STRATEGIES FOR DECREASING THE UNIT ENERGY AND ENVIRONMENTAL IMPACT OF HALL HEROULT CELLS

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Abstract

The electrolytic production of aluminum in a molten cryolite bath depends upon, as major raw materials, alumina, electrical energy, coke, pitch, and aluminum fluoride. From both economic and environmental aspects, conservation of these inputs, decreasing the energy in or operating voltage across cells, raising production, controlling and minimizing emissions from reduction plants are extremely important to every primary aluminum producer. Due to the complex and interactive nature of the parameters, fixed and variable, fundamental to the electrolytic process, there is a hierarchy of choices possible for addressing and improving, for instance, components of cell voltage, heat balance and conservation, variability amongst and stability within pots, consistency of high current efficiency, life of the cells, management of anode effects, etc. The impacts that operational procedures and work practices have on key parameters, their relationship to the inventory of basic knowledge about the Hall Heroult process and the expectations for relative improvements are identified and quantified to the extent possible. Additionally, with recent increased concern for global warming and environmental effects of CO_2 and CF_4 enlarging the industry's continuing concern and responsibility for the immediate surroundings of a plant, aspects for characterizing and decreasing fluorocarbons are discussed.

Introduction

Strategies to reduce the unit energy consumption and the environmental impact of the Hall-Heroult process are particularly relevant at present with oversupply of primary aluminum, economics, and availability of long-term power contracts more stringent, environmental regulations, and rising costs of labor. In light of these factors, it is the purpose of this presentation to point out technical choices to ameliorate these concerns.

Today, few actions or proposals beneficial to our rather mature electrochemical process can be unique or original.

The changes, variations, alternatives and the underlying fundamentals are not original but have evolved over the years, especially since 1962 when this venue began and in which much of the documentation has occurred. The expectation is that revisiting these strategies, prioritizing them and noting means for decreasing releases could prove helpful in responding to future challenges.

Energy Factors

Strategies and Impacts

In focusing on maximizing the current component of power to a potline, normally attention is paid to the minimization of the voltages across each individual cell, V, which can be expressed as,

$$V = E_o + \eta_A + \eta_C + I(R_A + 1/K \cdot \ell/A_B + R_C + R_{ex}) \qquad (1)$$

where E_o is the electrochemical decomposition potential of Al_2O_3 appropriate to the physicochemical state of the cell; η_A and η_C are anodic and cathodic overpotentials; I, the line current; R_A, resistance of the anode stem, stub(s), carbon to the bath level; K, electrical conductivity of the bath; ℓ, interelectrode distance; A_B, effective cross sectional area of the bath; R_C, resistance of the cathode system out to the busbars; and R_{ex}, allocated bus resistance. Minimizing V permits maximization of I which produces metal or lowers the power demand.

The anode overpotential is significant and consists of two important components, activation or reaction overpotential, η_{AC} and concentration overpotential, η_{CO}.

$$\eta_A \quad = \quad \eta_{AC} + \eta_{CO} \qquad (2)$$

$$= \quad a + b \, \ell ni + RT/nF \, \ell n[(i_c - i)/(i)] \quad (3)$$

where a is a constant 0.4 to 0.6V, b is about 0.3, i is the anodic current density and i_c is the limiting current density.

The cathode overvoltage has been confirmed small, viz., about 0.05V.

These equations (1 to 3) form the basis for classifying and prioritizing reductions in cell voltage. Productivity is well understood in terms of faradaic current efficiency (CE).

While a cell is rarely in a 'steady state,' we evaluate and project heat balances through the first law of thermodynamics. Electrical energy is process energy demand and heat losses or,

$$VI = Q_{PE} + Q_L \qquad (4)$$

where Q_{PE} is the energy essential for the electrolytic reduction and heating the components, while Q_L is the total conductive convection and radiation heat losses through the boundaries drawn around the cell. Depending upon the size, era of the design of the cell, and quality of operation, the ratio (Q_{PE}/VI) (sometimes called thermal efficiency) ranges from a poor 0.35 to an excellent 0.46. It is a significant achievement to raise this factor by 0.04 through voltage reduction or energy conservation.

The environmental considerations in the smelting process are mainly air and solid waste because the total process water usage is only 5.2 kg/MT Al; total effluents, 0.009 kg/MT Al. The total process air emissions including CO_2 and CO for smelting and ancillary processes for representative technologies (in North America) is about 1.56 kg/kg Al, of which 90% is CO_2. Fluorine releases are typically 1.64×10^{-3} kgF/kg Al including anode production. For process solid wastes, the corresponding approximation is 0.04 kg/kg Al, of which 62% is spent potliner. Effects of and ways of reducing some air and solid emissions, as relevant, will be mentioned in the following sections.

The Cell Voltage

Highest priority in reducing cell voltage and lower unit energy should be given to lowering the anodic current density. This is and has been done by enlarging the anodes, an essential consideration in conversions and modernizations of side worked prebake cells (SWPB) and center worked prebaked cells (CWPB) or modernizing the latter to point fed prebake (PFPB). The practice is also amenable to both horizontal stud (HSS) and vertical stud (VSS) Soderberg cells where the monolithic anode can be widened.

