

DEVELOPMENT AND DEPLOYMENT OF SLOTTED ANODE TECHNOLOGY AT ALCOA

Xiangwen Wang, Gary Tarcy, Stephen Whelan, Silvio Porto, Christopher Ritter, Bob Ouellet, Graham Homley, Andrew Morphet, Gilles Proulx, Steve Lindsay, and Jay Bruggeman
Alcoa Primary Metals, Alcoa, Inc. USA

Keywords: aluminum smelting, carbon anode, slotted anode, anode gas bubble, energy efficiency

Abstract

Alcoa started slotted anode development and plant trials in 1998. Nearly all Alcoa prebake smelters are now running with slotted anodes. Implementation of slotted anodes has required little or no capital investment and has generally achieved improvements in current efficiency, power efficiency and pot stability. The success was not completely incident free and it became clear that the slotted anodes changed the behavior of many factors in the pot. This paper provides a brief view of slotted anode development and deployment on different cell technologies at Alcoa. The chronological development is described along with comparative performance. Some of the negative aspects of slotted anodes in different technologies are also presented.

Introduction

The carbon anode is consumed to give off approximately 2.5m³ of CO₂ for every kg of Al produced. The release of the anode gas from the horizontal anode surface in a molten cryolitic electrolyte is not continuous, but occurs in a cyclic fashion.(1, 2). The gas blanket-like bubbles penetrate into bath about 1 cm (3-5), and can reach as deep as 1.5 cm into the bath at the leading edge prior to release (6). Large gas bubbles formation and release cause cyclic fluctuation/oscillations in anode current due to the bubble screening effect (7, 8). The cyclic large gas bubble release from the anode surface also induces vertical movements and turbulence at the bath-metal interface. This anode gas bubble phenomena on the carbon anode induces pot instability, reduces current efficiency and adds resistance as a result of a non-conductive gas bubble screening effect. Anode gas bubbles cover from 50 to as high as 90% of carbon anode surface (9, 10).

Minimizing of the anode gas bubble voltage drop may be one of the most economical ways to reduce energy consumption or improve energy efficiency by reducing overall cell voltage while maintaining optimal current efficiency for aluminum smelters.

Modification of the anode surface can effectively reduce both the bubble voltage drop and anode overvoltage by both facilitating the gas release to reduce the gas bubble coverage making more anode surface available for the electrolytic reactions, and by breaking up the blanket type of gas bubbles before being swept away.

Anode surface slots are an effective way to modify gas bubble formation, release and coverage.

This paper provides a description of slotted anode development and deployment on different cell technologies at Alcoa. R&D efforts in slotted anode development are described along with examples comparative cell performance improvements. The development and deployment of slotted anodes was not entirely without incident and in several cases the slots had to be removed and other factors corrected before they became a benefit.

Anode Overvoltage and Gas Bubble Voltage Drop

The overall cell voltage may be expressed by:

$$V_{\text{cell}} = E_{\text{Nemst}} + \eta_a + \eta_c + IR_c + \Delta V_{\text{bub}} + I(R_a + R_c + R_{\text{ext}}) \quad (1)$$

Where E_{Nemst} is theoretical decomposition potential (voltage) for Al reduction, η_a anode overvoltage, η_c cathode overvoltage, IR_c Ohmic drop through electrolyte, ΔV_{bub} anode gas bubble drop, R_a and R_c are anode and cathode resistance and R_{ext} cell external resistance.

The anode overvoltage, η_a , and anode gas bubble voltage drop, ΔV_{bub} , are particularly of interest in this study. Anode overvoltage may be generally expressed (11):

$$\begin{aligned} \eta_a = \eta_{\text{ar}} + \eta_{\text{ac}} &= \frac{RT}{nF} \ln(i/i_0) + \frac{RT}{nF} \ln [(i_c - i)/i] \\ &= a + b \ln(i) + \frac{RT}{nF} \ln [(i_c - i)/i] \end{aligned} \quad (2)$$

Anode gas bubble voltage drop may be estimated for conventional cells (9, 11):

$$\Delta V_{\text{bub}} = i/\kappa [d_b/(1 - \Phi) - d_b] \quad (3)$$

As seen from equations (2) and (3), anode current density, i , anode gas bubble thickness (d_b) and surface coverage (Φ) impact both the overall anode overvoltage and gas bubble voltage drop.

