

Studies on Background PFC Emission in Hall-Héroult Reduction Cells Using Online Anode

Current Signals

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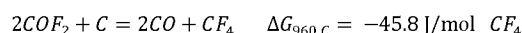
It is well established that maintaining magneto hydrodynamic stability over the life of an aluminium reduction cell is important for achieving optimum performance, and this includes having balanced cell current distribution. Dubai operates at the leading edge of current density, thanks to a state of the art control algorithm which also maintains low PFC emissions. As part of a continuing performance enhancement programme, we have been investigating temporal and spatial changes in cell conditions due to routine activities such as anode set, which can impose uneven distribution of current between operating anodes. During these investigations, we have found the occasional formation of traces of background anthropogenic PFC gases, namely tetrafluoride and hexafluoroethane, commonly referred to as non-AE PFC emissions. Further insights into the causes are presented from these studies.

Introduction

Industry practice has been to increase aluminium production through increasing operating amperage together with a proportional increase in anode size to maintain acceptable anode current density. To satisfy cell energy requirements while operating at higher amperages, cell anode cathode distance (ACD) is reduced which applies further limitation on the availability of electrolyte in a cell. Dissolution of alumina in electrolyte and subsequent mixing depend on several factors such as electrolyte temperature, chemical composition and alumina properties [1, 2]. However, the reduction of electrolyte volume combined with the increase in cell alumina daily shots can over stress the cell's ability to dissolve and mix the electrolyte uniformly. This can lead to concentration polarization on individual anodes where the transfer of oxyanions is inhibited [3, 4]. According to electrochemical principles, as illustrated in Figure 1, a rise in anode potential can enable new electrode products to be formed. It has been shown [2, 5 & 6], fluoride co-evolution can initiate at anode potentials below 2 volts, which is well below the voltage (<8 volt) normally used to define an anode effect in an industrial cell.

Recent studies [7, 8] have also demonstrated that individual anodes undergo a decrease in current prior to initiation of defined anode effects in cells. This indicates that an individual anode is responding to the increased interfacial anode potential whilst the localized voltage is controlled by the cell voltage.

Under such conditions, anode electrodes are more likely to evolve “non AE PFC emission”. Several publications have proposed mechanisms for the formation of non AE PFC emissions [9, 10 & 11]. Fluoride co-evolution starts and can continue indefinitely under certain conditions before the electrode becomes fully passivated and reaches the critical current density [12]. It has been demonstrated [13, 14] that COF_2 evolution can be detected prior to the anode effect onset. Due to its unstable thermodynamic condition, COF_2 can easily decompose at individual electrodes to CF_4



This gives an increase in CO co-evolution as has been observed [12] and simultaneously depolarizes the enabling reaction.

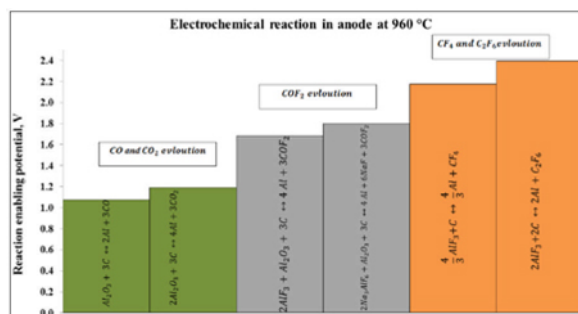


Figure 1: Electrochemical Potential gradients between surface anode electrode and electrolyte (v's Al ref.) corresponding products enabled.

Although “non AE PFC emissions” are not commonly measured in industry, Dubai Aluminium has contracted several independent studies as part of its overall efforts to reduce PFC emissions so it continues retaining its position as one of the leading smelters in operating cells at high

anode current density. Early surveys indicated our background emission was equivalent to 9 kg CO₂e / tonne of Al [15] versus the industry average equivalent of 404 kg CO₂e in 2013 [16], excluding background values in the calculations.

