

# Light Metals 2012

**ALUMINUM REDUCTION  
TECHNOLOGY**

**Cell Fundamentals,  
Phenomena and Alternatives I**

*SESSION CHAIR*

**Michel Reverdy**

Dubai Aluminium

Dubai, United Arab Emirates

## INFLUENCE OF THE SULPHUR CONTENT IN THE CARBON ANODES IN ALUMINIUM ELECTROLYSIS - A LABORATORY STUDY

Stanislaw Pietrzyk<sup>1</sup> and Jomar Thonstad<sup>2</sup>

<sup>1</sup>AGH-University of Science and Technology, 30 Mickiewicza Av., 30-059 Krakow (Poland)

<sup>2</sup>NTNU, Norwegian University of Science and Technology, 7491 Trondheim (Norway)

Keywords: aluminium electrolysis, carbon anodes, sulphur content, current efficiency, carbon consumption

### Abstract

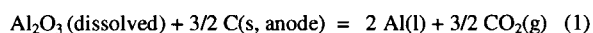
The chemistry of sulphur in carbon anodes is not fully understood, especially its influence on the electrolysis parameters. The results of this study are indicative of an important link between the sulphur content in the anode material and the carbon consumption as well as the current efficiency during aluminium electrolysis. By performing a laboratory scale investigation of different carbon anodes with sulphur contents ranging from 1.97 to 3.82 wt% S in addition to graphite anodes with sulphur content close to zero, it was found that increasing sulphur content contributes significantly to a decrease in the current efficiency and a rise in the carbon consumption. When going from 0 to 3.82 wt% S, the current efficiency decreased from 92 to 85% (1.8 % per 1 wt% S), and the carbon consumption rose from 108 to 128% (5.2 % per 1 wt% S).

### Introduction

Aluminium is produced by electrolysis of alumina dissolved in cryolite-based melts. The electrolyte also contains some impurities, i.e. iron, silicon, phosphorus, sulphur, etc. [1]. The impurities are introduced into the electrolyte with the alumina or fluoride salts or they originate from the carbon anodes. In the Hall-Heroult process we know that sulphur originates as sulphur in the anode carbon plus some sulphur contained in the alumina and in the aluminium fluoride (1-5 wt.% S).

Sulphur originates mainly from two sources. Petroleum coke used in the production of carbon anodes contains 0.7-3.5 wt.% sulphur (cokes with higher sulphur contents are usually blended with low-sulphur cokes). Cryolite and aluminium fluoride also contain sulphur, mainly as sulphate (up to 1 wt.%). The chemistry of sulphur in carbon anodes is not fully understood, especially its influence on the electrolysis parameters. Since the sulphur content in the crude oil used in the production of petroleum coke tends to increase with time, the effect of the sulphur content on the carbon consumption and the current efficiency was studied in the present work.

The main parameters affecting the current efficiency have been known for a long time. The concepts of loss in current efficiency were developed more than 50 years ago. The primary electrochemical reaction producing aluminium is:



and the main chemical back reaction causing loss of aluminium has traditionally been written as:



where Al(dissolved) is metal dissolved in the electrolyte [1].

In principle, the current efficiency can be determined from the weight of aluminium tapped from the cell, when knowing the quantity of electricity used. Reliable results for industrial cells can then be obtained for periods of several months, because the metal inventory in the cell is not known precisely. This method is also commonly used in laboratory cell experiments, where the weight increase of aluminium can be determined precisely after each short term experiment.

With the assumption that CO<sub>2</sub> (g) is the only primary anode product and that the main back reaction causing a loss of aluminium is (equation 2) producing CO(g), the current efficiency (CE) may be calculated by the well known Pearson-Waddington equation:

$$\text{CE}(\%) = 100\% - 0.5 [\% \text{CO}(\text{g})] = 50\% + 0.5 [\% \text{CO}_2(\text{g})] \quad (3)$$

This equation has traditionally been used to estimate current efficiency, with the use of various gas analysis techniques to determine the concentrations of CO<sub>2</sub>(g) and CO(g) in the anode gas. Thus, measurements of the CO<sub>2</sub>(g)/CO(g) ratios gives an instantaneous current efficiency determination. Prediction of current efficiency by this equation is usually believed to be accurate within a few per cent. Error limits are discussed in [1], and it is mainly due to difficulties in determining the exact extent of side reactions like: reaction between carbon, oxygen and CO<sub>2</sub>, electrolytic formation of CO, the back reduction of CO, oxidation of aluminium carbide, the effect of sulphurous gases etc.