The gains in voltage, performance and stability in all cases are synergistic because, in widening the anodes, the inner edges of the sidewalls have to be moved out which necessitates enlarging the cathode cavity. Thus, while designing for constancy of heat flow through the upper sidewalls to retain the protective layer of solid bath on those vertical surfaces through use of improved materials

and design (prebake carbon blocks, silicon nitride bonded silicon carbide, Sialon bonded silicon carbide, or composites) the effective cross section of the bath is also increased. Similarly, the area of the active cathode-metal pad is increased so that even without modifications to the external bus, the hydrodynamic force vectors (MHD) per unit volume in the cathode are decreased, resulting in a more stable metal pad within the original potshell because the vectors of current flow can be designed to be more vertical.

In all technologies where the heat balance and depth of cavity permits, MHD forces can also be reduced by increasing the depth of the metal pad. With decreased velocities and improved profile, the interelectrode distance can be reoptimized.

An empirical rule in designing PB cells in the late sixties was that there should be a gap of about 20 cm between the anode and the sidewall. This distance was perceived needed for the turbulence of gas and magneto-hydrodynamic flow to be damped sufficiently to ensure stability of the freeze layer. With advanced materials, more quiescent metal pads and consistent operating conditions, this distance can be decreased to ≤15 cm while still retaining solid bath on sidewalls.

Consider, for example, the order of consequences of increasing the anode area by 10%. These increments have ranged from 8% to 30% across the spectrum of technologies effecting, for instance, a decrease in current densities ranging 1.1 to 0.9 down to 0.85 to 0.68 amp cm^{-2}. Theoretically for a 10% reduction in i, the η_{RE} should decrease by 35 mV and the concentration polarization at 2.5% Al_2O_3 by only 1 mV. But because the coverage of the anode by bubbles, which ranges from 20% to at least 80% approaching i_C (the anode effect), the actual decrease in overvoltage obtained is 0.07 to 0.15V. In most instances, the effective cross section of the electrolyte will be increased similarly and, due to the fanning effect, a little more. Take the conservative case where the new dimensions of the anodes result in an overlap of the fanned projection in the center aisle, 8%. With the same bath composition and interelectrode distance, 8% reduction in V_B is about 0.15 volts.

Thus, the decrease in the ohmic resistance of the anode carbon, increasing anode area by 10%, and absent options for enlarging the cross sections of metal connections, will result in an improvement of at least 0.3 volts.

While this is a well established and proven economical practice, I perceive there are many potlines which would improve technically from this basic change. However, for a combination of reasons such as genuine obsolescence, uncertainties on "technomonics" (joint engineering and economics) such as meeting requirements on clean air

regulations, future power costs, upgrades in cathode materials and manpower commitments, these modifications may be delayed to the extent that a potline could become unsalvageable.

A few operational consequences of anode voltage reduction are, e.g.:

- There is a greater heat flow up through the anodes, so, for PBs, increased alumina cover is required and the bake dome of HSS and VSS has to be managed and monitored.

- Since the metal pad is more stable, the anode immersion might be increased which will further slightly decrease anodic current density and voltage drop through the bath and, therefore, cell voltage.

- If the option to increase the height of the anode block is elected concurrently to decrease the frequency of instabilities from anode change, even better protection from airburning by the use of alumina-crushed bath or sprayed aluminum could be necessary. Increased air burning could reduce the dimensions negating some of the gains.

The extent to which R_A in Eq. (1) can be reduced by increasing the cross section of anode rods and stubs can be modeled. Such modeling and balancing of the gains in voltage, cost of increased conductor, and predictions of the increased thermal conductivity and potential for thermal stresses in the anode are essential.

With such a retrofit of the anode system for a given power demand, I and therefore production could be increased 5-7%. Annual production increments of 2000 to 3500 tons/potline for such projects generally show an advantageous return on investment.

The semi-revolutionary retrofit of cathodes with TiB_2 wetted, stable refractory hard metal composites such as TiB-graphite has been demonstrated beyond the concept, but not yet proven to be both technically and economically feasible. Successful implementation could reduce voltage and unit energy 8-15% depending upon the design of the PB cell.

The Cathode

While only small increments in voltage can be achieved with increased area of the floor of the cathode cavity, significant gains can be made with choice of the material in the prebaked cathode blocks. Currently, these grades of carbonaceous materials are classified: amorphous (A), graphitic (AG) (meaning proportions of graphite added to the former) and semigraphitized SG (meaning either of the former, heated to above 2200°C to convert carbon to

graphite). Fully graphitized blocks (FG), petroleum coke, and graphitized materials which have been finished at 3000°C are becoming more common. Each of these categories has a differing combination of electrical, thermal, and mechanical properties in addition to sufficiently different expansion through absorption and reaction with codeposited sodium and resistance to abrasion, therefore the application to each type of cell or shell has to be thoroughly evaluated.

