OFF-GAS ANALYSIS OF LABORATORY-SCALE ELECTROLYSIS EXPERIMENTS WITH ANODES OF VARIOUS COMPOSITIONS

Ole S. Kjos, Thor Anders Aarhaug, Egil Skybakmoen, Asbjørn Solheim, Henrik Gudbrandsen

SINTEF Materials and Chemistry, P.O. BOX 4760 Sluppen, NO-.7465 Trondheim, Norway

Keywords: SO_2, COS, CS_2, industrial anodes, gas analysis, PFC

Abstract

The sulphur content of industrial anodes in the aluminium industry is usually between 1% and 2%. This sulphur is converted to different sulphuric gases which are released along with the other off gases from the cell. Although wet scrubbers in modern plants are capable of capturing the sulphur before it is released to the atmosphere, the equilibrium dynamics and production kinetics of the sulphurous gases are of vital interest in order to be able to predict acid dew point temperatures and other important parameters for the off gas suction system in a plant.

Controlled potential electrolysis with on line gas analysis was utilized to study the compositions of gas species produced in a laboratory cell during regular electrolysis conditions and during anode effects. A three-electrode setup with an Al reference electrode was used to monitor the anodic voltage. The combination of mass spectrometry (MS) and Fourier-transform infrared spectroscopy (FTIR) was used to characterize the off gas.

The dominant sulphur containing gas specie in the laboratory cell was COS. CS_2 was only observed during anode effect, along with small amounts of SO_2.

Introduction and Theory

Introduction

The role of sulphur in an aluminium cell is not fully understood today, but it is not seen as a problem for cell operations today. Sulphur is also easily cleaned from the off gases, and therefore, it does not have any large environmental impacts. Nevertheless, sulphur containing species can be of vital interest when it comes to scaling in the off gas system. It is also of fundamental interest to fully understand the processes occurring on the anode surface, and the role that sulphur plays.
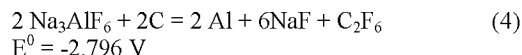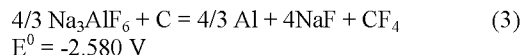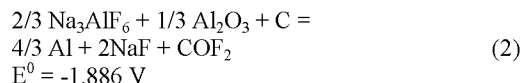
Background

The principal reaction in a Hall-Heroult cell is:

$$Al_2O_3 + 3/2C = 2Al + 3/2CO_2 \qquad (1)$$
$$E^0 = -1.192 \text{ V}$$
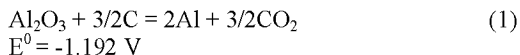
The standard cell voltage (E^0) was calculated by using FactSage [1] with pure solid α-Al_2O_3, graphite, Al and pure CO_2 gas as standard states.

When the supply of oxide to the anode surface gets below the consumption rate, other reactions will occur in order to sustain the line current in an industrial cell. These reactions will consume the electrolyte, and lead to fluoride emissions from the cell. The reactions might be:

$$2/3 \text{ Na}_3\text{AlF}_6 + 1/3 \text{ Al}_2\text{O}_3 + C =$$
$$4/3 \text{ Al} + 2\text{NaF} + \text{COF}_2 \qquad (2)$$
$$E^0 = -1.886 \text{ V}$$

$$4/3 \text{ Na}_3\text{AlF}_6 + C = 4/3 \text{ Al} + 4\text{NaF} + \text{CF}_4 \qquad (3)$$
$$E^0 = -2.580 \text{ V}$$

$$2 \text{ Na}_3\text{AlF}_6 + 2C = 2 \text{ Al} + 6\text{NaF} + \text{C}_2\text{F}_6 \qquad (4)$$
$$E^0 = -2.796 \text{ V}$$

All potentials above are calculated for 960°C, using FactSage [1], with pure gases, pure liquid NaF, Al and Na_3AlF_6, and solid C(graphite) and α-Al_2O_3 as standard states.

In a typical industrial cell the current densities will be about 1 A/cm^2, and the anodic overvoltage around 0.5 V. These cells are operated in the constant current regime. [2]

Typical anodes used in the aluminium industry today are made from petroleum coke which contains 0.7-3.5wt% sulphur, mainly in the form of CH_3SH [3]. Some of this sulphur burns off as the anodes are baked, but a content of up to 2wt% is expected in the finished anodes. All the sulphur leaves the cell as different sulphur-containing gases.