AE's, Non AE PFC emission, Background PFC's

Anode effects. Anode effects (AE's) are not unique to Al smelting and were discussed in literature for more than 30 years before aluminium smelting started. Bunsen [17] is generally acknowledged as the first person to observe an anode effect when he was trying to produce calcium metal by electrolysis molten calcium chloride in 1854. Throughout the literature there are three common indicators for anode effects, these being:

1. They are always associated with a rapid rise in cell voltage if operating at constant current. The interfacial gradient is sufficient for arcing to occur at the interface.
2. They are always associated with a dramatic reduction in current (towards zero) if operating under voltage limitation.
3. When measured, the potential gradient at the anode /electrode interface exceeds that necessary for fluorocarbon emissions.

Anode effects in molten salt electrolytes are always associated with carbon electrodes and pure halide or halide oxide mixtures [12, 18]. This combination clearly indicates the anode effect is associated with passivation of the electrode by a resistive surface film of reaction intermediates, but this film can be removed through the extra interfacial energy provided by the increased voltage and arcing. It is likely this is providing the extra enthalpy energy required for the entropic energy [19] and to accelerate the kinetics of the reaction intermediates.

Non AE PFC emission. What has been described as non-anode effect PFC emissions in recent times is confined to single or multiple parallel electrode cells operating under a controlled total cell voltage but with variations possible in electrolyte properties, or current/ current density. These tend to occur in the anode potential range where formation of COF₂ is enabled and are associated with the evolution of extra CO [12] and CF₄. Under such conditions complete passivation of the electrode has not occurred.

These observations clearly indicate that the onset of PFC emissions is linked with changes in the interfacial potential of individual anodes, occurring at a rate that does not necessarily fully passivate the electrode and initiate a complete AE.

Electrochemical fundamentals and detailed polarization studies indicate the most likely variables for bringing about this change during Al electro-winning include depletion of interfacial alumina concentration, changes in temperature,

excess aluminium fluoride concentration, current density and anode quality.

Background PFC's. This is probably inappropriate terminology as it implies continuous evolution within the cell. It is more likely to be intermittent unless a cell operates at very low average alumina concentration. Otherwise the emissions would be no different than "non AE PFC emissions".

Operating conditions that can change an individual anode potential include anode replacement and setting operations, depletion of electrolyte depth or volume, spatial or temporal variations in temperature or excess AlF₃ concentration, and barriers to alumina dissolution or electrolyte mixing. The aim of this work is to gain further understanding specifically on the spatial and temporal effects of anode setting practice and bath levels. This includes the consequential spatial MHD effects.

Experiment set up

Experimental investigation was performed on a modern magnetically compensated cell fitted with individually controllable point feeders and having the sensor of a Gasmeter DX4000 FTIR analyser positioned in the duct of the exhaust gases from the cell. The cell was fitted with an individual anode current monitoring system with the ability to sample at a high rate without filtering. The latest control Dubal logic was employed which included careful energy management. In order to enter the region where "non AE PFC's" could be generated, the cell's average alumina concentration was reduced to less than the desired target.

Part 1: PFC emission during anode setting.

It is well established that when new anodes are introduced to the cell they immediately form a freeze layer between the metal pad and the newly set anode surface which effectively insulates it, preventing significant electrochemical current flow in that zone. Not only does this impact the localised MHD stability and metal pad profile within the cell but it also results in a redistribution of the fixed total cell current, changing the electrode current densities, especially for the anodes near the newly set one. The anode change also introduces spatial and temporal effects within the cell that impact properties that cause changes in electrode potential. For example the freeze layout impacts the electrolyte flow and mixing of the alumina from feeders, but with this effect being different for different anode stall locations.

The thermal effect of anode setting also impacts the superheat and this can impact the dissolution of the alumina through any affected feeder holes. Consequently whilst it is normally expected each electrode operates under similar conditions of electrode potential and electrolyte compositions, during this period the behaviour of the individual anodes, and their potentials, will be quite individualistic. Some of them risk moving to a condition whereby the electrode potential could change to that necessary for PFC evolution.