In principle, because the ratio of electrical conductivities, SG/A, is in the range 2 to 3, the cathode drop without enlarging the collector bar or means of mounting can be reduced by up to 0.15 volts. But that gain does not come "free." The relative thermal conductivities have a similar ratio, so to preserve heat balance and not lose voltage savings, heat must be conserved in the cathode shell. This means redesign of the thermal insulation, particularly that in the lower sidewall and under the blocks. Materials SG and FG have been shown to have alkali metal expansions only 20 to 40% of A and AG, an asset which can be offset by the anisotropy of the thermal expansion coefficients of the former two.

For cells with an active metal pad induced from older bus designs, when metal pad velocities range 10-25 cm/s compared with 2-18 cm/s in modern cells with compensating bus bars, the reduced resistance to abrasion of the advanced materials may preclude adoption of advanced cathode materials.

Voltage savings of the order of 40 to 80 mV can be obtained through increasing the cross section of the collector bar, e.g., 50%. Gluing the bars with special carbonaceous resins has been proven equivalent to the best casting or ramming practices. Caution is again required because the amount of heat conduction along a bar can typically increase from 3% to 5% of the total heat losses. While gluing the bar and block components imposes no pre-installation thermal stresses on the blocks, the perception is that it requires more rigorous practices than the typical procedures for casting in collector bars. The optimized curing or baking procedure must be well understood.

There are economic and environmental consequences (besides possible redesigns) for the selection of cathode blocks. These stem from a realistic analysis of the cumulative energy saved by the projected over the past lifetimes of the prior and newly configured cathode hearth to which has to be added differences in the costs of disposal of the spent potliner (SPL).

For example, if we consider a 100 kA cell having an average pot life of 1500 days with type A cathode blocks, at 90% CE, 7.2 kwh/lb Al, there is no change in CE, heat loss, but a decrease of 0.15 in pot volts, and the SGs

providing this cost $500 more per ton, then if power costs 2.5¢/kwh, how much additional cathode life must be obtained before economic gains (not counting interest) are realized? Taking the charge for disposal of SPL at $200/ton for the 40 tons from the pot, the cathode life would have to become 1910 days. Extrapolation of the performance of a reconfigured cell, taking into account modeled stresses, heat and voltage distributions, has matured to the point of being quite reliable. This is particularly so if cathodes utilizing initially high quality materials are assembled with equally high quality care and precision.

A couple of additional points: we know that substitution of cold ram paste for seams (if not glued) has far less volatile organic emissions than hot ram paste and my sense is that experience has shown that it performs just as well. Secondly, when anodes are lengthened and sidewalls pulled back towards the potshell, longer blocks are needed. Blocks up to 330 cm can be obtained so that the length of flat, rammed material over electrical insulation around the collector bars can be decreased. The quality of seams has matured to the point that if mounting a single 330 cm long block on a bar presents a problem of either physical or thermal expansion nature, two or more shorter segments of the same high quality cathode material can yield cathode lives of >3000 days. Additionally, gluing blocks together is being evaluated at several plants. Success in these trials would allow elimination of the rammed seam. While not universally adaptable, there are indications that use of LiF-modified bath, particularly during start up, can promote longer cathode life.

With respect to power then, implementation of an improved cathode assembly could be converted to a negotiated decrease in demand on the order of 4% or a comparable increase in aluminum production depending upon anticipated economics.

The Heat Balance

From Equation 4, it is apparent that in considering a heat balance - a source of considerable economies - heat flows need to be reviewed and optimized. The key word in designing for and modifying a heat balance, which is actually a constantly changing condition buffered by the thermal inertia of the lining and the heats of fusion / solidification of cryolite, is "optimize," because the objective is to maintain the temperature of the bath with the appropriate superheat, deliberately lose heat through specific regions of the sidewalls to maintain the frozen ledge and keep the cathode blocks above 880°C isotherm.

Although process energy is largely set by the enthalpy of the reduction, it can be affected by raising the CE, by decreasing carbon consumption and lowering the current density. It is advantageous to increase the process energy while maintaining or decreasing the power input.

All components of the heat balance are synergistic. Improvements are readily modeled, compared, and obtained by modifying the thermal insulation. With a retrofit of bath anode area, size of cavity, cathode blocks and thermal insulation, heat losses can be reduced by 15%, thermal efficiency raised by 4%, and unit energy lowered by 0.5 to 1 kwh/lb Al through decreases in equivalent voltage. These changes may require no or minor changes only to the cathode shell.

Implementation is through allocation of materials in a sandwich configuration over the same depth under the cathode blocks as was previously used. Practitioners have selected low thermal conductivity, low density Moler bricks, slabs of Vermiculite or calcium silicate against the bottom of carefully refurbished shells to thicknesses of 7-10 cm as the ultimate insulation. The top of this layer should never exceed 700°C since that is the limit of practical service of these materials in this environment.

Prolonging these superior insulation characteristics can be achieved through installation of barriers which inhibit the rate at which molten and vapor fluoride compounds impregnate (and slowly degrade) the bottom insulation. Various barrier materials have been proposed and tested. For instance, steel plates, ceramic tiles, low water monolithic castables, and anorthite ($CaAl_2Si_2O_8$) all have been found to have adequate properties from laboratory tests and field trials. Both steel plates and low water castables remained effective for greater than 1500 days, although the latter are preferred. As an example of the effectiveness of a barrier, the heat loss was reduced by 14 kw (50%) in a 95 kA HSS cell using alumina only as cathode insulation.