It is reported that the main sulphur-containing species in the off gas form industrial cells is SO_2, while other species such as COS, CS_2 and H_2S only occur in smaller quantities. [3]
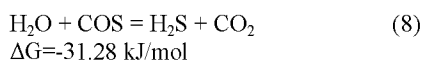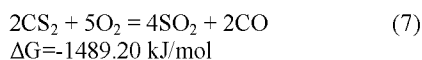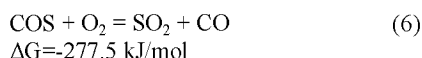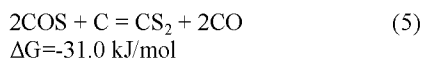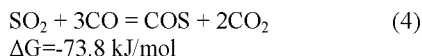
Emission of COS is of particular interest, as this substance is harmful to the ozone layer. [4] It is the only sulphur-containing gas that can escape into the stratosphere, where it oxidises to sulphates, which catalyze the breakdown of the ozone layer. COS is also poorly captured by the dry scrubber as well as the wet scrubber. [5]

However, in laboratory cells COS is often described as the only [4], or main [6], sulphur containing species. Common for all studies of off gases from closed laboratory cells is that there is very little, or no, SO_2 present in the off gas. [4,6]

An important goal of the laboratory investigation reported here was to see if there is any detectable difference in the onset potential for PFC production when using anodes that contain sulphur. Increasing sulphur content of anodes has been shown to reduce the reaction overpotential for CO_2 production as well as increase the general reactivity of the anode [7]. It was therefore of interest to see if any significant changes in the onset potential for PFC gas production from the anode could be measured. The onset potential for non-anode effect related PFC production has been studied earlier for graphite anodes [8].

<u>Theory</u>
Several equilibria exist between the sulphur species, CO / CO_2, C, and O_2. Some of these equilibria are listed below:

$$SO_2 + 3CO = COS + 2CO_2 \qquad (4)$$
$$\Delta G = -73.8 \text{ kJ/mol}$$

$$2COS + C = CS_2 + 2CO \qquad (5)$$
$$\Delta G = -31.0 \text{ kJ/mol}$$

$$COS + O_2 = SO_2 + CO \qquad (6)$$
$$\Delta G = -277.5 \text{ kJ/mol}$$

$$2CS_2 + 5O_2 = 4SO_2 + 2CO \qquad (7)$$
$$\Delta G = -1489.20 \text{ kJ/mol}$$

$$H_2O + COS = H_2S + CO_2 \qquad (8)$$
$$\Delta G = -31.28 \text{ kJ/mol}$$

All potentials are calculated for 960°C, using FactSage [1], with pure gases as standard states.

Equations (6), (7), and (8) are only relevant for industrial cells and larger open laboratory furnaces where air containing oxygen or moisture can react with COS and oxidize completely to SO_2. In these cells equilibrium (6) is shifted to the right and the main constituent in the off gases of industrial smelters is SO_2. [3]

Equation (4) indicates that COS should be the most stable gas specie as long as CO_2 is the dominating gas specie, which is the conditions that should be expected in closed laboratory furnaces.

In mass spectroscopy (MS) gas analysis it is possible that several different gas molecules have the same mass, or can split into fractions that have the same mass. Hence, great care must be taken to consider all possibilities when analysing the results, to ensure that the recorded signal is interpreted correctly. The relative height of a peak on the MS can be assumed to be linearly related to concentration.

For FTIR the signal is recorded as absorbance versus wave number (inverse wavelength), and different calibration spectra have to be recorded for all the gases that are going to be analysed. After the experiment the recorded spectra are compared to the calibration models, and gas species can be identified and quantified.

Experimental

A laboratory cell was constructed with a focus on rapid extraction and recovery of the anode gases. Therefore, a hollow anode rod was used as the gas escape vent, and the anode was sloped inwards with a hollow centre, directing most of the produced gases into the anode rod (see Figure 1). In addition, a Si_3N_4 shielding around the anode extending 0.5 cm below the anode helped direct the gases through the centre channel. On the lower part of the anode rod, just above the anode, a hole was drilled to allow the inert flushing gas to escape. This helped to increase the gas velocity through the rod. The furnace was flushed with 400 ml/min of Ar.