The first part of this investigation was to determine how stall location of the anode impacts the current pickup of new anodes and what the current redistribution was likely to be. A large number of new anodes which were set at a predetermined fixed reference were recorded. Figure 2 shows the typical pickup of current in three anodes. The pickup rate varied with stall location, but it always required a minimum of 24 hours to reach the target current.

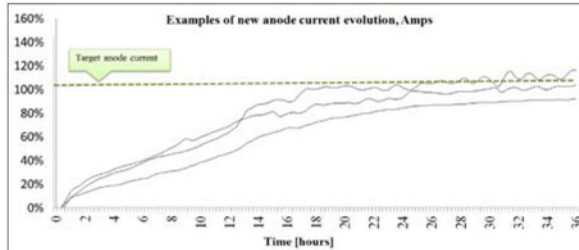


Figure 2: New anode current evolution

During the study some anodes were removed at different stages and from this that it can be concluded that the initial increase in current pickup is associated with the dissolution of the freeze on the sides of the anodes rather than the base (refer to Figure 3).

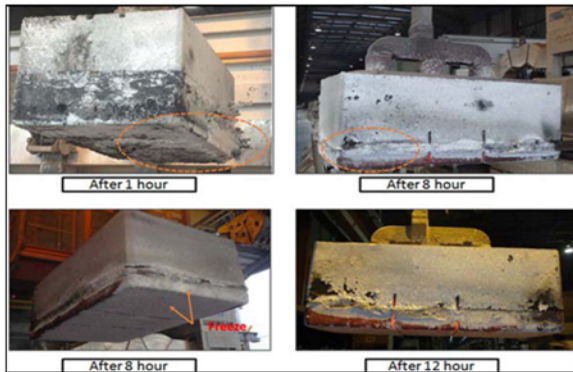


Figure 3: Anode freeze re-melting process following changing a new anode

Response to a double set.

In order to study the impact of changed conditions through anode setting, the duct gas composition was continuously monitored as well as the current of all anodes following a double anode set.

Figure 4 shows that the double anode set initiated PFC evolution under the experimental conditions, even though the emissions occurred on anodes in other stall locations. The change was obviously associated with changed electrolyte conditions since there was a time lag for the appearance of PFC's, and they appear well before the current density of the new anodes was significant enough. However it also shows other phenomenon occurring which cause PFC emissions later.

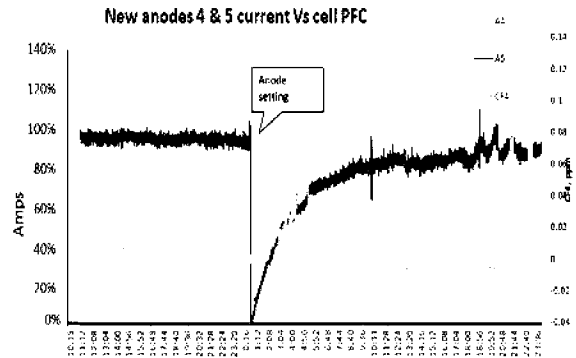


Figure 4: Non AE PFC emission analysis following double anode setting (Anodes 4 & 5)

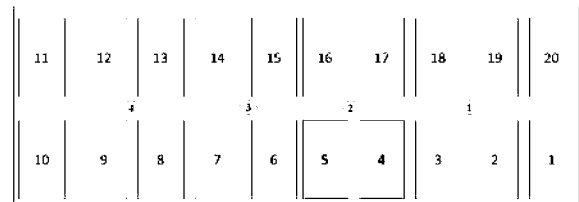


Figure 5: Anodes layout location in studied cell

During this anode change the cell control curves and behaviour were normal as illustrated by the voltage time curves in Figure 6.

While CF_4 appeared following anode change and remained measureable for 4-5 hours, this occurred despite the cell voltage remaining below 8 volts. Variations in cell voltage while anode setting are illustrated in Figure 6.