When lower sidewall insulation must be increased to conserve the increased heat flow associated with prebake blocks of lower electrical resistivity, the thermal resistance of the upper sidewalls needs to be decreased. Some heat has to be dissipated so there are practical constraints. One cannot overconserve heat flow through the bottom and lower sidewalls expecting to achieve both very low cell voltages and stability. Paraphrased, this implies that, given the practice of conserving upward heat flow through anodes and crust with increased and monitored alumina cover reducing the proportion of heat flux through one area of the cell may have to be offset by reduction in energy input or increases through another zone. This is exemplified in Table I for four technologies. The data shows that when the proportion of heat flow through the bottom is decreased by design, it increases through the sidewalls. This redistribution of heat flow is relevant for reductions in cell voltage in the range 5-8%. This is not to

imply that reconfiguration of sidewall or lower sidewall thermal insulation leads to an increase in the actual energy losses - these can be comparable to or less than a previous design - but it does mean a redistribution of the heat losses should be expected. It is also apparent that much more heat flows into the monolithic Soderberg anode where it affects baking, and an insulation might be evaluated for the permanent casing. This contrasts to the prebake cells where, even in the most modern cells, there seems opportunity to redirect or reduce heat flux through the bottom of the cell.

Table I. Distribution of Heat Loss (%) from
A Selection of Cell Types

Type of Cell	Top of Cell	Shell Sides, Ends, Collector Bars	Shell Bottom
		Heat Loss From	
HSS	62±2.8	23±3	15±3.5
Modified HSS	63.5±9	29±6	7.5±3
VSS	69±2	20	10.8
Modified VSS	66	28.4	5.6
CWPB	47.3±10	40.4±8	11.6±5
Modernized PFPB	47±7	41±6	12±1

Along with redistribution, considerable conservation of energy can be achieved from modifying the heat balance and running at lower cell voltages in all types of cells. There are still many potlines that either have not evaluated the returns or become convinced that economics warrant use of advanced carbonaceous blocks, thermal refractories, silicon carbides or composites for modifications. In face of increasing costs and availability of energy, more retrofits of cathodes should be expected.

The strategy for decreasing unit energy through improved design and materials in the cathode shell has another perspective -- positive environmental impact. Now that SPL is classified as a hazardous waste because of its trace cyanide and leachable fluoride content, its minimization becomes a priority.

Hence, all basic information and good practices need to be utilized in extending pot life. A degree of success has already been achieved in this through the principles outlined above, viz., inhibit the ingress of air into the

cathode lining and reduce the quantities of carbon, especially rammed carbon, through use of prebaked and SiC sidewalls, glued blocks, and longer prebaked cathode blocks.

Because the ingress of air into the cathode lining contributes significantly to the formation of the many compounds that fill the initial voids and porosity of the components, e.g., $NaAlO_2$, $NaCN$, AlN, means for inhibiting it should be addressed. Stuffing boxes at the entries for the collector bars, a cement seal or compressible ceramics between the deckplate and the top of the sidewall, are useful options. In this manner, the rate of increase of volume in and stresses on the potshell can be diminished. The amount of cyanide formed, particularly in the upper and lower sidewalls will be decreased. Consequently, all steps should be taken to improve the quality and longevity of the seals around collector bars and between deckplates and the top of sidewalls. These include, e.g., use of plates, mortars, stuffing boxes around collector bars and cryolite-resistant, compressible materials or refractories under the deckplate.

An idea of the consequence of modified cell linings, sidewall construction, and more attention to sealing and pot building is demonstrated by the fact that for one company the rate of SPL generation decreased by 44% from 1980 to 1992.

Power Efficiency

There are some paradoxes to the paradigms for reducing voltage and conserving energy. These derive from the structure of power contracts, the aluminum supply situation, and the extent to which value can be added to the aluminum in downstream processing by the initial producer.

Consider, for example, two contrasting cases. Through more consistent control of bath chemistry and anode cover, improved stabilities allow a thermally efficient PFPB potline a decrease of 12 volts across the 240 cell potline. With a fixed contract for, say, 185 megawatts of hydro power, this could be converted to a 0.6% increase in line current. This could easily be manifested in a comparable 0.6% increase in production and decrease in unit energy. But only if there is provision for credit for reduced power demand in the power contract is there a choice between maintaining production with the same line current at reduced unit energy costs or increasing production.

By contrast, for a less thermally efficient older potline, with power contracts comprising a mixture of firm hydro and interruptible hydro/nuclear, reductions in voltage achieved through any of the above means -- in addition to the very practical means of removing sludge

accumulations from under anodes -- are more often converted into higher line current and production rather than as a reduced power demand. When there are constraints on how credits can be obtained for incremental reductions in power, for these technological or market-based reasons, cursory analysis reveals that it is often advantageous to produce more metal because for such incremental changes, labor and operational costs generally can not be decreased.

When retrofits lead to significant decreases in power demand and manning, then the situation is different.