An alternative method of calculating the current efficiency, which is being used in the present work, is the oxygen balance method, based on a mass balance of the gaseous oxygen in the cell. This method (OxyB) calculates the current efficiency by comparing the total net oxygen production in the form of CO<sub>2</sub> and CO with the theoretical amount of oxygen that should be produced from the cell according to Faraday's law.

In a similar way a carbon mass balance can be made for the cell where the carbon consumption and the carbon dust formation can be determined independently of the current efficiency [2-5]. The theoretical carbon consumption (CC<sub>th</sub>) per second can be calculated by Faraday's law:

$$CC_{th} = \frac{M_c \cdot I}{4 \cdot F} \quad [\text{g/s}] \quad (4)$$

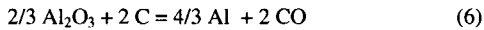
where  $M_c$  is the molar weight of carbon (12) and  $I$  denotes the total current.

In practice, it is known that the  $CC$  is generally higher than theoretical. This may be due to excess consumption in the form of excess carbon gasification ( $CG$ ), as outlined in the following, and the formation of carbon dust ( $CD$ ). A certain disintegration of the working face of the anode occurs, due to different rates of consumption of the two components in the carbon anodes [1,6] since the binder coke, originating from the pitch binder, is chemically more reactive than the aggregate coke.

Excess carbon gasification is mainly due to the Boudouard reaction:



It has been shown [1,7] that this reaction does not take place on the surface of the polarized anode, but  $CO_2$  can react inside the pores of the anode or with carbon dust floating in the bath. Exposure of the anode to air during electrolysis also causes excess consumption in the form of gasification (air burning) and dusting. It is possible that some primary  $CO$  may be generated at low current densities, according to:



The net result is the same as for reaction (1) followed by reaction (5), so it is not possible to distinguish unambiguously between primary  $CO$  and  $CO$  formed by the Boudouard reaction. However, there is strong evidence [8-10] that reaction (6) plays a very minor role, except at very low current densities ( $< 0.05 - 0.1 \text{ A/cm}^2$ ). Furthermore, the so-called back reaction, which causes loss in  $CE$ , i.e. reaction (2), produces  $CO$ , but it does not affect the gas volume or the  $CC$  as calculated by equation 4. However, if the  $CC$  is referred to the amount of aluminium produced, reactions (2) and (6) do affect the  $CC$ .

The above-mentioned reasons tell us why the carbon consumption in practice is generally higher than theoretical (as calculated by equation (1)).

Efforts have been made to develop a reliable method to determine the electrolytic carbon consumption in the laboratory. The most well known and publicized method is that of Alcan, sometimes known as the Hollingshead method [11,12]. An anode core sample is inserted in a bath contained in a graphite crucible and electrolyzed for a certain time (2-6 hours). The weight loss of the anode is determined. In industry the carbon consumption ( $CC$ ) is normally expressed as  $\text{kg C per tonne Al produced}$ , but in this work it was calculated referred to equation (1), i.e. to Faraday's law, and given in percent of  $CC_{th}$ .

Compared to the standard testing procedures for carbon materials, electrolytic testing is very time-consuming and expensive. Another shortcoming of this method is the fact that it does not distinguish between carbon gasification ( $CG$ , in the form of  $CO_2$  and  $CO$ ) and carbon dusting ( $CD$ ). Direct determination of carbon dust formation is not easily accessible. Therefore, at the aluminium laboratories in Trondheim a method to determine  $CG$

and  $CD$  in an indirect way was developed [13-15]. A closed furnace was used and all the anode gas was collected. The total carbon consumption was determined in the normal way, and the dusting was then found by difference between the total consumption and the carbon gasification,

$$CC = CG + CD \quad \text{in [g]} \quad (7)$$

This procedure adds considerable complexity and operating cost to the method, but on the other hand it yields more information.

The content of carbon dust is calculated according to the equation:

$$CD = 100 \cdot \{CC_{th} [\text{g}] - \text{Carbon in the gas phase} [\text{g}]\} / CC_{th} [\text{g}] \quad \text{in [\%]} \quad (8)$$

where  $CC_{th}$  represents the carbon consumption according to Faraday's law. Please note that all data are referred to Faraday's law, implicitly assuming 100% cathodic current efficiency, and the data are thus slightly lower than data referred to e.g.  $\text{kg Al produced}$ . The conversion factor is  $100\%CE$ , so for e.g. 95% current efficiency, the factor is 1.05.