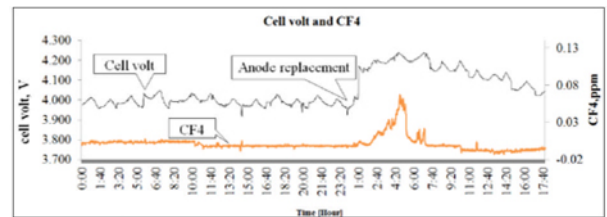


Figure 6: Cell volt and occasional CF_4 emission upon anode setting

The resulting redistribution of the current following anode set is shown by comparing the average current of each anode two minutes before starting the set to the two minute average 30 minutes after anode setting activity. This is plotted in Figure 7.

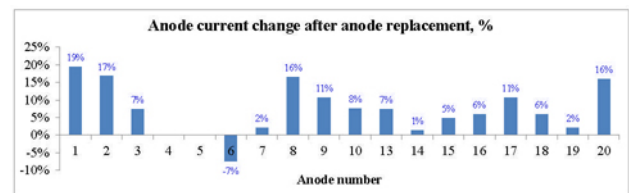


Figure 7: anode current of anodes before/after anode setting

It is observed that except for the neighbouring anode #6 all other anodes show an increase in current but of varying magnitude. This also shows the greatest increase in current after set occurred for anodes 1, 20 and 8. Anode 8 was adjacent to the feeder and also relatively far away from the zone where the anode changes were carried out. Therefore the impact of the decrease in super heat on the alumina solubility in that zone would be small. Furthermore this would be aided by the extra inter-electrode bath volume and the increased local heat generation resulting from the higher anode cathode spacing plus higher current density. Therefore alumina dissolution and mixing in that zone would be good. Some of the same arguments can be used for anodes 1 and 20 which are at the end of the cell. However, it is worthwhile to note that these anodes are located in zones where the metal pad velocities are higher and consequently local heat transfer and mixing will also be enhanced.

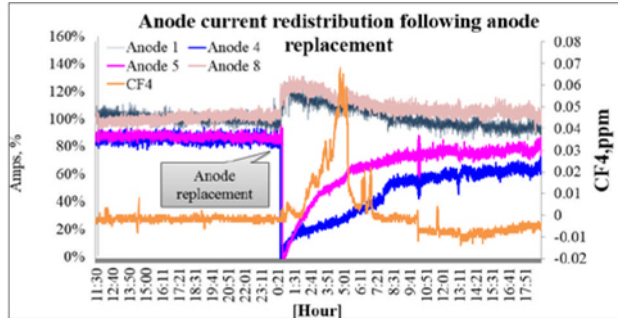


Figure 8: Illustration of current redistribution following anode replacement.

The redistribution of current decayed substantially after seven hours and this coincided with the disappearance of the PFC's (Figure 8). At this time the current flowing through the newly set anodes was between 40 & 60% of final target and rising at a decreasing rate.

After more than 12 hours the current through some of the anodes appeared to develop a cyclical wave, and this initiated a small increase in background PFC again (see right hand side of Fig. 8). Initiation of the cyclic behaviour coincided closely with the completion of the reduction of the anode setting voltage.

Removing the anode set voltage would result in another change in bath flow and mixing. This coincides with the circled region of the control curves presented in Figure 9.

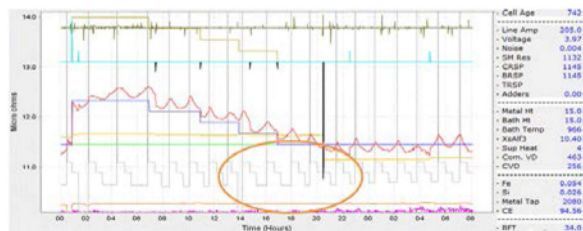


Figure 9: Highlighting the alignment of the initiation of the superimposed cyclic behavior in the newly set anodes with the minimization of anode-cathode spacing.

As has been found in other studies [25] cyclic individual anode current patterns occur through redistributions of current when the electrode potentials are impacted through spatial alumina concentration gradients. The anodes that are deficit in alumina show a decrease in current during the under-feed and those with adequate alumina shed load and increase current.

This effect is clearly demonstrated by two of the anodes (anodes 1 and 8) that had significant increases in current following the anode set, as shown in Figure 10.