It is well documented (11) that in addition to anode current density, i , bath chemistry (alumina concentration and bath ratio) also plays a dominant role in changing the anode gas CO₂ wetting characteristics and therefore the bubble coverage. In these previous studies, the gas bubble coverage or volume fraction is only a function of current density, cell temperature and bath chemistry (ratio and alumina concentration), independent of either anode size or shape of anode surface.

Physical modification of the anode surface with the introduction of slots is another way to break up gas bubbles covering the anode

surface. Slots result in both an overall smaller gas bubble, and channel the gas off the surface instead of traveling along it. The slots can be designed so that both gas bubble thickness, d_b , and coverage, Φ , can be minimized.

Development of Slotted Anode

Slots in Anode Surface

The “slots” are pre-made deep channels across anode surface in either longitudinal or transverse arrangement as illustrated in Figure 1. The slots can be either formed during anode forming or cut by saw after baking.

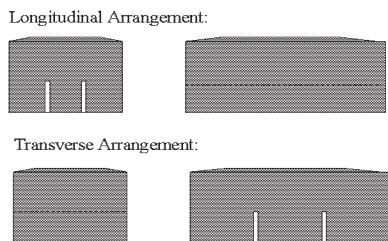


Figure 1. Typical slotted anodes showing slots arrangement in the anode surface.

Basic requirement of the slots includes:

- Effectively breaking up anode gas bubbles,
- Effectively channel anode gas off the anode surface,
- Maintaining anode structural and electrical integrity
- Introduce no extra C-dust.

The slots also allow for some simple engineering of the fluid flow in the pot which in principle can help with both heat balance and chemical issues associated with the process. Conventional anodes do not have this capability.

Earliest Plant Trial and Deployment

Alcoa started slotted anode development and plant trials in 1998. One of impressive early results was a significant reduction of pot noise. Other observations included:

- Change in gas bubble release and direction,
- No increase in carbon dusting,
- No change in slot size before being consumed,
- No visible change in pot ore cover and side ledge,
- No increase of Fe content in metal,
- Decrease in the anode effect alumina concentration,
- Increase in the Na concentration in the Al metal.

One other observation was not every slot configuration that was tried gave the expected results (especially the noise reduction).

Parallel to the potroom trial, methods and processes in making and handling slotted anodes were finalized at our carbon plant. A plant wide deployment of slotted anodes was carried out in September 1999 without road blocks.

Based on the early development and performance results Alcoa started a systematic approach from slotted anode development to deployment at other locations. The systematic approach included R&D development, design, plant trial, field verification

measurements, and finally implementation and fine tuning of the pot operation.

Understanding Slotted Anodes

A study was conducted in Feb 2000 to determine which slot configuration gave the maximum benefits.

Figure 2 presents fluctuations of individual anode resistance as impacted by anode gas bubble formation and release patterns on anode surfaces. For the traditional flat anode, the magnitude of resistance oscillated cyclically from a low of -0.02 to a high of 0.015, a swing of over 0.03. One cyclic swing represents a dominant blanket type of gas bubble formation (high resistance) and release (low resistance). Slot configuration 1 significantly reduced the magnitude of oscillation to a range of -0.005 to 0.005, a swing of 0.01. Slot configuration 2 reduced the oscillation even further to a swing of 0.005. Slots on anode surface not only reduced the anode gas bubble size and coverage (as represented as the magnitude of oscillation), but also facilitated in getting the gas out of the anode surface faster (in a higher frequency). Slot configuration 2 apparently is a better arrangement in modifying anode gas bubbling pattern in reducing anode current oscillations.

Change in individual anode will result in a cell with different noise level. Figure 3 shows a typical result of short term noise with and without using slotted anodes.

