

Low-Cost PFC Analyzer for Early Anode Effect Detection

Hervé Roustan

R&D Process Control Team Leader

Rio Tinto Aluminium Pechiney, Saint Jean de Maurienne, France

Corresponding author: herve.roustan@riotinto.com

Abstract



The anode effect is a major and unfortunately recurrent malfunction of aluminum reduction cells. Process control algorithms implemented in the pot controller can detect this problem and eliminate it. However, detection is based on the resulting significant increase in the voltage of the pot, and this increase is generally very fast: the nominal voltage is increased to 8 Volts (the detection threshold commonly used by ALPSYS[®], for AP technology pots) in just a few seconds, which is not enough to permit a preventive treatment of the anode effect.

However, several minutes before the anode effect can be detected with certainty by a rise in the pot voltage, the unwanted electrochemical reaction is already present and gases such as CF₄ or C₂F₆ are already being produced by the pot. This phenomenon has been clearly demonstrated on prototype pots equipped with Fourier transform infrared analyzers (FTIR). Unfortunately, such analyzers cost too much to allow equipping all the pots in a smelter with them. We have therefore worked in partnership with the Mirsense company to develop a low-cost device for continuously sampling and analyzing pot gases in order to detect CF₄. The principle of the device is photo-acoustic detection: a laser emitting at a carefully chosen frequency will selectively excite CF₄ molecules so that they emit a sound whose amplitude is directly related to the quantity of CF₄ present. The development of this device also includes the sampling equipment, in order to obtain a solution able to work continuously over a long time without manual intervention.

To date, the performance of our photo-acoustic device is very good and its results consistent with those of an FTIR placed in parallel for comparison.

Keywords: Anode effect, PFC. Low-cost PFC analyser.

1. Introduction

The anode effect is a phenomenon which appears in aluminum reduction cells due to the depletion of oxygen-containing ions at the anode. It is generally considered that the effect occurs when the alumina concentration in the pot is less than 1 to 1.5 % wt. [1], [2], [3], [4], [5]. At the beginning of the aluminum industrial era, there was no automated alumina feed, and the anode effect was awaited in order to know when to add more alumina to the pot. For several decades now, thanks to automation, the pots have been equipped with either continuous or semi-continuous alumina feeding systems. The appearance of anode effects is therefore no longer necessary to ensure the proper functioning of the pots and is clearly not desirable, because the phenomenon has negative consequences on the robustness of pots (release of intense thermal energy which deteriorates ledge and crust) and on their performance (higher energy consumption and lower current efficiency). Moreover, the anode effect causes a release of CF₄ and C₂F₆ instead of the CO₂ normally produced at the active surface of the anodes. These two perfluorocarbons (PFCs) have a global warming potential of respectively about 7 000 to 12 000 times that of CO₂ and have an extremely long lifetime in the atmosphere, reaching respectively 50 000 and 10 000 years. This is why it is important to limit the occurrence of anode effects as much as possible (expressed in number of anode effects per pot and per day). Much progress has been made in this field since the 1990s, in particular by trying to improve the operating conditions of the pots.

Numerous scientific studies have been carried out to explain the origins of anode effects [6], [7], [8], [9]. All these studies clearly show that the primary cause of the anode effect is the lack of alumina in the pot or more precisely under certain anodes. It seems that since alumina is delivered at the center of the pot, an anode effect is very often triggered under the anodes at the end of the pot, in areas where the bath stirring is less powerful and where enriching the bath with alumina is therefore more difficult. As soon as the alumina concentration under these anodes drops below approximately 1 to 1.5 % wt., the anodic current density limit is reached and the first bubbles of CF_4 and C_2F_6 begin to form [4], creating a resistive layer under these anodes which further reduces their current. This current reduction is distributed to the other anodes, increasing their current densities and hence making them more sensitive to the anode effect. A chain reaction then occurs, generalizing the anode effect to all the anodes of the pot [3].

However, as the first anodes undergo the anode effect, the new current distribution in the other anodes is not clearly visible in the pot voltage, because other phenomena such as magnetic instability lead to noise in the voltage greater than the variations resulting from the onset of the anode effect on the first anodes [10]. For this reason, the anode effect is only clearly detectable in the very last seconds before it generalizes, when the cell voltage begins to increase rapidly.

