Influence of carbon dust in the electrolyte on aluminium electrolysis parameters

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Abstract

This paper presents the results of the influence of the presence of carbon dust in the electrolyte on cell and electrolyte voltage during aluminium electrolysis. The voltage drop in the cell was determined by the current interruption method. The tests were performed in a laboratory cell with prebaked anodes with varying content of carbon dust added to the electrolyte. The experimental results are indicative of an important relationship between the carbon content in the electrolyte and the cell voltage at constant anode-cathode distance (ACD). The results show that carbon dust in the electrolyte increases electrolyte resistance and consequently electrolyte voltage drop and cell voltage. Despite the fact that carbon is an electrical conductor, carbon particles suspended in the electrolyte under the influence of a DC electric field act as being non-conductive, due to the polarization resistance at the electrolyte/carbon interface.

Keywords: Aluminium electrolysis; carbon dust in electrolyte; electrolyte voltage drop; cell voltage.

1. Introduction

In the aluminium industry carbon dust floating in the electrolyte is regarded as a nuisance, and large accumulation of dust is considered to be detrimental to the current efficiency, and it can lead to overheating of the cell [1]. If the amount of dust floating on top of the bath in a cell accumulates, it may then have to be skimmed off. This operation is a very disagreeable job, and the skimming is normally being dumped, representing a loss of bath material. Carbon dust can also accumulate underneath the anodes, apparently increasing the bath resistance [2, 3], causing overheating and possibly uneven current distribution by inhibiting the supply of dissolved alumina to the anode surface. By compensating for the increased resistance, cells with much carbon dust will be operating at a shorter anode-cathode distance, leading to loss in current efficiency.

Anodes are made up of particles of petroleum coke bonded together by a mixture of pitch and fines, forming the so-called binder phase. In the literature it is generally agreed that the cause of carbon dust formation is the fact that the binder coke is more reactive than the aggregate petroleum coke, so that the binder phase is preferentially consumed, and grains of petroleum coke can then be detached, falling into the bath [1].

Carbon dust may also be trapped underneath the anodes, and this dust is regarded as being particularly deleterious, by increasing bath resistance and leading to uneven current distribution. Such accumulation of dust may set up a concentration gradient in the vicinity of the anode with respect to dissolved alumina (risk of anode effect). It may also initiate anode spike formation by inhibiting the normal anode reaction.

Dusting in aluminium reduction cells is one of the visual signs of unwanted anode consumption. Operational irregularities originating from excessive dusting by selective anode oxidation have been experienced by most aluminium plants, particularly in Soderberg cells. Soderberg cells generate more carbon dust than prebakes, due to the higher pitch content required in soft paste formulation and due to a lower baking temperature.

The amount and behavior of carbon dust depend on several factors, such as: the quality of the anode material, cell design and the operating conditions (the current density, electrolyte composition and electrolyte temperature). Intensive carbon dust formation can be observed prior to or during anode effect, when the carbon is poorly wetted by the electrolyte due to a low alumina concentration. Most of the carbon dust combusts at the surface of the electrolyte, while the remaining part is being skimmed off by the operators. Typically the amount of dust that is being skimmed off can be 20 - 40 kg per tonne Al [4]. However, nowadays the dust problem is more sporadic, but equally damaging for cell performance when it occurs. At reduced inter-polar distance or at a particular bath composition, the content of carbon in the electrolyte may increase up to 1 wt. %. This phenomenon has been named carbonation of the electrolyte [5].

The objective of the present work was to measure the voltage drop (IR_{el}) in the electrolyte as a function of different contents of carbon dust in the cryolite melt during laboratory experiments of 6 hours duration.

2. Experimental

2.1. Experimental cell

The voltage drop experiments were performed in an air-tight laboratory furnace. Argon (99.999 %) was used as a flushing gas. The cell, shown in detail in Figure 1, consists of a graphite crucible, where the inner wall was covered by a sintered alumina lining. The side of the anode was shielded by a sintered alumina tube, and the top was covered with loose alumina (2 - 3 cm thick layer) in order to prevent any reaction between CO_2 and the carbon anode body. The completely flat anode (made so in order to trap carbon dust underneath the anodes) was 42 mm in diameter and had a threaded hole at the top to connect it to the threaded stainless steel rod (shielded by a sintered alumina tube), which served as the current lead.

