# Next Generation Vertical Electrode Cells

**Craig Brown**

*The concept of the vertical electrode cell (VEC) for aluminum electrowinning is presented with reference to current research. Low-temperature electrolysis allows non-consumable metal-alloy anodes to show ongoing promise in laboratory tests. The economic and environmental advantages of the VEC are surveyed. The unique challenges of bringing VEC technology into practice are discussed. The current status of laboratory research is summarized. New results presented show that commercial purity aluminum can be produced with promisingly high current efficiency.*

## INTRODUCTION

In recent years, the emphasis in aluminum smelting research has moved away from the view that retrofit non-consumable, or so-called inert anodes, alone represent the next milestone in emerging cell technology.[1] This change in focus comes in part from the realization that non-consumable oxygen-generating anodes require additional free energy for electrolysis compared to conventional technology.[2] In order to derive the benefits promised by inert anodes, system designs must overcome this additional energy requirement. Thus, the realistic approaches to next generation smelters must be systems approaches.

One approach currently being researched is the vertical electrode cell (VEC).[3] Such a cell employs both inert anodes and wetted cathodes in a vertical arrangement. The wetted cathodes allow the anode-cathode distance (ACD) to be kept small and fixed. The oxygen bubbles generated on the anodes are quite small compared to the ACD. The resulting voltage drop in the electrolyte across the ACD can be kept small enough that these cells show promise of reducing the energy intensity of aluminum smelting despite the free energy penalty. In principle, the VEC approach could be implemented with any inert-anode material, thus with conventional electrolytes at conventional temperatures. However, demonstrably suitable anode materials for this type of system remain elusive. For this reason, low-temperature electrolysis (LTE) is being researched as a basis for the next generation cell.[4] LTE is based on changing the electrolyte composition to one that is much more acidic than what is used in conventional smelting, and that exhibits a much reduced liquidus temperature. The lower temperature increases the number of materials that might succeed as inert anodes.

The conditions for successful LTE differ significantly from the conditions for conventional electrolysis. Establishing the limits on these conditions is a challenge. Maintaining these conditions in practice will be a challenge for successful commercialization of the technology. The traditional cell geometry cannot sustain LTE. The concept of the VEC emerges as the alternative.

## CELL CONCEPT

The LTE approach opens the possibility that metal alloys will succeed as inert anodes.[5] Charles Martin Hall himself had attempted to use copper as the anode material.[6] However, at the traditional temperatures of over 950°C, the corrosion rate is too high for copper to be suitable as an anode. Alloying copper with other metals can improve the stability of metal anodes, but not enough to allow their use in conventional systems. With LTE conditions, however, commercial purity aluminum has been produced in laboratory experiments with metal alloy anodes, as is reported below. Since the product purity is related to the corrosion rate of the metal anode,[7] metal anodes show true promise if used in an overall LTE systems approach.

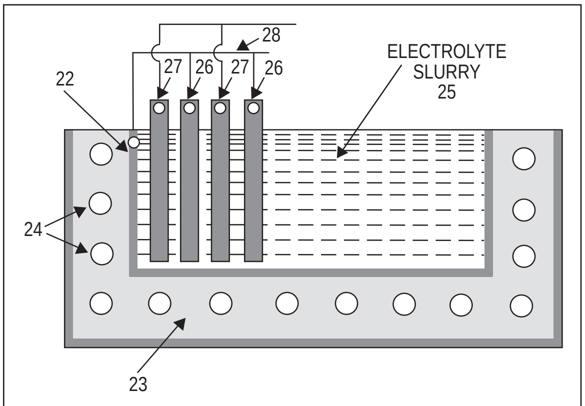

Figure 1. A depiction of a vertical electrode cell with an inert anode lining; adapted from Beck.[4]

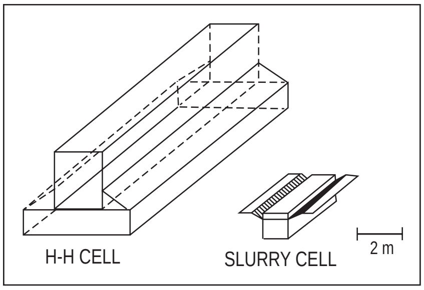

Figure 2. An isometric comparison of a large Hall cell and a small vertical electrode cell of equal capacity; adapted from Beck.[4]