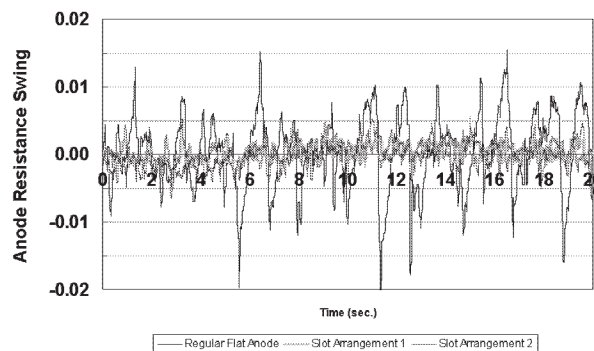


Figure 2. Pseudo resistance swings on individual anode as affected by the presence of slots on anode surface.

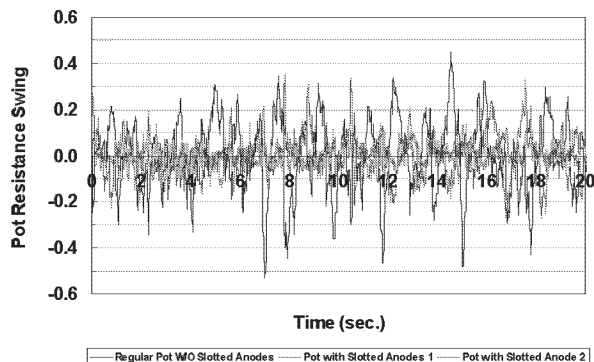


Figure 3. Cell pseudo resistance swing as affected by the slots on anode surface.

For the cell running with regular flat non-slotted anodes, cell resistance can oscillate from a low of -0.5 to a high of 0.5, a swing as great as 1.0. The cell running with slotted anodes

(configuration 1) had oscillation to below 0.5. The cell running with slotted anodes of design 2 had the even lower noise <0.25. The short term noise level was reduced from 1.0 for regular cell to below 0.25, a reduction of over 70%.

Physical Modeling of Slotted Anodes:

Alcoa owns prebaked smelters with many different cell and anode technologies. Due to uniqueness of each smelter and its carbon plant, one slotted anode design was not optimal for all plants. In 2001, R&D efforts were spent to study anode gas bubble phenomena including physical modeling of real size slotted anodes in laboratory to gain understanding of the optimal slot anode design for each smelter.

Figure 4 shows a diagram of an experimental setup for physical modeling of the gas release from an anode. In the setup, the bubbling phenomena (bubble size and thickness) were recorded by videoing gas formation and release patterns as well as influences by various slot arrangements. At the same time, gas bubble resistance was measured to evaluate the gas bubble coverage.

Using the physical model, all anodes used within Alcoa prebaked cells were studied and influences by various slot configurations were evaluated. This allowed us to use optimal slot configuration tailored to each smelter technology.

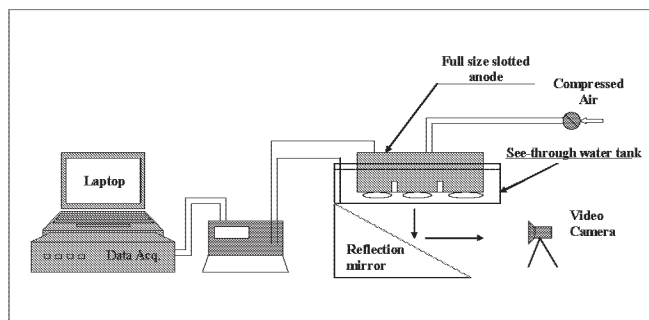


Figure 4. An experimental setup for physical modeling of full size slotted anode.

Figure 5 shows an example in comparing anode resistance as impacted by gas bubble effect between a regular flat anode and anodes with two different slot configurations. The presence of slots not only reduced the resistance fluctuations, but also reduced the overall resistance. The anode resistance fluctuations as shown in Figure 5 are analogous to the anode stem current fluctuations as measured in actual cells (as shown in Figure 2).

