

**REDUCTION OF CF<sub>4</sub> EMISSIONS FROM THE ALUMINUM SMELTER IN ESSEN**

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**Abstract**

Perfluorcarbon (PFC, e.g. tetrafluoromethane and hexafluoroethane) emissions are harmful to the environment because of their global warming potential and, therefore, it is a challenge for the aluminum industry to reduce the evolution of such gases. Based upon this background, two measurement campaigns of CF<sub>4</sub> emissions were carried out at ALUMINIUM Essen GmbH during the spring of 2001. In the first campaign the current level of emissions was fixed and different strategies of automatic anode effect treatment were analyzed and compared. Special attention was paid to the success rate and CF<sub>4</sub> emission levels with respect to the anode effect quenching strategies. Afterwards the most successful method with the lowest emissions was implemented in all process computers. In the second campaign the perceived improvements were verified. This paper shows the correlation between anode effect overvoltage and CF<sub>4</sub> emissions during these trials. In addition, the merits of various anode effect quenching strategies are discussed.

**Company Information**

ALUMINIUM Essen GmbH is a privately owned smelter with no up or down-stream fabrication. The plant is located in Essen, at the heart of the industrial Ruhr area of Germany, near to Cologne and Düsseldorf. The smelter was commissioned between 1971 and 1973. Today, ALUMINIUM Essen GmbH produces 155,000 mt (metric tonnes) per year of primary aluminum on three potlines. The annual casthouse production amounts to 230,000 mt, consisting of mainly billets and slabs. The pots are of the Alusuisse technology, with end-to-end cells having prebaked anodes, built for 140 kA (EPT 14). Following major modernization in 1986 the cells were equipped with point feeders and pot controllers. The line amperage is currently 157 kA in lines 1&2 and 165 kA in line 3 (EPT 17 since 1998). The history of our company has been quite turbulent in the last 10 years. Due to the crisis in the aluminum market in the early nineties, the former owner Alusuisse decided to close the plant in 1994. As a result Line 3 was shut down in 1992. Afterwards Line 1 was taken out of operation in 1993. Line 2 was also gradually shut down during the spring of 1994. With only 51 of the 360 original pots still in operation, a management buy-out took place in May 1994. Following the change of ownership, Lines 1&2 were restored to full operation by the end of 1994.



Figure 1: ALUMINIUM Essen GmbH

Following further modernization of the busbar system, Line 3 was finally restored to operation in 1998. Nowadays, our company belongs to the TRIMET AG, which is 100% owned by the Schlüter family. In the past 3 years production at ALUMINIUM Essen GmbH has been the highest in the history of the plant.



Figure 2: View of potline 3

### Measurement methodology

A photo-acoustic gas monitor, Innova Airtech Instruments (formerly Bruel & Kjaer), model 1302, was chosen as the measuring instrumentation, because of its low detection limit, appropriate range of measurement and reliability of performance reported at many other aluminum smelters [1-2, 4, 9].

The principle of the measurement is infrared absorption. In order to analyze PFC emissions an IR-wavelength of 7.7  $\mu\text{m}$  was used. The resulting analysis is a sum of  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  because this method is not able to detect these gases selectively (100 % of  $\text{CF}_4$  and 75 % of  $\text{C}_2\text{F}_6$ ) [4]. For this reason, values measured in the present paper are termed “ $\text{CF}_4\text{-m}$ ”.

The conditioned gas sample is pumped into a gas and pressure-tight thermostatic measurement cell. The gas is exposed to infrared light of the appropriate IR-frequency range. IR-absorption causes pressure fluctuations, which can then be detected by microphones.

In the aluminum industry  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  gases only occur during the anode effect phase. PFC measurements in smelters of similar technology to ALUMINIUM Essen GmbH show an average  $\text{CF}_4/\text{C}_2\text{F}_6$  ratio between 4% and 10% [9, 12]. This variation can be explained by the influence of different circumstances, e.g. anode effect duration and anode effect overvoltage. The analyses in this report assume a relative content of 10 %  $\text{C}_2\text{F}_6$  in relation to the content of  $\text{CF}_4$ .

### Sampling/Interferences

Prior to starting the measurements, checks were made to ensure that there was no interference from other gases generated in the aluminum smelting process, ( $\text{HF}$ ,  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}_x$ ). After a 2-point-calibration test with 20 and 800 ppm of  $\text{CF}_4$  gases in nitrogen, the instrument was discharged with a gas mixture equal to the composition of the process gases. The gas was completely dried to avoid moisture interference.

Gas samples were taken from various locations in the duct system. Some samples were extracted from the duct that connects two electrolysis cells (about 3m distance from the pots), some from a duct collection pipe for 60 pots (before the dry scrubber system) and some were taken in the stack at the 45-m level, where the other emission measurement instruments are installed.

The gas had to pass through a crystal filter and NaOH for removing HF. Then the gas went through the gas cooler (5° C, dew point) including the air trap and an additional filter. After passing a cartridge filled with magnesium perchlorate to remove any remaining humidity the gas entered the measurement instrument.

