

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 SO₂ emissions was confirmed by analysis of the gasses, the major sulphurous compound was SO₂. 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 SO₂ 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 SO₂, with minor amounts of COS, CS₂ and H₂S (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 % AlF_3 and 5 mass % 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 SO_2 and COS were absorbed and analysed. After electrolysis the solidified electrolyte was analysed for the content of sulphur.

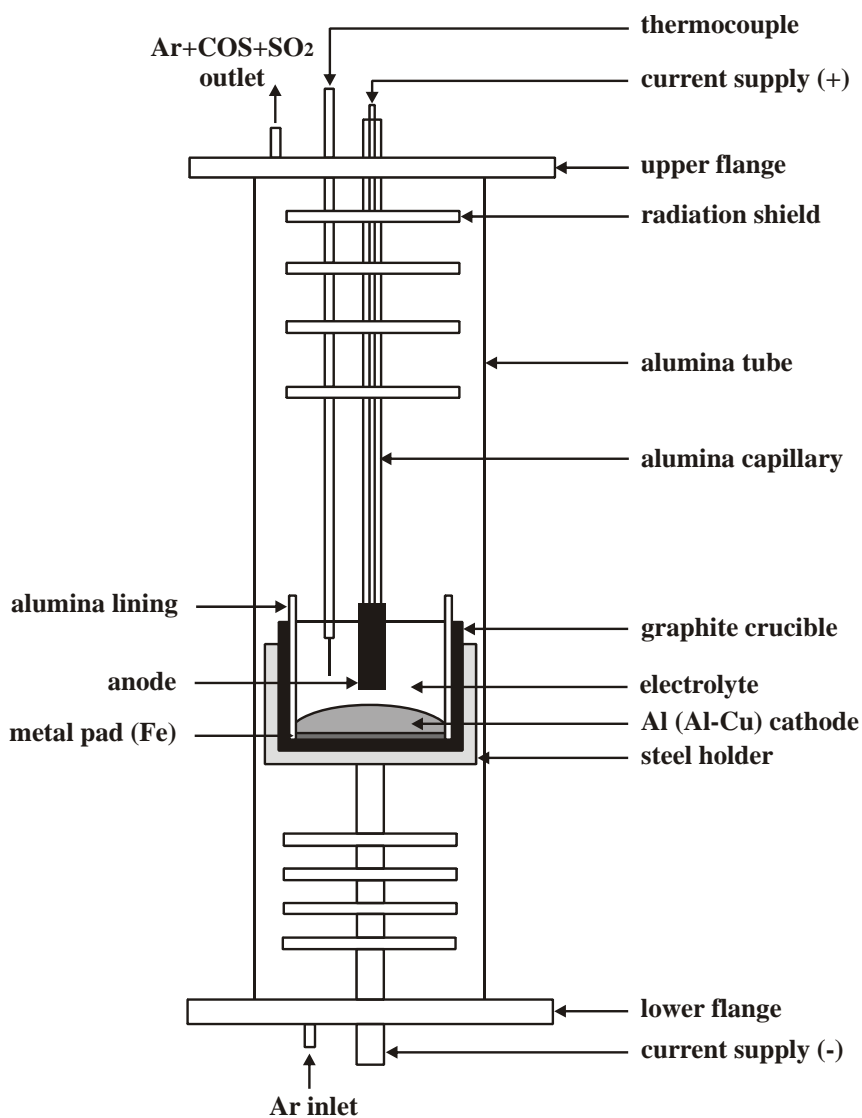


Fig.1. Scheme of the experimental equipment.

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 in anode	Total mass of S / mg	Sulphur in COS / mg	Sulphur in gas / mg	Sulphur in electrolyte / 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, SO₂) 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, SO₂ 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 SO₂ 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.