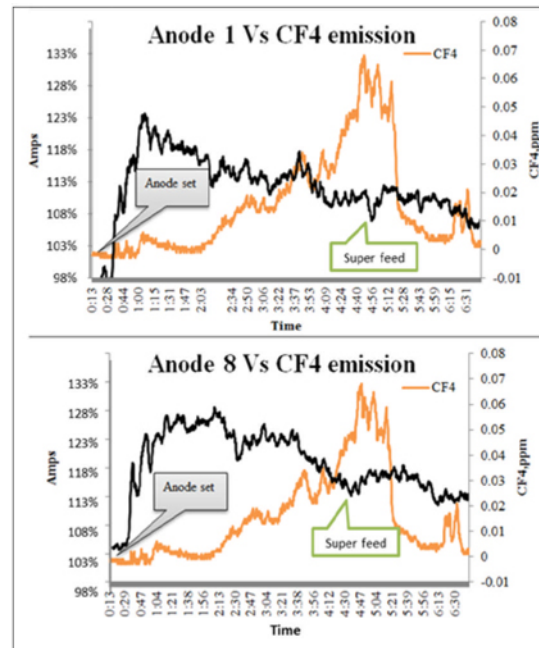


Figure 10: Anodes 1 & 8 current dynamic with respect to CF4 emission following anode replacement activity

The general explanation given above is also supported by the metal velocity profiles from the MHD model of this cell, (see Figure 11). These show that the back wall area of Anode 6 experiences relatively slow movement which suggests lower heat transfer from metal to bath [22] during the double anode setting of anodes 4 and 5.

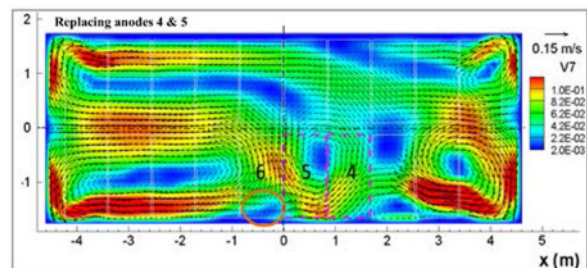


Figure 11: Metal velocity profile in the cell after replacing anodes 4 & 5, [23]

Furthermore, the sudden reduction in the temperature of neighboring anodes due to anode replacement will lower superheat, hindering alumina dissolution and electrolyte mixing.

In terms of changes in metal contour profile after replacing Anodes 4 & 5, it is seen the anode 6 area does not experience a dominant change, (see Figure 12).

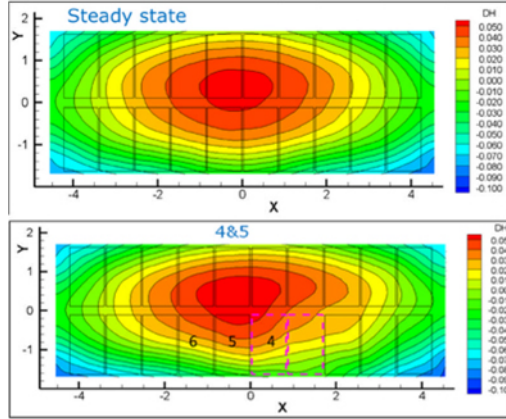


Figure 12: Metal contour profile in the cell after replacing anodes 4 & 5, [23]

Part 2: The impact of electrolyte volume / higher current density on non AE PFC emission

The continuous increase in anode size of modern cells in order to maintain acceptable current density while increasing operating amperage has resulted in reducing the amount of electrolyte volume. Moreover, it results in a narrower central channel which impacts alumina dispersion and homogeneity in the electrolyte [24]. This issue is magnified in this cell because of the low ACD and cell energy input. Consequentially, it would have a higher propensity for rapid anode electrode polarisation increases which result in non AE PFC emissions.

Trial set-up – Part 2

The first phase was to ensure the cell had an adequately balanced current and was operating at normal voltage, but with 3 cm less depth of electrolyte. The alumina feeding and control parameters were such that the average alumina concentration was lower than normal.