Bath Chemistry

Selection or optimization of electrolyte is constrained by some parameters that are fixed properties of the particular cell. For a given cell, there can be multiple compositions of bath that, based on both modeled prediction and industrial trials, give equivalent technical but different economic results.

In assessing whether changing bath chemistry will benefit an operation energetically, economically, or environmentally, one has first to measure and quantify all the cell parameters with the bath used currently. Haupin's (1) recent summary on bath properties is an excellent resource.

The objectives in changing the bath composition are to lower the temperature, raise the CE, lower the voltage, maintain operating stability and decrease emissions while maintaining proper ledge and not generating alumina sludge under the metal pad.

For all cells, the prime question is, will the modified bath under evaluation be an adequate reservoir for alumina (dissolve it at a sufficient rate) for a mass and energy balance at the line current? For instance, an HSS 95kA cell at 92% CE with 3650 kg bath must dissolve 55 kg Al_2O_3/hour (1.5 wt.%/hr); a 180 kA PFPB at 95% with 3650 kg bath must dissolve 109 kg Al_2O_3/hour (3 wt.%/hr). This calls for either widely differing baths or management of alumina. Additives reduce the saturation solubility of Al_2O_3 in all baths and greater proportions of excess AlF_3 depress the rate of solubility of Al_2O_3.

Next, the electrical conductivities and equivalent alumina metal solubilities need to be compared in the likely range of operating temperatures, 10°-15°C above freeezing point for cells over 120 kA and 15°-25°C for smaller cells. The conductivity inserted into Eq. (1) allows assessment of either the interelectrode distance at constant voltage or vice versa. If the cell had been operating at the 'critical ACD' for the hydrodynamic forces in the cathode and bath, indicated by a variably acceptable level of noise or standard deviation in cell voltage, then empirically a

shorter interelectrode distance could result in a decrease of CE at the rate of 4%/cm. Widening the A-C distance would increase the CE, not at the same rate, but risks raising the temperature of the bath.

The level of the calculated total equivalent dissolved Al_s (Al + Na + Li) will be indicative of the trend in CE. Using Wang, et al., (2) Eq. (2), Al_s increases 3 ±.5%/°C for all of low (1.1), medium (1.25) and high (1.4) ratio baths with 2.5%Al_2O_3. The temperature coefficient for CE over a 20-30° range of temperature in each of these families of baths is 0.2%/°C based on mass transfer mechanisms. This could indicate that the rate determining step(s) governing the CO_2 reoxidation of Al_s allows extraction with only 7% of the available dissolved aluminum.

This approximation can be extrapolated for testing the trends in CE with increasing proportions of AlF_3, which is highly effective in lowering Al_s, because while Al solubility goes up slightly, Na solubility is strongly suppressed with decreasing ratio. For example, at 965°, Al_s decreases -6% per 0.1 ratio or -2.1% per wt.% AlF_3 suggesting an increase of CE, 0.15% per wt.% AlF_3. At 940°C, this correlation would project CE increasing by 0.24% per wt.% AlF_3. Analyses of some industrial experience has indicated +0.6% per wt.% AlF_3. With a -1.3%/wt.% AlF_3 coefficient for conductivity, maintaining constant voltage drop across the bath would result in a -0.05 cm decrease in interelectrode distance, or potentially -0.2% CE. However, with increasing AlF_3, the average concentration of Al_2O_3 would likely decrease, resulting in a net gain in CE.

There is little variation in Al_s with addition of LiF. Therefore, enhancements in CE obtained with LiF modified bath are attributable to the lower operating temperature, -8.6°C per wt.% LiF, that can be achieved. The advantageous properties of this additive through increased conductivity give the options of a wider interelectrode distance, or lower cell voltage. The lowering of saturation solubility of Al_2O_3 has never seemed to impede the rate of solubility of Al_2O_3 in such baths, but distinct disadvantages derive from partitioning Li to the aluminum (LiF%/1250), its subsequent removal, and the cost of Li_2CO_3.

To achieve the significant and less costly gains in CE with baths containing 10-14 wt.% AlF_3, the cell must operate with a virtually flat, quiet, metal pad because the interelectrode distance must be short to 3.5 ±.2 cm for the correct bath voltage. To minimize fluoride emissions, excellent hooding, and an efficient dry scrubber are required since the vapor pressures of such melts are 37 and 100% higher than those with 7% and 2.8% excess AlF_3, respectively. Cells exploiting high AlF_3 baths require point feeders which have the capability and advantage of

maintaining almost constant bath composition; an important factor for stable and consistent operation.

There are practical means for improved utilization of AlF_3 and conservation of fluoride in existing sideworked or centerworked cells. When the metered or specified quantity of AlF_3 is added to the frozen crust just after a break as a windrow, then Al_2O_3 can be added to cover it. Sintering reactions between Al_2O_3, AlF_3, $NaAlF_4$ and percolating bath will occur. Losses of F by hydrolysis which can amount to 10% of the available fluoride may be reduced. The gain can amount to 0.015 kg F/MT Al.