Likewise we can calculate how much of the primary  $CO_2$  has reacted according to the Boudouard reaction (equation 5) [5,16]:

$$DBR = 100 \cdot (n_{CO_2} + n_{CO} - n_{th}) / n_{th} \quad \text{in [\%]} \quad (9)$$

where:  $n_{CO_2}$  and  $n_{CO}$  represent the number of moles of  $CO_2$  and  $CO$  in the outgoing gas, and  $n_{th}$  represents primary  $CO_2$  according to Faraday's law ( $It/4F$ ), i.e. it is the molar equivalent of  $CC_{th}$ .

The objective of the present work was to measure the carbon consumption ( $CC$ ), the carbon dust formation ( $CD$ ) and the current efficiency ( $CE$ ) in a laboratory cell using the techniques outlined above, in order to study the effect of the anode sulphur content during experiments of 6 hours duration.

## Experimental

The  $CC$  and  $CE$  experiments were performed in an air-tight laboratory furnace attached to a gas line for continuous analysis of the anode gas.

The cell, shown in more detail in Fig. 1, consists of a graphite crucible, where the inner wall was covered with 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 mm thick layer) in order to prevent any reaction between  $CO_2$  and the carbon anode body. The anode was 42 mm in diameter and had a threaded hole in the top to connect it to the threaded stainless steel tube (shielded with a sintered alumina tube) with a closed end, holding the anode and serving as current lead. A Pt-Pt10Rh thermocouple placed inside a sintered alumina tube was used to record the electrolysis temperature. Argon (99.999 %) was used as a carrier gas at a flow rate of  $200 \text{ cm}^3 \text{ min}^{-1}$ . The gas analysis was performed continuously by means of an IR gas analyzer. The experimental conditions are listed below.

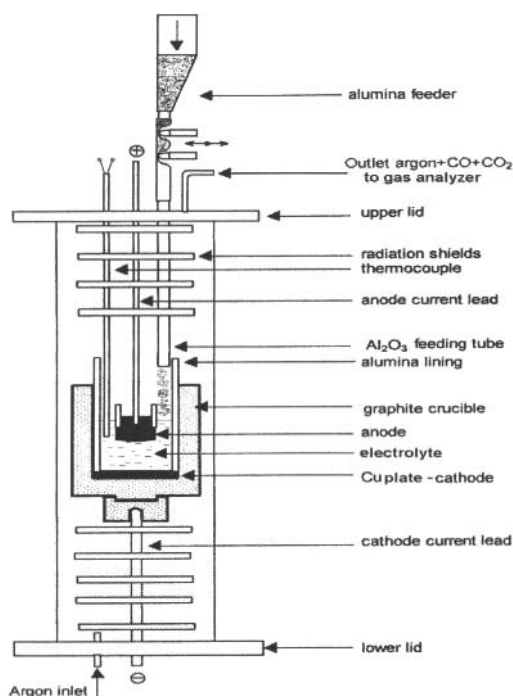


Figure 1. The experimental cell.

#### Experimental conditions

Cell current - 27 A

Anode current density -  $0.86 \text{ A} \cdot \text{cm}^{-2}$

Cathode current density -  $0.3 \text{ A} \cdot \text{cm}^{-2}$

Anode-cathode distance - 40 mm

Anode- Graphite and prebaked

Cathode- Copper plate

Melt composition:  $\text{AlF}_3$  -12%,  $\text{CaF}_2$  -5%,  $\text{Al}_2\text{O}_3$  - 8.36% (sat.),

$\text{Na}_3\text{AlF}_6$  -74.64% in wt%

Working temperature - 960 °C

Electrolysis time - 6 hours

Data sampling frequency - 20s

Alumina was fed by a fully automated feeding device (feeder). The feeding parameters were: batch size: 0.3 g, feeding rate: 14 g  $\text{Al}_2\text{O}_3$  /h at 78 s intervals, in amounts corresponding to approximately 80% of the consumption, and the remaining 20% is then dissolved from the cell and anode lining. The anode materials were supplied by Hydro Aluminium.

Anodes with different sulphur contents were prepared by mixing a low-sulphur coke with a high-sulphur coke in different proportions and supplied by the Carbon Laboratory of Hydro Aluminium in Årdal, Norway. Four runs were made with graphite anodes as a zero sulphur carbon material. The sulphur contents in the carbon anodes are given in Table I.

Table I. List of tested anodes.