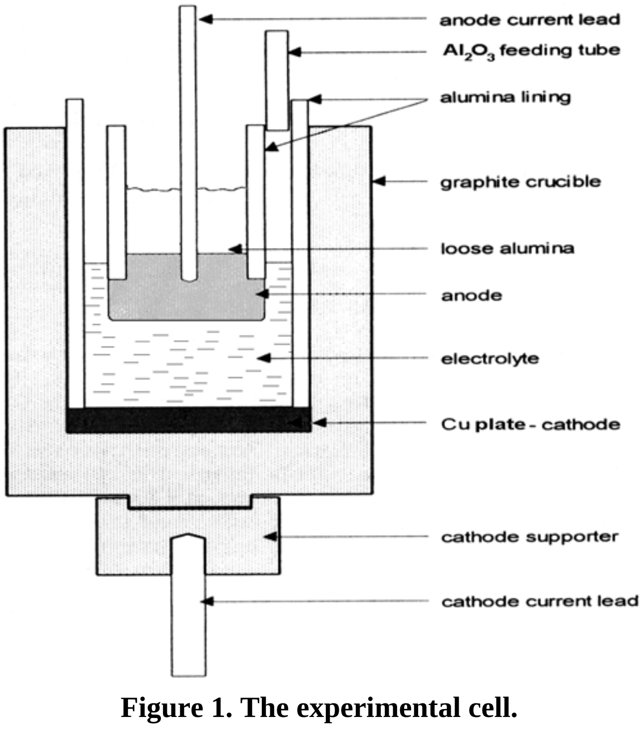

Figure 1. The experimental cell.

A Pt-Pt10Rh thermocouple placed inside a sintered alumina tube was used to record the electrolyte temperature. Alumina was fed by a fully automated feeding device (feeder). The feeding parameters were: batch size: 0.3 g, feeding rate: 10 g/h at 108 s intervals in amounts corresponding to approximately 80 % of the consumption.

2.2. Apparatus

The experimental set-up was composed of:

- Power supply- Hewlett Packard 6032 (0 - 60 V/0 – 50 A, 1000 W),
- Current interrupter - Model 810 IR Measurements System - Scribner Associates Inc.,
- Digital oscilloscope - Le Croy LS -140 ™ Scope Station,
- GPIB (General Porpose Interface Bus) Controller - National Instruments,
- PC computer equipped in the EMDAQ program for data acquisition,
- Multimeter-Keithley 2000-Scan with 10 channel multiplexer on GPIB,
- Equipment for batch-wise alumina feed control - digital-analog card, computer boards.

The scheme of the apparatus is shown in Figure 2.