The physical model allowed us to estimate the gas volume fraction (12) at the anode surface and the gas bubble coverage (10) as a function of slot configurations. Figure 6 gives an example of gas bubble coverage as a function of current density for one full size anode. Higher anode current density results in higher gas bubble coverage. For the regular flat anode without any slots, the gas coverage was about 0.94 at current density of 0.9 A/cm². Slot configuration A reduced the coverage to 0.89 (6% drop) while slot configuration B reduced the gas coverage to 0.76 (16% drop). Apparently, slotted anode configuration B is more effective than slotted anode configuration A in breaking up large anode gas bubble formation and facilitating in removing gas

from anode surface to reduce anode gas bubble resistance drop as evidenced by the higher gas bubble release frequency.

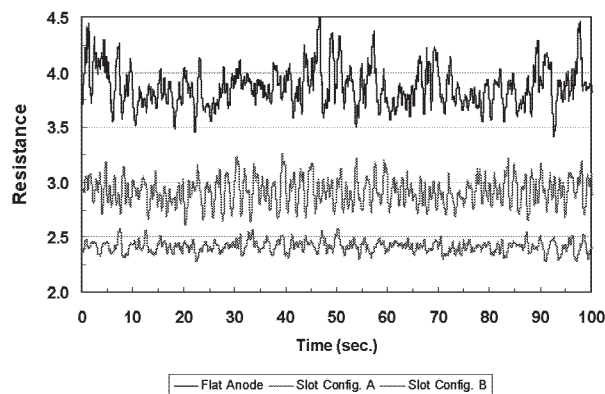


Figure 5. Physical model results: anode (cell) resistance as influenced by gas bubble formation/release processes.

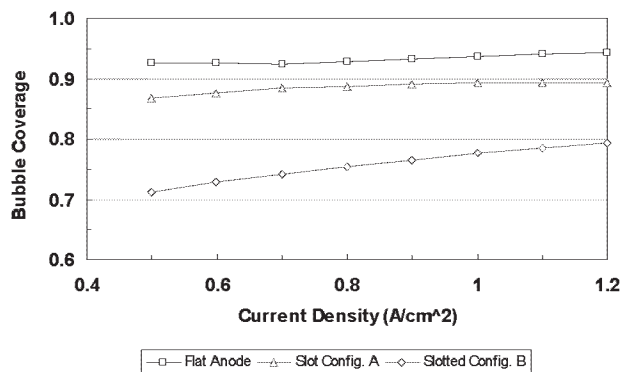


Figure 6. Comparison of regular flat anode and slotted anode: Anode gas coverage as a function of current density.

Anode Gas Bubble Measurements in Industrial Cells

Physical modeling is limited and can only provide us with preliminary understanding in slotted anodes. Numerous field studies were carried out during plant trials and deployment process for each cell technology to determine the optimum design for each condition.

One of the special measurements was to determine depth of anode gas bubble penetration into the electrolyte and anode gas bubble voltage drop using a specially designed scanning reference electrode (3).

Figure 7 shows a time recording of typical anode potential fluctuations obtained at a location on a flat anode surface. The potential fluctuates cyclically from a low of 2.65V to a high of 3.45V at a constant frequency when anode gas bubble forms and leaves. The magnitude of the potential oscillation was 0.8V. The low potential (2.65V) represents a potential free of bubbles while the peak potential (3.45V) is the potential when the bubble grows to its maximum before being swept away.

When slots are present in the anode surface, the bubble formation and release pattern is significantly modified. Figure 8 shows typical anode potential fluctuations for the identical anode, but

with the presence of slots. The potential fluctuates cyclically from a low of 2.55V to a high of 2.85V also at a constant frequency. The magnitude of the oscillation, however, was only 0.3V. The low potential (2.55V) is identical to the low potential for the flat anode and represents a potential free of bubbles while the peak potential (2.85V) is the potential when the bubble grows to its maximum. This substantially reduced anode potential oscillation indicates slots effectively break up or prevent formation of large gas bubbles before being swept away or channeled out of the surface. The overall effects are that significantly reduced anode current oscillation as seen in Figure 2 and reduced anode gas bubble voltage drop as shown in Figure 9.

