The fluorocarbon surface compounds continually decompose into CF_4 and C_2F_6, which escape with the cell gas, but the surface compounds are continually reformed by the discharge of fluoride ions. The gas produced at the anode changes from essentially all CO_2 before anode effect to 10–20% CF_4 by volume, 1–3% C_2F_6, 2–10% CO_2 and the balance CO. Once a cell is on anode effect, simply restoring the alumina concentration will not terminate the anode effect. However, interrupting the current for as little as 10 ms (as by splashing aluminum) will kill the anode effect.

Anode effect generally occurs at between 1 and 2 wt% alumina concentration, depending upon electrolyte temperature and flow, anode balance and bath additives. However, anode effects can be produced at higher alumina concentrations if the anode current density at any location is sufficiently high. The authors have seen the high-localized anode current densities that accompany a severe electromagnetic disturbance trigger an anode effect at over 4% alumina bulk concentration. Of course diffusion of alumina across the boundary layer at the anode surface makes the alumina concentration much lower at the reacting surface.

In this document when percents are given with no qualification they are weight (mass) percents.

Use of anode effect to control alumina concentration

In the early days cells were batch fed about 4 hours worth of alumina. Then the operators waited for an anode effect at which time they fed another batch of alumina. The heat of the anode effect helped dissolve the alumina. If an anode effect came too quickly, the amount of alumina being fed was increased and vice versa. Anode effects were killed (extinguished) by raking the bottom of the cell with an iron rake without prongs. The raking action stirred the bath helping dissolve the alumina and splashed aluminum against the anode, momentarily short circuiting the cell. The short circuit killed the anode effect. Of course dissolution of the rake increased the iron impurity in the aluminum. Some smelters used green wood poles instead of the iron rake. The boiling action caused by moisture and volatile organic material from the wood accomplished the same result. Killing anode effects was a hot and potentially hazardous job. In the late 20s, the time between anode effects was increased by making one or two feedings between anode effects. This reduced the number of anode effects and saved electric power.

Automatic killing of anode effects

With the introduction of automatic feeders and computer control it became possible to reduce greatly the frequency of anode effects. Also, automatic killing of anode effects was introduced. It is important not only to minimize the number of anode effects but also to kill each anode effect as quickly as possible to minimize the generation of CF_4 and C_2F_6. This will also minimize waste of electrical energy and overheating the cell. Overheating the cell lowers current efficiency, increases fluoride emissions, increases electrolyte penetration into the lining and melts ledge, which in turn alters the electrolyte composition. The fastest anode effect killing technique in practice today for cells with prebake anodes is to simultaneously fast-feed alumina and lower the anodes rapidly until momentary short circuiting occurs as the undulating aluminum pad contacts one or more anodes. This extinguishes the anode effect. The anodes are then raised back to the set point voltage (or pseudo resistance). Some companies prefer to use a slower technique. They feed alumina and lower, then raise the anodes, first a small amount, then progressively greater amounts, in sort of a pumping action, until the anode effect is extinguished. Computer control, point feeders and automatic quenching of anode effects have lowered the anode effect frequency of prebake cells from over one anode effect per day to less than 0.2 per day. The average time for each anode effect has been lowered from over 5 minutes to less than one minute. Söderberg cells have not achieved these low values, but the introduction of computer control and point feeders to these cells is bringing them closer.

It is important not to add an excessive amount of alumina when killing an anode effect because the excess will form muck. It is particularly harmful when the muck recrystallizes into a hard glass-like coating. Muck causes horizontal current flow in the aluminum pad, and this produces electromagnetic disturbances that can trigger anode effects. It is better to use a smaller amount of alumina to kill the anode effect and then let the normal control algorithm adjust the alumina concentration.

Lowering the anodes to kill an anode effect raises the electrolyte level and has a danger of causing electrolyte to overflow, if the initial electrolyte level was too high. Overflowing electrolyte can damage bus bars and collector bar straps or get between the cell walls and shell causing distortion and heat-balance-altering gaps between the shell and the wall, and ultimately wall failure. Some companies avoid this problem by lowering one end of the anode beam (support mechanism) while raising the other. Other smelters have a cell so designed that half the anodes can be lowered while the other half are raised an equal amount. Still other smelters have cells so designed that an anode pair can be lowered rather than all the anodes. In Söderberg cells, anode effects usually are killed by blowing air down a pipe through the anode.