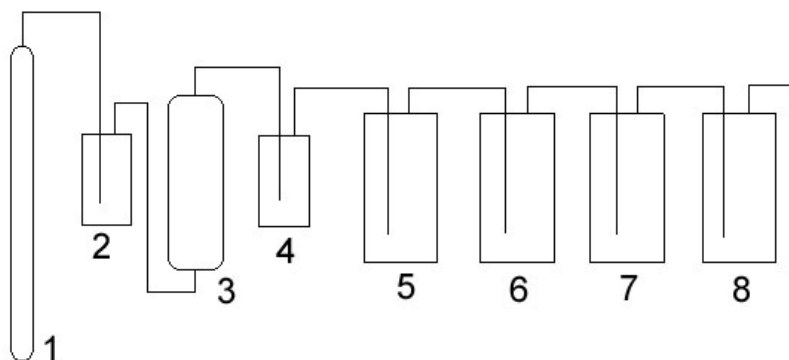


Fig. 2. Arrangement of absorption solutions in experiment A1: 1 – argon, 2 – gas washing bottle filled with H₂SO₄, 3 – furnace, 4 – safety bottle, 5 – gas washing bottle with 35 % solution of KOH, 6 – safety bottle with 35 % solution of KOH, 7 – gas washing bottle with 5 % solution of MEA, 8 – safety 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 H₂O₂, as shown in Fig. 3.

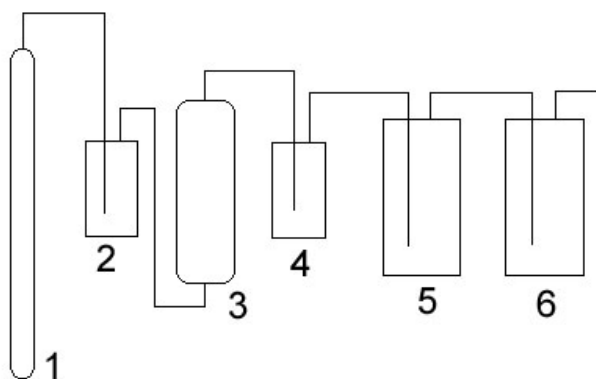
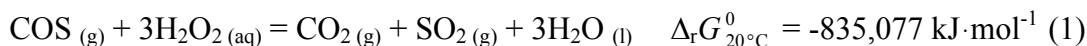


Fig. 3. Arrangement of absorption solutions in experiment A2: 1 – argon, 2 – gas washing bottle filled with H_2SO_4 , 3 – furnace, 4 – safety bottle, 5 – gas washing bottle filled with 6 % solution of H_2O_2 , 6 – safety gas washing bottle filled with 6 % solution of H_2O_2 .

It is known that SO_2 is then oxidized to H_2SO_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 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 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 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 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 H_2O_2 , as shown in Fig. 4. This experiment was to prove that only SO_2 reacts with a solution of KOH and that COS is quantitatively oxidized by H_2O_2 .

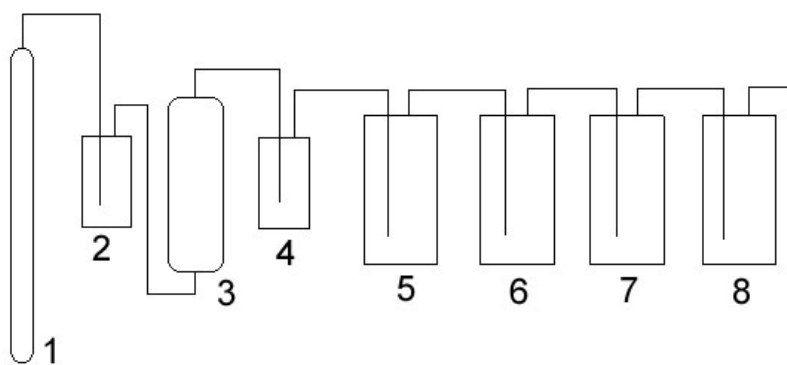


Fig. 4. Arrangement of absorption solutions in experiment A3: 1 – argon, 2 – gas washing bottle filled with H_2SO_4 , 3 – furnace, 4 – safety bottle, 5 – gas washing bottle filled with 35 % solution of KOH, 6 – safety gas washing bottle filled with 35 % solution of KOH, 7 – gas washing bottle filled with 6 % solution of H_2O_2 , 8 – safety gas washing bottle filled with 6 % solution of H_2O_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 H_2O_2 followed by a solution of MEA, see Fig 5. This experiment was to prove that COS reacts quantitatively with the H_2O_2 solution.