Thus, the initiation of the anode effect results in a drastic drop in current density in a limited number of anodes. Studies have therefore been carried out to detect the phenomenon by monitoring the current in each anode [11] [12]. This method is very effective but requires equipping each pot with anode current sensors, which is quite costly.

Other authors have used statistical methods, in particular principal component analysis [12] [13], or the calculation of third-order coherence functions [14] in order to detect drifts in the process and in particular in alumina depletion. However, the monitoring of these indicators is not sufficient because many exogenous phenomena can intervene. For example, monitoring the number of alumina shots introduced into the pot per unit of time is a good indicator of the quantity present in the pot, but a significant reduction in this value will not necessarily mean a reduction in the concentration, as this may be caused by a collapse of the cover in the bath (the regulation algorithm then decreases the alumina shot frequency to take account of this parasitic alumina feeding). It is also possible to estimate the alumina concentration in the pot using a linear Kalman filter, in order to increase the feeding rate (i.e., overfeeding) in case of lack of alumina [15], [16]. However, these estimators need to be readjusted periodically.

Studies using machine learning techniques have also already been used in order to predict the anode effect [17]. We can cite the work of Meghlaoui et al. in 1998 [18]. These authors used neural networks for the prediction of cell resistance at the 15-minute horizon. Their one-layer neural network uses as input data the instantaneous resistance value and its value 5, 10 and 15 minutes before, the instantaneous alumina feed rate and that, 20 minutes before, as well as the slope of the resistance and its deviation from the minimum recorded value. It should be noted that the authors claim good results in reducing anode effects thanks to their algorithm which imposes alumina overfeeding as soon as the prediction foresees an increase in resistance above a critical threshold. Nevertheless, this algorithm is open to criticism because, although the numerous overfeeds avoid the anode effects, their high frequency leads to an excess of alumina in the pots causing sludge. This algorithm has never been put into production on an industrial scale. More recently, Zhou et al. [19] used a generalized regression neural network. They also used aggregated input data (13 in total) such as average voltage for the last 3 hours, average voltage for the last 8 hours, average alumina feed rate for the last 24 hours, etc. As output, the model predicts a probability of occurrence of an anode effect in the next 30 minutes. Once again, the number of false positives seems too high to consider applying this method to all the pots in a plant.