Industrial-grade anodes with approximately 1.8% sulphur were used; the active anode area was approximately 25 cm^2.

The cell was contained in a cylindrical furnace with inner diameter 10 cm, and assembled as shown in Figure 1. The crucible was made of graphite and lined with Si_3N_4.

A reference electrode was utilized to be able to distinguish changes in the voltage at the cathode, and at the anode. The reference electrode was a boron nitride (BN) tube with closed bottom, where a small pool of pure Al (0.5 g) was the active electrode. A hole in the BN tube 1 cm from the bottom allowed electrolyte to flow into the reference electrode.

The cell potential or current (depending on experiment conditions) was supplied with a Hewlett Packard 6032A power supply controlled by a computer. All potentials were recorded with a Keithley 2000 multichannel data logger. The cell potentials were changed in a random order in order to separate the effects of longer term operation, i.e., alumina depletion or geometric change of the anode, from those directly linked to the anode properties.

The gas composition was analysed with mass spectrometry (MS) and Fourier-transform infrared spectroscopy (FTIR). The combination of the fast response of the MS and the high resolution of the FTIR comprises a powerful tool for analyzing gas composition.

The electrolyte used in the laboratory cell was 80% Na_3AlF_6, 12%AlF_3, 5%CaF_2, and 3%Al_2O_3 of industrial quality. The cell was kept at a temperature of about 960 °C.

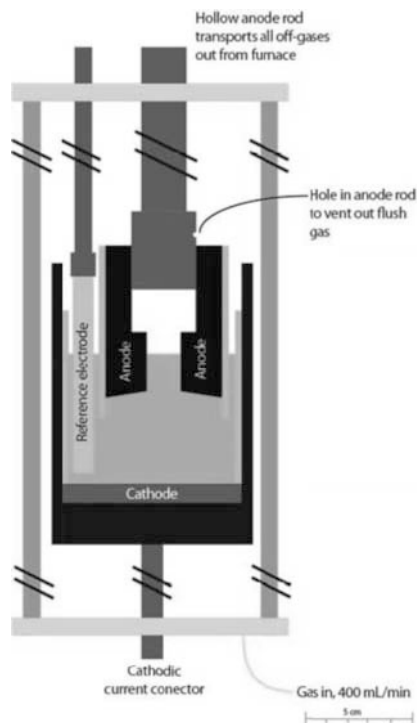The FTIR unit used was a Protea Protir 204m.

Figure 1. Laboratory cell setup.
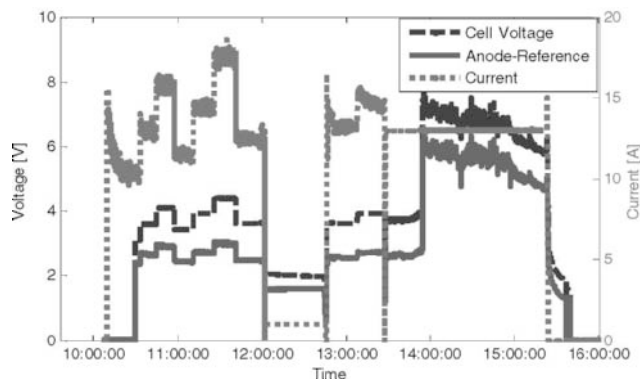
Results and Discussion

Figure 2. Current and voltage plot VS time.

All graphs and data presented here are from the same experiment, unless otherwise stated, to simplify the discussions. The first part of the experiment was run in constant voltage mode; see Figure 2. At 12:00 the experiment was stopped and some additional alumina was added. The experiment then continued at 12:45 and some voltage steps were repeated before a constant current of 13 A was set until an anode effect occurred at approximately 13:55.

The ohmic losses in the anode and anode connections are not possible to eliminate completely. Equipment to precisely determine the ohmic losses were not available during these experiments, but the resistance was estimated to be around 0.05Ω, giving between 500 mV and 750 mV in voltage loss depending on the current. None of the reported voltages are corrected for these losses due to the uncertainty in the magnitude.