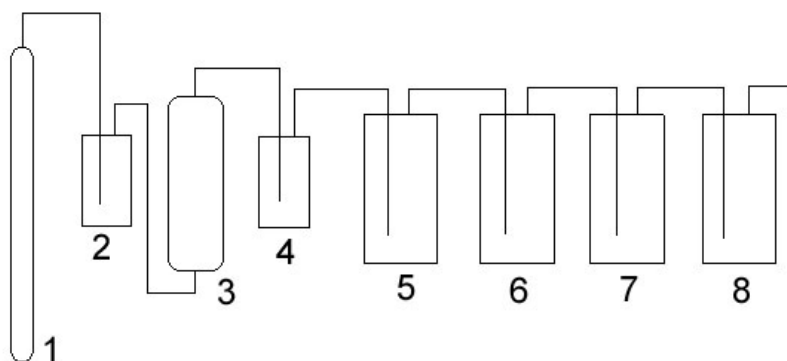


Fig. 5. Arrangement of absorption solutions in experiment A4: 1 – argon, 2 – gas washing bottle filled with H_2SO_4 , 3 – furnace, 4 – safety bottle, 5 – gas washing bottle filled with 6 % solution of H_2O_2 , 6 – safety gas washing bottle filled with 6 % solution of H_2O_2 , 7 – gas washing bottle with 5 % solution of MEA, 8 – safety gas washing bottle with 5 % solution of MEA.

It follows from the results that no COS was found in the MEA solution. This means that COS reacts quantitatively with H_2O_2 . However, two gas washing bottles filled with H_2O_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 in anode	Input of S / mg	Sulphur in 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.

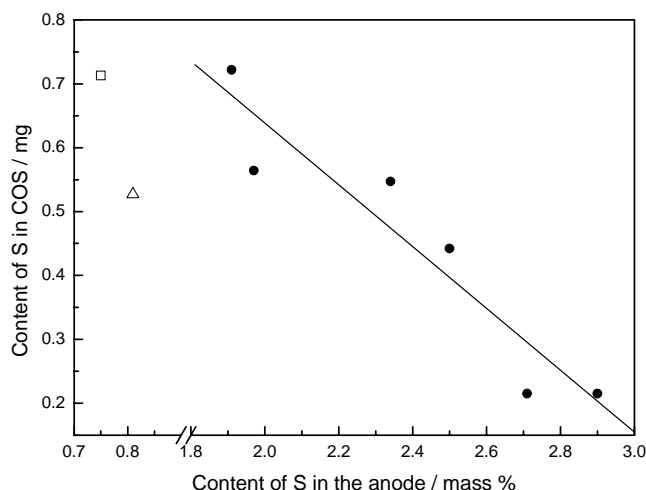


Fig. 6. Dependence of content of sulphur in COS on the content of S in the anode.
• – anode B, □ – anode C, Δ – anode A.

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 ₂ , Fe ₇ S ₈ , FeS _{0,9} Al, Al ₁₃ Fe ₄ Cu, intermetallic compounds:	Al ₁₃ Fe ₄ , Al, FeS, FeS ₂ , Fe ₇ S ₈ , FeS _{0,9} Al,
B3	Cu + Al, Cu + Al + Fe, CuFeS ₂ , Cu ₂ S	intermetallic compounds: Cu + Al, CuFeS ₂

Acknowledgement

This work was supported by courtesy of the Slovak Grant Agency (VEGA 1/0535/08) and MPO ČR 2A-ITP1/067.

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