

CURRENT EFFICIENCY STUDIES IN A LABORATORY ALUMINIUM CELL USING THE OXYGEN BALANCE METHOD

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Abstract.

There have been many studies investigating the effects of various parameters on the current efficiency in aluminium smelting cells. One of the most important and most widely debated of these parameters is alumina concentration, because of its implications in feed strategies and cell management. This paper presents the results from a study investigating the effects of alumina concentration, bath chemistry, current density and anode-cathode spacing on current efficiency. Gas emissions from a laboratory scale cell were measured by on-line mass spectrometry, current efficiency was determined by an oxygen balance method.

Electrolysis was performed from various starting alumina concentrations of 6 - 8 wt% until anode effect was reached. After initial start-up periods there was no variation in current efficiency as the alumina was depleted and anode effect approached.

Increasing the cryolite molar ratio, in agreement with other reports, has a strong negative effect on current efficiency. Results also show a strong increase in current efficiency with increasing current density. No effect of electrode spacing was detected.

Introduction.

For simple economic reasons there is a drive to maximise current efficiency, the measure of how efficiently the vast electric currents are used to reduce alumina into aluminium. There has been considerable effort made to study current efficiency, both in laboratory and real cells [4-6,11-13], using a variety of methods and in both batchwise and continuous modes.

There have been many previous studies on the alumina concentration-current efficiency relationship, with somewhat conflicting results. The results of some of the earlier studies are listed by Lillebuen et al. [2], which all report either a current efficiency minimum or linear increase with increasing alumina concentration. Grjotheim et al. [3] reviewed laboratory studies, most of which indicate a current efficiency increase with increasing alumina concentration or a minimum from 4-8 wt% alumina. Leroy et al. [4] directly contradicted those findings by showing that current efficiency increased strongly when the alumina concentration decreased. Alcorn et al. [5] summarised the methods used in a large number of current efficiency studies on industrial cells. More recently Solli et al. [6] provided a good review of studies investigating current efficiency with alumina concentration, temperature, bath chemistry, anode-cathode spacing and current density. They report their results, showing current efficiency increasing with current density, decreasing with cryolite ratio, and being unaffected by both anode-cathode

spacing and alumina concentration. These experiments were of the batch type and the efficiency was calculated by weight gain of cathodic metal.

The effect of bath chemistry on current efficiency has also been widely reported and reviewed [3,6,8,9,12,13]. It has clearly been shown that there is an increase in current efficiency with decreasing cryolite ratio (increasing excess AlF_3 content in the electrolyte), generally attributed to the decreased solubility of aluminium in lower ratio electrolytes.

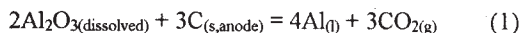
The objective of the work presented here was to develop a system for measuring current efficiency on a laboratory scale cell using the continuous oxygen balance method, and to study the effect of changing cell parameters. The focus has been on obtaining rapid current efficiency measurement, so that the effects of changes in the cell can be seen instantaneously.

A key feature of the equipment is that experiments can be run from a starting alumina concentration and then with electrolysis the alumina is depleted until anode effect occurs. In this way a single experiment covers a range of alumina concentrations, rather than discrete experiments at different concentrations.

An advantage of the system developed is that it also allows other studies to be made, such as of other gases given off during electrolysis and of particular interest anode effect emissions. The oxygen balance current efficiency method is also not confined to the laboratory, it would be possible to refine the equipment and use the method on an industrial cell.