Non AE PFC emission remains measurable while operating with these conditions. However, once a bath transfer was used to restore target electrolyte level, an immediate reduction in cell non AE PFC emission occurred as seen in Figure 13. Throughout the experiment the cell current distribution was fairly even and did not fluctuate significantly as is normally experienced when a single anode starts emitting low levels of PFC's.

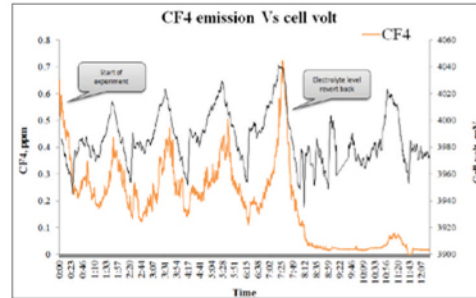


Figure 13: Cell non AE PFC emission against cell volt

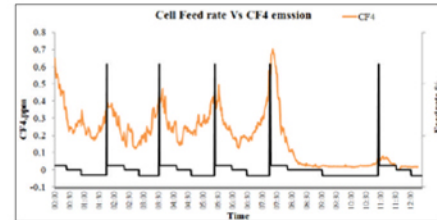


Figure 14: Cell non AE PFC emission at different feed window

It is observed that the non AE PFC emission (CF_4) and cell voltage has the same cyclic behaviour. With successive cycles there is a progressive increase in amplitude, this being due to a progressively small decrease in alumina concentration arising from the faster rate of change during underfeed for the changed conditions, (see Figure 14).

The background PFC evolution immediately reverted to zero level once liquid electrolyte was added to return the level to target, thus lowering the current density and anode potential simultaneously.

Discussion & Conclusions

The results presented in this study clearly demonstrate that background PFC emissions are both repeatable and reversible and can be initiated by a number of work practices that trigger process condition changes. These changes can be throughout the cell or localized, some of a short term nature and others long lasting, unless the root-cause is rectified. They include alumina concentration, current density, superheat, electrolyte flow and mixing conditions, and conditions that impact the feeding, dissolution and dispersion from feeder locations.

Each of these variables alters the electrode potential individually for each anode. It has been demonstrated that when the electrode potential exceeds ~ 1.85 V, the reversible Al/Al^{3+} electrode formation of COF_2 is enabled [12,13] although it readily decomposes to CO and CF_4 [13]. Conversely anode potentials above ~ 2.1 V enable direct formation of CF_4 , and this is known to rapidly passivate the electrode and initiate a full anode effect. In support of this it has been demonstrated by [26] that there is a stable potential zone between where carbon oxides are evolved and that at which an anode effect occurs which enables background PFCs to be co-evolved in a stable manner. Since the trend to operate at high current densities

automatically narrows the window before PFC evolution initiation, cell control and work practices need to be modified.

Minimising spatial concentration gradients and changes in superheat are needed through improved design and work practices.