7. References

1. Jomar Thonstad, Pavel Fellner, Geir Martin Haarberg, Ján. Híveš, Halvor Kvande and Åsmund Sterten, *Aluminium Electrolysis — Fundamentals of the Hall-Héroult Process*, 3rd Edition, Aluminium-Verlag, 2001, 359 pages.
2. Alton T. Tabereaux, Anode effects, PFCs, global warming, and the aluminum industry, *Journal of the Minerals, Metals and Materials Society*, Vol. 46, No. 11 (1994), 30-34.
3. Helmut Vogt, Contribution to the interpretation of the anode effect, *Electrochimica Acta*, Vol. 42, No. 17 (1997), 2695-2705.
4. Helmut Vogt, Effect of alumina concentration on the incipience of the anode effect in aluminium electrolysis, *Journal of Applied Electrochemistry*, Vol. 29 (1999), 779-788.
5. Helmut Vogt and Jomar Thonstad, Review of the causes of anode effects in aluminium electrolysis, *Aluminium*, Vol. 79, No. 1-2 (2003), 98-102.
6. Jomar Thonstad, F. Nordmo et K. Vee, On the anode effect in cryolite-alumina melts - I *Electrochimica Acta*, Vol. 18, No. 1 (1973), 27-32.
7. Jomar Thonstad, F. Nordmo and J. K. Rødseth, On the anode effect in cryolite-alumina melts - II The initiation of the anode effect, *Electrochimica Acta*, Vol. 19, No. 11 (1974), 761-769.
8. F. Nordmo et J. Thonstad, On the anode effect in cryolite-alumina melts – III Current voltage behaviour during anode effect, *Electrochimica Acta*, Vol. 29, No. 9 (1984), 1257-1262.
9. F. Nordmo et J. Thonstad, On the anode effect in cryolite-alumina melts - IV Gas composition and faradic efficiency, *Electrochimica Acta*, Vol. 30, No 6 (1985), 741-745.
10. Helmut Vogt and Jomar Thonstad, The voltage of alumina reduction cells prior to the anode effect, *Journal of Applied Electrochemistry*, Vol. 32, No. 3 (2002), 241–249.
11. Lukas Dion, Charles-Luc Lagacé, Laszlo Kiss and Sandor Poncsak, Using Artificial Neural Network to Predict Low Voltage Anode Effect PFCs at the Duct End of an Electrolysis Cell, *Light Metals* 2016, 545-550.
12. C. Cheung, C. Menictas, J. Bao, M. Skyllas-Kazacos and B. J. Welch, Frequency response analysis of anode current signals as a diagnostic aid for detecting approaching anode effects in aluminium smelting cells, *Light Metals* 2013, 887-892.
13. Nazatul Aini Abd Majid, Mark P. Taylor, John J. J. Chen and Brent R. Young, Multivariate statistical monitoring of the aluminium smelting process, *Computers and Chemical Engineering*, Vol. 35 (2011), 2457- 2468.
14. N. Aini Abd Majid, M. P. Taylor, J. J. J. Chen, M. A. Stam, A. Mulder and B. R. Young, Aluminium process fault detection by Multiway Principal Component Analysis, *Control Engineering Practice*, Vol. 19 (2011), 367-379.
15. Lucas José da Silva Moreira, Gildas Besançon, Francesco Ferrante, Mirko Fiacchini and Hervé Roustan, Model Based Approach for Online Monitoring of Aluminium Production Process, *Light Metals* 2020, 566-571.
16. Lucas José da Silva Moreira, Mirko Fiacchini, Gildas Besançon, Francesco Ferrante and Hervé Roustan, Modeling and observer design for aluminum manufacturing, *European Journal of Control*, Vol. 64 (2022), 100611.
17. Ron Kremser, Niclas Grabowski, Roman Düssel, Albert Mulder and Dietmar Tutsch, Anode Effect Prediction in Hall-Héroult Cells Using Time Series Characteristics, *Applied Science*, Vol. 10 (2020), 9050.
18. Abdelhamid Meghlaoui, Jules Thibault, R. T. T. Bui, Laszlo Tikasz and Renaud Santerre, Neural networks for the identification of the aluminium electrolysis process, *Computers & Chemical Engineering*, Vol. 22, No. 10 (1998), 1419-1428.
19. K. Zhou, D. Yu, Z. Lin, B. Cao, Z. Wang and S. Guo, Anode effect prediction of aluminum electrolysis using GRNN, *Chinese Automation Congress (CAC)*, Wuhan, China, 2015.

20. A. Johnson et L. Ching-Chung, Wavelet Packet Timeseries Analysis of Aluminum Electrolytic Cells, *Proceedings of The International Society for Optical Engineering*, Vol. 4391 (2001), 228-237.
21. Y. Zhang, Study on Anode Effect Prediction of Aluminium Reduction Applying Wavelet Packet Transform, *Advanced Intelligent Computing Theories and Applications*, (2010), 477-484.
22. W. Haupin, E. J. Seger, Aiming for Zero Anode Effects, *Essential Readings in Light Metals: Volume 2, Aluminum Reduction Technology*, Springer International Publishing, Berlin/Heidelberg, Germany, 2016, 767-773.
23. Thor A. Aarhaug, Alain Ferber, Heiko Gaertner, Steinar Kolås, Sven Olof Ryman, and Peter Geiser, Validation of Online Monitoring of PFC by QCL with FTIR Spectroscopy, , *Light Metals* 2018, 1487-1493.
24. Jomar Thonstad and Sverre Rolseth, Low Voltage PFC Emission from Aluminium Cells, *Journal of Siberian Federal University - Chemistry*, Vol. 10, No. 1 (2017), 30-36.
25. Wangxing Li, Qingyun Zhao, Jianhong Yang, Shilin Qiu and Xiping Chen, On Continuous PFC Emission Unrelated to Anode Effects, *Light Metals* 2011, 309-314.
26. David S. Wong, Paul Fraser, Pascal Lavoie, and Jooil Kim, PFC Emissions from Detected Versus Nondetected Anode Effects in the Aluminum Industry, *Journal of the Minerals, Metals and Materials Society*, Vol. 67, No. 2 (2015), 342-353.
27. Alexander Graham Bell, On the Production and Reproduction of Sound by Light, *American Journal of Science*, Vol. 20 (1880), 305-324.
28. Stefan Palzer, Photoacoustic-Based Gas Sensing: A Review, *Sensors*, Vol. 20 (2020), 2745.
29. Mirsense OEM gas analyser, <https://mirsense.com/liste-produits/371-2/>