Theory

The main reactions occurring in an alumina reduction cell are the primary reaction producing aluminium metal:



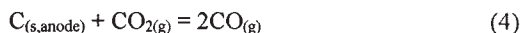
and the main back reaction causing a loss in aluminium metal:



Assuming that these are the only reactions that occur in the cell, the current efficiency can be calculated from the well known Pearson-Waddington equation [7]:

$$\begin{aligned} \text{CE} &= 1 - 0.5(\% \text{CO}_{(\text{gas})}) \\ &= 0.5 + 0.5(\% \text{CO}_{2(\text{gas})}) \end{aligned} \quad (3)$$

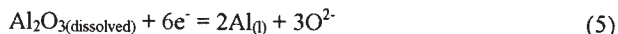
The Pearson-Waddington equation has traditionally been used to calculate current efficiency, with previous studies using various gas analysis techniques to obtain the CO and CO_2 gas concentrations. However, due to the occurrence of the Boudouard reaction (4) to a varying and unknown



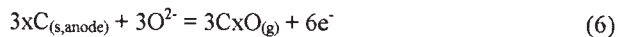
but significant extent [15], and the possibility of numerous other reactions that either consume current or alter the ratio of carbon dioxide to carbon monoxide, use of the Pearson-Waddington equation introduces an error in to the calculation of current efficiency. With the Boudouard reaction favouring the production of CO at the temperatures encountered inside the cell,

and the incorrect assumption of only reactions 1 and 2 occurring, the Pearson-Waddington equation becomes invalid.

If the reduction of alumina is written as two half reactions, then at the cathode alumina is reduced producing aluminium:



and at the anode carbon is oxidised:



According to Faraday's law, at the cathode a known cell current will deposit a known amount of aluminium metal, and a known amount of oxygen will be liberated from the anode. If the current is integrated with time, then Faradays law can be used to calculate the total amount of aluminium that should have been produced. The current efficiency can be calculated by weighing the actual amount of aluminium produced and comparing to the theoretical amount, as is practiced in smelters. This batch-wise method has been used in many laboratory studies, but has limitations that a continuous method overcomes. If the oxygen liberated from the cell can be measured, then a mass balance can be made to determine the efficiency based on oxygen instead of aluminium.

The anodic half-reaction (6) shows that the oxygen liberated is not bound in any particular form. Thus the oxygen balance method calculates the current efficiency by comparing the total net oxygen production from the actual cell (regardless of the form of this oxygen when analysed) to the theoretical oxygen that should be produced from the cell current. In a similar way a carbon mass balance can be made around the cell to calculate the carbon consumption independently of the current efficiency.

Obviously when performing an oxygen mass balance around an industrial cell all of the sources of oxygen entering the cell from pot-room air must be accounted for, as must any leakage of cell reaction products from the cell other than in the duct gas. However when using a laboratory cell the oxygen mass balance around is considerably simpler, as there is no external source of or oxygen if the cell is sealed and inert conditions are maintained. Simply, the total oxygen contained in the gas flushed from the cell is compared to the theoretical oxygen to give a continuous measure of the current efficiency. The occurrence of any of the unwanted reactions mentioned earlier does not affect the current efficiency as they are all accounted for in the oxygen balance. The current efficiency can be measured continuously if the gas is purged and analysed on-line.

Equipment & Procedure

A detailed description of the equipment and procedures developed and used is given in reference 1. Briefly, a laboratory furnace is used to house a small scale cell, electrolysis is performed, the gases produced are continuously flushed from the cell and analysed with a mass spectrometer.

The significant difference between this cell and many previous ones is the larger size. The crucible/cathode has internal diameter 138mm, and with boron nitride shielding on the sides an anode of 75mm diameter can be accommodated. This allows currents of up to 75 amps to be passed through the cell, so the

amount of off-gas generated is large, aiding analysis. Also a larger volume of electrolyte can be contained, so longer electrolysis times before anode effect are possible. The cell is shown in figure 1, illustrating the BN shielding on the sides of the cathode to eliminate horizontal current and over the top of the anode to reduce reactions with exposed carbon. The cathode BN shield also increases the cathodic current density. The carbon anode is suspended into the electrolyte from the lid above, and temperatures are measured at the top of the anode, cathode and in the electrolyte.