Experiment No.	Anode material	Anode sulphur content, wt. %	Butts content wt. %
1	Graphite	0	0
2	Graphite	0	0
3	Graphite	0	0
4	Graphite	0	0
5	B -09	1.97	0
6	B-64	3.82	0
7	B-09	1.97	0
8	B-64	3.82	0
9	B-09	1.97	0
10	B-64	3.82	0
11	B-30	2.09	20
12	B-65	2.33	20
13	B-56	2.62	20
14	B-36	2.64	20
15	B-58	2.69	20
16	B-30	2.09	20
17	B-65	2.33	20
18	B-56	2.62	20
19	B-36	2.64	20
20	B-58	2.69	20

#### Results

The experimental results are summarized in Figs. 2-4. The experimental data presented in Figs. 2-4 indicate a relationship between the sulphur content in the anode material and the current efficiency as well as the carbon consumption during aluminium electrolysis. It may be disputed whether the data obtained with graphite anodes should be directly compared with data obtained from prebaked anodes, because the two carbon materials have different structure and different impurity levels. However, this argument may not apply to the current efficiency data shown in Fig.3, because the back reaction determining current efficiency is not a part of the anode reaction.

If we consider the CC data in Fig. 2, the dotted line shows the overall trend. However, when neglecting the graphite data, we see that there is no significant rise in CC when going from 2 % S to 3.8 wt.% S. The same conclusion can be drawn from Fig. 4, i.e., the degree of the Boudouard reaction and carbon dust formation do not rise significantly with increasing sulphur content in the range between 2 and 3.8 wt.% S.

If we include the graphite data, we see from Fig. 2 that increasing anode sulphur content leads to increasing CC. The correlations between the CC and the sulphur content are then:

$$\text{CC from gas analysis} = 0.8241[\text{wt}\% \text{ S}] + 107.66; [\%] \quad (10)$$

$$R^2 = 0.131$$

$$\text{CC from weight} = 5.205[\text{wt}\% \text{ S}] + 108.06; [\%] \quad R^2 = 0.508 \quad (11)$$

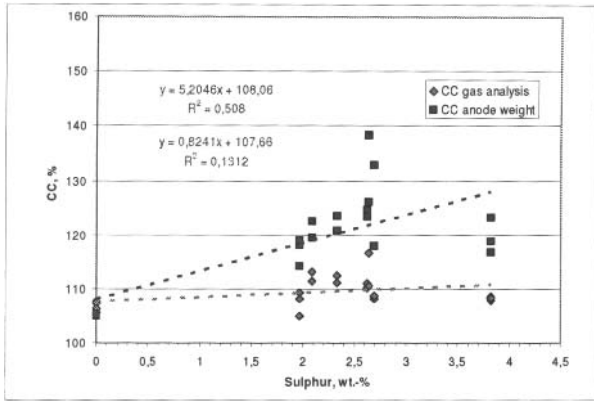


Figure 2. Influence of the anode sulphur content on the carbon consumption (CC).

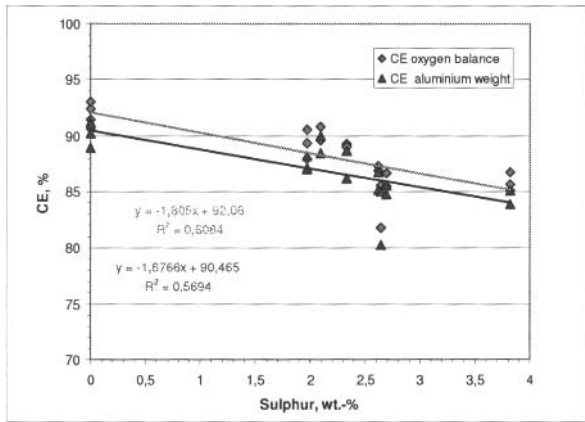


Figure 3. Influence of the anode sulphur content on current efficiency (CE).

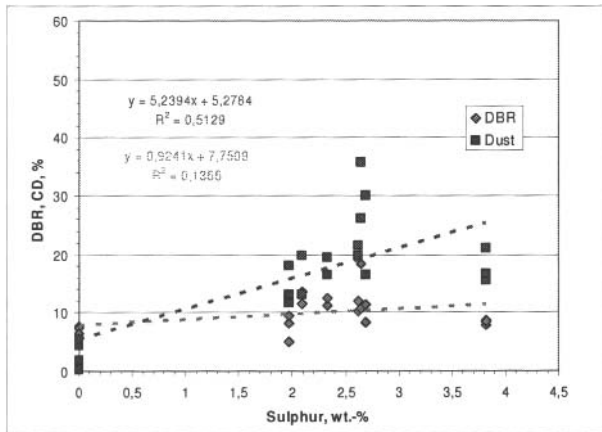


Figure 4. Influence of the anode sulphur content on the degree of the Boudouard reaction (DBR) and carbon dust formation (CD).

