

CONTINUOUS MEASUREMENT OF CURRENT EFFICIENCY, BY MASS  
SPECTROMETRY, ON A 280 KA PROTOTYPE CELL

Michel J. LEROY - Theodoros PELEKIS - Jean-Michel JOLAS  
Aluminium Pechiney  
Laboratoire de recherche des Fabrications  
B.P.114 - 73300 SAINT-JEAN-DE-MAURIENNE - France

Continuous analysis, by mass spectrometry, of the composition of the fumes emitted by a 280 KA cell enabled us to determine precisely a mass balance of oxygen and carbon, thus the current efficiency and net carbon consumption of the cell.

Results show that current efficiency increases strongly when alumina content of bath decreases (by about 2 % for 1 % variation of alumina content).

A parallel increase of net carbon consumption is noticed, which may be attributed to a strong enhancement of the Boudouard reaction at low alumina content.

Thus, the Pearson-Waddington relation is not valid.

We demonstrate, too, the existence of a critical Anode/Cathode Distance (ACD), under which current efficiency steeply decreases.

#### INTRODUCTION

In 1980, ALUMINIUM PECHINEY began trials for direct measurement of the current efficiency by analysing the fumes extracted from the 175 KA experimental pots of the LRF.

But, it is by the end of 1983 that the apparatus (mass spectrometer) and the interpretation, correction and calculation softwares were sufficiently improved to make it possible to obtain results with the accuracy required.

At that time, the 175 KA pots had been replaced for 2 years by the 280 KA pots described at the AIME Congress in 1986 (ref. 1).

#### 1. PRINCIPLE OF THE MEASUREMENTS

The gas is extracted from the pots by the dry scrubbing system after it has been previously mixed with a known flow of a tracer gas, and is then analysed.

In such a case, this tracer gas is either Argon, which has the advantage of being little expensive, or Helium, which is more precise.

Firstly, the extracted flow of the fumes, as well as the flow of atmospheric air which entered the pot are determined, using a balance on Argon, Helium and Nitrogen.

Once the flows and the analyses of the entering air and the getting out fumes are known, it is thus easy to evaluate the quantity of oxygen and carbon entering and getting out from the pot. Hence, by comparing it with the intensity through the pot, the current efficiency as well as the anode carbon consumption can be determined.

#### 2. PRECISION OF THE MEASUREMENTS

The causes of mistakes as far as measurements are concerned are numerous and it is possible to distinguish among them : the level and the fluctuations of the magnetic field due to the experimental potline which entails a parasite deviation of the ions fed in the spectrometer ; the temperature in the ionization chamber ; the voltage and the age of the filament ; the fluctuations in the composition of the atmospheric air, which is not to undervalue, close to a plant giving off CO<sub>2</sub> and CO, etc ...

We called the precision and the reliability of the measurements the "atmospheric current efficiency", that is to say the fluctuations in oxygen and carbon balances when some surrounding atmospheric air is taken instead of fumes and when current efficiency is then calculated as if air was fumes emitted by the pots. This integrates all the experimental errors and uncertainties, and fluctuations in the composition of air.

These measurements gave us standard deviations of about  $\pm 0.1$  % on the current efficiency and  $\pm 0.5$  kg/ton on the carbon consumption, as far as the results of the years 1984, 1985 and 1986 are concerned.

It seems difficult to improve this precision.

#### 3. RESULTS OBTAINED

We will successively show three groups of results proving the influence of the operative parameters :

- alumina content of the bath
- anode/cathode distance
- temperature of the bath.

3.1. INFLUENCE OF THE ALUMINA CONTENT OF THE BATH

Alternating overfeeding and underfeeding, sometimes interrupted by complete stoppages of feeding in alumina, we monitored the alumina content of the bath, keeping however the anode/cathode distance (ACD) constant.

We can evaluate the variations of alumina content of the bath by tracking the pseudo-resistance of the pot, which increases when the alumina content decreases, and decreases when the alumina content increases.