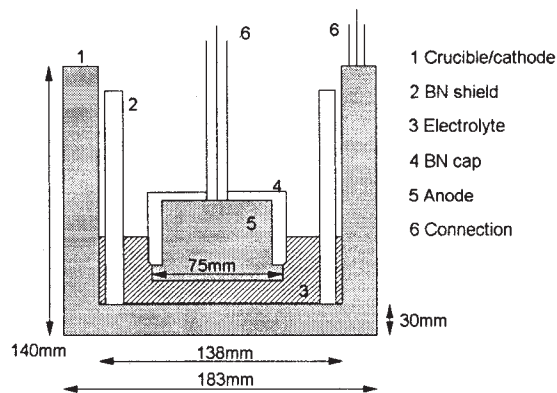


Figure 1: The electrolysis cell.

The cell is placed in an inonel container which is sealed with a gas tight lid, as shown in figure 2. The gas inlet and outlet ports allow for continuous purging of the cell with argon, and the electrolyte access port allows samples to be taken before electrolysis is started and after anode effect is reached, giving accurate alumina concentrations.

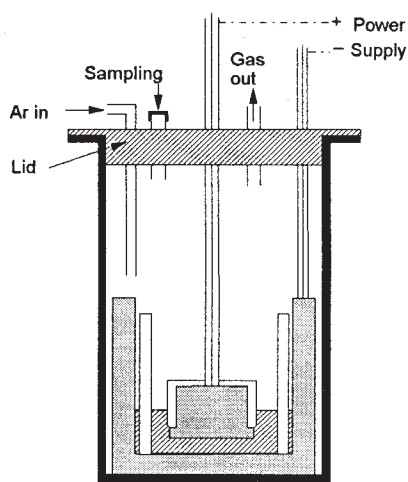


Figure 2: Furnace container, lid and electrolysis cell.

The gas analysis is performed using a mass spectrometer operated in tabular mode to follow up to twelve gas species simultaneously. The instrument is calibrated at the start and end of each experiment to account for any drift, and corrections are made for ion fragmentation and overlapping peaks.

Experimental Conditions.

The mass spectrometer data from each experiment is processed by an algorithm to provide results in the form of concentrations of CO and CO₂ and the current efficiency with respect to time (increasing time corresponds to depleting alumina concentration).

The conditions used for experiments were:

Cell current (A):	20, 37.5, 58, 75
Anode current density (A/cm ²):	0.295, 0.554, 0.856, 1.107
Cathode current density (A/cm ²):	0.210, 0.395, 0.610, 0.789
Anode-cathode spacing (mm):	30, 35, 40, 45
Excess AlF ₃ (wt%):	0.0, 2.7, 8.2, 9.0, 11.7, 15.0
Cryolite molar ratio:	3, 2.78, 2.39, 2.33, 2.17, 1.99
CaF ₂ (wt%):	4.0
Starting Al ₂ O ₃ (wt%):	6.0 - 8.1
Cell temperature (°C):	965 - 985
Electrolyte superheat (°C):	10 - 25

Results and Discussion.

Cell Performance.

The anode gas concentrations are calculated for each experiment. An example is given in figure 3, showing the carbon monoxide being of higher concentration than the carbon dioxide. This is typical of all the experiments, as is the shape of the curves, especially the rise in CO and drop in CO₂ in the last few minutes before anode effect is reached.

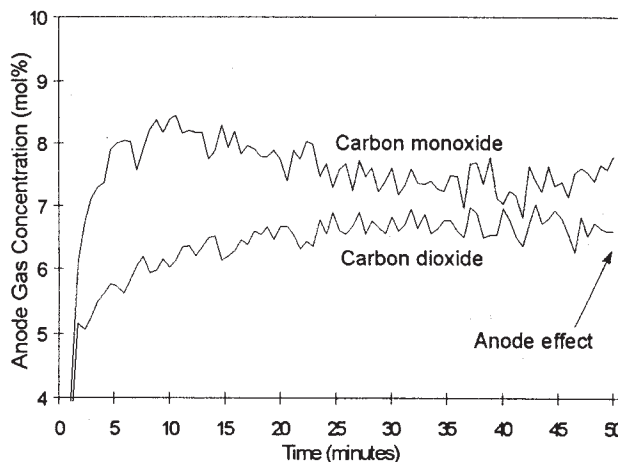


Figure 3: Typical anode gas concentration for the duration of an experiment.