More focus is needed on maintaining alumina concentration. The driving forces are combinations of lowering total anode overvoltage, lowering the vapor pressure, impacting Al solubility and decreasing the variations in the resistivity of the bath which, when coupled with a more constant liquidus temperature, results in less temperature fluctuations and more stable electrolysis. Whatever means of adding Al_2O_3 may be in use in a potline, periodic, continual, breaking by machine or bar on PF, all can be modified slightly against a data base to realize more consistent levels of dissolved Al_2O_3.

Within a given technology, the most important point is to strive for consistency, uniform bath depths, narrow distribution of bath temperatures, continual awareness of the Na_2O and CaO in the alumina so that the AlF_3 compensation is continually adjusted for these variations and the specific near-term history of temperature and ledges for each cell. Some retrofits will permit better magnetic compensation; others only anode, cathode and superstructures which are generally coupled with improved hoods. Hence, in the next decade, two categories of baths will be viable: low ratio baths (1-1.20) for all greenfield and fully modernized capacity; higher ratio electrolytes (1.25-1.4) for technologically enhanced PB, HSS, VSS cells and those potlines committed to wet scrubbers.

Environmental Factors

Anode Effects

During an anode effect (AE), some CF_4 and C_2F_6 are formed. Both gases absorb in the ultraviolet and therefore contribute to the global warming potential (GWP) of the earth from atmospheric effects. Carbon dioxide is the GWP gas at greatest concentration in the atmosphere. While the debate continues about the impact of upward trends in concentrations and destinies of accumulating GWP gases (3) the aluminum industry has undertaken a comprehensive assessment of the amounts of CF_4 and C_2F_6 produced and evaluations of options for decreasing these emissions. Further, the industry is supporting studies offering a better understanding of the radiative

characteristics, lifetime and distribution gradients of these gases in the atmosphere and exchange with the stratosphere.

While the quantities of CF_4 and C_2F_6 worldwide are small, .070 ppb in the atmosphere (cf, 3.5×10^5 ppb CO_2) the problem is that whereas the lifetime of CO_2 is listed as 2 years, the lifetimes for CF_4 and C_2F_6 are, by current estimates, greater than 100 years (4). Considering using fossil fuel for power at the IAPI mix of hydroelectric, nuclear, etc., and the combustion of carbon anodes, the aluminum industry could be contributing up to 1.5% of the total CO_2 sourced from fossil fuels used in the world. Given a GWP factor of 5100 (4) for world emissions of 10^4 tons $CF_4 \times 5100$, this would add an equivalent 5×10^7 tons CO_2 making the industry's possible contribution to the total GWP gases larger.

Until analyses are completed on the gases in ice cores from Greenland and Antartica, there is no data on atmospheric CF_4 before the industrial revolution. However, the simplistic estimates in Table II suggest that the aluminum industry has been a major contributor to atmospheric CF_4.

Table II. Probable Emissions of CF_4 from Anode Effects, World Aluminum Capacity Since 1900

Period	Tons Al made x 106	CF_4lb/ Ton Al	Total lb CF_4x10^6	Contribution to Atm ppt
1900-1950	23.2	10	231	20
1951-1960	34.5	3	103.5	9
1961-1992	420	1	420	37
Total CF_4 Estimated				66

There are strategies for decreasing CF_4 emissions. Again, these differ depending upon the extent of mechanization of a potline but all have the objective of raising the average concentration of alumina and decreasing the incidence and duration of anode effects. For example, the insertion of tubes as ducts for compressed air in VSS anodes has been very successful in decreasing the duration of an anode effect. These air lances are effective in terminating about 95% of all anode effects within 2-3 minutes compared with the 4-6 minutes when attended to manually.

The correlation of the rate of change in cell resistance with alumina to the automated incremental kilogram additions of Al_2O_3 every minute or so is the key to the consistent

quality of operations in these technologies. The automated anode effect suppression routines, whereby the anodes are driven into the bath in two or three steps each lasting 10 seconds or so, are very effective in quenching and abbreviating an anode effect. With these procedures, the virtually unpolarized sidewall area of the anodes is increased. The momentary and necessary shorting to aluminum occurs and the alumina needed is supplied from both the crust and the point feeders. This normal electrolysis can be restored in 40-80 seconds with such systems. At 0.1 AE/day on a 180 kA cell lasting 1 minute, the CF_4 generation would be 0.025 kg/T Al.

The average increment in Al_2O_3 concentration needed to effect a significant reduction in AE would need to be about 0.5% Al_2O_3 only. Achieving such an increase, given that it is reasonable to attain dissolved Al_2O_3 70% of saturation with minor risk of sludging, seems a reasonable goal. There is a body of evidence that suggests that there could be an attendant small increase in CE (and decrease in η_A). Those cells needing very clean hearths for high stability may require more monitoring.

In all cases, benefits can be realized from enhancing pot operators' knowledge about the process, origin and suppression of anode effects and the fact that there should be a shared responsibility to reduce anode effects. Solutions belong in the "age of information." The tradition of using AE as a check point on dissolved alumina has to be abandoned. Using consecutive AE's to deplete accumulation of sludge under metal pads must be reconsidered.