One of the most significant aspects of the LTE system is that the electrolyte exhibits relatively low solubility of alumina. Even if the electrolyte is kept saturated with dissolved alumina, the low solubility prohibits operation at a reasonably high current density. This limitation is overcome by maintaining an excess of undissolved alumina in the electrolyte.[4] It is essential that the excess not settle in the cell, however. Rather, a slurry-electrolyte should be maintained. In a slurry, the undissolved particles can circulate through the reaction zones near the electrodes. In these zones, the dissolved alumina is below saturation, so the slurry particles are driven to dissolve. This dissolution supplements diffusion of dissolved alumina from the bulk electrolyte, and a reasonable current density is possible.

Of course, as is generally the case with oxygen-generating anodes, the free energy penalty associated with oxygen-generating anodes must be overcome. Moreover, the electrolysis process enthalpy must be considered. In particular, the standard enthalpy for the process corresponds to an electrolysis voltage of around three volts at 750°C.[3] If the cell is run with lower voltage, the electrolyte will freeze. If the cell is operated at a higher voltage, the excess heat will keep the electrolyte molten as long as the cell has a proper thermal design.

As mentioned previously, the free energy penalty is overcome by using wetted cathodes. With these, the ACD

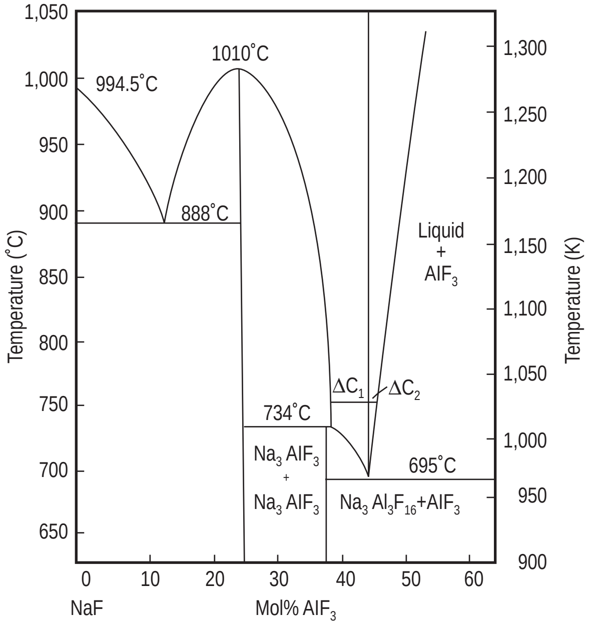

Figure 3. The phase diagram of the NaF:AlF$_3$ system.[4] $\Delta C_1$ and $\Delta C_2$ indicate change limits for the AlF$_3$ concentration that must not be exceeded within a LTE cell.

can be kept small enough to compensate for the free energy penalty associated with the non-consumable anodes. Thus, the LTE system has three main components: low-temperature slurry-electrolyte, non-consumable metal anodes, and wetted cathodes.

Could a modified traditional cell configuration succeed with these three components? For instance, could a drained bottom cell succeed as an LTE system? The answer is no as long as the slurry is required to support a reasonable current density. The requirement that the undissolved alumina in the LTE system not settle implies that a traditional cell configuration is not suited for LTE. This is because the traditional arrangement places the cathode, which is not gas-evolving, on the cell bottom.

The VEC concept allows the LTE conditions to be put into practice. In the VEC, the slurry is kept suspended by exploiting the oxygen bubbles produced. In particular, the liner of the cell is chosen to be anodic, thus gas-evolving. The bubbles from the bottom of the liner can indeed lift undissolved alumina particles and prevent settling.

Figure 1 depicts the VEC concept. This figure shows the anodic liner embedded in insulation, and a multiplicity of vertical electrodes suspended into the slurry-electrolyte. The vertical electrodes alternate between being cathodes and anodes. For a given cross-sectional area of an individual vertical electrode, the total number of such electrodes employed determines the capacity of the cell. Although there is a multiplicity of vertical electrodes, this VEC is not a multi-polar cell in that all of the cathodes are at an equal potential, and all of the anodes are at an equal potential to each other.