In this particular experiment the anode effect was of a "soft type" without any extreme rise in voltage. However, the voltage rose by approximately 3 V.

COS
COS is the only sulphur containing specie that follows the potential and current in rapid response (Figure 3). The formation is directly related to the current passing through the anode. In the short term, a change in voltage (and current) will lead to a change in the COS produced.

However, the overall trend during the timeframe of the experiment was that the detected amount of COS decreased gradually. In Figure 3 it can be clearly seen that COS production at the highest voltages in the middle of the experiment, between 11:30 and 11:45 was significantly lower than that at 0.5 V lower anode voltage in the beginning of the experiment, between 10:30 and 10:45.

The evolution of COS is particularly interesting during the anode effect. As mentioned, in this particular experiment the anode effect gave a rather moderate increase in cell voltage of only 3 V. Therefore the power supply managed to keep the current constant throughout the AE. The AE started just before 14:00, and it can be seen that the COS concentration drops immediately, and then gradually rises to a higher value than before the AE. This is despite of the current being constant and the overall trend for COS to decay when current / voltage is unchanged in these experiments.

It is expected that all available sulphur at the anode surface reacts, and, that the rate of COS formation will be proportional to the anode wear. The rate of sulphur-containing gas formation would therefore be proportional to cell current. This seems to be true for the short term trends, but the underlying decay in the total sulphur content in the off gas cannot be explained by this hypothesis.

It could not be determined from these experiments if formation of COS is a direct electrochemical reaction, or if sulphur on the anode reacts with CO_2 to form COS and CO.
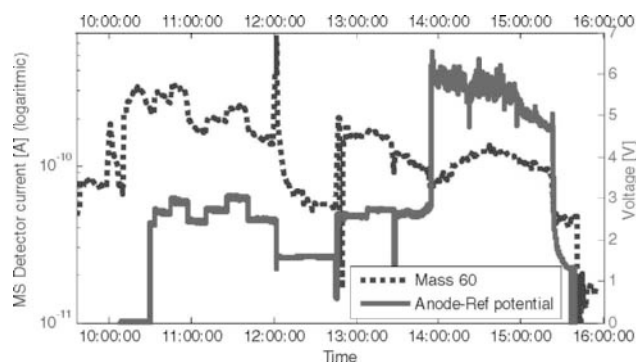

Figure 3. Plot of signal from COS (Mass 60), left axis, and voltage measured between anode and reference electrode on the right axis.

CS_2
There are no indications of CS_2 formation during the regular electrolysis. However during the anode effect the CS_2 signal starts to rise slowly. The slow rise is significantly different from the rise of, *i.e.*, CF_4 (Mass 69, Figure 5), which shows an abrupt increase at the time the cell goes into an anode effect, and hence the formation of CS_2 cannot be explained by the voltage increase itself.

CS_2 formation is not expected to involve electron transfer, but rather reaction of COS with C, reaction (5), or direct decomposition of sulphur-containing species in the anode to form CS_2. During the AE a significant increase in temperature can be expected in the anode, and that could probably explain the production of CS_2 as the spontaneous reaction between C and S is thermodynamically more favourable at higher temperature.
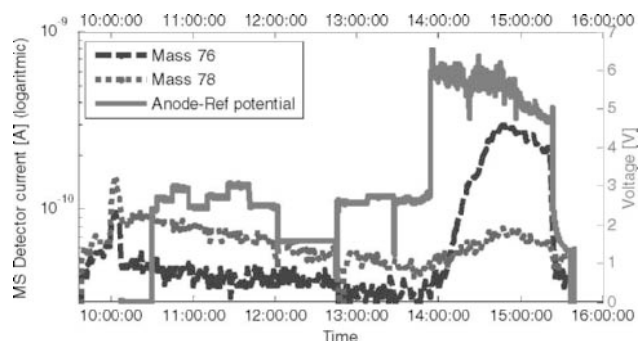

Figure 4. Plot of the primary CS_2 mass (76) along with the additional mass (78), representing signal from CS_2 with ^{34}S isotop.