It is thought that the initial large difference in the amounts of CO and CO₂ may be due to the condition of the anode carbon. A new anode is used for each experiment, machined from an anode butt from a smelter. The initial anode surface is new, and there may be preferential consumption of the binder pitch until an equilibrium state is reached. According to Sadler et al. [10] CO formation is favoured on the less ordered carbon in the anode

structure. Also the Boudouard reaction occurs preferentially with binder carbon.

From these gas concentrations the current efficiency is calculated, as shown in figure 4. The current efficiency calculated by the Pearson-Waddington equation is also shown for comparison. There is a significant difference, obviously due to the inability of the P-W equation to account for the high CO concentration, formed by the Boudouard reaction and possibly electrolytically at lower current density areas such as the sides of the anode. The oxygen balance gives a current efficiency with a greater deviation. Both calculations are based on the same gas concentration data, but the oxygen balance also uses a gas flow rate term. This is back-calculated from the gas flow into the cell, and causes the increase in the deviation. The flow rate must be back-calculated because of the difficulty in measuring it directly, on-line, and without causing interruption of the flow to the gas analyser.

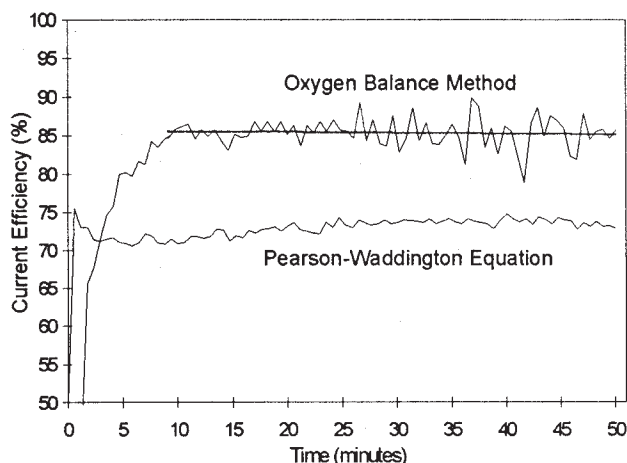


Figure 4: Current efficiency calculated by the oxygen balance method and Pearson-Waddington equation.

It was thought that the saw-tooth type variations in gas concentrations could be caused by the bubble release frequency being similar to the gas analysis frequency. This could have been falsely adding to the variation in the current efficiency measurement. The bubble release frequency was determined by measuring the voltage rise and fall due to the formation and release of bubbles under the anode. At $1.107\text{A}/\text{cm}^2$ current density it was approximately 0.9Hz , many times more frequent than the gas analysis, as the mass spectrometer sampled every $35\frac{1}{3}$ seconds (0.0283Hz). Thus many bubbles were released and mixed between gas samples. Even at the lowest current density used the bubble release was still an order of magnitude faster than the gas sampling. Therefore the variation in gas concentration is real and not affected by the bubble release frequency from the cell.

With the oxygen balance method there is an initial period when the current efficiency builds up before reaching a steady value, a trend that was also seen by Castellano et al. [11]. There is some gas mixing as the anode products blend with the purging flow, and some resistive heating of the electrolyte, which may contribute to this starting effect.

The overall current efficiency value for each experiment was obtained by averaging the readings after an initial 10 minute period. This current efficiency then encompassed an alumina concentration range of at least 4 wt%.

Current efficiencies were obtained ranging from 70 to 90%, which is at the low end of efficiencies for real cells but similar to other laboratory cell studies, especially those without a cathodic aluminium pad. There was good agreement between current efficiencies determined by the gas analysis/oxygen balance method and calculated from the starting and final Al_2O_3 concentrations.