For potlines that are manually broken, equipped with computer control, and to which alumina is added by way of a mobile ore dolly or hoppers, means must be added for knowing or calibrating the weights of alumina to the productivity of the cells. This, in combination with the data available on voltage/resistance tracking in a straightforward anode position control system, should result in more consistent and quantitative control of alumina and sludge and the heat balance. Old, but highly reliable practices that are inclined to be neglected, like using rods to keep track of ledge configuration, the extent and location of sludge encroaching under Soderberg anodes and in center aisles, should be done on each cell at least twice a week. Decreasing frequency of AEs on older potlines will require more focus and attention than has been customary. There will have to be an enhanced level of integration of real-time numerical and physical knowledge about each cell, and astute communication of the observations by dedicated people on the status of cells.

Some plants, HSS, VSS, and SWPB, have mechanized bar breakers and aluminum hoppers within hoods which have resulted in more efficient fume capture. Revision of the break protocol or interval in perspective with the onset of

sludge production, cell stability and adding supplementary Al_2O_3 within the period of regular breaks is recommended. Breakers operated by computers can be used with one end only activated. Forcing part of the crust down promotes more self-feeding over the interval between normal breaks with negligible disturbance on the cell.

Another practical modification to a mechanized bar breaker is to add teeth or spikes to its lower edge so that it can, for instance at half-stroke, simulate a point feeder. This action of adding or forcing a fraction of the alumina crust towards the bath promotes more uniform concentration of Al_2O_3 thus lowering AE frequencies. HSS cells have the advantage of a reservoir of alumina in a beneficial windrow of sludge along the sidewall outside the anode, so have AE frequencies 0.25 to 0.5/day. Better quantification of Al_2O_3 additions and improved control over metal pad and base depths can lead to reductions in AEs. Consistent side ledges and anode immersion are paramount in achieving stable operations and high productivity in Soderberg cells. Yet with break/feed operations at 2 to 4 hour intervals, the cyclical Al_2O_3 concentrations <u>cause</u> cycles in temperature, voltage, and CE that, in turn, affect the stability of the ledges. Absent greater sophistication in automated break/feed systems, the uniformity in Soderberg operations could be improved using a labor-efficient device such as a wheel breaker to promote more self-feeding and uniform Al_2O_3 concentration without major disruption of the sealing/insulation characteristics of the alumina crust.

For fully mechanized, automated, well-hooded CWPB and PFPB cells where the anode effect may range 0.2 to 0.5, 0.1 to 0.2/day, respectively, the criterion of keeping the cathode hearth clear of sludge remains paramount to good operation. Partial breaks can be evaluated for CWPB. Slight changes in the protocols for diagnosing the Al_2O_3 concentration and hence refinements in feeding could also be tested.

Irrespective of the cause of an anode effect, e.g., genuine shortage of dissolved Al_2O_3, temperature too low to dissolve Al_2O_3, metal pad unstable due to cathode deposits or poor anode current distribution, the amplitude of modulations in the cell voltage normally increases with these events. This sinusoidal pattern, variously called noise, standard deviation, or stability indices, has become an important tool in detecting and diagnosing abnormalities in cells. There are opportunities to use these signals in combination with trend analyses to improve the early detection of such events, allowing more opportunity for man/machine interactive decisions and choice of remedial actions. Successes would yield more consistent operations and reduced AEs.

Fluorine Emissions

Each AE also represents an unrecoverable loss of fluoride irrespective of the type of scrubber. For example, using the correlation presented elsewhere in these proceedings, an AE lasting 2 minutes for a 150 kA cell will result in the loss of 0.35 kg F. At one such AE/day/cell, this extrapolates to 116 kg AlF_3 for a 200 cell potline. Thus, all means for minimizing fluoride losses should be exercised -- keeping hoods and seals in good condition, maintaining complete alumina or alumina/crushed bath coverage of the space between the anodes and deckplates, keeping the ratios in a narrow range (a tight Gaussian distribution) and the superheat to a workable minimum. The latter two points of control are particularly important for cells using low ratio bath because the rate of increase of vapor pressure with AlF_3 increases from +6%/wt.% AlF_3 at 1.4 to +10%/wt.% AlF_3 at 1.1. One could argue that this is of no consequence with an efficient dry scrubber but there are always leaks and anomalies in operations. Despite the economics of controlling ratios that may result from correlations of pot temperature with excess AlF_3, better management and conservation of fluoride is likely to result from fairly frequent direct chemical analysis of the bath, e.g., once per week. The temperature coefficient of vapor pressure ranges 1 to 2%/°C depending upon the ratio in the range 1.4 towards 1.1.

A high proportion of fluoride losses can occur during anode changing because of the combination of time, area of exposed bath, and absence of hoods. The replacement of an anode must be a high quality job -- all of production, stability, and smooth progression to a new pseudo-steady state, depend on this so it cannot be rushed. Upon removal, the hot crust adhering to the butts emits fluoride vapor which escapes to the monovents. These butts could be encapsulated in airtight metal bins while cooling, thus decreasing total fluoride emissions.