## CELL ADVANTAGES

The advantages of the VEC over a conventional cell are many, and all yield economic benefits. Some advantages derive from the inert anode, some from the wetted cathode, and some from the cell configuration.

The VEC has the potential to reduce energy consumption by up to 30% as a result of the relatively low operating voltage obtained using wetted cathodes. But the smelting technology offers other cost reductions as well. These include reductions in operating costs, capital costs, and total costs, which can potentially lower the price of the aluminum produced and yield several environmental advantages.

The operating cost reductions, which include the reduction in energy consumption, can potentially be as great as 25%. The anodes are non-consumable, which eliminates the traditional carbon manufacture process. This also reduces the cell maintenance since anode replacement is much less frequent. That the cells remain on-line continuously for longer periods with the longer anode life, and also that there are no anode effects with a slurry cell, improves the productivity of the smelting process. Finally, since the cells are well insulated, energy modulation becomes possible.

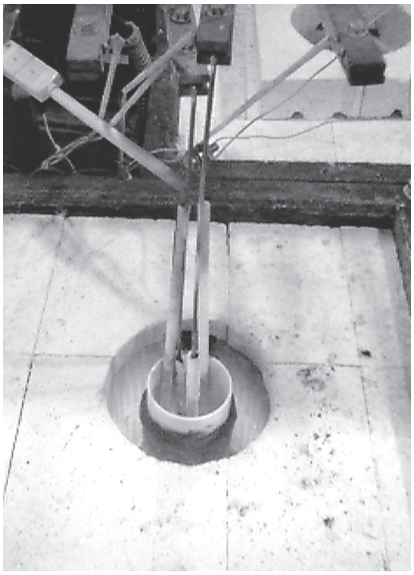

Figure 4. A photograph of the 10-ampere cell test stand used in the laboratory. The alumina crucible is contained in a steel can and placed in a furnace. The anode specimen resides on the bottom of the crucible. The cathode is suspended vertically above this. A thermocouple and a reference electrode, both housed in closed-end alumina tubing, are also placed in the cell.

Because the active electrode area is redistributed, the VEC configuration yields a large reduction in cell footprint (Figure 2). In a conventional cell, the area is horizontal. The area footprint of the cell is thus larger than the active area of the electrodes. In the VEC, the electrode area is redistributed, and is vertical. Thus an equivalent electrode area fits within a much reduced cell footprint area.

Due partly to the reduced footprint, the capital cost for new smelters can potentially drop by 30–40%. VEC smelters require less land, and the smaller cells reduce the infrastructure requirements. Another factor reducing capital costs is elimination of carbon plants.

The VEC can potentially retrofit existing smelters, also. The strategy is to replace existing cells with VEC cells, but use existing power supplies. This strategy will, in effect, reduce the size of the smelt per cell.

If a 25% reduction in total costs is realized with VEC technology, the potential exists to open new markets for primary aluminum. In particular, the reduced cost matches the cost the automotive industry has stated would be required to use aluminum as a primary structural material. It has been estimated that such use would increase aluminum content from around 113 kilograms per car today to as much as 317 kilograms per car by year 2020.[8] The reduced price could facilitate aluminum penetrating into other markets, such as packaging, as well.

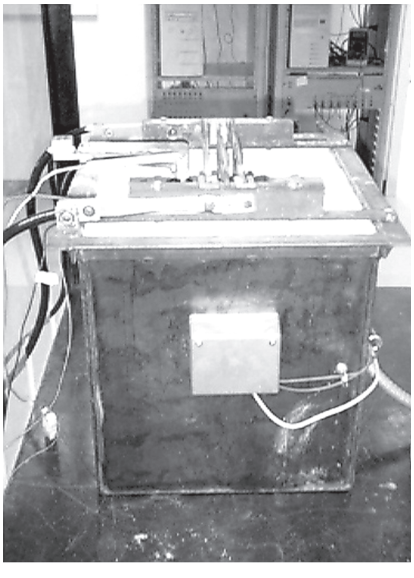

Figure 5. A photograph of the 200-ampere cell test stand. This uses a metal alloy liner instead of the alumina crucible in Figure 4. This cell also used two vertical cathodes and one vertical, center anode plate.