Small traces of SO_2 were identified in the off gases on the FTIR measurements; the SO_2 seems to be present after an anode effect. It was not possible to positively identify SO_2 using MS data, as

the MS signal for SO_2 overlaps with the signal generated by SiF_4 $SiF4$ could be formed from Si containing impurities in the electrolyte, or by reaction of the Si_3N_4 ceramics as described in [8] Were you able to identify SO_2 using the FTIR?

In industrial cells SO_2 is the main sulphuric compound in the off gas. This agrees with our results, as COS will oxidize in the presence of O_2, and produce SO_2 and CO_2. The equilibrium between SO_2 and COS is determined by temperature, but under no conditions it is likely that all SO_2 formed in the laboratory furnace reacts to give COS, if we assumed that SO_2 were the primary formed species.

We were not able to positively identify H_2S from any of our data. On the MS H_2S should have signal on both mass 34 (H_2S), mass 33 (HS^-) and 32 (S), these should all follow the same trend, and 32 and 33 should have an intensity of approximately 40-50% of the signal from mass 34. However, mass 32 has too much signal from all the other sulphur containing gas species, along with a background signal of O_2. Comparing mass 33 and mass 34 gives a significantly higher signal on mass 33 than mass 34, indicating that mass 33 has a significant contribution from something other than H_2S. The signal at mass 34 can not alone positively identify H_2S, as sulphur has an isotop, ^{34}S, with the mass of 34 a.u., and which can originate from all the other sulphuric species identified.

H_2S is difficult to detect on FTIR due to a spectrum which contains few distinct features, and is located in the wave number region where there is much noise. The presence of H_2S therefore could not be completely ruled out. However in a closed laboratory cell, H_2S is not expected to be one of the off gas components.

PFC
The first sign of PFC production that was detected in this experiment was at a potential as low as 2.9 V measured between the anode rod and the reference electrode, when small amounts of CF_4 were measured. This is more or less identical to the results obtained on graphite, where CF_4 also could be detected in the off gas before a full blockage of the anode with high voltage or current drop occurred at 2.9 V [8], both potentials uncorrected for ohmic losses. With estimated ohmic losses in the area of 750 mV the actual anodic voltages were in the range of 2.1 V to 2.2 V However, the uncertainty in determination of the ohmic losses can be as great as 150mV, which easily would mask smaller trends in the onset potential.
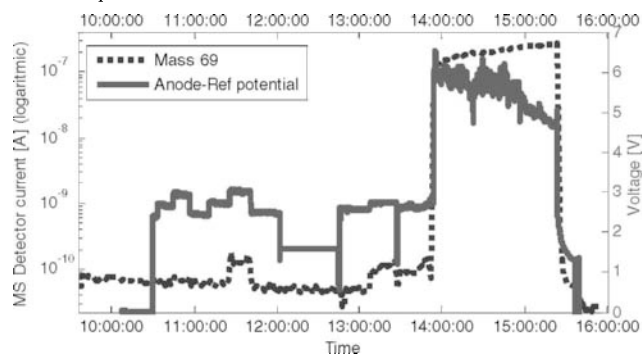

Figure 5. Mass 69 (CF_4) on left axis, and anode – reference potential on the right axis.

In any event, these potentials are too low to directly form CF_4 (E^0= 2.6 V) and the most probable formation route is through decomposition of COF_2, which can be formed at anode potentials as low as 1.9 V.

SiF_4
Significant amounts of SiF_4 were also identified in the off gas from the laboratory cell. Si(IV) is expected to be present as an impurity in the electrolyte, the Si_3N_4 cell lining could also be a Si source, even if there is no visible corrosion to the lining during the experiments. The release of SiF_4 from the laboratory cell seems to be continuous rather than following the applied voltage / current profile. This suggests that the SiF_4 is formed in a chemical rather than an electrochemical reaction.