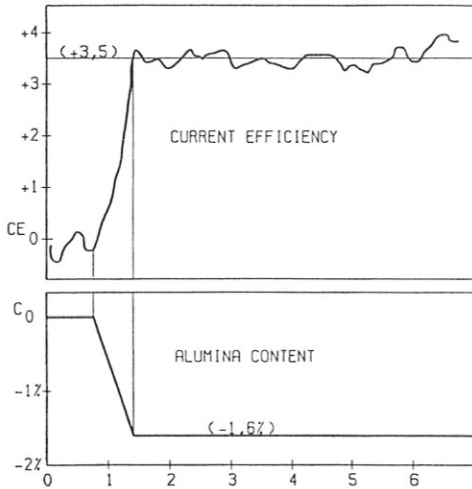


Figure 1 - CE variations induced by a rapid decrease of alumina content in bath

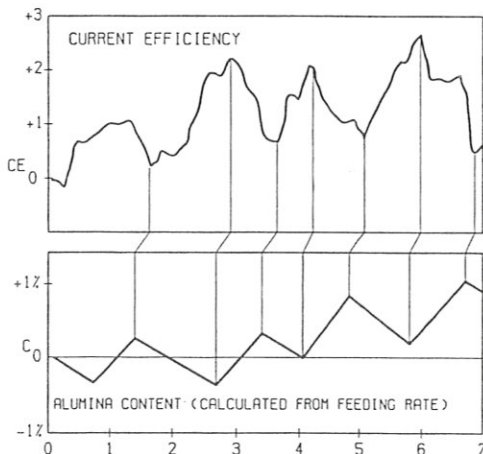


Figure 2 - CE variations induced by alternating underfeeding and overfeeding.

There is an outstanding parallelism between the variations of the measured current efficiency and the alumina concentration of the pot (Fig 1 and 2). In the same way, we can notice an outstanding parallelism between CE and the net consumption in carbon, which is completely unexpected and contrary to the basis hypotheses of the PEARSON WADDINGTON formula (Fig. 3).

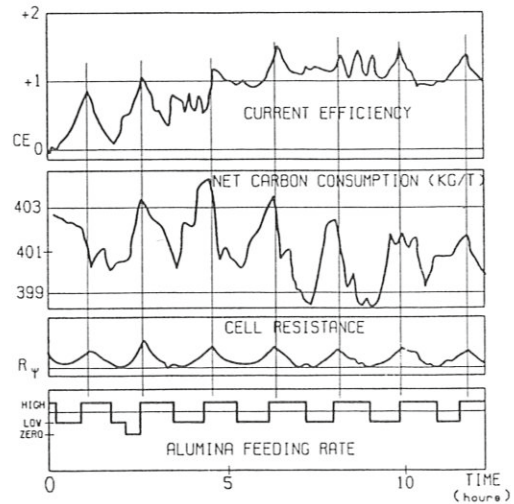


Figure 3 - Parallel evolution of cell Resistance ( $R \psi$ ), Net carbon consumption, and current efficiency (CE) when alternating overfeeding and underfeeding.

Let us however notice that this formula supposes that the Boudouard reaction doesn't exist, which is obviously wrong if we consider the important internal porosity of the basis of the anodes after the electrolysis, that can only be explained by this reaction.

So, we have many good reasons to suppose that, when the alumina content of the bath decreases, the contact surface between the anode bubbles and the anode basis increases, which entails the interdiffusion between the  $CO_2$  (contained in the anode bubbles) and the  $CO$  produced by Boudouard equilibrium (contained in the anode porosity)(Fig 4)

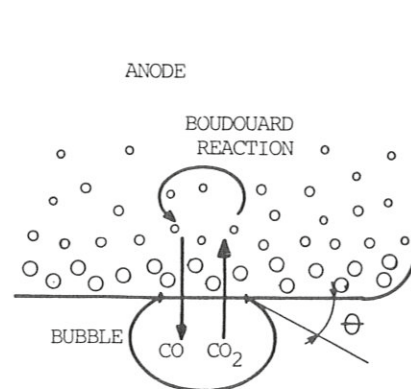


Figure 4 - Proposed exchange mechanism

This interdiffusion fluctuates very quickly according to the wetting angle bath/anode carbon, which is known to change strongly at low alumina content, until it reaches the anode effect.

As a consequence, the CO content of the electrolysis gases would be more an image of the wetting angle bath/carbon than an image of the current efficiency, at least for these magnetically well balanced pots.