Figure 9 shows the calculated anode gas bubble voltage drop on the specific anode based on measurement results as shown in Figures 7 and 8. Basically, the bubble voltage drop was averaged at 0.24V for flat non-slotted anode, and averaged 0.08V for the slotted anode. The bubble voltage drop was decreased by 0.16V. There was more scatter in the data for the flat anode primarily due to anode age, large bubble (blanket like) formations and its non-uniform nature on the large surface area.

Plant measurements and physical models showed slotted anodes work on most prebaked smelters with anode size big or small. Physical modeling together with the numerous plant measurements allowed us to develop an overall model to optimize slot configuration tailored for each individual smelter and to predict the voltage/energy savings. Figure 10 shows the predicted voltage savings using optimized slotted anodes for different cell technologies. For simplicity, the voltage savings are plotted against a normalized anode. The voltage saving is different ranging from a low below 30 mV to a high of over 160 mV depending on its cell technology. As will be shown in the later section of cell performance, the overall model proved to be accurate and realistic.

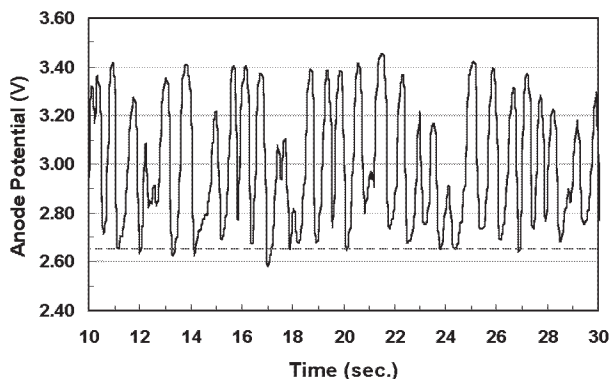


Figure 7. An anode potential time recording on anode surface of regular flat non-slotted anode.

Slotted Anode Deployment and Cell Performance

Since 1999, almost all Alcoa prebaked smelters have been deployed with slotted anodes. Implementation of slotted anodes has generally achieved improvements in current efficiency, power efficiency and pot stability. Figures 11 to 13 show examples of pot performance in one of Alcoa smelters before and after slotted anode deployment as well as during slot optimization.

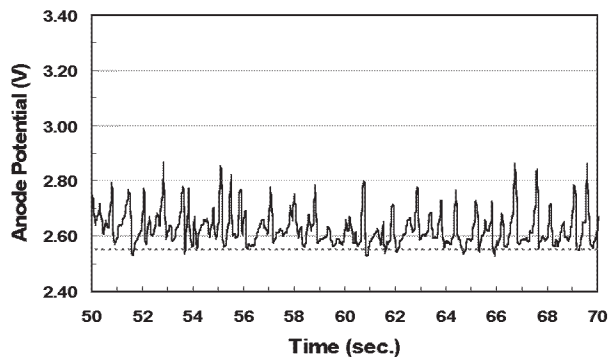


Figure 8. An anode potential time recording on anode surface of a slotted anode.

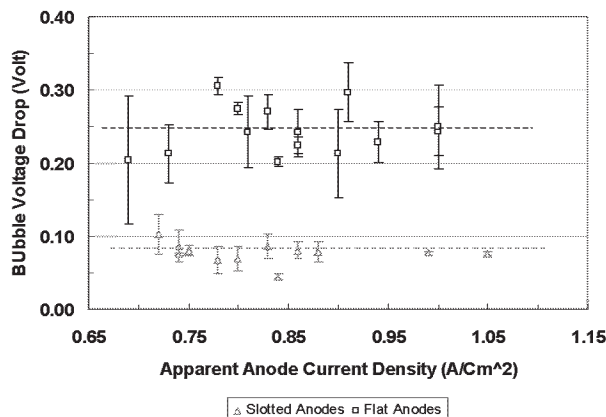


Figure 9. Comparison of anode gas bubble voltage drops on regular flat and slotted anodes in one prebaked smelter.