All of these cost advantages are enhanced by the environmental advantages associated with VEC technology. With metal alloy anodes, greenhouse gases from the smelting process itself are eliminated. Another large environmental advantage is the elimination of spent potliner, a hazardous waste. Because the cells are smaller, run at lower temperatures, and are rarely opened, VEC technology also promises improved working conditions in smelters.

It should be pointed out that inert anodes do not totally eliminate $CO_2$ generation due to aluminum smelting. This is true because generating the power input for the process can generate $CO_2$. However, if the cost reductions result in widespread use of aluminum to fabricate high-mileage automobiles, a substantial impact can be made on reducing $CO_2$ generation worldwide.

## UNIQUE CHALLENGES

The advantages of the vertical electrode LTE cell make it quite attractive to pursue. But the practical implementation of such a cell presents a great number of challenges. These can be thought of as belonging to three classes: Fundamental challenges, process control challenges, and engineering challenges.

The first fundamental challenge is realizing a working inert anode. This involves not only determining a suitable chemistry for the material, but also fabricating this material. While the vertical anodes may be fairly straightforward to fabricate, the anode liners may present a unique challenge in VEC technology, in particular, understanding the way the anode passivates and corrodes in the electrolysis process.

A second fundamental challenge is to understand VEC alumina feeding. Are the alumina types now used widely suited for slurry cell applications? If not, what are the requirements on the alumina, and how can these be met? Are existing feeders, such as point feeders, the best technology for VEC feeding? If not, what are the requirements for feeder technology? These questions are ultimately tied to the physical and chemical behavior of alumina in the slurry cell.

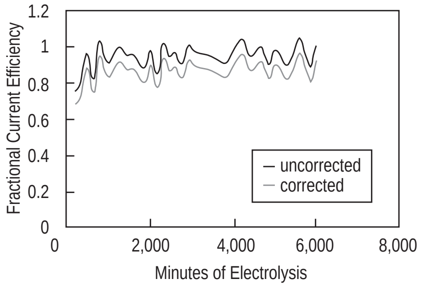

Figure 6. A plot of cell current efficiency vs. time for a 100-hour electrolysis test in the 10 A cell. The upper curve includes the weight of electrolyte extracted along with the product metal. The lower curve is corrected for this electrolyte weight using a constant factor.

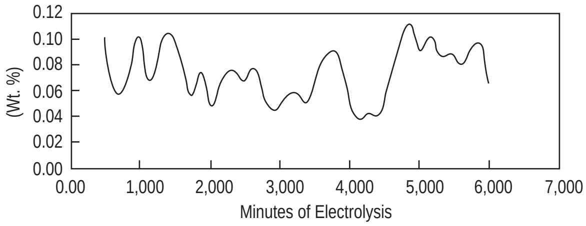

Figure 7. The product metal contamination vs. time for a 100-hour electrolysis test in the 10 A cell. The plot shows the combined weight percent of all anode components in the product metal, and is not corrected for additional sources of these metals. The commercial purity target of 0.1 wt.% with respect to anode metals was maintained essentially throughout the test.

A third fundamental challenge is to realize the best cathode. While titanium diboride ($TiB_2$) is usually nominated as a suitable material,[9,10] it may not be the best for VEC applications.[11] Finding ways in which any candidate material can be fabricated for VEC use is an additional challenge. Understanding the way the material and fabrication method combine to yield a wetted and dimensionally stable cathode is a significant fundamental challenge.

A fourth fundamental challenge that is unique to the VEC approach is removing the product metal. Unlike a conventional cell, the VEC has no metal pad that forms on the bottom. Rather, the liquid product metal is formed on the vertical cathodes, and could be lost if it detaches. If the aluminum contacts the anode, the cell could short and the anode could be destroyed. Even in the laboratory, product metal extraction is a challenge requiring solutions that enable relatively long-term tests of the VEC approach.

