

## **Aluminium Electrolysis with Carbon Anode Containing Sulphur**

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### **Abstract**

The gases evolved from an aluminium laboratory cell were investigated. Carbon anodes contained different amounts of sulphur were used. The presence of COS and SO<sub>2</sub> emissions was confirmed by analysis of the gasses, the major sulphurous compound was SO<sub>2</sub>. The content of sulphur in the electrolyte was measured by classical iodometry. The formation of metal sulphide was confirmed by XRD analysis of solidified cathode.

**Keywords:** aluminium electrolysis, anode gases, COS and SO<sub>2</sub> emissions

### **Introduction**

In the electrolyte used for the production of aluminium, sulphur originates mainly from two sources. Petroleum coke used for the production of carbon anodes contains 0.7 – 3.5 mass % sulphur. Cryolite and aluminium fluoride and a minor extent alumina also contain sulphur, probably in the form of sulphate (up to 1 %) (LaCamera et al. 2004). Alumina may contain 0.04 mass % S. Sulphur leaves the aluminium reduction cell predominantly as SO<sub>2</sub>, with minor amounts of COS, CS<sub>2</sub> and H<sub>2</sub>S (Fellner et al. 2005, Utne et al. 1998). These substances can partly be adsorbed on alumina (Fellner et al. 2006, Burnakin et al. 1979) and returned back to the cell. However, part of them passes through the scrubbers and escapes into the atmosphere. COS is considered as a greenhouse gas, the other compounds contribute to acid rain and pollution of the atmosphere. In this paper, results of the investigation of anode gas from aluminium laboratory cell with the carbon anode contained different amount of sulphur are discussed.

## **Experimental**

The experimental equipment consisted of a furnace equipped with a sintered ceramic tube that enabled use of the inert atmosphere (argon) and an analysis of the gases leaving the electrolysis cell (see Fig. 1). The temperature was regulated with a controller. The gas leaving the cell was absorbed in a battery of washing bottles. The thermocouple for temperature regulation was placed in the heating element. The temperature in the cell was measured with a PtRh10-Pt thermocouple placed in the melt near the carbon anode.

### *Working Procedure*

In the first series of experiments, electrolysis was carried out with the cathode formed by molten aluminium placed on a steel pad. The carbon anode contained a defined amount of sulphur. The anode material was supplied by aluminium industry and the other anodes were made by the Slovak company Elektrokarbon a.s. Topoľčany. The anodes denoted A and B contained sulphur in the same form as in industrial anodes (probably in the form of thiophene and thiol). The third type (C) contained elemental sulphur. The content of sulphur in the anodes A and C was determined in Slovalco a.s. by coulometric titration. The content of sulphur in the anodes B was determined in Hydro Aluminium by XRF analysis.

In order to decrease the activity of aluminium (and therefore also its solubility in the electrolyte) we used as a cathode the Cu-Al alloy (50 mol % Cu initial concentration). 50 g of aluminium (or 50 g of Cu-Al alloy) was weighed-in and placed in the crucible. The electrolyte (90 g) consisted of 85 mass % cryolite, 10 mass %  $\text{AlF}_3$  and 5 mass %  $\text{CaF}_2$ . To this pre-melted electrolyte 8.36 mass % of alumina was added.

The heating rate was  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . The electrolysis was carried out at a constant temperature of  $970\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$ . Normally, the electrolysis current was 4 A. The interpolar distance was 1.5 cm; electrolysis was carried out for 2 h. During electrolysis, the gas leaving the cell passed through washing bottles, and  $\text{SO}_2$  and  $\text{COS}$  were absorbed and analysed. After electrolysis the solidified electrolyte was analysed for the content of sulphur.