When comparing CC data based on analysis of the outgoing gas (integral) method with the CC based on anode weight loss, it is

clear that for industrial type anodes, dusting is much higher than for graphite anodes. This was further confirmed by the results of carbon dust content (CD) in Fig.4.

The CC results obtained for experiments 11 to 20 were more scattered, and the range of sulphur content was quite narrow (2.03 - 2.69 wt.% S) so a proper correlation could not be made. The scatter was probably due to the fact that the anodes used in experiments 11 to 20, contained butts, introducing new impurities.

The results show that increasing anode sulphur content leads to decreasing CE, independently of the method applied for its determination. The correlations between current efficiency in relation to the sulphur content are:

$$\text{CE: weight} = -1.677 \cdot [\text{wt.\% S}] + 90.465; [\%], R^2 = 0.569 \quad (12)$$

$$\text{CE: OxyB} = -1.805 \cdot (\text{wt\% S}) + 92.06; [\%], R^2 = 0.608 \quad (13)$$

Fig. 4 makes it clear that the presence of CO in the outgoing gas is caused not only by the back reaction but also by side reactions (mainly the Boudouard reaction). According to literature data [5] this difference can be even higher, i.e. in the range 4 to 10% (data not related to anode sulphur). When comparing CE data based on oxygen balance (integral) and on aluminium weight, differences are observed (except in the case of Exp.2) in the range from 0.56 to 3.34 %, while in ref. [5] this difference is in the range 2 - 7%. Table II presents the CE data obtained for experiments 1 to 10.

The carbon consumption was found to increase by 6.5% (average from CC gas analysis and CC weight) with increasing sulphur content, while the current efficiency decreased by 1.7% (average) per 1 wt% increase in the sulphur content in the range 0 - 3.8 wt.% S, according to equations (10) to (13). However, the CC and CE results obtained for experiments 11 to 20 are more scattered, and the correlation coefficients ( $R^2$  - equation of linear regression analysis) for all results were lower than for experiments 1 to 10, especially for anodes containing butts, within the small differences in sulphur content (2.03 to 2.69 wt.%). The current efficiency and the carbon consumption varied significantly for anodes B-36 (2.64 wt.% S) and B-58 (2.69 wt.% S). One reason could be the occurrence of anode effects when running experiments with anode B-36.

Table II. CE data obtained for experiments 1 to 10.

Parameter	Method	Relationship	
		Results for experiments 1 to 10	
	[%]		
Al weight		CE = - 1.471 [S] + 90.34	
		R <sup>2</sup> = 0.9153	
Oxygen balance		CE = -1.558 [S] + 91.99	
		R <sup>2</sup> = 0.8735	
[S] denotes weight percent sulphur in the anode material			

Reactivity data for the anodes used in experiments 11 to 20, determined by the Årdal Carbon Laboratory are presented in Fig. 5.

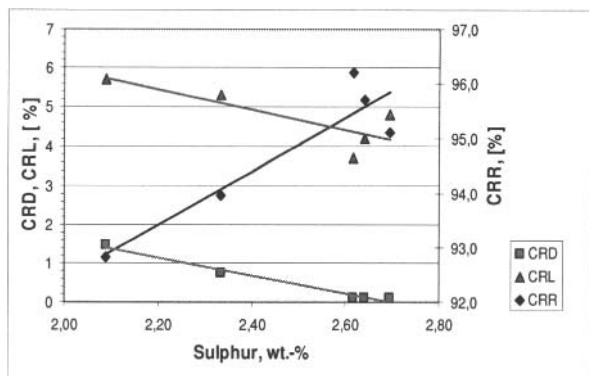


Figure 5. Reactivity data for anode materials containing 20% butts for anodes used in experiments 11-20. CRR - CO<sub>2</sub> reactivity residue, CRL - CO<sub>2</sub> reactivity loss, CRD - CO<sub>2</sub> reactivity dust.

