

SULPHUR CONTAINING COMPOUNDS IN THE ANODE GAS FROM ALUMINIUM CELLS,

Introduction

## A LABORATORY INVESTIGATION

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Abstract

Anode gas from a laboratory electrolysis cell (985°C) was sampled without any contact with oxygen and analysed by gas chromatography. Prebaked anodes with 1-2 wt% sulphur were used. Apart from CO<sub>2</sub> and CO the following gas species were found: CS<sub>2</sub>, H<sub>2</sub>S, COS and SO<sub>2</sub>. For CO<sub>2</sub>/CO ratios that are normal for aluminium cells (4-5) the major sulphurous compound was COS. The total sulphur content in the anode gas was high at the beginning of electrolysis with a new anode, and it decreased gradually during 2-3 hours reaching a steady state in accordance with the mass balance. Thermodynamic calculations for the equilibria between CO<sub>2</sub>/CO and the various sulphurous gas species are compared with the experimental results.

In the last decade there has been an increase in the average sulphur content of the petrol coke used for anode production in the aluminum industry. At present a sulphur level of 2-3 wt% is normal for prebaked anodes and a further increase is anticipated. At present roughly 200 000 tons of sulphur is dealt with in the primary aluminum smelters per year. Due to environmental regulations much work has been done on scrubbing of SO<sub>2</sub> from off gases in general, and also from anode gas in the aluminum industry. In comparison, the research on the primary reaction of sulphur in the carbon anode is rather limited.

Henry and Holliday (1) examined both slightly burned and completely burned anode gas from industrial aluminum cells by means of a mass spectrometer, and CS<sub>2</sub>, H<sub>2</sub>S, COS and SO<sub>2</sub> were detected. CS<sub>2</sub> appeared only during anode effect, H<sub>2</sub>S only in slightly burned gas while SO<sub>2</sub> was only found in completely burned gas. COS was the major sulphur containing species in slightly burned gas.

Some of the major producers have carried out extensive studies of the effect of sulphur on anode consumption, current efficiency and cell performance. According to the latest work (2) based on Söderberg plant tests the sulphur content of the anode has no significant negative effect. This conclusion is partly in conflict with earlier work mostly based on data from prebaked plants and laboratory studies (3,4,5).

In a series of three papers (6,7,8) Burnakin and coworkers treated some of the effects of the anode sulphur content on the electrolytic process. In the first paper (6) a laboratory study of anodic overvoltage was reported, showing a decrease in overvoltage with increasing sulphur content amounting to 38 mV/wt% S for current densities below 0.7 A/cm<sup>2</sup>. It was pointed out that the gain in overvoltage was less at higher cd being negligible at around 0.9 A/cm<sup>2</sup>. Furthermore, the benefit of lower overvoltage was more than counterbalanced by a nearly linear increase in the ohmic resistance of carbon with increasing sulphur content from 0.073 Ω cm<sup>-1</sup> with 0.33 wt% S to 0.093 Ω cm<sup>-1</sup> with 2.52 wt% S.

High sulphur contents also cause increased corrosion of metallic parts of the cells (6,7). The most dramatic negative effect of increasing anode sulphur content was observed in a laboratory study of anode consumption (8). The consumption increased from 0.45 kg C/kg Al at 0.94% S to 0.622 kg C/kg Al at 2.92% S, i.e. a 38% increase. The sulphur containing gaseous species were analysed and only H<sub>2</sub>S and COS were found (6,7). The contents of these species increased linearly with increasing sulphur content, the H<sub>2</sub>S/COS ratio being close to seven.

In the present study the composition of the sulphur containing species in the anode gas from a laboratory cell was analysed and compared with thermodynamic data.

Experimental

The experiments were performed both in a pot furnace flushed with helium (~ 5 l/h) and in a closed tubular furnace with helium atmosphere. A sketch of the cell and the sampling tubes for the pot furnace and the tubular furnace are shown in Figs. 1 a and b. Listed from the carbon anode, the different parts of the sampling tubes (5 mm i.d.) were made of sintered alumina, copper and glass. Fig. 2 shows a sketch of the cell and the lower part of the gas sampling tube which was the same in all experiments.