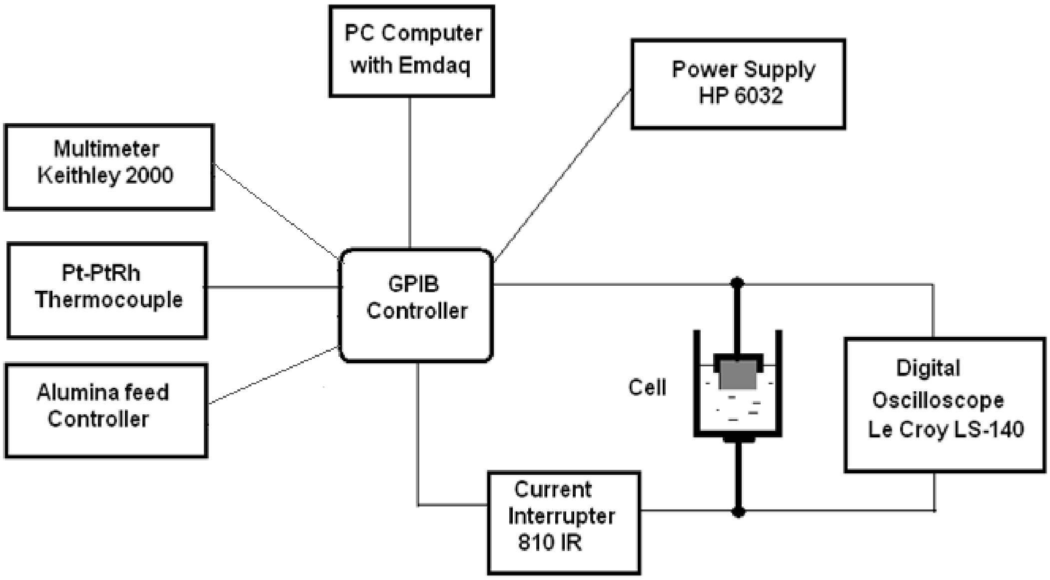

Figure 2. Scheme of the apparatus.

The ohmic voltage drop IR_{el} across the cell between anode and cathode was determined by means of a current interruption technique. The only variable was in this case the electrolyte resistance, so it was recorded as electrolyte resistance, IR_{el}. Switching time: 0.2 µs, duration of current interruption 170 µs. The measurements were started 30 minutes after the anode was immersed in the melt. The results were stored on the digital oscilloscope.

2.3. Experimental conditions

The experimental conditions are shown in Table 1.

Table 1. Experimental conditions.

Parameter	**Unit**	**Value**
Cell current	A	27
Anode current density	A/cm²	0.86
Cathode current density	A/cm²	0.3
Anode-cathode distance (ACD)	cm	4
Anode: prebaked and graphite (as reference)		
Cathode: copper plate		
Melt composition:	wt. %	
AlF_3		12
CaF_2		5
Al_2O_3 (saturation)		8.36
Na_3AlF_6		74.64
Working temperature	°C	960
Electrolysis time	h	6
Recorded data: I = current, U_{el} = cell voltage IR_{el} = voltage drop in the electrolyte, Temperature of the electrolyte		
Data sampling frequency	s	20
For IR by current interruption	min	15 - 20

2.4. Anodes

To avoid having too many variables, the same anode quality was used in all tests. Selected properties of the anode material are given in Table 2.

Table 2. Properties of anodes used.

Physical Properties			Reactivity		
Electrical Resistivity	µΩm	51.3	CO_2 Reactivity Residue	%	83.0
Compressive Strength	MPa	46.3	CO_2 Reactivity Dust	%	6.6
Real Density	g/cm³	2.077	CO_2 Reactivity Loss	%	10.5
Thermal Properties			**Ash and sulfur contents**		
Thermal Conductivity	W/mK	3.9	Ash	%	0.41
Thermal Expansion	m/K	4.6×10^{-6}	S	%	1.705

2.5. Carbon dust

Due to the short duration of the laboratory experiments, it would not be realistic to generate sufficient quantities of dust in situ by electrolysis, so the scheme was to add dust that has been skimmed off industrial cells as carbon froth. Samples of the carbon dust were incinerated for 10 hours at 700 °C to determine the carbon content. The average carbon content in the carbon dust was 16 wt. %. Subsequently the carbon dust was crushed by a manual crusher. Finally the carbon dust was mixed together with the components of the electrolyte to be melted in the experimental crucible.

In the following the amount of dust added will be given in terms of wt.% C, obtained by multiplying the percentage of dust added by 0.16.

3. Results

An example of a typical cell voltage (U_{el}) decay after current interruption is presented in Figure 3. It is seen that disconnection of the polarized electrodes (mainly anode) results in an oscillating decay (ringing). Customarily a graphical extrapolation to time zero is used in current interruption measurements in order to determine the voltage drop IR_{el}.