Fig. 5 shows that the CO<sub>2</sub> reactivity of the anodes decreased appreciably with increasing sulphur content, i.e. the reactivity residue (CRR, material not reacted) increased and the dusting (CRD) decreased. For the anodes used in experiments 5 to 10 without butts the available reactivity data are incomplete, but the positive effect of sulphur seems to be much less pronounced. The positive effect of sulphur in anodes with butts is usually attributed to sulphur neutralizing the negative effect of sodium coming from the butts, probably binding sulphur as Na<sub>2</sub>S. The average sodium content in anodes without butts was 94 ppm, while it was 237 ppm in anodes containing 20 % butts. Sodium is known to be a catalyst for the Boudouard reaction with CO<sub>2</sub>.

The positive effect of sulphur on CO<sub>2</sub> reactivity is not reflected in what we may name “electrochemical reactivity”, expressed in terms of electrolytic carbon consumption (CC), as shown in Fig. 2, since CC was found to increase with increasing sulphur content. This topic will be further treated in the Discussion.

Increasing anode sulphur content caused enhanced surface roughening and more dusting (CD), according to the relationship (including the graphite data):

$$CD = 5.239[\text{wt.}\% \text{ S}] + 5.278 \quad R^2 = 0.513 \quad (14)$$

as well as increased degree of the Boudouard reaction, according to the relationship:

$$DBR = 0.924[\text{wt.}\% \text{ S}] + 7.751 \quad R^2 = 0.135 \quad (15)$$

The influence of addition of butts on CC, DBR and CD, shown in Table III, represents the CE data obtained in experiments 5 to 10 (except the data for graphite) and 11 to 20 separately.

Table III shows that the CC, DBR and CD increased appreciably (especially for the two last parameters) by addition of butts. The CC, DBR and CD were found to increase by 5.65 %, 50.45 % and 37.06 % respectively in the range 1.97 to 3.8 wt. % S.

Table III. The influence of the addition of butts on CC, DBR and CD, based on data obtained for experiments 5 to 10 (no butts) and for experiments 11 to 20 (20 wt. % butts addition).

Anodes	CC anode weight (average)	DBR (average)	CD (average)
	%	%	%
No butts (6 experiments)	118.31 ±7.14	7.93 ±1.39	15.95 ±7.30
20 wt. % butts (10 experiments)	124.97 ±6.25	11.93 ±2.63	21.86 ±6.91
Increase after butts addition	5.63	50.45	37.06

After the experiments the graphite anodes exhibited a smooth surface, representing a material that is less prone to disintegration than prebaked anodes. The prebaked specimens, showing fairly high excess carbon consumption, were visually associated with marked surface roughening. This is the reason why the degree of the Boudouard reaction and the amount of carbon dust was lower for graphite compared to prebaked anodes.

### Discussion

As shown in the discussion of Figs. 2 and 4, it makes a difference whether we include the data obtained with graphite anodes or not. For current efficiency the graphite data should be relevant, because the red-ox reactions causing loss in current efficiency are not linked to the anode reaction, so these data have been included. However, it is far more uncertain whether data on carbon consumption for graphite are directly comparable with those for prebaked samples. The safest approach is probably to exclude the graphite data from a direct comparison. We then see from Figs. 2 and 4 that going from 2 to 3.8 % S, does not have any significant effect on carbon consumption, dusting or degree of the Boudouard reaction.

In the comments to Fig. 5 it was mentioned that although sulphur has a positive effect on CO<sub>2</sub> reactivity, it has a negative effect on what we can name “electrochemical reactivity”, expressed as carbon consumption (CC), as shown in Fig. 2. We are here considering two entirely different reactions. The CO<sub>2</sub> reactivity tests the Boudouard reaction, producing CO, while the electrochemical reaction produces CO<sub>2</sub> with sulphur mainly bound as COS [17]. While the theoretical carbon consumption is 333.3 kg C per tonne Al produced, a sulphur content of 2 wt.%, yielding COS, raises that number to 341.4 kg, i.e. by 1.2% per wt. % S. Part of the increase in carbon consumption may be explained in this way.

At this stage a further explanation of the reaction mechanism involving sulphur species can hardly be given. A proper interpretation of all aspects of the mechanism would require further studies.

### Conclusions

- 1) The results of this study are indicative of an important link between the anode sulphur content and the current efficiency during aluminium electrolysis.
- 2) Increasing anode sulphur content lowers the current efficiency.
- 3) In the tested range of 2 - 3.8 wt.% S, the carbon consumption did not change significantly, while it was considerably higher than for graphite anodes. The same conclusion applies for the degree of the Boudouard reaction and carbon dusting.

### Acknowledgements

Excellent cooperation with Dr, Lorentz Petter Lossius at the Hydro Aluminium Carbon Laboratory in Årdal is gratefully acknowledged.

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