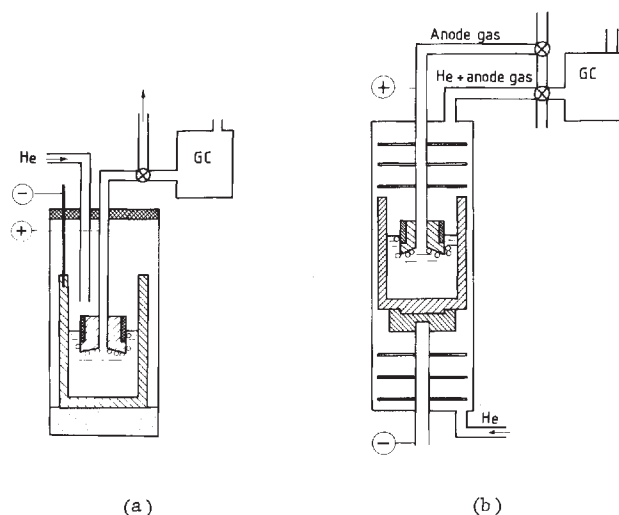


Figure 1 - A sketch of the cell and the sampling tubes for a) the pot furnace experiments, b) the tubular furnace experiments, GC = gas chromatograph.

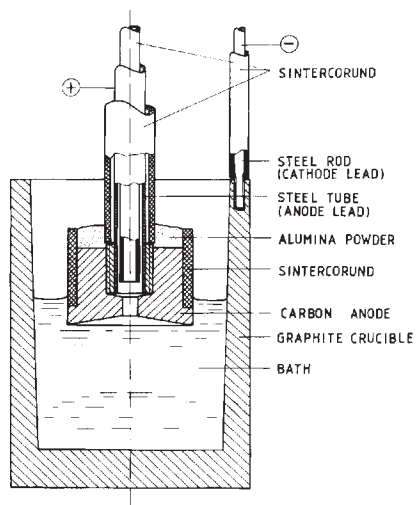
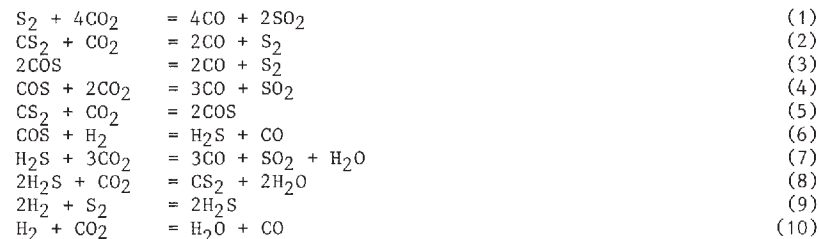


Figure 2 - The experimental cell.

Core samples of two different industrial anodes were machined to the shape shown in Fig. 2. The slightly concave ( $\sim 3^\circ$ ) anode allowed direct sampling of undiluted anode gas through the centrally located sintered alumina tube. About 50% of the gas produced underneath the anode escaped this way. In the closed tubular furnace the gas which escaped to the furnace compartment and mixed with the helium gas could also be analysed. Gas samples taken at arbitrary time intervals were analysed by means of a Hewlett Packard 5840 A gas chromatograph equipped with a flame emission detector used for the sulphur compounds and a thermal conductivity detector used for CO and CO<sub>2</sub>. The bath was prepared by mixing 79 wt% Na<sub>3</sub>AlF<sub>6</sub>, 5 wt% CaF<sub>2</sub>, 6 wt% AlF<sub>3</sub> and 10 wt% Al<sub>2</sub>O<sub>3</sub>, all of technical grade. The graphite crucible (100 mm i.d.) served as a cathode. No aluminum was present in the crucible in the beginning of electrolysis. The total current 30 A, corresponding to an anodic current density of 0.8 A/cm<sup>2</sup>, was supplied by a Hewlett Packard 6261 B Power Supply. The cell voltage and the temperature ( $983 \pm 3^\circ\text{C}$ ) were recorded on a two channel strip chart recorder.