The lack of a metal pad at the start of each experiment meant that as aluminium was produced it would have formed small droplets on the non-wetting cathode surface. This increased the mass transfer area between aluminium and electrolyte, so allowing a greater opportunity for back reaction and current inefficiency. This was reflected in the relatively low current efficiencies observed, but was expected by design.

The trends observed for current efficiency with cryolite ratio and current density discussed below agree well with many previous studies. This gives further confidence that the method is working correctly and the current efficiency values gained are reliable.

The high currents used meant that resistive heating of the electrolyte was observed. Because of this it was difficult to accurately control the electrolyte temperature during electrolysis, so the effect of temperature on current efficiency could not be determined with the present arrangement.

Anode-Cathode Spacing.

Experiments were performed with an anode current density of $1.107\text{A}/\text{cm}^2$ (75 amps) and excess AlF_3 of 8.19 or 9 wt%. The effect of anode-cathode spacing on current efficiency is shown in figure 5.

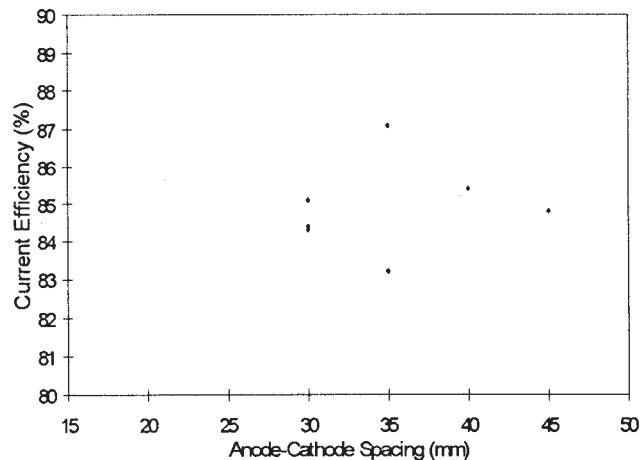


Figure 5: Effect of anode-cathode spacing on current efficiency.

There is clearly no discernible effect of electrode spacing. This is to be expected by the design of the cell, as with no cathodic metal pad the mass transfer conditions will be the same at all the

electrode spacings used. No attempt was made to determine if there was any limiting or critical electrode spacing as this would have required much smaller electrolyte volumes resulting in shorter electrolysis times. The strength of this method is the ability to measure the current efficiency over a longer period as the alumina concentration is changing. It is expected that the critical spacing for this cell would be very small, as there is no metal pad to disturb and become unstable, as opposed to a real cell where the metal pad wave can cause droplets of aluminium to break free and circulate in the electrolyte.

Current Density.

The average current efficiencies from different current density runs are shown in Table 1. Each run was performed under constant current conditions with the voltage floating until anode effect was reached.

Table 1: Average current efficiencies as a function of anodic current density.

Current density (A/cm ²) (Current A)	Current Efficiency (%) (Std. Dev.)	Current density (A/cm ²) (Current A)	Current Efficiency (%) (Std. Dev.)
0.295 (20)	71.3 (2.55)	1.107 (75)	85.4 (1.82)
0.295	69.2 (2.75)	1.107	84.8 (1.78)
0.554 (37.5)	77.0 (2.11)	1.107	83.2 (2.47)
0.554	76.1 (1.96)	1.107	84.4 (1.84)
0.856 (58)	80.9 (2.82)	1.107	84.3 (1.58)
1.107 (75)	87.1 (1.95)	1.107	85.1 (3.05)

This data is plotted in figure 6. The gradient appears to be at the higher end of the range of laboratory studies shown by Grjotheim et al. [14], but agrees well with the predominant increasing trend.