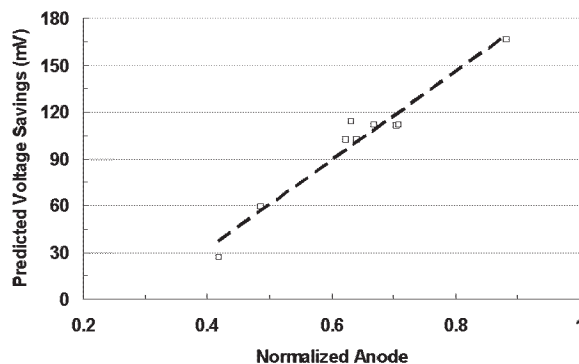


Figure 10. Predicted voltage savings from using optimized slotted anodes for each smelter technology.

Figure 11 shows pot noise reduction after the use of slotted anode. In general, the overall pot noise on average was reduced from above 0.25 to below 0.20, an over 20% reduction. This overall pot noise reduction is primarily a result of reduction of anode gas bubble noise reduction, and the reduction can only be seen if the overall slot design for the pot whole meets some minimal criteria.

Slotted anodes have allowed us to reduce pot voltage in many cases. Figure 12 shows the plant cell voltage reduction trend as a function of slotted anode deployment. An average, the pot

voltage was able to be reduced by 0.15V when the slotted anode design met the optimal requirements.

Slotted anode allows us to reduce pot voltage without sacrificing current efficiency. Figure 13 shows that at least 0.5% improvement in current efficiency was seen after slotted anode efficiency reached a critical level. The improvement in current efficiency was believed to be a result of reduction in pot noise. Slots break and prevent large blanket type gas bubble formation, which also reduces the buoyancy force during bubble releases and minimizes metal pad turbulence or bath/metal interface interactions.

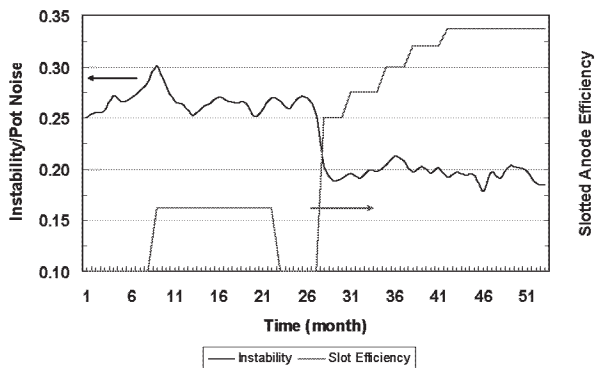


Figure 11. Pot instability/noise before and after slotted anode deployment.

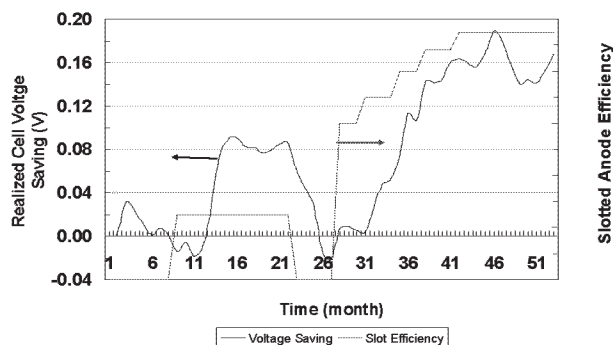


Figure 12. Average pot voltage saving/reduction before and after slotted anode deployment.

Issues and Negative Aspects

The success was not completely incident free and it became clear that slotted anodes changed the behavior of many factors in the pot. Adjustments have to be carried out to avoid some undesirable upsets. As seen in Figures 11 to 13, in a period when slotted anode efficiency was below the critical threshold. The realization of pot voltage reduction brought in process instability. The current efficiency became more erratic. Adjustments had to be made to both the green anode and potroom operations. Adjustments in slotted anodes included:

- Slot width: either too wide or too narrow slots would not improve but hurt process stability and cell performance,

- Slot depth: slots have to have a certain life span of the set cycle, no benefit could be seen if slots too shallow.