The averages obtained with many tens of 8 hours' continuous measurements give us a current efficiency variation of about + 2 % for an alumina content drop of 1 %, when the alumina content is in the range between 3.5 % and 1.2. %.

The rise in the anode carbon consumption is of + 3 to + 4 kg/ton for this alumina content drop of 1 %, below 2.5 % of  $Al_2O_3$ . Consumption seems constant over this content.

These last results are compatible with that revealed by Norsk-Hydro at the AIME Congress in 1986 (ref. 2) even though our interpretation is different.

These measurements show why it is so important to maintain an alumina content as low as possible in the bath, which has been our policy for many years and has entailed the implementation of potline operation softwares, adapted to this walk "on the edge of the razor", very close to the anode effect (ref. 4 and 5)

3.2.-INFLUENCE OF THE ANODE/CATHODE DISTANCE

The alumina content of the bath being kept constant by a nominal rate feeding - that is to say equal to the consumption rate - we made the anode/cathode distance fluctuate.

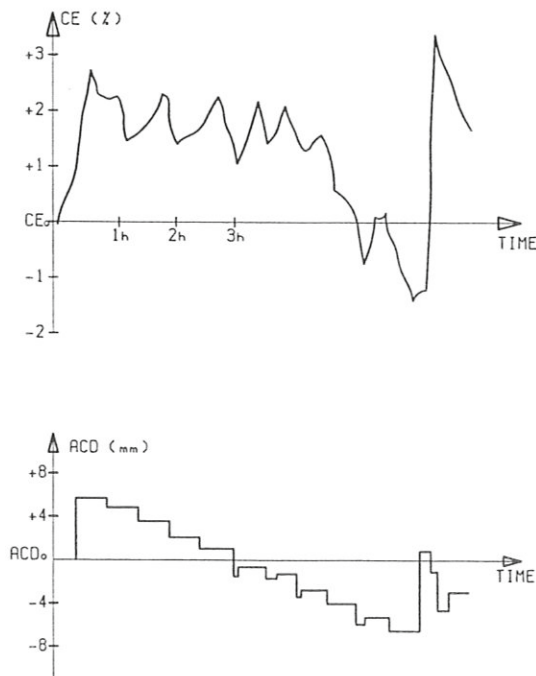


Figure 5 - Evolution of CE when changing ACD at constant alumina content of bath

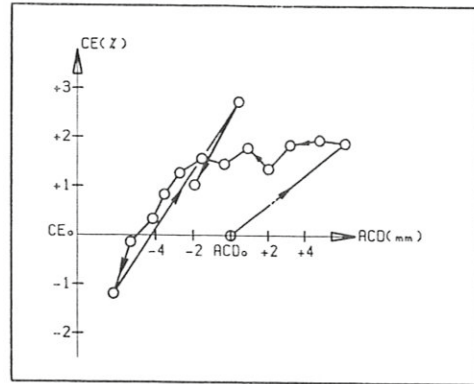


Figure 6 - Same results as Fig. 5, giving CE as a function of ACD.

The results obtained show that, as long as this anode/cathode distance exceeds a critical value (ACD) crit, the current efficiency remains roughly constant. On the contrary, if the anode/cathode reaches a value inferior to (ACD) crit, the efficiency decreases quickly, by about 0.7 % per millimeter (fig 5 and 6).

These results are very similar to those revealed by GRJOTHEIM and Als in the case of laboratory minicells. (ref. 3).

3.3.- TEMPERATURE OF THE BATH

In order to modify the temperature of the bath, without altering its composition, we fed the pot with a solid grinded bath with the same composition than the liquid bath, keeping on the alumina feeding to a rate equal to the consumption rate.

We noted an efficiency rise of about 1 % while the temperature of the bath had dropped by 4°C close to the bath feeding crustbreaker and by 2°C close to the tapping hole.

This result is entirely compatible with the previous results of regression (CE increase of 0.2. to 0.3 % for a drop of 1°C of the bath temperature).

There has not been a rough variation of the consumption of anode carbon (taking into account the precision of the measurements).

#### 4. CONCLUSION

Mass spectrometry has proven to be an invaluable tool for understanding and quantifying the influence of major parameters on the performance of full size cells.

Work is presently in progress for the characterization of operating modes (tapping, anode changing) and for quantifying the consequences of disturbances (instabilities, anode effects).

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