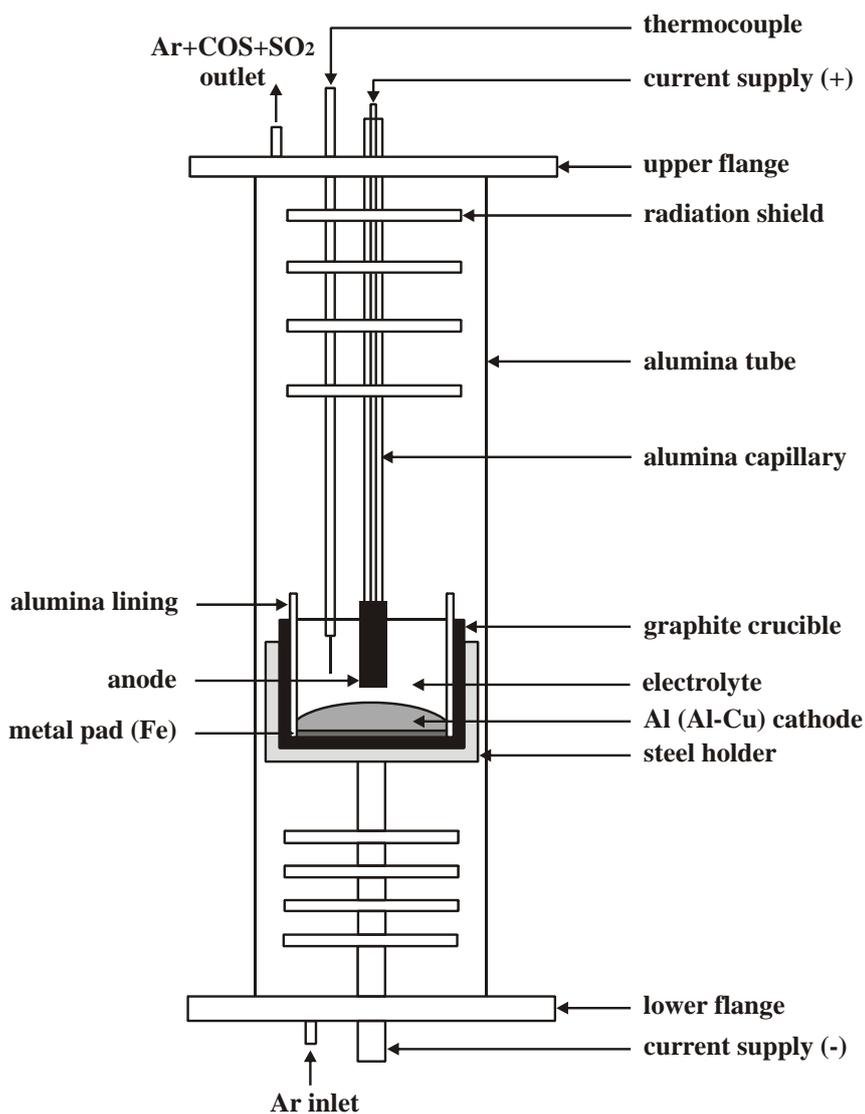


Fig.1. Scheme of the experimental equipment.

## Results and Discussion

### *Electrolysis with aluminium cathode and with anodes having the same content of sulphur*

The results of these series of experiments are summarized in Table 1. The experimental determination of the anode consumption was rather inaccurate. This made it difficult to estimate the amount of sulphur entering the system during electrolysis. This parameter, viz. the amount of sulphur originating from the anode, was estimated on the basis of the theoretical carbon consumption of 100 % current efficiency. Of course, it is not realistic but it gives a basis for a comparison of the obtained data.

Table 1. The content of sulphur in COS and in the melt after electrolysis (Al cathode).

| Anode | mass % S<br>in anode | Total mass<br>of S / mg | Sulphur in<br>COS / mg | Sulphur in<br>gas / mg | Sulphur in electrolyte /<br>mg |       |
|-------|----------------------|-------------------------|------------------------|------------------------|--------------------------------|-------|
|       |                      |                         |                        |                        | initial                        | final |
| A1    | 0.81                 | 7.32                    | 0.41                   | –                      | 226                            | 361   |
| A2    | 0.81                 | 7.32                    | –                      | 2.83                   | 226                            | 273   |
| A3    | 0.81                 | 7.32                    | 0.42                   | –                      | 226                            | 262   |
| A4    | 0.81                 | 7.32                    | –                      | 2.67                   | 226                            | 324   |

In these experiment, different analytical procedures were used to determine the sulphur species (COS, SO<sub>2</sub>) in the gas. In Fig. 2, the arrangement of washing bottles used in the experiment denoted as A1 is shown. (The analysis is based on the Slovak Technical Norm STN EN ISO 6326-3). According to this recommendation, SO<sub>2</sub> is absorbed in a KOH solution and COS is quantitatively absorbed in a solution of monoethanol amine (MEA).

In this experiment (A1) the amount of SO<sub>2</sub> absorbed in KOH could not be determined because of high concentration of KOH that was applied. The content of COS was determined by potentiometric titration. The content of sulphide in the solidified electrolyte was determined by iodometry.