Used measurement range:	0.03 – 1000 ppm $\text{CF}_4$ or 0.1 – 3900 $\text{mg}/\text{m}^3$
$\text{CF}_4$ calibration:	2 – point
Quantity of gas per sample:	140 ml
Flushing the line:	30 ml/s
Accuracy:	11 – 12 %

The frequency of analyses was every 30s whilst the sampling procedure lasted 10s.

After interpreting the results from the three measurement locations, the duct that collects the exhaust gases from 60 electrolysis cells was chosen for the second measurement campaign. This duct was selected because the level of concentrations was most appropriate (range between 10 and 60  $\text{mg}/\text{m}^3$ ) at this location.

### Efficiency of the electrolysis hooding system

To determine the efficiency of the electrolysis hooding system  $\text{SF}_6$  was selected as tracer because it is an inert and easily detectable gas.

Gas samples were taken in the connecting duct of two pots. Samples were extracted using an airtight syringe located in a bypass of the  $\text{CF}_4$  measurement assembly.

Before starting the measurement program it was necessary to establish that there was no  $\text{SF}_6$  generated during the electrolysis process, therefore the first samples were taken without dosing in  $\text{SF}_6$ . A defined quantity of  $\text{SF}_6$  was blown under the hooding lid in the middle of the electrolysis cell. Pots in normal production and those in anode effect phase were evaluated.

The analysis of the gas samples was determined in a certified official agency laboratory. A gas chromatography instrument (Fisons GC 8000) with a detection limit of 0.1 ppm and an accuracy of 10 % was used. The result of the “zero measurements” showed no  $\text{SF}_6$  was evolved in neither the normal aluminum production nor the anode effect phase.

In the efficiency test, about 98 % of the added tracer gas was detected. These results agreed with expectations.

### Correlation overvoltage – PFC emissions

The correlation between overvoltage and PFC emissions was clearly identified. There was a time delay between the overvoltage signal and the PFC measurement signal because of the distance between measurement location and instrument, which varied between 50 – 300 m.

To permit comparison of voltage development and concentration of PFC the time shift was taken into account, thus enabling both sets of data to be plotted on the same time scale.

### Mechanism of Anode Effect Generation and Quenching

The production of aluminum using the Hall-Héroult process with carbon anodes is even today accompanied by the so-called anode effect. Only frequency and duration of anode effect vary from smelter to smelter and between the different technologies. The worst effect of anode effects is the evolution of  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ . These greenhouse gases are harmful to the environment due to their global warming potentials which are 6500 and 9200 times higher than that of  $\text{CO}_2$  for  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  respectively [8-9]. The emission levels that are reported, varies from 0.005 kg  $\text{CF}_4$  per ton of aluminum to about 2 kg/t [2-3, 5-6]. The level of perfluorocarbon emissions is dependent upon the length of time and magnitude of voltage during the anode effect.

The physical reason for the occurrence of an anode effect is because the critical current density (CCD) is exceeded somewhere in the pot. The CCD is dependent upon the amount of dissolved

alumina in the bath. With this background there are different practical reasons for the cause of anode effects. These reasons can be classified in two groups:

1. Depletion of Alumina over Time (Case 1):

- a) clogging of the feeders
- b) empty feeder-silos
- c) malfunction of the breakers
- d) changing alumina qualities → dissolution problems
- e) lack of superheat
- f) extended underfeeding of alumina

All these reasons lead to decreased concentration of dissolved alumina in the bath. Figure 3 shows the relationship between alumina concentration and CCD [10-11]. The “bubbles” represent the distribution of current density and alumina in the pot. When the concentration decreases, the anodic over voltages increase leading to a more equalized current distribution. But when the “bubble” touches the CCD curve an anode effect will occur, although average current distribution and average alumina concentration are not critical.

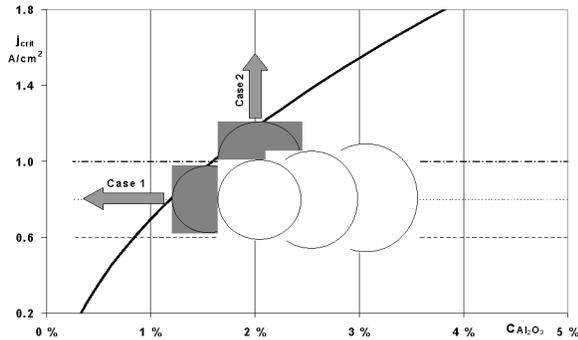


Figure 3: Approaching an Anode Effect

An alternative cause of anode effects originates from increase in current density.

2. Change in Current Distribution or Current Density (Case 2):

- a) anode change
- b) anode burn off
- c) beam raising
- d) line current variations
- e) beam movements
- f) tapping of bath or metal

All the above reasons will increase current density or deviation of current distribution. This consequently leads to an anode effect if the “bubble” touches the critical curve. Regardless of the cause of anode effects, there is a need to extinguish them as soon as possible. Quenching an anode effect needs in principal these two steps:

- 1. increasing alumina concentration (ultra rapid feeding)
- 2. short-circuit between cathode (metal pad) and anode, thereby removing the gas film under the anodes

Anode Effect and Pot Performance

Figure 4 shows an anode effect that was deliberately provoked for measurement purposes. The solid black line represents the pseudo resistance curve (moving average over 10 minutes) and the solid gray line shows the feeding cycle status. The dotted (red) line displays the alumina concentration (analyzed with an oxygen analyzer LECO RO 416).