Control by Computer

Since no sensor can survive long in the aggressive environment of the cell, both the control of alumina concentration and the control of anode-to-cathode distance, ACD, is based upon continuous measurement of the cell's voltage and current. As the alumina concentration falls, the polarized cell voltage (equilibrium or reversible potential plus overvoltages plus bubble voltage drop)[4] increases as shown in the upper curve of figure 1. At

the same time, the electrical resistivity of the electrolyte decreases with decreasing alumina concentration. Hence the ohmic voltage, IR, of the electrolyte at a constant ACD decreases as shown in the lower three curves of figure 1. Below approximately 4.5% alumina, the increasing polarization voltage, overrides the decreasing IR and causes cell voltage to rise as alumina is depleted further. The combined effect is shown in figure 2.
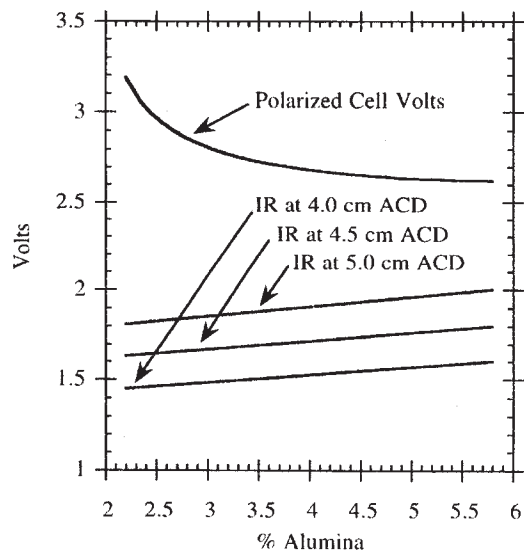

Figure 1. The components of cell voltage for 12% AlF₃, 6.5% CaF₂ and 15°C superheat. [4]
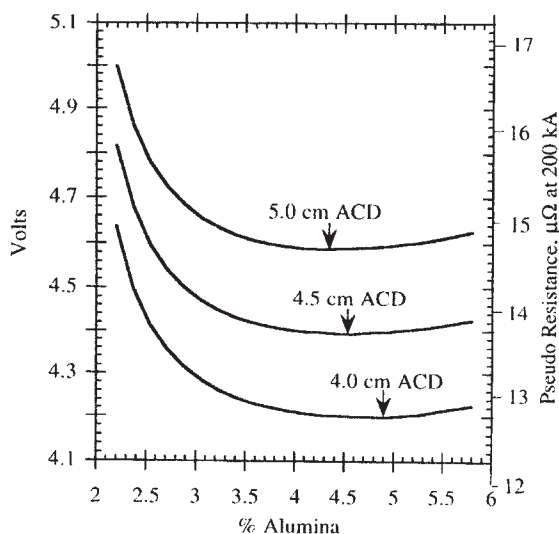

Figure 2. Adding together the polarized cell voltage and the ohmic resistance from figure 1 gives figure 2. These curves are

typical for computer control. The left axis is in volts and right axis is in pseudo resistance calculated for a 200-kA cell using equation 3. Pseudo resistance values will vary with cell size, but the shape of the curves will remain the same.

Early control by computer

An early type of control was a repeating cycle of feeding alumina until the voltage started to rise (on the right hand side of the minimum in figure 2). Then feeding would stop and not start again until the voltage started to rise on the low alumina side of the curve. The minimum in the curve was an indication of the ACD and used for its adjustment. This technique was often referred to as "rocking chair" control. At the high alumina concentrations used in this technique, 4.5 ± 1%, accidental anode effects were rare, but there was danger of forming muck (un-dissolved alumina) under the aluminum causing unstable operation. Therefore, anode effects were scheduled, usually one each day, by discontinuing the feeding of alumina to at least partially clean the cell.

Modern control

Today, most point-fed, computer-controlled cells operate on the low alumina side of the minimum in the curve. Although the details and special features vary, patents [5–11] indicate that the following features are common to all: The computer employs two feed rates, one greater than the normal alumina requirement and the other less. Starting with the low feed rate, the computer follows the rate of change in voltage (pseudo resistance) with time as alumina is consumed. When the rate of voltage rise exceeds a set value, the computer switches to the high feed rate. The high feed rate is continued for a set period, calculated to restore the electrolyte to the desired alumina concentration. Next the computer checks the cell voltage and adjusts the ACD to bring the cell voltage to a set value. Then the process is repeated. This technique can hold the alumina concentration to within about a half a percent of the set point, which can range from about 2.5 to 3%. There are fewer anode effects at higher set points, but Alcoa and Pechiney find that higher alumina concentrations produce lower current efficiencies[12].