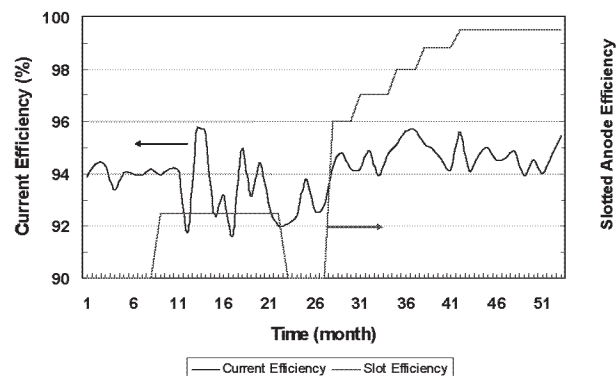


Figure 13. Current efficiency before and after slotted anode deployment.

The success of slotted anode deployment at some smelters did not guarantee success at others. It became apparent to us a success at one pot technology does not mean the same story for another pot type. Each pot technology was unique and therefore had to be treated differently. Some of the negative aspects of slotted anodes in different technologies are presented below.

Slotted Anode Manufacturing

Slotted anodes can be made either in the green anode forming process or by sawing baked anodes.

Slotted anodes manufactured in the green anode forming process requires a much stricter requirement in process control and a high level of quality assurance. Slots can sometimes result in a more variable anode quality such as density unevenness across the anode. The uneven density is more prone for spike formation and carbon dusting. Because of heavy dusting and extra sets due to spike/point formation, process upsets occurred in the potroom resulting in reduced current efficiency.

Additionally, the former/pusher arrangement limits how slots can be made. The slot depth is limited due to integrity issues. The slot's width is also critical as they can sometimes pitch during the baking process. A cleaning device may need to be installed to remove packing coke from the slots after baking, which increases steps of operation and results in additional operating cost.

Sawing the slots is the preferred method of manufacture. This is done after anodes are pulled from the baking furnace. The cutting method allows making uniform, clean slots to exact specification. However, this is an added expense due to additional equipment expenditure and sawing blade consumption.

Potroom Operation

Slotted anodes change many characteristics of pot operation. Some undesirable aspects include tendency towards increasing C dusting. The C dusts may result from packing coke inside the slots or increase Boudouard reaction ($C + CO_2 \Rightarrow 2CO$) due to increased CO_2 gas contact with Carbon by the gas traveling through the slots). The reaction would increase carbon consumption and bring extra C dust in pots especially when anode

quality has variability. Figure 14 shows a net carbon change before and after use of slotted anodes in three of our smelters. Plant 1 and 3 saw an increase in net carbon after the use of slotted anodes while plant 2 saw an improvement, further illustrating the uniqueness of each implementation.

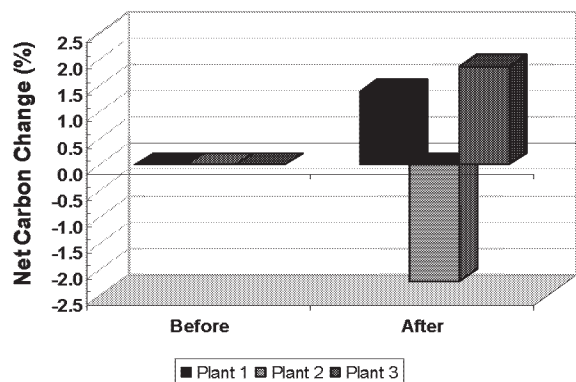


Figure 14. Net carbon consumption change before and after slotted anode deployment.