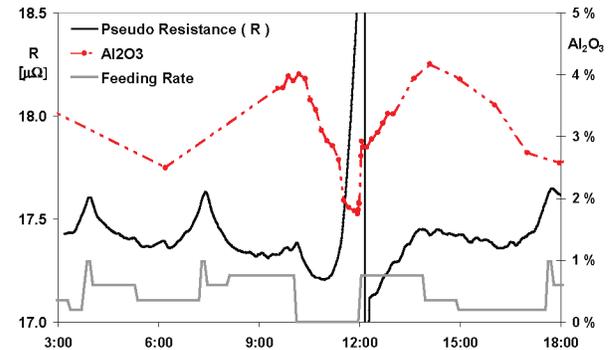


Figure 4: Pot 2045: Anode Effect (Resistance and Al<sub>2</sub>O<sub>3</sub>)

The pot was overfed by 150 % for a period of three hours in order to pass through the minimum of the resistance curve and on to the high Al<sub>2</sub>O<sub>3</sub> concentration side. Subsequently, the feeding was switched off and two hours later the anode effect occurred. On this occasion the anode effect was manually quenched without pumping the beam. (anode effect data: duration: 4.63 min. / energy: 304 kWh → with the regression parameter set 1 (Table 1) the emissions can be calculated to CF<sub>4</sub>-m = 1.36 kg for this anode effect).

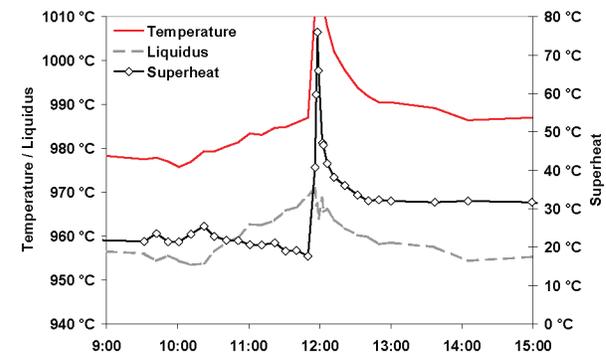


Figure 5: Pot 2045: Anode Effect: Manual Kill (Temperature, Liquidus and Superheat)

From 09.30 am to 01.00 pm superheat measurements (made with Heraeus Electro-Nite Multi-Lab 2 Cry-O-Therm device) were made every 10 minutes. Before and after this time period additional measurements were made, but not as frequent. Figure 5 demonstrates the influence of an anode effect on the pot performance. During the zero feeding period bath temperature and liquidus increased but superheat remained almost constant. During the anode effect superheat climbs steeply before settling afterwards at a higher temperature level. This indicates that besides the PFC emissions, an anode effect also represents a waste of energy. This anode effect experiment was repeated on pot 2058 as shown in Figure 6.

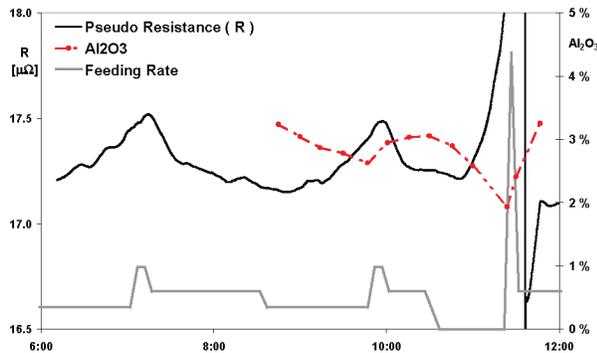


Figure 6: Pot 2058: Anode Effect (Resistance and  $Al_2O_3$ )

This time the anode effect was quenched by pumping the beam. (anode effect data: duration: 2.28 min. / energy: 112 kWh  $\rightarrow$  with the regression parameter set 2 (Table 2) we calculate  $CF_4 = 0.43$  kg for this anode effect).

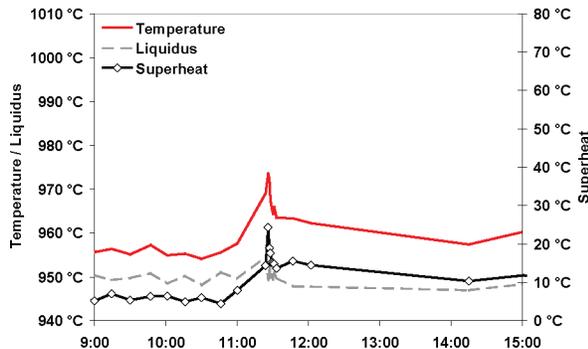


Figure 7: Pot 2058: Anode Effect: Automatic Quenching (Temperature, Liquidus and Superheat)

In contrast to the earlier quenching strategy, vigorous pumping of the beam, resulted in acceleration in the rate of alumina dissolution and, as a consequence, the anode effect produced a relatively low increase in bath temperature and superheat. A further contributory factor was the increase in bath height and additional alumina dissolution from the upper crust, leading to a further increase in alumina concentration of the bath. As a result of the collapsing voltage and subsequent low voltage periods, the total energy input was lower, further supporting the pumping strategy.