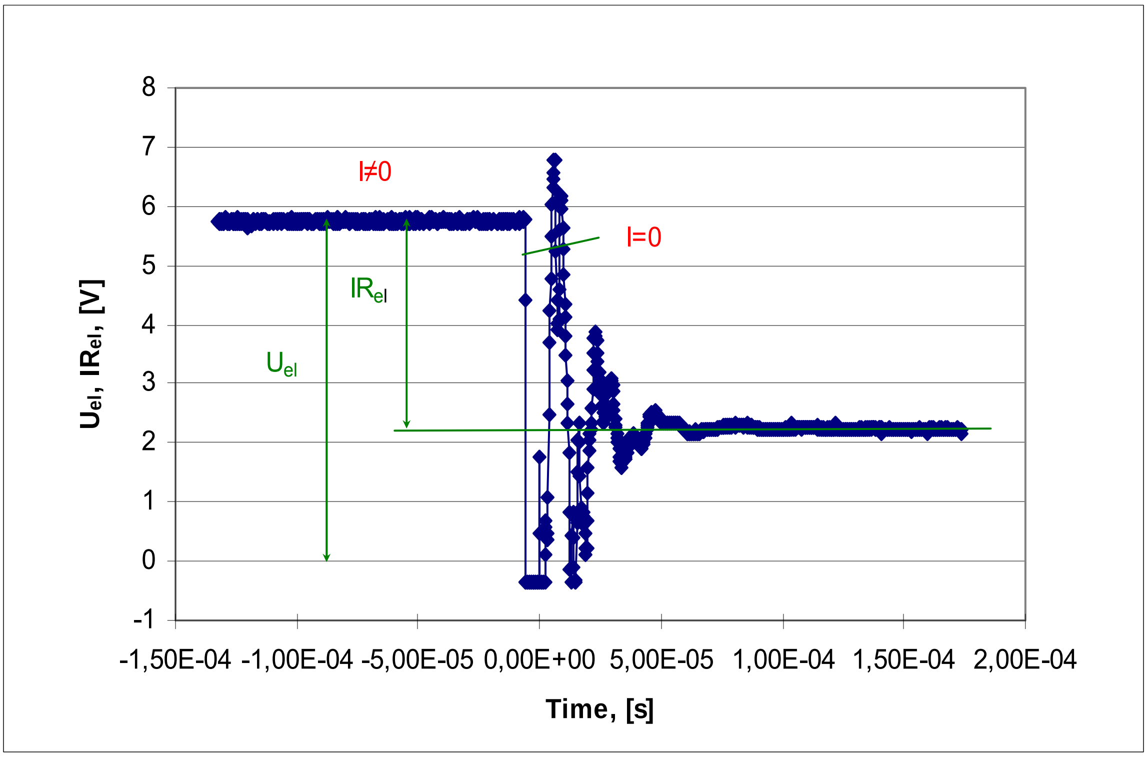

Figure 3. Typical cell voltage decay after current interruption.

The results of the study of the influence of the carbon content in the electrolyte on the cell voltage and the voltage drop in the melts by the current interruption method are summarized in Table 3 and in Figures 4 and 5.

Table 3. Results (average) of cell voltage and voltage drop in the electrolyte as a function of the carbon content.

C added	U_{el}		IR_{el}		ratio IR_{el}/U_{el}
		std. dev.		std. dev.	
%	V	± %	V	± %	%
0.00	5.87	0.90	3.45	0.79	58.72
0.67	6.88	4.71	4.20	4.07	60.36
1.39	6.22	4.75	3.94	4.65	63.35
2.18	5.86	0.20	3.62	0.19	61.87
4.00	7.94	0.07	5.41	0.28	62.20
5.92	8.46	1.83	5.49	1.48	62.48
8.00	8.68	0.04	5.74	0.09	66.05