Fluoride emissions as indicated above can also be reduced by modified bath. For instance, it is possible that a target for fluoride emissions could be met without the capital expense of an upgraded fume capture system, but with a bath of decreased vapor pressure. There is ample evidence and experience demonstrating that LiF at levels of 2-3 wt.% can reduce fluoride emissions by 30-40% in comparison with Na_3AlF_6-CaF_2 baths, weight ratio 1.3 to 1.4. Choice of the solution to the problem depends upon the economics.

When reviewing alumina addition strategies and deciding what the optimum average concentration of Al_2O_3 is for a potline, it is constructive to recall that Al_2O_3 also affects vapor pressure and hence fluoride losses. The coefficient for decreasing vapor pressure ranges 3 to 6%/wt.% Al_2O_3

-- with the rate of change becoming greater approaching AC -- another reason for trying to minimize the time a cell is depleted of Al_2O_3.

The total CO_2 releases from unit processes, bauxite mining to molten Al in a crucible representing a blend of technologies in North America, are 11.7 kg CO_2/kg Al. Only 1.4 kg CO_2 of this is associated with the actual smelting process. Inclusive of CO_2 from fuel and transportation, bauxite mining, alumina production and smelting account for 3.2%, 16.1% and 81.6%, respectively. Power for smelting at the mix of the North American grid accounts for 69% of the total CO_2. Thus, if reducing CO_2 becomes an issue, the aluminum industry is predominantly impacted by sourcing of power. Decreasing unit carbon consumption 0.03 kg/kg Al will reduce the total CO_2 by 0.08% only.

Conversion to non-consumable anodes (NCAs) would decrease CO_2 by 1.4 kg due to carbon anodes -- less the CO_2 evolved in processing the revolutionary anodes. This substitution would also reduce fluorine releases from better hooding and elimination of anode baking, and drastically reduce organic emissions (currently about 6.7×10^{-4} kg/kg Al). However, considerably more basic material science, pilot testing and transitioning remains to be completed before NCAs become commercial.

Cell Control

Given the increased capacity, speed, and application of powerful microprocessors in the interpretation and control of pot voltage, there will be both wider application and refinements in the sensitivity and structure of the algorithms used. There should be expanded utilization of the range of the amplitude of a statistically treated noise signal in pot voltage (e.g., ±15 mV, ±30 mV, ±60 mV) because with correlative information and diagnostics this can be used to automatically re-select an optimized set point or widen the deadband within which anode moves are ordered. We can also expect refinements in voltage/resistance trend analysis for determining the rate at which point or bar breaker feeders are activated. These enhancements will be mandated, not only by economic pressures but also ecological pressures.

Most automatic anode position control systems, although closed loop, are neither predictive nor self optimizing. In some systems a running average of "noise," or a stability factor is used advantageously. When above a prescribed threshold, these factors can be used to change the logic. For instance, controls can be made to proportionately raise or lower set points, open or close control bands for cell voltage, modify or delay alumina additions. Generally these algorithms restore control parameters to the norms as stability indices decrease to and below the threshold value.

Measurement and assessment of the characteristics of "noise" in pot voltage is an area for discovery. With further studies, analysis and correlations of the periodicity of fluctuations in pot voltage, it can be anticipated that frequencies in the range 0.01 to 0.04 hertz will be correlatable with the most likely cause of undesirable conditions in the cell.

There is a rich database on the physicochemical properties of bath, the mechanisms and interactions of electrode processes, the dynamics of dissolution of alumina, and interchange between solid and liquid states for the Hall Heroult process. The algorithms to utilize all this knowledge to characterize, develop into a means of predictive control, and optimization of the state of the reduction cell in real time need to be developed.

Summary

For the Hall Heroult process, immediate options for effecting unit energy reduction include,

- Voltage and unit energy reduction:

  By decreasing anodic current density,
  Simultaneously increasing bath area,
  Decreasing the resistivity of the carbon hearth, and concurrently reducing overall heat losses with improved thermal insulation.
  Decreasing the ohmic resistance of electrical connections,
  Enhanced algorithms in computer control systems.
  Increasing the CE by modifying the bath chemistry, pursuing lower operating temperatures, reoptimizing interelectrode distance as a consequence of more stable metal pads and enhanced consistency in operations.

- Improvements in ecological factors can be obtained through:

  Decreasing the frequency and duration of anode effects to reduce CF_4.
  Reviewing and revising the extent to which cells are open and components with hot bath are in an unprotected environment.
  The electrolyte of choice, for a given gas scrubbing system ensuring that it is monitored and maintained to a consistent composition to reduce fluorine.
  F emissions can also be decreased through electrolytes of lower vapor pressure, temperature and higher Al_2O_3 concentration.
  Organic releases can be decreased through use of cold ram pastes, dry anode pastes, better hooding and automated proportioning of air flow to HSS cells on flex raise.

Apart from substitution of hydro for fossil fuel power, units of CO_2 can be decreased slightly by decreasing consumption of anode carbon.
Unit spent potliner can be decreased by designing and building energy conserving cathodes assured to obtain longer lives, operating these within narrow preferred limits and implementing sealing of the cathode shell to inhibit ingress of air.

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