### Perfluorocarbon Emissions from Essen – A Review

The development of PFC emissions in Essen is a reflection of production and modernization over a period of time. This is illustrated in the following graphs. Figure 8 shows the development of specific  $CF_4$ -m generation in Essen. In these measurements the sum of  $CF_4$  and  $C_2F_6$  (100%  $CF_4$  and 75%  $C_2F_6$ ) was determined and displayed as  $CF_4$ -m in the graphs, Figures 8-10. A hooding efficiency of 98% was assumed. Due to a lack of information, the emissions from 1985 to 1999 were estimated from the number of anode effects multiplied by a fixed factor of 0.92 kg  $CF_4$  per anode effect (determined in the measurement campaign in 1996). The data for 2000 and 2001 were calculated from the anode effect duration. The different

slope values took the change of anode effect treatment into account. All data displayed for 2001 are forecasts on the basis of the data from January to September 2001.

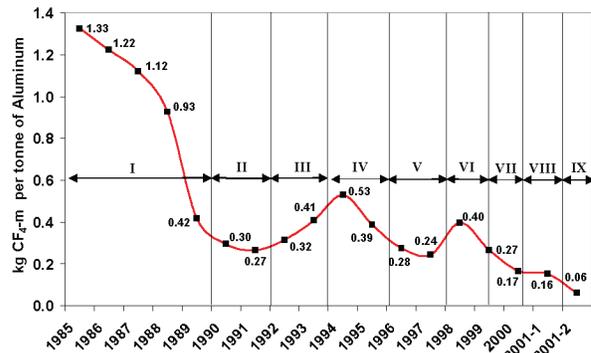


Figure 8: Development of  $CF_4$ -m Emissions

- I. Installation of point feeders and training of people
- II. Stable operation in 1990 and 1991
- III. Shut down of pot lines:
  - a. line 3 in 1992
  - b. line 1 in 1993
  - c. line 2 in 1994 (in May: only 51 pots in operation)
- IV. Restart of potlines 1 and 2 in 1994
- V. Stable operation in 1996 and 1997
- VI. Restart of potline 3 after retrofit
- VII. Stable operation in 1999
- VIII. Reducing scheduled anode effects
- IX. Change of anode effect treatment method

From Figure 8 it can be seen that the biggest steps in reducing the specific  $CF_4$ -m emissions were made between 1985 and 1990. Neglecting the disturbances (production cut backs) the emission level between 1991 and 1999 was nearly constant with about 0.25 kg  $CF_4$ -m per ton of aluminum. The reduction in scheduled anode effects from one per week to one per month provided a further reduction to 0.17 kg  $CF_4$ -m per ton of aluminum for the year 2000 and the first four months in 2001. The introduction of a new anode effect pumping strategy brought the emission level down further to 0.06 kg  $CF_4$ -m per ton of aluminum.

Figure 9 shows the aluminum production (solid line) and the  $CO_2$  emissions (dotted line) ( $CO_2$  from net anode consumption as well as  $CO_2$  equivalents originated from  $CF_4$  and  $C_2F_6$ ). Calculations of  $CO_2$  emissions are described in the following formulas: ( $CO_2$  in mt and  $CF_4$ -m in kg)

$$CO_2 = \text{net anode consumption} \times \text{carbon content} \times 3.67 \quad (1)$$

The factor 3.67 (44/12) is the ratio between oxygen and carbon if all the carbon is transferred into  $CO_2$  [9]

$$CF_4\text{-m} = \text{number of anode effects} \times 0.92 / 0.98 \quad (2a)$$

The factor 0.92kg  $CF_4$ -m per anode effect is from the measurements in 1996. This factor is assumed to be valid for the years 1985 to 1999. The factor 0.98 represents the hooding efficiency of 98%.

$$CF_4\text{-}m = \text{anode effect minutes} \times (0.27 + 0.13) / 0.98 \quad (2b)$$

The factors 0.27 and 0.13 originate from a regression analysis (from the measurements in March 2001: Table 1). They are valid for the year 2000.

$$CF_4\text{-}m = \text{anode effect minutes} \times (0.16 + 0.07) / 0.98 \quad (2c)$$

The factors 0.16 and 0.07 originate from a regression analysis (from measurements in May 2001: Table 2). They are valid for the year 2001.

$$CO_2\text{-}e = CF_4\text{-}m / 1.075 \times (6500 + 0.1 \times 9200) / 1000 \quad (3)$$

In Equation 3 the ratio of 1:10 (C<sub>2</sub>F<sub>6</sub>:CF<sub>4</sub>) and the measurement principle of analyzing the sum of 100% CF<sub>4</sub> and 75% C<sub>2</sub>F<sub>6</sub> was taken into account.