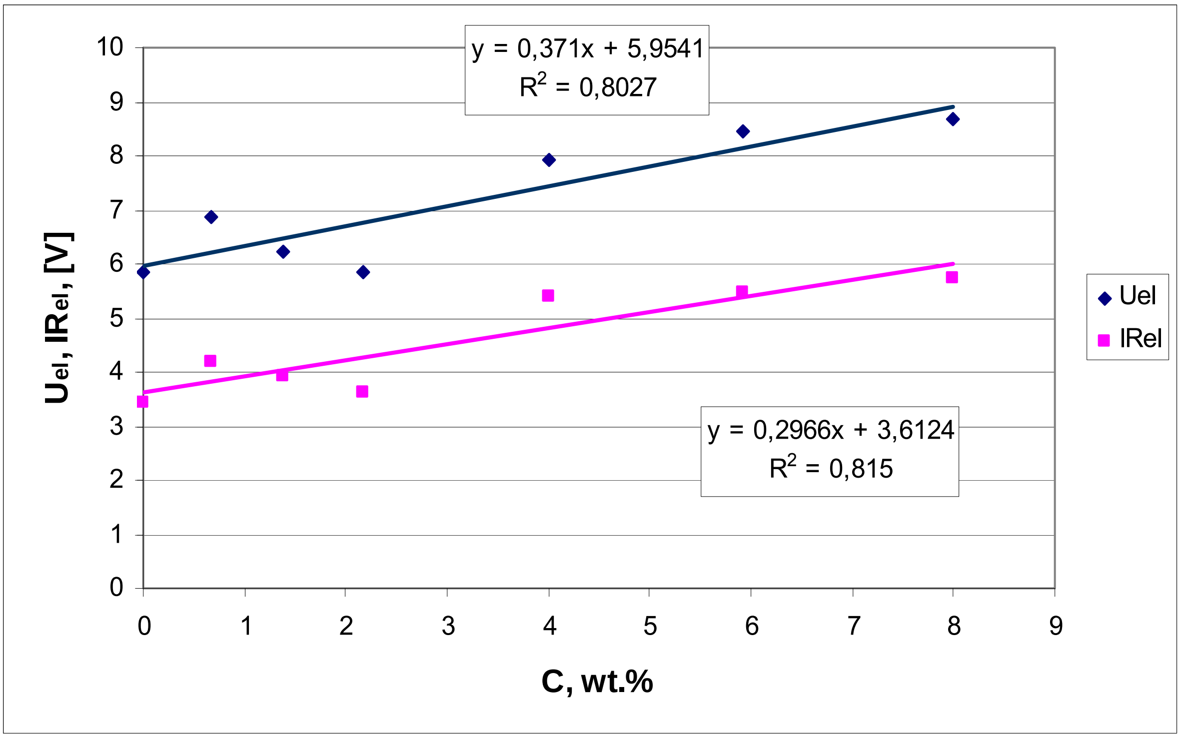

Figure 4. The influence of the carbon addition to the electrolyte on the cell voltage and on the voltage drop in the melt.

The experimental data presented in Table 3 are indicative of an important relationship between the carbon content in the electrolyte and the cell voltage at constant ACD, as well as the voltage drop in the electrolyte during aluminium electrolysis. Despite the fact that carbon is an electrical conductor, carbon particles suspended in the electrolyte under the influence of a DC electric field act as being non-conductive, due to the polarization resistance at the electrolyte/carbon interface. As we can see, increasing carbon content in the melt leads to increasing U_{el} and IR_{el}. The correlations between the earlier mentioned parameters in relation to the carbon content are:

$$U_{el} = 0.37(wt.\%C) + 5.95\ ,\quad [\mathrm{V}] \qquad R^2 = 0.80 \tag{1}$$

$$IR_{el} = 0.29(wt.\%C) + 3.61\ ,\quad [\mathrm{V}] \qquad R^2 = 0.81 \tag{2}$$

The higher coefficient for Uel than for IRel is probably due to increased polarisation by the presence of carbon dust under the anode.