Thermodynamic Calculations

Equilibrium pressures in gas mixtures of CO<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S, CS<sub>2</sub>, COS and SO<sub>2</sub> can be determined from the following equilibria:



The thermodynamic data were taken from JANAF (9).

The equilibrium pressures of hydrogen- and sulphur-containing gases were calculated for 750 K, 1000 K and 1250 K. The results are presented in Fig. 3 a - c and in Fig. 4 as a function of the CO<sub>2</sub>/CO ratio in the gas mixture. The calculations were conducted for two different sets of data concerning sulphur and hydrogen contents,

case A

$$\begin{aligned} P_{\text{S}_2} + P_{\text{SO}_2} + P_{\text{CS}_2} + P_{\text{COS}} + P_{\text{H}_2\text{S}} &= 0.04 \text{ atm.} \\ P_{\text{H}_2} + P_{\text{H}_2\text{O}} + P_{\text{H}_2\text{S}} &= 0.01 \text{ atm.} \\ \text{Total pressure: } &1.00 \text{ atm.} \\ P_{\text{CO}_2} + P_{\text{CO}} &= 1.00 \text{ atm.} - (\sum P_{\text{S}(g)} + \sum P_{\text{H}(g)}) \\ \sum \text{S}(g) &\approx 15 \text{ wt\% sulphur in anode gas} \end{aligned}$$

case B

$$\begin{aligned} P_{\text{S}_2} + P_{\text{SO}_2} + P_{\text{CS}_2} + P_{\text{COS}} + P_{\text{H}_2\text{S}} &= 0.01 \text{ atm.} \\ P_{\text{H}_2} + P_{\text{H}_2\text{O}} + P_{\text{H}_2\text{S}} &= 0.01 \text{ atm.} \\ \text{Total pressure: } &1.00 \text{ atm.} \\ P_{\text{CO}_2} + P_{\text{CO}} &= 1.00 \text{ atm.} - (\sum P_{\text{S}(g)} + \sum P_{\text{H}(g)}) \\ \sum \text{S}(g) &\approx 3 \text{ wt\% sulphur in anode gas.} \end{aligned}$$

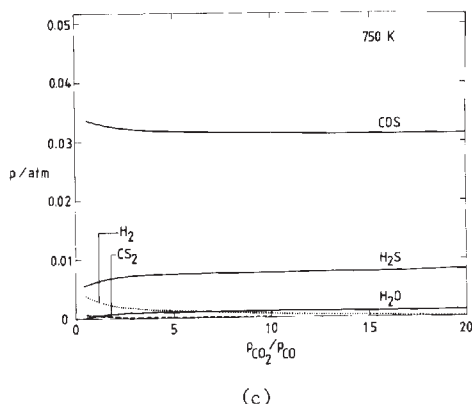
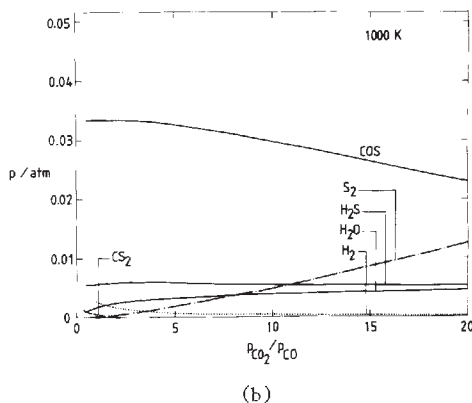
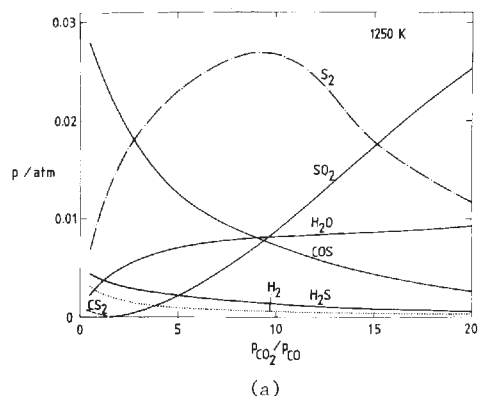


Figure 3 a - c - Calculated equilibrium pressures of sulphur- and hydrogen-containing gas species in accordance with eqs. (1-10) for case A (see text) as function of the  $\text{CO}_2/\text{CO}$  ratio for three different temperatures.