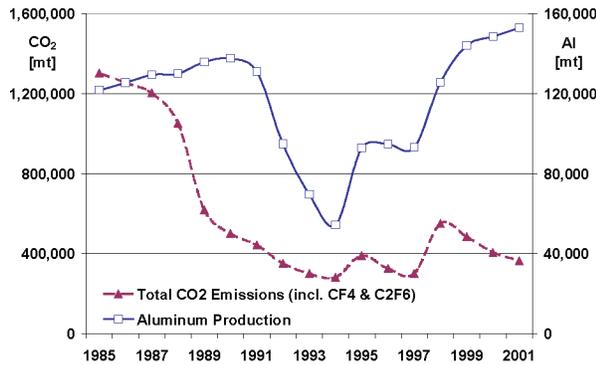


Figure 9: Primary Al-Production and total CO<sub>2</sub> Emissions

From 1985 to 1990 aluminum production increased steadily by 2-3 % per year to a level of 137,700 mt by 1990. During this period, a modernization project was completed. The pots were hooded and equipped with point feeders. Further, a dry scrubber was introduced and a dense phase transport system were installed for alumina and aluminum fluoride. Due to changing from SWPB (Side Worked PreBaked) to CWPB (Center Worked PreBaked), major reductions in PFC emissions were achieved between 1985 and 1990. From 1991 to 1994 production was reduced and, therefore, CO<sub>2</sub> emissions also decreased. During the restart periods 1994-95 for potrooms 1 and 2, and 1998 for potroom 3, PFC emissions increased temporarily. The reasons being start-up anode effects as well as unscheduled anode effects after temporary power-down situations.

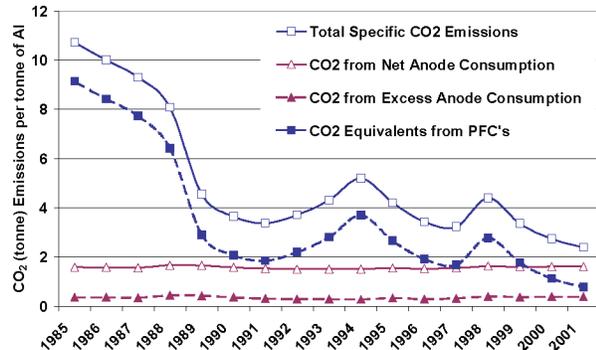


Figure 10: Equivalent and Direct CO<sub>2</sub> Emissions

Figure 10 shows the evolution of CO<sub>2</sub> emissions divided into primary source (anode consumption) and secondary source (CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>). Today, the CO<sub>2</sub> evolution from excess carbon consumption and the equivalent CO<sub>2</sub> emissions from PFC's getting close. Further reductions are possible, but the reduction potential is becoming less significant.

Switching to non-carbon anodes will superficially give greater improvements but the overall benefit might be questionable. Today, the aluminum industry uses waste products from the oil industry; petroleum coke is a by-product from the oil refining industry, as a good raw material to produce anodes. The application of petroleum coke in the aluminum industry is much more energy efficient than its use in a coal power plant.

**Phase I: Measurement Campaign in 1996**

The first time that the anode effects were systematically investigated for their PFC emissions was in the summer of 1996. The measurement instrumentation was the same as in the campaigns in 2001. The sampling location was in the stack of the central dry scrubber. In earlier days tilting the beam quenched the anode effect. During beam tilting one side drives gradually down whilst the other side moves up. After 100 seconds the movement is inverted. The success with this strategy was relatively low (about 60%) and therefore the anode effect duration were quite long. The average CF<sub>4</sub>-m emission of 28 anode effects was determined to be 0.92 kg per anode effect with a standard deviation of 63 %. Unfortunately no voltage information was available for these anode effects, therefore, it is not possible to correlate these data to any other process parameter. The yearly PFC emissions were calculated from the number of anode effects multiplied with the above-mentioned factor of 0.92 kg CF<sub>4</sub>-m per anode effect.

**Phase II: Measurement Campaign in March 2001**

The objective of this measurement campaign was to determine the present situation and find out how this might be improved. At the end of the year 2000 tests were already being made with a moderate pumping strategy. A typical anode effect with this strategy is shown in Figure 11.

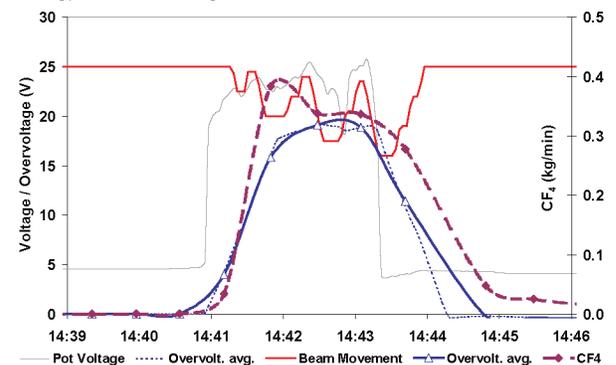


Figure 11: Pot 1068: Version 0: 0.98 kg CF<sub>4</sub>

In this figure pot voltage (solid gray line), anode beam position (solid red line; starting position is always 25 on the left y-axis), CF<sub>4</sub>-m emission (dashed red line with solid square marks) and one minute moving average (solid blue line with open triangle marks) of the overvoltage (voltage above 7.5 V) are displayed.