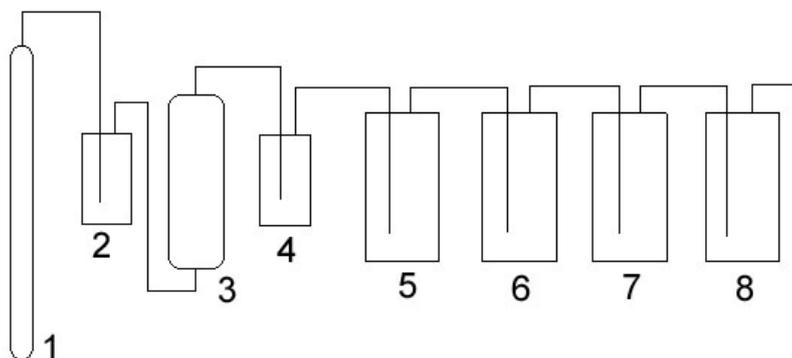


Fig. 2. Arrangement of absorption solutions in experiment A1: 1 – argon, 2 – gas washing bottle filled with H<sub>2</sub>SO<sub>4</sub>, 3 – furnace, 4 – safety bottle, 5 – gas washing bottle with 35 % solution of KOH, 6 – safety bottle with 35 % solution of KOH, 7 – gas washing bottle with 5 % solution of MEA, 8 – safety gas washing bottle with 5 % solution of MEA.

The electrolysis in the next series A2 was made in the same way as described above. Only the gas analysis was different. The gas leaving the cell was bubbled through a solution of H<sub>2</sub>O<sub>2</sub>, as shown in Fig. 3.

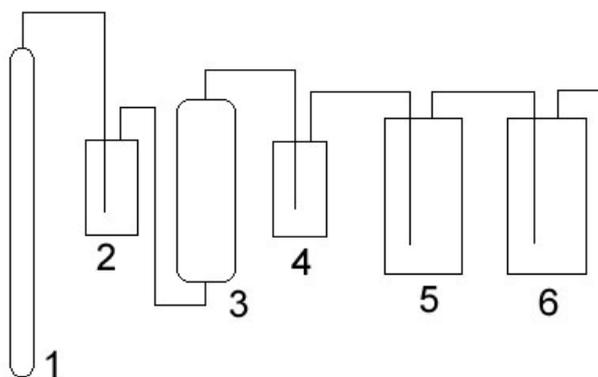
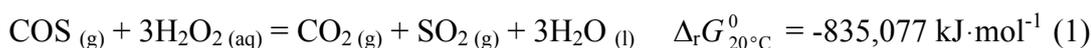


Fig. 3. Arrangement of absorption solutions in experiment A2: 1 – argon, 2 – gas washing bottle filled with  $\text{H}_2\text{SO}_4$ , 3 – furnace, 4 – safety bottle, 5 – gas washing bottle filled with 6 % solution of  $\text{H}_2\text{O}_2$ , 6 – safety gas washing bottle filled with 6 % solution of  $\text{H}_2\text{O}_2$ .

It is known that  $\text{SO}_2$  is then oxidized to  $\text{H}_2\text{SO}_4$ . It was not clear if also COS is oxidized in the same way. Thermodynamics suggests (eqns. 1 and 2) that this is possible.



From the previous experiment we knew the amount of COS. Thus the difference between the total sulphur leaving the cell and the sulphur in COS gives the sulphur in  $\text{SO}_2$ .

It was found that total amount of sulphur in the gas phase was 2.83 mg. It follows that the main sulphur-containing gas was  $\text{SO}_2$  (2.42 mg S), which is six times more than the amount of sulphur in COS.

These results just confirmed that the amount of  $\text{SO}_2$  and COS depends very much on the experimental conditions of the electrolysis. However, under constant conditions of electrolysis, the reproducibility of the results was good. Kimmerle et al. 1997 performed similar measurements with industrial pre-baked anodes. They found that only 4 % of sulphur was in the form of COS while 96 % was present as  $\text{SO}_2$ . However, when collecting gas samples under the crust of industrial cells, Tveito et al. 2001 found much higher COS contents, so this question requires further studies.

In the next series of experiment denoted as A3, the gas was bubbled first through a solution of KOH and then through a solution of  $\text{H}_2\text{O}_2$ , as shown in Fig. 4. This experiment was to prove that only  $\text{SO}_2$  reacts with a solution of KOH and that COS is quantitatively oxidized by  $\text{H}_2\text{O}_2$ .