Since this procedure maintains a constant average voltage and current is constant, the average power input to the cell is constant. Any drift in temperature is slow and can be corrected by changing the voltage or pseudo resistance set point. Electrolyte temperature is generally measured manually and seldom more often than once a day. Bonnardel and Homsi [13] describe an automatic device for measuring electrolyte temperature and electrolyte height every 8 hours. They claim that its use lowered the standard deviation of temperature by 75%, the standard deviation of aluminum fluoride concentration by 50% and improved current efficiency 0.6%. Although not stated, presumably the more constant conditions would lower the frequency of anode effects.

Heraeus Electro-Nite [14] sells disposable probes to measure both electrolyte temperature and liquidus temperature. This information is very valuable for cell control and for diagnosing problem cells. Unfortunately the present price of these probes limits their use. Presumably, increased use of these probes would lead to mass production and lower prices.

Pseudo resistance

In the previous discussion, "pseudo resistance" can be substituted wherever voltage is mentioned. Pseudo resistance is so called because it is not true ohmic resistance but contains components of overvoltage. Pseudo resistance, R_P, is calculated:

$$R_P = (E_{cell} - Vext) / Current \qquad (3)$$

The term "Vext" (voltage extrapolated) is determined by extrapolating the slope of the volts vs amps curve over the operating range back to zero amps. While cell current is nominally constant, it does fluctuate over a narrow range. Pseudo resistance varies with alumina and ACD in the same manner as cell voltage but the noise caused by short-term fluctuations in cell current is removed.

Alumina quality and feeders

In order to approach zero anode effects a consistent supply of high quality alumina is required. In general the overall alumina quality has improved in recent years. However some Bayer plants add to the product, electrostatic precipitator, ESP, dust from the calciner. This dust contains a high percentage of -20 micron alumina. It produces a cell feed that does not flow well, is slow to dissolve in the bath and causes an increase in anode effects in nearly all cells, especially in side-worked prebake and Söderberg cells[15]. The dust can be recycled to the Bayer plant at some added cost. However, ESP dust can account for 2% of the production and thus has an important impact on the Bayer plant costs/profits. A cost-effective treatment of ESP dust needs to be found.

Present feeders are volumetric and depend upon the bulk density of the alumina remaining constant. Reliable gravimetric feeders have not been demonstrated for industrial aluminum cells, but may be needed to approach zero anode effects.

Operators must routinely inspect the feeders and crust breakers to assure that they are operating properly and that the feed holes in the crust remain open. The computer can aid by observing the small transient in pseudo resistance that follows each alumina addition. If this is not seen, the computer's announcenator can summon the pot operator to check the feeders on this cell.

Obviously, the crust breaker must be electrically isolated, especially if it is to operate during anode effects.

Necessity for anode effects

It was once thought that occasional anode effects were essential for good operation. However, prebaked anode cells have operated for over a month without an anode effect with no loss in performance. Modern cell control does not depend upon anode effects. Today, anode effects are accidental. The control algorithm depends upon sensing the rapid rise in voltage or pseudo resistance that occurs close to anode effect to signal a switch to a rapid feed rate. Sometimes this switchover comes too late and the cell goes on anode effect. Electrical noise is the usual reason for missing the rapid rise of voltage. Noise reduces the accuracy of the slope (rate of rise) determination. An additional signal is needed to help anticipate the approach of an anode effect.

Hysteresis in volt amp curve

One such signal requiring no additional equipment comes from the increased hysteresis in the volt amp curve, figure 3, that occurs approximately 5 minutes before anode effect in the tracking mode (all feeding stopped) or as much as 15 minutes before anode effect in the slow feed mode. To use this signal, the current must periodically be lowered about 5% for 30 seconds to 1 minute every 15 to 20 minutes. The current is then restored to its previous value. If the cell's pseudo resistance comes back to a lower value than that before the current was lowered, the cell is close to anode effect and rapid feeding should be started. When using this technique the nominal current must be increased slightly to avoid loss of production. A 5% reduction in line current for one minute every 15 minutes would require a 0.33% increase in nominal current. Because this indicator measures transients, a rapid scan rate is required.

An indicator that tolerates both a slower scan rate and more electrical noise can be calculated from the same current reduction data. The computer extrapolates back to zero current the voltages at points "a" and "c". Point "a" is the average voltage determined just before the current was reduced. Point "c" is the average after the voltage has stabilized at the lower current. Very noisy cells may require as much as a 10% reduction in current to give an accurate prediction.

$$E_{XT} = (E_c * I_a - E_a * I_c) / (I_a - I_c) \qquad (4)$$

Voltage and current pairs must be measured simultaneously. An extrapolated value, E_{XT}, less than a set value (typically about 1.45 V) indicates that the cell is close to anode effect and the computer should start a fast feed cycle.