From Figure 11 it can be seen that only after the fourth stage in beam movement the voltage collapsed and the necessary short circuit occurred. To make this data easier to compare with other data and due to the fact that the measurements were carried out at different locations (with different volume rates), the CF<sub>4</sub>-m emissions were converted into kg per minute; (concentration multiplied by the gas volume per minute). In the present paper all of the voltage-emission-diagrams are plotted with the same scales on the axis.

Due to the type of measurement and the nature of the CF<sub>4</sub>-m evolution, there is good agreement between the one-minute moving average of the overvoltage and the CF<sub>4</sub>-m emissions. To reduce the CF<sub>4</sub>-m emissions the anode effect treatment strategy had to be changed. The first idea was to reduce just the overvoltage during anode effect with fast down moves. But there were several concerns about a more aggressive pumping strategy:

1. bath overflow of pots and loss of bath volume due to absorption of bath while pumping into the crust
2. increase of carbon dust because of overflowing of the anodes with bath
3. iron contamination due to stub erosion while in contact with the bath
4. no confidence in the general mechanism and correlation between CF<sub>4</sub> emissions and overvoltage

It was decided to start with the observation of bath height while moving the beam. The anode current distribution was also monitored. Both results (average of several trials) are shown in Figure 12.

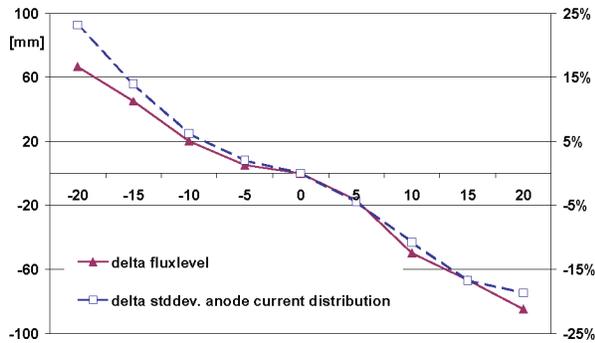


Figure 12: Bath Level Variation

With a reduction in beam height of 20mm, the bath level increases about 60mm while the standard deviation of anode current distribution increases by about 25%. Increasing the beam height by 20mm results in a decrease in bath level of 80mm and reduction of anode current deviations of 20%. With a pot cavity of 580mm and a metal / bath level of 180 / 220mm there is a nominal space of 180mm for the bath during pumping. All of the other arguments against pumping were also in the meantime rejected. Bath levels were regularly measured directly after anode effects but no significant changes were observed. Metal quality was unchanged during the last year. No correlation existed between carbon dust accumulation in pots and the frequency of anode effects.

During this measurement campaign some of the anode effects were provoked because the different quenching parameters were only downloaded to selected pots. Figures 13 - 15 demonstrate the effect of these different quenching strategies.

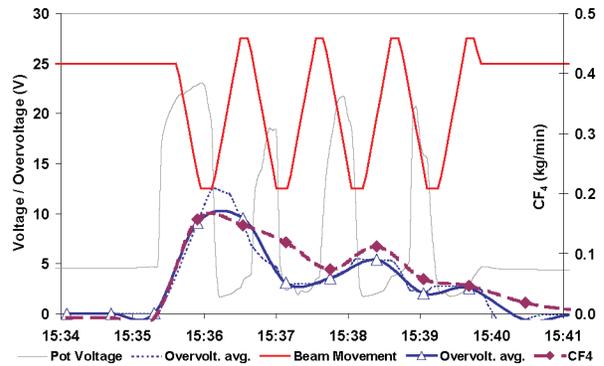


Figure 13: Pot 3017: Version 2: 0.46 kg CF<sub>4</sub>-m

The quenching Version 2 was successful after the fourth stage. The maximum emission level and the total emission were low. The ratio of high voltage periods to low voltage periods is about 50% resulting in a low value of averaged overvoltage and emissions. The development of the voltage and the CF<sub>4</sub>-m emissions curves follow each other closely.

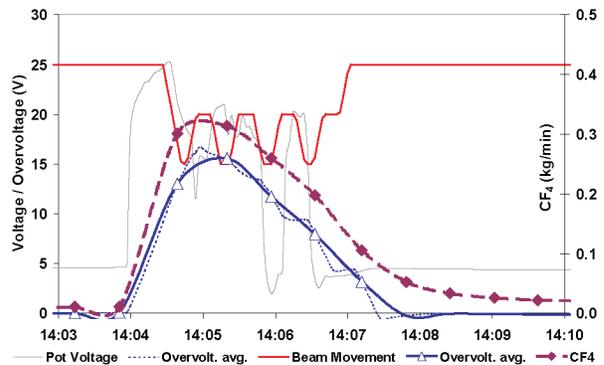


Figure 14: Pot 1070: Version 4: 0.95 kg CF<sub>4</sub>-m

Figure 14 displays a good correlation between CF<sub>4</sub>-m and overvoltage moving average. The voltage signal from the beginning of the anode effect initially remains quite stable and the first break down in voltage is only achieved after 2 minutes. As a result the total emissions become substantially high.