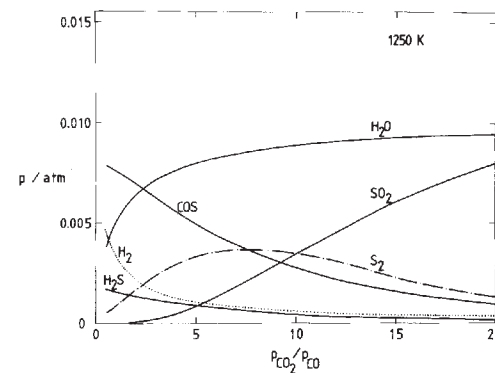


Figure 4 - Calculated equilibrium pressures of sulphur- and hydrogen-containing gas species in accordance with eqs. (1-10) for case B (see text) at 1250 K.

The following comments can be made regarding Figs. 3 and 4:

If the gas mixtures at 1250 K or 1000 K were quenched the  $\text{S}_2$  gas would condense.

As the temperature is reduced there is a dramatic change in the equilibrium gas composition towards COS and  $\text{H}_2\text{S}$ .

From a thermodynamic point of view, very little  $\text{CS}_2$  should be present in the anode gas at normal  $\text{CO}_2/\text{CO}$  ratios.

If the total pressure of sulphur-containing species is reduced (Fig. 4 compared to Fig. 3 a), there is no striking change of the equilibrium curves. It should be noted, however, that the pressure of  $\text{S}_2$  and  $\text{CS}_2$  are proportional to the square of the sulphur content. Consequently these pressures are reduced far more rapidly with a decrease in total sulphur content compared to the pressures of COS,  $\text{SO}_2$  and  $\text{H}_2\text{S}$  which are directly proportional to the sulphur content.

### Results and Discussion

In Figs. 5 a - d are shown some typical gas chromatograph responses for the analysis of sulphurous species in samples of anode gas collected through the central sintered alumina tube during electrolysis in a pot furnace. The duration of electrolysis before sampling is indicated on each graph. After analysis of CO and  $\text{CO}_2$  (chromatograph responses not shown) the  $\text{CO}_2/\text{CO}$  vol. ratios and S/(S+C) weight ratios were calculated. Table I gives the amounts of COS,  $\text{CS}_2$ ,  $\text{SO}_2$ , CO and  $\text{CO}_2$  in the various samples together with  $\text{CO}_2/\text{CO}$  and S/(S+C) ratios. In addition to the analysed gases given in Table I,  $\text{H}_2$  was detected qualitatively. S(s) was not found in the furnace or in the gas sampling tubes.

Fig. 6 shows plots of the S/(S+C) ratio derived from the gas composition as a function of time for two different anodes with 2.0 wt% (Table I) and 1.3 wt% sulphur. The dotted lines represent the S/(S+C) ratios based on uniform sulphur consumption of the anodes.