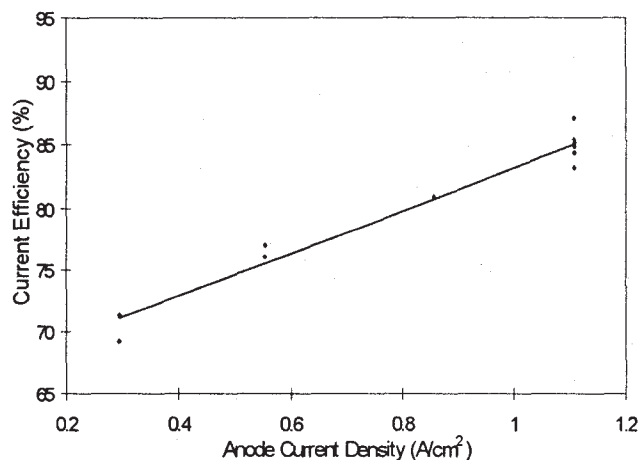


Figure 6: Effect of current density on current efficiency. Gradient = 17.25, linear fit R² = 0.9617.

The large effect on current efficiency may be accentuated by the mass transfer conditions present in the cell. At the lower current densities the aluminium produced will form into droplets more slowly, thus there will be a greater ratio of surface area to volume, effectively giving a larger mass transfer area for the metal to dissolve. No drop-off in current efficiency was detected at lower current densities as been seen by some previous studies.

Bath Chemistry.

The cryolite molar ratio was varied at the same current density (1.107A/cm²) by changing the excess AlF₃ in the electrolyte. The extremes were 0 and 15wt% AlF₃ (CR = 3, 1.98), with the majority experiments at 8.19 or 9wt% (CR = 2.35).

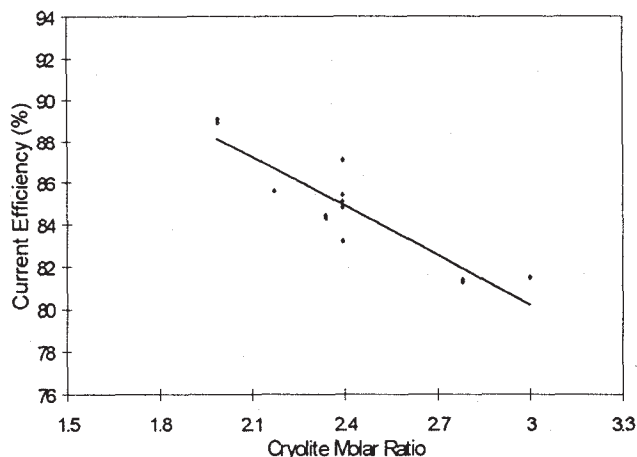


Figure 7: Effect of cryolite ratio on current efficiency. Gradient = -7.84, linear fit R² = 0.8093.

The results are given in figure 7, showing a clear pattern. The trend of increasing current efficiency with increasing excess AlF₃ is well established, and is not surprising as the solubility of aluminium is decreased in the lower ratio electrolytes. As well as being shown in many specific laboratory studies, the trend has also been observed in smelters as a result of operational changes. Kvande [8] describes a current efficiency increase as the AlF₃ was increased on a 180kA cell line. Welch [9] shows graphically the clear response of current efficiency to a step increase in excess AlF₃ for an entire smelter. Welch also demonstrates another advantage of higher excess AlF₃, which is a lower concentration of contaminant metal (calcium, lithium and magnesium, from their fluoride additives) in the aluminium produced. This can be an important consideration when the goal is production of high purity aluminium.

Alumina Concentration.

The technique involved measuring current efficiency as a function of time as the alumina concentration is depleted from its preset initial value and electrolysis was invariably continued until an anode effect occurred. From a knowledge of the initial mass of electrolyte and alumina, and also the analysed final alumina concentration, the total number of moles of alumina

electrochemically removed can be calculated. This gives an integrated overall measure of current efficiency for the duration of the experiment. For the series of experiments conducted, the integrated instantaneous values of current efficiency compared well with the values determined by the alumina depletion.