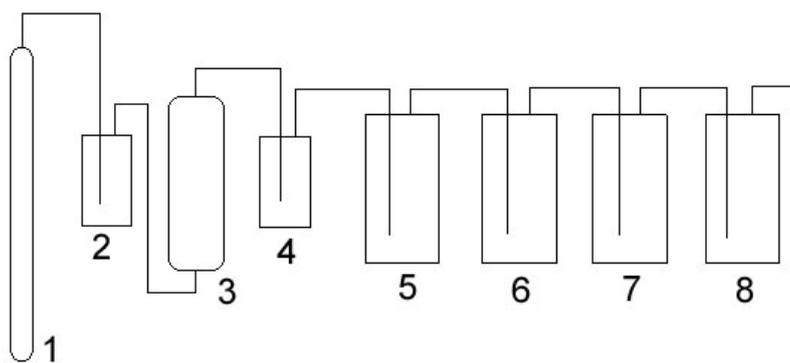


Fig. 4. Arrangement of absorption solutions in experiment A3: 1 – argon, 2 – gas washing bottle filled with  $\text{H}_2\text{SO}_4$ , 3 – furnace, 4 – safety bottle, 5 – gas washing bottle filled with 35 % solution of  $\text{KOH}$ , 6 – safety gas washing bottle filled with 35 % solution of  $\text{KOH}$ , 7 – gas washing bottle filled with 6 % solution of  $\text{H}_2\text{O}_2$ , 8 – safety gas washing bottle filled with 6 % solution of  $\text{H}_2\text{O}_2$

As follows from the results, both analytical methods gave, within the limits of error, the same results. It also proves that the experiments were reproducible.

In the last series of experiments, denoted as A4, the gas was bubbled through a solution of  $\text{H}_2\text{O}_2$  followed by a solution of MEA, see Fig 5. This experiment was to prove that  $\text{COS}$  reacts quantitatively with the  $\text{H}_2\text{O}_2$  solution.

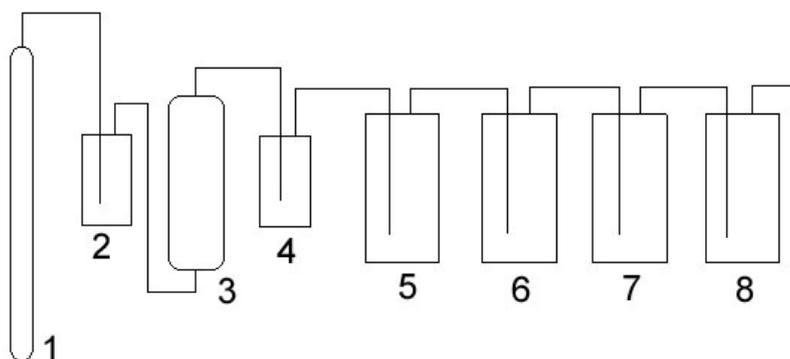


Fig. 5. Arrangement of absorption solutions in experiment A4: 1 – argon, 2 – gas washing bottle filled with  $\text{H}_2\text{SO}_4$ , 3 – furnace, 4 – safety bottle, 5 – gas washing bottle filled with 6 % solution of  $\text{H}_2\text{O}_2$ , 6 – safety gas washing bottle filled with 6 % solution of  $\text{H}_2\text{O}_2$ , 7 – gas washing bottle with 5 % solution of MEA, 8 – safety gas washing bottle with 5 % solution of MEA.

It follows from the results that no  $\text{COS}$  was found in the MEA solution. This means that  $\text{COS}$  reacts quantitatively with  $\text{H}_2\text{O}_2$ . However, two gas washing bottles filled with  $\text{H}_2\text{O}_2$  must be used. The analytical method described in Fig. 2 (STN EN ISO 6326-3) seems to be better, so it was used in the experiments to follow.

It is not clear why the content of sulphur in the solidified electrolyte is so high. Several explanations can be suggested. The most probable is that the content of sulphur in the carbon anode is higher than presented in Table 1. The petroleum coke, which was used to prepare the anode, contained 4 mass % S. As has been shown later the composition of the anode gas was consistent with a content of sulphur in the anode greater than 2 mass %. Apparently the analysis of the anode has to be repeated. This, however, does not influence the main result of this chapter, viz. that the gas analysis is reliable.

*Electrolysis with the cathode consisted of a Cu-Al alloy and with anodes having different contents of sulphur*

In this series of experiments, the Cu-Al cathode was used. In this cathode the activity of aluminium is decreased. This means that also the dissolution of aluminium into the electrolyte was low, so that the current efficiency of aluminium increased. This also means that the anode gas was reduced by dissolved metal to a lesser extent (eqn. 3) than when pure liquid aluminium was used as a cathode. One may expect that the content of COS in the anode gas will increase.