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References

1. O. Kobbeltvedt, S. Rolseth, J. Thonstad. The dissolution behaviour of alumina in cryolite bath on a laboratory scale and in point fed industrial cells. Department of Electrochemistry, Norwegian Institute of Technology, N-7034 Trondheim, Norway SINTEF Materials Technology, N7034 Trondheim, Norway'
2. R. G. Haverkamp, Surface studies and dissolution studies of fluorinated alumina. PhD thesis, University of Auckland, 1992
3. N.E. Richards, and B.J. Welch. "Anodic Overpotentials and Mechanisms of the Anode Process on Carbon in Cryolite-Alumina Electrolytes". In *"Electrochemistry" Proc. 1st Australian Conference*, (Eds. Gutmann and Friend), Pergamon Press, pp 901-922 (1964).
4. W.E. Haupin, "Polarization in an Aluminium Reduction Cell", *Journal of the Electrochemical Society*, 174-178, 1956.
5. E.J. Frazer, and B.J. Welch, "Reactions Occurring at the Anode During Aluminium Electrowinning", *Proc. Aus. I.M. & M.*, 260, pp. 17-22 (1976).
6. A J Calandra, C.E. Castellano, C M Ferro, and O Cobo "Experimental and Theoretical Analysis of the Anode Effect in Industrial Cells" *TMS Light Metals 1982*, p345 – 358.
7. A. Lützerath, J. Evans and R. Victor, On-line monitoring of anode currents: experience at Trimet, *TMS Light Metals, 2014*, pp. 739-741.
8. D. S. Wong, A. Tabereaux, P. Lavoie, "Anode effect phenomena during conventional AEs, low voltage propagating AEs & non-propagating AEs," *TMS Light Metals, San Antonio, TX*, pp. 529–534, 2014.
9. A.A. Zarouni, and A.A. Zarouni. "DUBAL's Experience of Low Voltage PFC Emissions," *10th Australasian Aluminium Smelting Technology Conference*. 2011. Launceston, Tasmania.
10. Chen X., Li W., Zhang Y, Q. "Investigation on formation mechanism of non-anode effect related PFC emissions from aluminium reduction cells," *TMS Light Metals, San Antonio, TX*, pp. 877–881, 2013.
11. Li W., Chen X., Yang J., Hu C., Liu Y., Li D., Guo H"Latest Results from PFC Investigation in China," *TMS Light Metals, TMS, 2012*, pp. 617-622.
12. D. M Stütt "A study of anode reactions during the electrolysis of divalent metal oxides in molten fluoride solvents" PhD thesis UNSW (1971).
13. M. M. R. Dorreen, "Cell performance and anodic processes in aluminium smelting studied by product gas analysis". PhD thesis, The University of Auckland, 2000.
14. Ole S. Kjos, Thor A. Aarhaug, Henrik Gudbrandsen, Asbjorn Solheim and Egil Skybakmoen, "Fundamental studies of perfluorocarbon formation,"*10th Australasian Aluminium Smelting Technology Conference*. 2011. Launceston, Tasmania.
15. Abdalla Zarouni, Reverdy M., Ali Al Zarouni, K.G. Venkatasubramaniam, "A study of low voltage PFC emissions at Dubai" *TMS Light Metals, TMS, 2013*, pp 859-863.
16. "Results of the 2013 Anode Effect Survey", International Aluminium Institute, London, U.K., <http://www.worldaluminium.org>, Publications.
17. R Bunsen . *Annag*. 92 (1854) p 251.
18. C Krohn, "On the Anode Effect in Some Fused Chloride Mixtures" PhD thesis NTNU (1965)
19. A. Solheim "A Practical implication of some interfacial processes in alumina reduction cells" *11th Australasian Aluminium Smelting Technology Conference*. 2014. Dubai, UAE.
20. M. Segatz, C. Droste and D Vogelsang.. Magnetohydrodynamic effect of anode set pattern on cell performance. *TMS Light Metals, TMS, 1997*, pp 352-358.
21. Ali Jassim, S Akhmetov., B. Welch, M. SkyllasKazacos, Jie Bao, Yuchen Yao, "Studies toward balancing the current in smelting cells," *11th Australasian Aluminium Smelting Technology Conference*. 2014. Dubai, UAE.
22. G. Vanderlei, "Modelling the mass and energy balance of aluminium reduction cells" Ph.D. thesis, School of Chem. Eng., University of New South Wales, Australia, 2014.
23. A. Arkhipov, "Calculation of metal heave and metal velocities for different AS patterns in D20 technology". Industrial presentation in Dubai aluminum, Dubai, 2011.
24. R Kaenel, Jacques Antile, V. Romerio, B. Olivier, "Impact of magnetohydrodynamic and bubbles driving forces on the alumina concentration in the bath of an Hall-Héroult cell". *TMS Light Metals, TMS, 2013*; pp 585-590.
25. C. Y. Cheung Private communications (2014).
26. H Asheim, T Aarhaug, A Ferber, O Kjos & G Haarberg. "Monitoring Continuous PFC Formation in Small to Moderate Size Aluminium Electrolysis Cells" *TMS Light Metals 2014*, pp. 535–539.