Figure 8 displays the current efficiency for three experiments with 9wt% excess aluminium fluoride but with different starting alumina concentrations. In order to prevent confusion in the data points (because of good repeatability), the three curves are offset and the left hand abscissa gives the absolute efficiency for each curve, whereas the right hand scale can be used to calculate the change in efficiency. There are three basic characteristics of the curves. Initially the mixing of the reaction product gas with the cover gas shows an apparent build up in efficiency. During this period the metal dissolution and reoxidation will be moving to its steady state. Thereafter the second characteristic becomes apparent, namely the scatter in the data. The third characteristic shows that generally there is very little variation between efficiency and time.

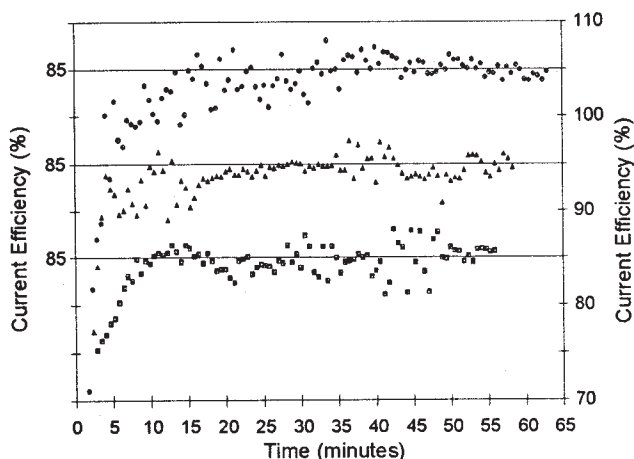


Figure 8: The effect of depleting alumina on current efficiency.

The rate of change of efficiency with time gives the rate of change of alumina with time and therefore that co-efficient can be determined. However, from an examination of the data points in Fig 8, it is evident that the effect of alumina concentration on efficiency is small. A series of seven experiments with similar solvent electrolyte composition, but with minor differences in other process conditions, have been processed by calculating the average rate of change in efficiency with alumina concentration. This data is presented in Table 2, along with its standard deviation. In all situations the trend is very small, sometimes it being positive slopes and in other cases, negative. Averaging all the slopes (the bottom row) indicates that the rate of change is virtually zero. Certainly it is smaller than the effect of other variables that can change with alumina concentration changes. Thus, the present study supports the argument of Solli et al. [6] who concluded that alumina concentration does not have a significant effect on the efficiency. It is also interesting to note that the range of slopes calculated in Table 2 all fall within the small variable group as characterised by Kvande [8]. Perhaps the third curve of Fig. 8 combined with the changing ratio of CO to CO₂ as the anode effect is approached explains the reasons

why some researchers have reported positive effects of alumina concentration and others negative. Interpreting the data over a limited alumina concentration or time basis can lead to differing slopes because of inherent standard deviations in this, and all other methods used for current efficiency determination.

Table 2: The effect of alumina concentration on current efficiency.

Current Efficiency (Oxygen Balance) (%)	Std. Dev. (%)	dCE/dc _{alumina} (%/wt%)	Current Efficiency (P-W Equation) (%)
85.1	3.05	0.6846	73.4
87.1	1.95	0.3669	74.3
85.4	1.82	0.1026	73.2
84.8	1.78	-0.1717	73.5
83.2	2.47	-0.2794	75.0
84.3	1.84	-0.5608	75.1
84.3	1.58	-0.2804	75.2
84.9	2.07	-0.0197	74.2

Conclusions.

A system has been developed for measuring current efficiency in a laboratory scale Hall-Heroult cell using the oxygen balance method. The results show good consistency with established trends from previous studies. The most important findings are:

- There is no effect of anode-cathode spacing on current efficiency, although this is as expected by the design of the cell.
- There is a strong increase in current efficiency with current density, the gradient being 17.25% CE per A/cm² at the anode.
- There is a strong decrease in current efficiency with cryolite ratio, the gradient being -7.84% CE per cryolite molar ratio.
- The Pearson-Waddington equation gives current efficiency values that are erroneously low, in this cell by approximately 10%.
- Within the normal alumina operating range, there is no effect of alumina concentration on current efficiency.

Acknowledgments.

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