Table 2. Content of sulphur in COS and in the solidified electrolyte before and after electrolysis.

| Anode | mass % S<br>in anode | Input of S<br>/ mg | Sulphur in<br>COS / mg | Content of S in electrolyte / mg |       |
|-------|----------------------|--------------------|------------------------|----------------------------------|-------|
|       |                      |                    |                        | initial                          | final |
| A     | 0.81                 | 7.32               | 0.53                   | 226                              | 575   |
| B1    | 1.91                 | 17.46              | 0.72                   | 226                              | 206   |
| B2    | 1.97                 | 18.02              | 0.56                   | 226                              | 155   |
| B3    | 2.34                 | 21.48              | 0.55                   | 226                              | 180   |
| B4    | 2.50                 | 22.99              | 0.44                   | 226                              | 147   |
| B5    | 2.71                 | 24.98              | 0.22                   | 226                              | 177   |
| B6    | 2.90                 | 26.78              | 0.22                   | 226                              | 199   |
| C     | 0.75                 | 6.78               | 0.64                   | 226                              | 169   |

The results are summarized in Table 2 and in Fig. 6. Also in this case the input of sulphur from the anode was estimated under the assumption of 100 % anodic current efficiency. It may be more realistic to add 20 % to this value.

It follows that the content of COS depended on the content of sulphur in the anode. Strangely enough, the higher the content of sulphur in the anode the lower is the content of COS in the anode gas, according to the relationship:

$$y = (1,61 \pm 0,21) + (- 0,48 \pm 0,09)x \quad (4)$$

where y is the content of sulphur in COS and x is the content of sulphur in the anode.

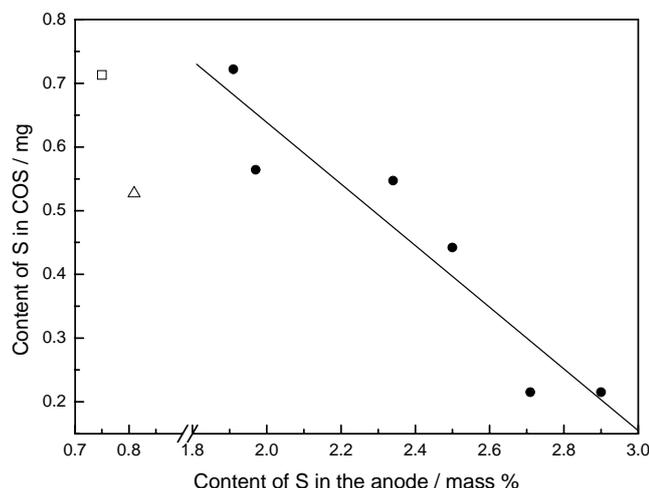


Fig. 6. Dependence of content of sulphur in COS on the content of S in the anode.  
• – anode B, □ – anode C, △ – anode A.

It can be also seen that anodes prepared in different way yield rather different production of COS for the same content of sulphur. This may partly explain why the results obtained by different authors are so different. Only general trends can be stated. The results suggest that the sulphur content in the anode A was not 0.81 mass % (see Table 1) but (based on Fig. 9) about 2.2 mass %. This would make the material balance of sulphur presented in Table 1 more realistic. It is interesting to observe that the content of sulphide in the electrolyte decreased during the experiments. This might be explained by the reaction of sulphide with iron pad and/or with copper. This assumption viz. formation of metal sulphides was confirmed by XRD analysis of solidified cathode (see Table 3).

Table 3. Phase composition of the cathode according to XRD analysis.

| Sample | Surface   | Bulk   |
|--------|---|--|
| A1     | FeS, FeS <sub>2</sub> , Fe <sub>7</sub> S <sub>8</sub> , FeS <sub>0,9</sub><br>Al, Al <sub>13</sub> Fe <sub>4</sub><br>Cu, intermetallic compounds: | Al <sub>13</sub> Fe <sub>4</sub> , Al,<br>FeS, FeS <sub>2</sub> , Fe <sub>7</sub> S <sub>8</sub> , FeS <sub>0,9</sub><br>Al, |
| B3     | Cu + Al, Cu + Al + Fe,<br>CuFeS <sub>2</sub> , Cu <sub>2</sub> S  | intermetallic compounds: Cu + Al,<br>CuFeS <sub>2</sub>  |

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