A fifth fundamental challenge is to generate reliable physical measurements for the LTE system. Since the electrolyte and cell temperature are quite different from those in conventional cells, there is no body of data in the literature to supply this background information. Thus, measurements of physical parameters such as alumina solubility, diffusion coefficients, densities, and so on, must be made especially for the LTE systems being researched.

Unique process control challenges arise with the VEC and LTE technologies. An example is that with a slurry cell, alumina depletion and anode effect are not elements of the system. Rather, strategies for monitoring and controlling the excess alumina in the slurry will be required. So with next-generation cells, one of the process control challenges is to identify the crucial parameters that must be controlled for successful cell operation. The next challenge is to associate measurements with these parameters, then, the control limits must be determined for each such measurement. And, finally, strategies must be developed for using the measurements for process control.

An excellent example of these process control challenges is found by looking at the electrolyte used in LTE. A suitable electrolyte comprises the sodium fluoride (NaF): aluminum fluoride ($AlF_3$) two-component system near its low-melting eutectic composition. As shown in the phase diagram of Figure 3,[4] this occurs near 44 mole% $AlF_3$. As shown also in Figure 3, the composition cannot deviate from this but by a few mole% in either direction. If the composition becomes too low in $AlF_3$ within some limit denoted as $\Delta C_1$, cryolite can freeze. This typically occurs on the cathode, and is effectively irreversible at 750°C. If the composition becomes too rich in $AlF_3$ within some limit denoted as $\Delta C_2$, the excess $AlF_3$ precipitates onto the anodic bottom of the cell. Both of these conditions are to be avoided, and the actual limits on the change in composition depend on various factors in the cell. Identifying all of the conditions, identifying useful measurements, relating the measurements to control limits, and implementing bath composition control are all key challenges to successful operation of a VEC utilizing low-temperature electrolyte.

Once the fundamental and process control challenges have been met, the final set of challenges leading to a commercial smelting process can be addressed. These are the engineering challenges. They involve embodying the specifications given by the fundamental and process control challenges in cost-effective and practical ways.

Two of the most crucial engineering challenges envisaged currently follow from the previous discussion. One is fabricating the electrodes themselves. This involves not only consolidating or casting the materials chosen, but also doing so in shapes that embody other factors, such as product metal removal. The second challenge is developing the alumina-feeder technology appropriate for the specifications of the overall VEC.

It was mentioned that the VEC must be insulated well in order to the meet the enthalpy requirements that ensure a molten electrolyte. In a VEC, a frozen ledge is to be avoided. The design of an insulated hood that incorporates dry scrubbing of the cell offgas, yet controls heat loss, is one of the engineering challenges.

The multiple electrodes of the VEC reside beneath this insulated hood. Thus, an additional engineering challenge is connecting these electrodes to a power

### PROGRESS UPDATE

Given this overview of the nature of the VEC being researched presently, the question may be asked: Where does the research effort stand at this time?

The types of experiments and cells used in the laboratory experiments to date are described more fully elsewhere.[3] Two types of cells have been employed. One, shown in Figure 4, uses a 500 ml alumina crucible to hold the electrolyte. Experiments in this cell typically draw around 10 amperes of electrolysis current, and it is called the 10 A cell. These experiments are typically of five-hour duration. They focus on surveying anode and cathode materials and investigating LTE slurry-electrolytes. A larger cell, in which currents of 100–300 amperes are used, is shown in Figure 5. This 200 A cell uses a metal alloy liner and vertical electrodes. In this way, it embodies the VEC concept. It is being used to address issues of long-term tests and product-metal extraction. Both of these cells use ovens with resistance heaters embedded in firebrick. For the tests conducted with these cells, an insulated hood is not used; the heaters are relied upon to maintain system temperature.

One year ago, five-hour tests in the 10 A cell exhibited current efficiencies as high as 90%. These efficiencies are determined by weighing the actual product metal, not by analyzing for oxygen in the offgas. These efficiencies were achieved concurrently with producing metal that nearly reached program goals for purity (ie., no more than 0.1 wt.% contamination by anode components). It was anticipated that the corrosion of the anodes and the associated contamination of the product metal would drop in time. However, no continuous aluminum extraction method was in hand to enable longer tests. It was also not known if the 90% efficiencies observed were limited in a fundamental way by the VEC approach. In particular, was a 10% loss of current efficiency the result of the product metal back reacting with oxygen in the electrolyte?