Raising the current produces even more sensitive indicators. Unfortunately raising the current can, in itself, trigger an anode effect; hence it is not recommended.
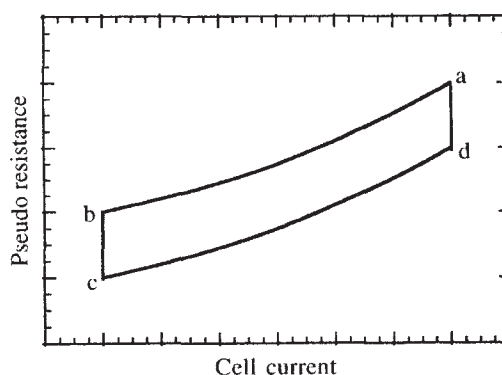

Figure 3. Hysteresis Curve. At point "a" the current is reduced 5%. With the reduction in current, pseudo resistance falls to the value at "b". Over the next 30 seconds pseudo resistance falls to the value at "c". When the current is restored to its original value, pseudo resistance rises to the value at "d". Over the next 30 seconds pseudo resistance rises back to the value at "a". Normally b-c and d-a are very small. When they become large

enough to be detected by the computer (eg. larger than random noise), the cell is close to anode effect.

Other potential anode effect predictors

Tadaaki Toyoshima of Mitsubishi disclosed in 1977 a predictor for cells with prebaked anodes that anticipated anode effects 10 to 30 minutes in advance[16]. It was based upon the increased in the non-uniformity of anode currents that precede an anode effect. Today this could be accomplished by having the computer calculate the standard deviation, S, of anode currents each time it scanned the cell.

$$ S = \sqrt{\frac{1}{n}\left\{\sum_{i=1}^{n}\left(Ii - Ia\right)^2\right\}} \qquad (5) $$

where, Ii is the current in anode i, Ia is the average anode current and n is the number of anodes in the cell.

Three-minute averages of S would be compared. If the average increased more than a fixed amount, say 30%, and this was not associated with an anode bridge movement or other cell operations, it would indicate an anode effect was imminent and would trigger the fast feed routine.

While hysteresis analysis requires only an addition to the control algorithm, this indicator requires also anode current sensors and additional inputs to the computer. Universal Dynamics Limited [17] makes non-contacting sensors that can be permanently mounted behind the position of each anode rod to measure its current without altering the anode change routine. In addition to detecting impending anode effects, monitoring anode currents can detect improperly set anodes, especially those carrying excessive currents that may trigger anode effects.

E. W. Greenfield of Kaiser Aluminum [18] patented in 1960 an anode effect predictor that measured the high frequency noise, "hash" above 20 kHz in the cell's voltage. He claimed that a marked increase in "hash" occurred up to 30 minutes before anode effect. If this claim is valid, its implementation will require special equipment because high frequency noise is filtered out of the computer readings. This and also the use of anode current distribution as an indicator of impending anode effects may depend upon non-uniform anode currents and/or a non-uniform alumina concentration to cause some particular anode to approach anode effect ahead of the others. If we achieve ideal uniform anode currents and a uniform alumina concentration these two indicators may not work.

Jilai Xue and H.A. Øye [19] used acoustic signals from anodes to measure the bubble release rate. Since bubble size increases greatly as anode effect is approached, this type of measurement has the potential of predicting an impending anode effect.

In theory, a small "pilot" anode operating at slightly higher current density than the main anodes should go on anode effect ahead of the regular anodes[20]. The pilot anode could get its current from the adjacent upstream pot and be controlled by a variable resistor. A drop in current to the pilot anode would signal that the cell was close to anode effect. In practice, there are many problems that must be solved to make the pilot anode a reliable predictor. As the pilot anode is consumed, its current must be reduced to maintain constant current density. Consump-

tion of the pilot anode could be minimized by operating at very low current density except for a few seconds every 10 to 15 minutes to test for anode effect. Multiple pilot anodes may be required because alumina concentration often is not uniform throughout the cell.

Careful Relining and Careful Startup Requirement

There has been little reported on the correlation between lining condition and anode effect frequency. Avoiding anode effects requires close, accurate control of alumina, close control of anode current distribution and close control of ACD. This is impossible with a cell having a damaged lining. For a cell to operate well, all collector bars must carry their proper loads. Non uniform collector bar currents can be caused by internal defects, such as cracked cathode blocks or leaking seams or external defects such as loose or dirty electrical contacts (collector bar to strap or strap to bus bar). A poorly conducting collector bar affects the anode above it. The aluminum pad only partly redistributes the current. Moreover, the redistribution of current produces horizontal currents in the aluminum pad. This creates electromagnetic disturbances producing an electrically noisy cell. Excessive electrical noise makes close control impossible. Although the authors have had no experience with cells having deep metal pads, this problem probably is less severe in these cells.