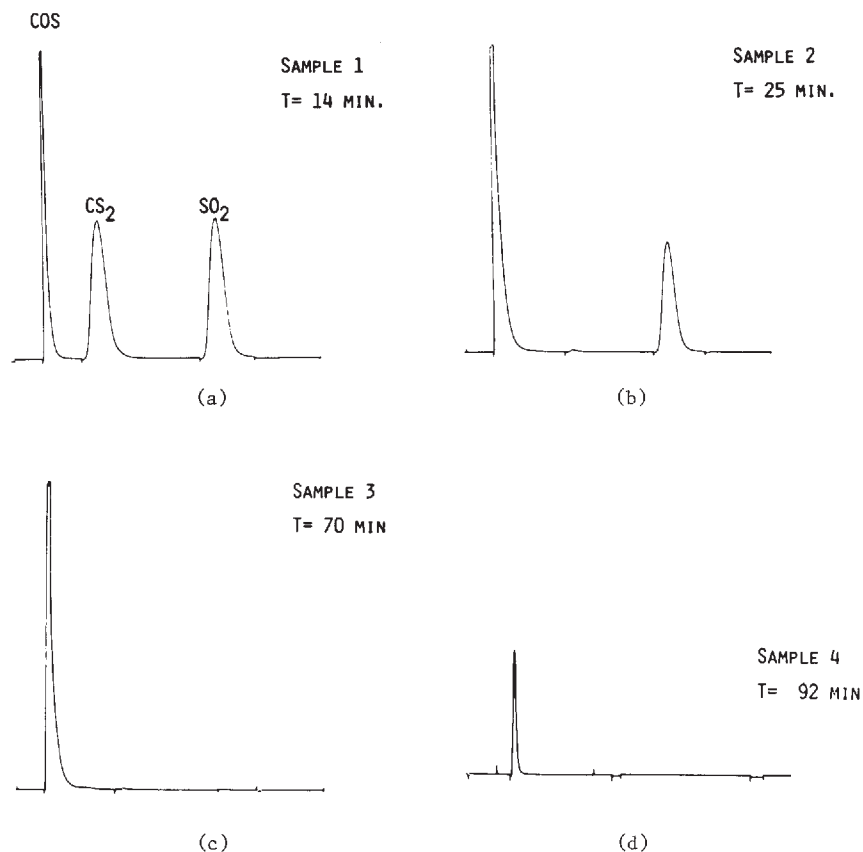


Figure 5 a - d - Typical flame emission detector responses for gas chromatographic analysis of anode gas produced during electrolysis at  $984 \pm 2^\circ\text{C}$  and  $0.8 \text{ A/cm}^2$ . Duration of electrolysis before sampling is indicated on each graph.

Table I - Chromatographic analysis of anode gas during electrolysis in a pot furnace at  $984 \pm 2^\circ\text{C}$  and  $0.8 \text{ A/cm}^2$ . Sulphur content of the anode = 2.0 wt%. Duration of electrolysis before sampling is given.

Time, min.	Vol. %				$\text{CO}_2/\text{CO}$		$\text{S}/(\text{S}+\text{C})$
	COS	$\text{CS}_2$	$\text{SO}_2$	CO	$\text{CO}_2$	Vol. ratio	Weight ratio
14	2.7	1.8	2.7	8.44	84.4	10.0	0.20
25	5.6	0.02	1.7	9.94	82.8	8.3	0.17
70	1.6	0.03	-	13.6	82.1	6.0	0.044
92	0.9	0.003	-	52.0	47.0	0.9	0.025

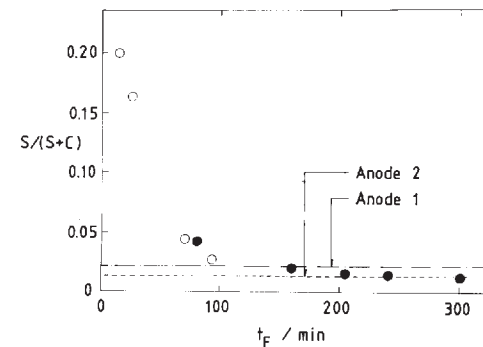
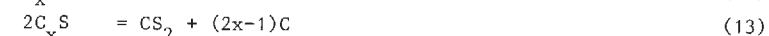
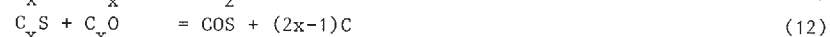


Figure 6 - The S/(S+C) weight ratio in the gas phase as a function of time of electrolysis with  $0.8 \text{ A/cm}^2$  at  $983 \pm 3^\circ\text{C}$ . Two different anodes with 2 wt% S (o) and 1.3 wt% S (●) were used. The dotted lines indicate a sulphur level of 2.0 wt% and 1.3 wt%.

Fig. 6 demonstrates clearly that considerably higher amounts of sulphurous compounds escaped from the anode in the first period after start of electrolysis than would be for uniform consumption of the anode sulphur. After a period of 3-4 hours of electrolysis a stable level was finally reached in accordance with the mass balance.