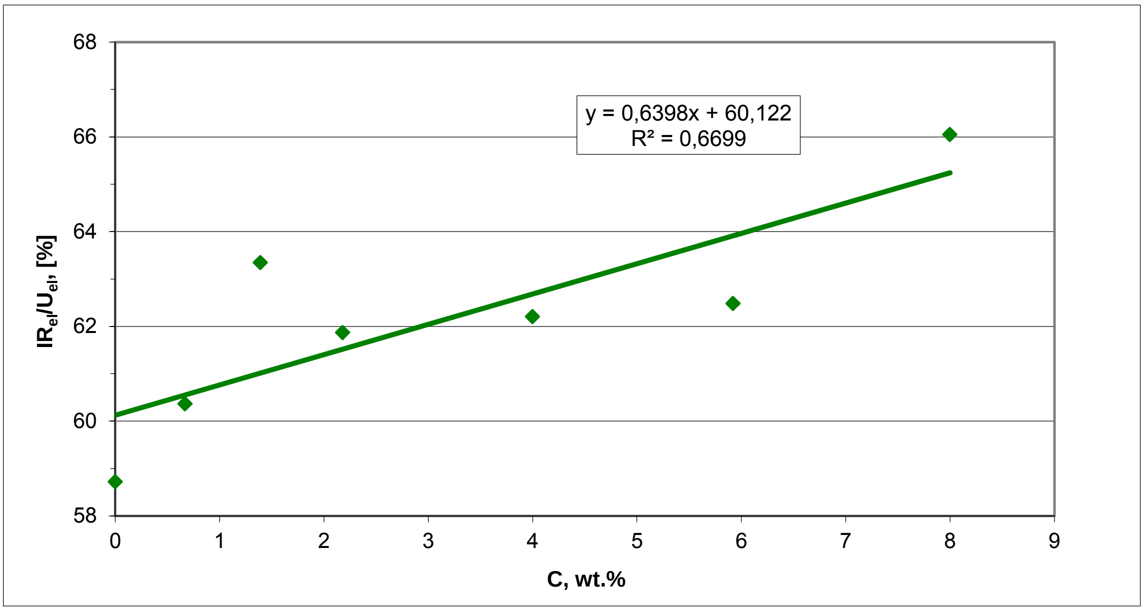

Figure 5. The influence of the carbon addition to the electrolyte on the IRel/Uel ratio.

When melting the electrolyte the carbon particles are distributed all across the depth of the bath. As explained in the Introduction the carbon particles then become partly suspended in the electrolyte, but mainly concentrated near the surface of the electrolyte and at the anode/electrolyte boundary (Figure 6). This causes increased electric resistance in the melt, resulting in increasing voltage drop in the electrolyte and consequently increased cell voltage.

A. B.

Figure 6. A crucibles after an experiment with carbon dust at the surface of the electrolyte (A), and loose grains of carbon dust (non-wetted by the melt), collected from the surface of the frozen electrolyte after the experiments (B).

Carbon dust has also been trapped underneath the anodes, and it is this part of the dust that is regarded as being particularly deleterious, by leading to uneven current distribution and hence uneven anode consumption. This effect can be seen in Figure 7.

Figure 7. Uneven anode consumption caused by carbon dust trapped underneath the anode after experiments with 8 wt.% C addition, compared with a new anode.

Accumulation of carbon dust underneath the anode may set up a concentration gradient in the vicinity of the anode with respect to dissolved alumina, and eventually initiate an anode effect. This kind of anode effect was very hard “to kill”, and this was the reason for finishing some experiments earlier than after 6 hours.

4. Conclusions

1. The results of this study are indicative of an important link between the presence of carbon dust in the electrolyte and the cell voltage at constant ACD as well as the voltage drop in the electrolyte.
2. The study of current interruption shows that the presence of carbon dust in the electrolyte causes increased voltage drop in the electrolyte.
3. The results indicate that accumulation of carbon dust in the electrolyte has a detrimental effect on the behavior (uneven consumption) of the anode and on important parameters of electrolysis, such as cell voltage and ohmic voltage drop in the electrolyte, resulting in increased energy consumption.

5. Acknowledgement

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6. References

1. K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky, and J. Thonstad, Aluminium Electrolysis – Fundamentals of the Hall-Heroult Process, 2nd Ed., Aluminium-Verlag (1982), ISBN: 0-9960035-4-1.
2. M.M. Vetyukov, M.M. Tsyplakov, Nauch. Dokl. Wysch. Shk. Metallurgija, 1, (1958), p. 247.
3. M.M. Vetyukov, R.G. Chuvilyaev, Izv.Vyssh.Ucheb. Zav. Tsvetnaya Metallurgiya, 6, (1964), p. 74.
4. E.R. Cutshall, Influence of Anode Temperature and Current Density Upon Sloughing, Light Metals 1986, pp 629-637.
5. K. Grjotheim, and B.J. Welch, Aluminium Smelter Technology. A pure and applied approach, Aluminium-Verlag (1980), p. 47, ISBN: 3-87017-132-4.