CH4
One interesting observation that was made through interpretation of the FTIR data is the presence of small amounts of CH_4 in the off gas. In an industrial cell, CH_4 would probably get burned together with COS and CO. CH_4 peaks as high as 450 mg/m^3 were observed when the anode was lowered into the melt and the current was turned on. The CH_4 formation rate rapidly decayed, and stabilised at around 40-50 mg/m^3. (Figure 6)
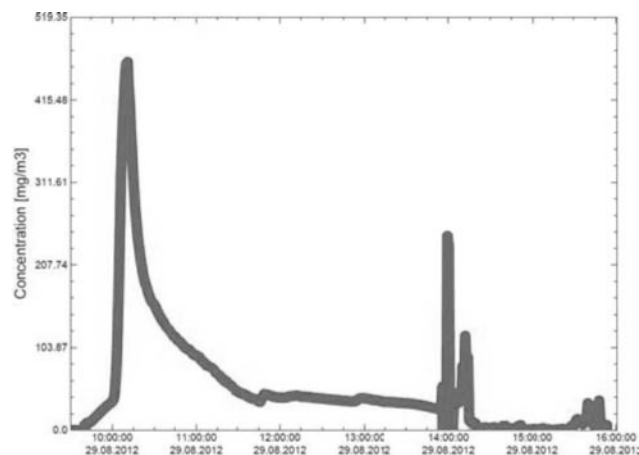

Figure 6. CH_4 concentration in the off gas as a function of time.

When re-examining older data where graphite anodes were used instead of industrial quality carbon, we discovered that CH_4 was detected in the off gas from these graphite anodes in the same part of the experiment as well. The formation of CH_4 can therefore be attributed to carbon reacting with some hydrogen source. The hydrogen source for CH_4 formation is however unknown. Thermodynamically water dissolved in the melt could form CH_4 when exposed to graphite, but CO and H_2 are thermodynamically favoured.

Conclusions

Industrial quality anodes were studied in a laboratory furnace, and produced anode gases were collected and analysed online by means of FTIR, MS. It was demonstrated that the primary sulphur specie produced at the anode is COS, while CS_2 was detected only in the later part of a fully developed anode effect.

During an anode effect there was somewhat higher release of sulphur from the anode compared to before and after the anode effect.

It was not possible to detect any significant difference in the onset or production of non-AE related PFC gases in these industrial anodes compared to the graphite anodes studied earlier within the measurement uncertainties in the experiment. Small amounts of CF_4 were detected at anode voltages as low as 2.2 V when corrected for IR loss.

CH_4 was found in the off gas upon anode lowering into the melt.

Further work

Based on these initial experiments, a better understanding of gas composition and evolution from a laboratory electrolysis cell was achieved.

In order to more accurately determine the impact of anode quality on gas evolution, experiments with potentiostatic control of the potential between the anode surface and reference electrode should be performed. The anode potential should be systematically recorded by using a separate electrical connection to anode surface. Such approach will compensate for the differences in ohmic losses between different experiments, and will enable a direct comparison of evolved gases for the same anodic potential and different anode qualities. In addition these experiments should all be conducted under similar potential / time cycles so the only difference will be the anode quality.

Acknowledgement

References

1. FactSage 6.1, Thermodynamic software, Thermfact and GTT-Technologies, (2009)

2. J. Thonstad, et.al., *Aluminium Electrolysis*, 3. edition (Aluminium-Verlag, Düsseldorf 2001)

3. M. Ambrova, J. Jurisova, P. Fellner, "Aluminium Electrolysis with Carbon Anode Containing Sulphur", Acta Chimica Slovaca, Vol. 1, No. 1, 2008, 3-11

4. M. M. Hyland, B.J. Welch, J.B. Metson "Changing knowledge and practices towards minimising fluoride and sulphur emissions from aluminium reduction cells", *Light Metals 2000,* (2000), 333

5. K. Tveito, J. Tonheim, K.A. Paulsen, "Carbonyl sulphide (COS) emissions from prebake aluminium cells", Com2001 proceedings, (2001), 291

6. R. Odegard, S. Roenning, A. Sterten, J. Thonstad, "Sulphur Containing Compounds in the Anode Gas from Aluminium Cells", *Light Metals 1985,* (1985), 661

7. R. J. Thorne, C. Sommerseth, E. Sandnes, O. Kjos, T. A. Aarhaug, L. P. Lossius, H. Linga, A. P. Ratvik, "Electrochemical Characterisation of carbon anode performance", Submitted for light metals 2013

8. O. S. Kjos, T.A. Aarhaug, E. Skybakmoen, A. Solheim, "Studies of perfluorcarbon formation on anodes in cryolite melts", *Light Metals 2012,* (2012)