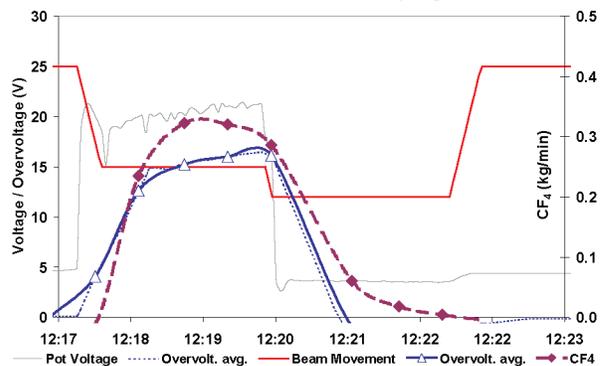


Figure 15: Pot 2029: Version 7: 0.78 kg CF<sub>4</sub>-m

Figure 15 shows a special test for anode effect quenching. The idea was to move the beam down, immediately after an anode effect was detected. The beam remains in this lowered position for three minutes. In this particular case the downward movement was not sufficient to achieve the voltage collapse. After three minutes the beam was manually driven down until the voltage broke down and immediately CF<sub>4</sub>-m generation stopped.

During the first measurement campaign in 2001, 30 anode effects were analyzed with an average emission level of 1.02 kg CF<sub>4</sub>-m per anode effect. The standard deviation of the emission level was 59%.

Table 1: Set 1 of data: Results from Campaign March 2001

Correlation	Linear Regression	R
Time [min]	Y = 0.27 * X + 0.13	0.90
Voltage [Vh]	Y = 0.51 * X + 0.34	0.91
Energy [kWh]	Y = 0.0034 * X + 0.33	0.90

Table 1 shows the results from regression analysis of the above-mentioned 30 anode effects. The emission level was correlated with time, voltage and energy of the anode effects. The correlation factors |R| are very good for all three correlations, however all the regression curves have quite high offsets.

**Time [min]:** calculated in minutes. Represents the portion of the anode effect while the voltage is above 7.5V

**Voltage [Vh]:** integration of the voltage signal while the voltage is above 7.5V. Converted into voltage hours. Hereby, the complete voltage signal is integrated. This gives a better correlation factor than subtracting 7.5V or the set-point-voltage from the signal.

**Energy [kWh]:** anode effect energy while the voltage is above 7.5V.

**Phase III: Measurement Campaign in May 2001**  
**Verification of Improvements**

After evaluating the results of this measurement campaign Version 2 was installed on all process computers. This strategy showed the lowest emissions and the highest success rate. To verify this newly implemented anode effect treatment strategy another measurement campaign was carried out in May 2001. At this time all pots had been running with this strategy for over two months. During these two months the anode effect quenching time was reduced by approximately two minutes while the success rate increased by more than 30%. Today, the failure in automatic anode effect quenching is less than 5%. These performance indicators also infer good results for the emission measurements. During the campaign in May 2001 the measurements were done at each duct system of the three potlines (about 50 m before the entrance to the dry scrubber) in order to get the most representative results for the Essen smelter. Each of these locations connects 60 pots from one potroom. There were no anode effects provoked during these measurements.

Table 2: Set 2 of data: Results from Campaign May 2001

Correlation	Linear Regression	R
Time [min]	Y = 0.16 * X + 0.07	0.81
Voltage [Vh]	Y = 0.55 * X + 0.03	0.92
Energy [kWh]	Y = 0.0036 * X + 0.03	0.91

27 anode effects were investigated during this verification campaign. The average emission level was 0.43 kg CF<sub>4</sub>-m per anode effect with a standard deviation of 58%. The results of the regression analysis are displayed in table 2. The correlation factor between time and emissions was low, only 0.81 but still representing a good indication of a positive correlation. The correlation factors for voltage and energy turned out to be high with up to 0.92. The next charts show some examples of this newly implemented successful quenching strategy.

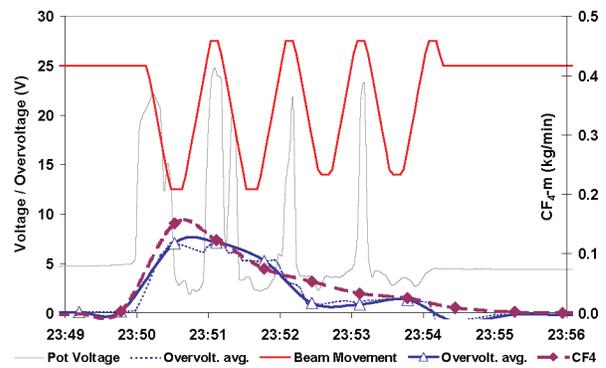


Figure 16: Pot 1117: Version 2.2: 0.31 kg CF<sub>4</sub>-m

Figure 16 shows a successful example of the newly installed quenching sequence. Important for the low emission level is the high ratio of low voltage times in relation to high voltage peaks. The agreement between the one-minute-moving-average of the voltage signal and the CF<sub>4</sub>-m emission is excellent.