Since then, several principles and methods for continuous metal extraction have been studied and shown to be feasible. One of these has been used to enable longer tests in the laboratory. These longer tests have been conducted both with the 10A cell and the 200A cell. Other advances have resulted in current efficiencies for five-hour tests as high as 95%. This last result indicates that the current efficiency losses typically experienced seem not to be due to back-reaction, but to other factors.

The best results to date can be summarized in terms of two tests, one in the 10 A cell and one in the 200 A cell. The best 10 A cell test lasted 100 hours. All indications were that the cell would continue operating without problems, but the test was halted once the targeted duration was reached. The average electrolysis voltage for this test was 3.716 V. This is above the 3.5 V target overall, but is an appropriate voltage for the geometry of the 10A cell because the ACD is not uniform in this test stand.

The average current efficiency over the 100-hour period was 87%. Figure 6 is a plot of current efficiency with time. Two traces are shown. The upper trace includes the weight of electrolyte that is removed with the metal extraction technique employed. The lower trace is corrected with an average factor for this electrolyte.

The product metal collected in this 100-hour test was at or below the target contamination level for essentially the entire test. This is shown in Figure 7, which plots the contamination by anode materials against time. The target is 0.1 wt.%, which is exceeded only slightly in four of the metal-collection cycles throughout the entire test. It should be noted that iron is a component in the anode tested, and iron is present in the electrolyte regardless of the anode used. The results in Figure 7 include any iron contamination from sources other than the anode.

The best test to date with the 200 A cell lasted 88.5 hours. The test was halted due to freeze on the cathode, which underscores the need for better process control. The overall current efficiency, corrected for electrolyte removed, was 84%. This relatively low value is probably due in part to the inefficiency of the metal-removal method. During some portions of this test, the product-metal purity reached the targets, but this purity was not maintained throughout. The variable product purity is probably tied to difficulties with process control.

---

bus that lies outside of the hood. The connections must be of suitably low resistance and compatible with the materials of the electrodes.

### ACKNOWLEDGEMENT

*This paper was prepared with the support of the U.S. Department of Energy (DOE) Award No. DE-FC07-98ID13662 and Award No. DE-FC07-00ID13901. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author and do not necessarily reflect the views of DOE.*

## References

1. R.E. Hanneman et al., "Inert Anode Technologies Report," *Report CRTD,* Vol. 53 (New York: American Society of Mechanical Engineers, July 1999).
2. W. Haupin and H. Kvande, *Light Metals 2000,* ed. R.D. Peterson (Warrendale, PA: TMS, 2000), p. 379.
3. C.W. Brown, *Light Metals 2000,* ed. R.D. Peterson (Warrendale, PA: TMS, 2000), p. 391.
4. T.R. Beck, *Light Metals 1994,* ed. U. Mannweiler (Warrendale, PA: TMS, 1994), p. 417.
5. T.R. Beck and R. Brooks, U.S. patent 5,006,209 (1991).
6. C.M. Hall, U.S. patent 400,664 (1989).
7. R. Keller et al., *Electrochimica Acta,* 42 (12) (1997), p. 1809.
8. *Aluminum Industry: Industry/Government Partnerships for the Future* (Washington, D.C.: The Aluminum Association, 1996).
9. R.P. Pawlek, *Light Metals 2000,* ed. R.D. Peterson (Warrendale, PA: TMS, 2000), p. 449.
10. K. Billehaug and H.A. Øye, *Aluminum,* 56 (1980), pp. 642–698 and 713–718.
11. C.W. Brown, *JOM,* 50 (5) (1998), p. 38.

---

*Craig Brown is Manager of Research at Northwest Aluminum Technologies.*

**For more information, contact Craig Brown, Northwest Aluminum Technologies, 1080 West Ewing Place, Suite 202, Seattle, WA 98119; cbrown@nwat.net.**