Steps to assure a good cathode lining

Lining design and the preheating and startup procedures vary from company to company. All agree, however, that a good cathode starts with a good design, the best available materials and carefully supervised workmanship[21]. The need for slow, uniform, very well controlled preheating to near operating temperature and a slow, smooth, carefully controlled startup cannot be over emphasized. The benefit to cathode life is well appreciated, but the benefit to cell control is often overlooked. Thermal excursions and bath composition excursions must be avoided during startup. The first 60 days of operation are crucial. In fact the uniformity of collector bar currents at 60 days is a good predictor of how long the cathode will last. Skimping on supervision during startup is poor economics. After 90 days the cell is more tolerant of temperature and aluminum fluoride fluctuations, although these fluctuations still are undesirable. It is a difficult economic decision to shut down a cell with a damaged lining that is not leaking. It is far better to increase supervision and avoid damaging the lining.

Ledge Control

Ideally the ledge should extend out to the projected image of the anode or anodes[22]. Too little or too much ledge causes horizontal currents in the aluminum pad that result in electromagnetic disturbances and poor control. Good ledge control is obtained by carefully controlling bath composition, cell kW, and avoiding extended anode effects. It is a cumulative relationship. While a proper ledge minimizes anode effects, anode effects melt ledge and in doing so change bath composition, increase aluminum pad undulations and therefore lead to more anode effects

Additional Requirements for Point Feed Prebake Cells

Avoiding anode effects requires that the concentration of dissolved alumina throughout the cell be as uniform as possible. Any location with low alumina concentration or high anode current density can trigger a local anode effect. This shifts increased current onto other anodes and forces the entire cell onto anode effect.

Here are some questions to consider. Are we employing enough feeders? Are our feeders so strategically located that the alumina is carried uniformly to all parts of the cell? Should each feeder be controlled individually? Can we feed alumina continuously?

When setting new prebaked anodes, care must be taken to assure that, when they come to temperature and start to carry current, they carry the proper current. It is a common belief that an anode set a bit too low will burn off to the proper ACD. This takes much longer than most people believe and during this time this anode carries a higher current density and can act as a trigger for anode effects.

As anodes age their cross sectional area decreases 20 to 25 percent depending upon anode size. Hence to maintain a uniform current density and not trigger an anode effect, mature anodes should carry proportionally less current. If rebalancing of anode currents is performed, this factor should be kept in mind. Anodes that were set properly initially, will not require rebalancing. Manual rebalancing is difficult and should be rare.

Preemptive Kill of Incipient Anode Effects.

Many Söderberg and side-worked prebake anode cells do not have automatic (point) feeders. Usually they still use the anode effect as part of their control philosophy. Generally they do have a computer tracking cell voltage. The authors propose that the computer should track the rate of rise in voltage following each feeding. When the voltage shows a high rate of rise indicating that the cell soon will have an anode effect, the computer should trigger a preemptive anode effect quench and call for the feeding of this cell. With side-worked prebakes and Söderbergs with movable casings, lowering and raising the anode will cause self-feeding and thereby hold the cell off anode effect for a short time until the cell can be fed. Hopefully the preemptive anode effect quench will work also for Söderberg cells that use compressed air to terminate anode effects.

Summary

Modern computerized control does a good job of minimizing anode effects. However, because modern control operates best at low alumina concentration and therefore close to anode effect, accidental anode effects do occur. Measuring hysteresis in the volt-amp curve in addition to measuring the rate of voltage (or pseudo resistance) rise is recommended to help avoid accidental anode effects. An increase in the variance of anode current distribution, high frequency electrical noise, acoustic noise and pilot anodes provide other potential indicators of an approaching anode effect. Near zero anode effects can accomplish this only if the cell's lining and electrical connections to the collector bars are in good condition. Moreover, it is essential that the alumina feed be of high quality and the feeders properly maintained. Maintaining a uniform anode current density throughout the cell

and a proper ledge also will help avoid anode effects. Preemptive killing of incipient anode effects is suggested as a way of preventing anode effects in cells that do not have automatic feeders.

The mention of company names and products does not constitute an endorsement by the authors or by The Minerals, Metals & Materials Society.

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