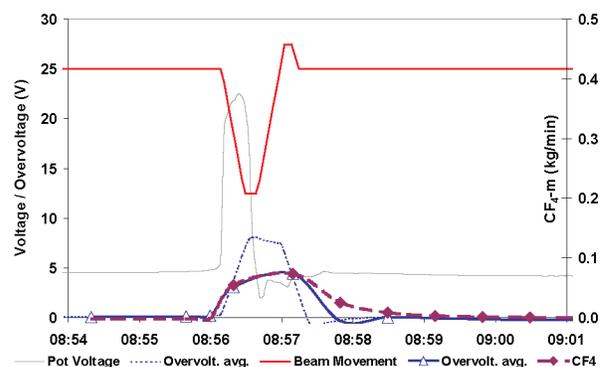


Figure 17: Pot 3063: Version 2.2: 0.10 kg CF<sub>4</sub>-m

The best results with anode effect quenching were achieved in potroom 3, (see Figure 17), which has the highest line amperage and the lowest interpolar distance. Quite often these anode effects were already extinguished after the first moving sequence (about 40s).

**Slope Method and IPCC Recommendation**

In this section the data from this work are compared with the “slope method” [7] and the values recommended by IPCC. The slope method is defined as:

$$\left( \frac{kg\ CF_4}{metric\ ton\ Al} \right) = S * \left( \frac{anode\ effect\ (min)}{cell\ day} \right) \tag{4}$$

Equation 4 is best applicable if during the evaluation measurements a whole potline or smelter is observed over a longer period of time and the emissions are integrated. Another approach is the investigation of single anode effects. To evaluate these single anode effects in the same way and calculate a comparable “S”-factor, the equation 4 has to be rearranged:

$$kg\ CF_4 = S * \left( \frac{metric\ ton\ Al}{cell\ day} \right) * anode\ effect\ (min) \tag{5}$$

The factor (mt Al)/(cell day) depend on potline performance and amperage. For the following calculations a three-month average was used. With Equation 5 the anode effects were analyzed in a regression analysis. Table 3 shows the slope values that result from our two measurement campaigns and compare these values with IPCC recommended values and the linear regression parameters from table 1 and 2. The pots produce about 1.1 to 1.2 ton Aluminum per cell day. Therefore the slope values and the data from table 1 and 2 are quite similar.

Table 3: Comparison of Slope-Factors

	Slope	Linear Regression
IPCC	0.14	
March 2001	0.26	Y = 0.27 * X + 0.13: Table 1
May 2001	0.17	Y = 0.16 * X + 0.07: Table 2

Table 4 demonstrates the development of CF<sub>4</sub>-m emissions for the years 2000 and 2001. The reasons that are mentioned earlier in this paper for the reductions of PFC emissions from the smelter Essen are also valid for Table 4.

Table 4: Emissions from Essen

	AEmin/ Cell-day	kg CF <sub>4</sub> -m/ mt Al	kg CF <sub>4</sub> -m/mt Al/ AEmin/Cell-day
1 <sup>st</sup> Quarter 2000	0.63	0.15	0.24
2 <sup>nd</sup> Quarter 2000	0.64	0.15	0.24
3 <sup>rd</sup> Quarter 2000	0.65	0.15	0.24
4 <sup>th</sup> Quarter 2000	0.84	0.20	0.24
1 <sup>st</sup> Quarter 2001	0.65	0.15	0.23
2 <sup>nd</sup> Quarter 2001	0.57	0.10	0.17
3 <sup>rd</sup> Quarter 2001	0.45	0.06	0.14

**Conclusion**

Figure 18 shows the excellent correlation between the integrated voltage signal and the CF<sub>4</sub>-m emissions. The influence of a change in anode effect quenching can clearly be seen from this

graph. In particular, the second set of data (valid for the new pumping strategy) represents a very consistent relationship between the emissions and the integrated voltage and the energy. The regressions for Voltage and Energy for both sets of data exhibit a better fit than the regressions for “Duration”. In this paper it has been demonstrated that it is possible to achieve a considerable reduction in PFC emissions by changing the anode effect quenching strategy. Furthermore, the strong relationship between the voltage signal and the CF<sub>4</sub>-m emissions has been identified. From Figure 18 it can be seen that the voltage gives a very reproducible and convincing regression.

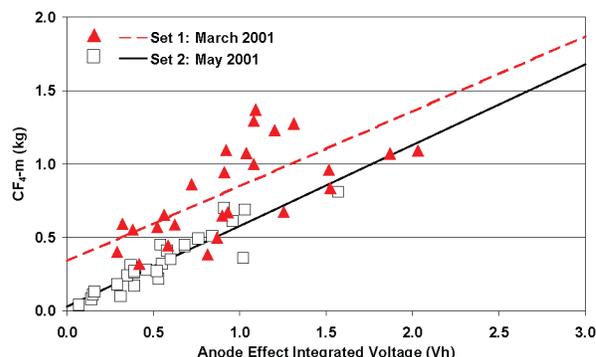


Figure 18: Regression / Voltage

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