Probably one of the most pronounced negative aspects is the uneven burn off rate for anodes with and without slots in the same cell. Slotted anodes and non-slotted anodes co-exist at all times. Unlike the traditional cell in which every anode behaves the same, the “anode resistance” is inherently different between slotted anodes and non-slotted anodes. Given the same anode potential and operated at the same anode – cathode distance, the slotted anodes will carry greater current load. Varied current loading would change cell current flow pattern, which in turn would result in some different magnetic field distribution. Different current loads would also result in uneven anode surfaces (different ACD under slotted and non-slotted anodes) with the ACD of slotted anodes being greater. Unless special care is taken with the parameter changes used around setting anodes this change could lead to anode deformations and spikes.

Potroom process upsets did occur due to use of slotted anodes of poor anode quality. Figure 15 shows current efficiency loss due to a process upset that occurred in one smelter. The current efficiency loss, as high as 4%, was due to slotted anodes with low density zones adjacent to slots. The bad anodes introduced heavy carbon dusts due to slot erosion and air burning, and also resulted in extra sets due to spike formation. The slotted anodes did not improve, but reduced current efficiency and resulted in production loss. We had to take the slots out in order to get the process back to normal.

Some other negative aspects that have been observed

- Reduced butt thickness and increased tendency of higher Fe in metal due to carbon loss by slots,
- Reduced set cycle and so anode production requirements due to loss of carbon by slots,
- Changed bath (heat) flow due to slot arrangement with potential for increased sidewall erosion, blocked feeders and thinning of the anode cover from bath splash,
- Changed load up anode curve.

Slotted anode does not work effectively on cells where long term noise (metal pad) is dominant in the overall noise or the pots

which are magnetically instable. For the same reason, slotted anode does not cure pot ill.

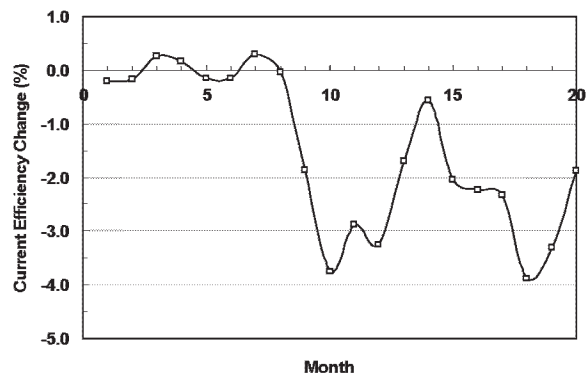


Figure 15. Current efficiency loss due to use of bad slotted anodes.

Summaries

This paper briefly described activities in slotted anode development and deployment at Alcoa. In general the slotted anodes provided benefits to the operation of prebake cells but each implementation had to be treated individually and an array of pitfalls had to be overcome in order for the benefits to be obtained.

Acknowledgements

Successful deployment of slotted anode projects requires involvement and the close co-operation with personnel from R&D and operations. Authors wish to thank those who were and continue to be involved in this project. There are simply so many to be mentioned. Appreciation also goes to Alcoa Primary Metals for allowing publishing this work.

References

1. E. W. Dewing: Canadian Metallurgical Quarterly, Vol. 30, No. 3, 1991, pp153-161.
2. S. Fortin et al: Light Metals 1984, pp712-741.
3. W. E. Haupin: JOM, Oct. 1971, pp46-49.
4. G. J. Houston et al: Light Metals 1988, pp641-645.
5. R. C. Dorward: J. Applied Electrochemistry, No.13, 1983, pp569-575.
6. Lagon B. and J. M. Peyeau: Light Metals 1990, pp267-274.
7. J. Xue and H. A. Oye: Light Metals 1995, pp265-271.
8. X. Wang and A. T. Tabereaux: Light Metals 2000, pp239-247.
9. R. J. Aaberg et al: Light Metal 1997, pp341-346.
10. T. Hyde and B. Welch: Light Metals 1997, pp333-340.
11. W. Haupin: Light Metals 1998, pp531-537.
12. C. W. Tobias: J. Electrochem. Soc. Vol. 106, No. 9, 1959, pp1207-1218.