Elemental analysis of surfaces of used anodes on an Auger scanning microprobe showed only carbon and no sulphur in the surface layer, within the detection limit of the instrument ( $\sim 0.5\%$ ). The interior of the anode was found to contain  $\sim 2 \text{ wt}\%$  S, in agreement with the chemical composition, and also some oxygen was detected. By means of scanning electron microscopy a mapping of elements was made on cross sections of used anodes showing lower sulphur concentration in the outer layer near the anode surface. The formation of such a sulphur concentration gradient should correspond to an initially high rate of sulphur removal from the anode and then a gradual decrease to a steady state value and a stationary gradient, in accordance with the data given in Table I.

The nature of the sulphur bonds in the calcined anode coke is not known. Some kind of carbon-sulphur bonds must be present in the prebaked anodes since there are very small amounts of inorganic sulphur compounds. We will denote this by  $\text{C}_x\text{S}$ . Several primary reactions may be proposed, i.e.



Acknowledgement

The composition and type of bonds in the intermediate compound  $C_xO$  proposed in the primary  $CO_2$  forming anode reaction is also unknown (10). The structure of  $C_xO$  and  $C_xS$  need not be the same although similarities are to be expected.

It is commonly accepted (10) that the primary anode product is predominantly  $CO_2$  and that the  $CO$  present in the anode gas is formed in secondary reactions. Therefore, oxidizing conditions will prevail at the anode surface where the primary anode reaction takes place, and a high content of  $SO_2$  should be expected according to eqs. (11) and (15) and the equilibrium data shown in Fig. 3 a.

The question arises to what extent the gas analysis results reflect the situation at the anode surface or if reactions occur during the cooling of the gas samples. As can be seen from Fig. 3 a - c the equilibria are strongly shifted with decreasing temperature. For instance, if  $SO_2$  is taken to be the only sulphurous gas product, cooling of a  $CO_2$ - $CO$ - $SO_2$  mixture from 1250 K at equilibrium would transform it to a  $CO_2$ - $CO$ - $COS$  mixture without any detectable amount of  $SO_2$  present. However, Table I shows that the oxidizing agent  $SO_2$  coexists with the reducing compound  $CS_2$  in the samples taken during the initial period of electrolysis. From an equilibrium point of view the two gases should not coexist at any temperature (see Fig. 3). This coexistence indicates that  $CS_2$  and  $SO_2$  should both be considered as primary formed sulphurous compounds. Another indication for non-equilibrium conditions is that  $H_2$  has been identified without any  $H_2S$  being present. This is not in accordance with the equilibrium (6), see Figs. 3 and 4. The results, therefore, indicate that the high temperature gas composition is fairly well preserved during cooling.

Eqs. (11) and (12) are related to the primary  $CO_2$ -forming anode reaction taking place on the active carbon surface. However, the sulphur gradient observed may indicate that there is rather little sulphur present at the electrode surface where the  $CO_2$ -formation takes place. This means that reaction (11) and (12) hardly will be of any significance.

The thermal desulphurization reaction (13) may be important in the initial period of electrolysis as indicated by the high content of  $CS_2$  found in that period. Due to the high rate of sulphur removed in this period, the equilibria in the gas phase are probably not established. Therefore, reactions (13,14 and 15) may all be important since  $SO_2$ ,  $COS$  and  $CS_2$  all are present in larger amounts in the analysed gas. However, there will also be some attack of  $CO_2$  on the anode surface due to the Boudouard reaction;



The  $CO$  formed (and  $CO_2$ ) will penetrate into pores in the anode (10), and a gradually increasing  $CO/CO_2$  ratio will be established in the anode microstructure close to the active surface (10). The sulphur gasification reactions (14) may then be favoured, since the partial pressure of  $CO$  in the pores is increased. This mechanism agrees with the observation that the  $COS/\Sigma P_g$  ratio increases with time as shown in Table I. However, the present data do not allow any firm conclusions to be drawn with regard to the reaction mechanism for the removal of sulphur from the anode during electrolysis, and further work is needed.

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