

Chemical Reactions of Sulphur Species in Cryolite-Based Melts

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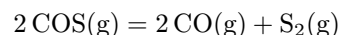
Chemical reactions of sulphur compounds in the electrolyte used for electrowinning of aluminium were investigated. It was found that sulphate ions are reduced both by carbon and by aluminium under the formation of sulphides and SO₂. The amount of sulphur reduced to sulphides was in some cases as high as the amount of sulphur escaping in the form of SO₂.

Aluminium is produced by the electrolysis of alumina dissolved in cryolite-based melts. The electrolyte also contains impurities, like 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. The main constituents of the gas leaving the cell are as follows: CO₂, CO, CF₄, C₂F₆, HF, SiF₄, H₂O, hydrocarbons, SO₂, H₂S, COS, CS₂, together with some solid particulate emissions. In this paper we will discuss the behaviour of the sulphur compounds in aluminium cells.

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 also contain sulphur, mainly as sulphates (up to 1 %). Sulphur leaves the aluminium cell mainly as SO₂, with minor amounts of COS, CS₂, and H₂S [2, 3]. *Henry* and *Holliday* [4] examined the composition of gases leaving aluminium reduction cells by mass spectrometry. CS₂ occurred only during anode effect. *Ødegård et al.* [5] investigated the composition of anode gas leaving a laboratory cell. They found that the anode gas consisted of COS with some traces of CS₂. *Dorreen et al.* [6] also observed that the only species containing sulphur in the anode gas is COS. *Harnish et al.* [7] determined the content of COS in the gas leaving industrial cells with prebaked anodes. When the anode contained 1.1 mass % sulphur, 1.6 kg of COS emissions per tonne of aluminium produced was determined. *Kimmerle* and *Noel* [8] monitored the levels of COS, CS₂, and SO₂ in the gas from prebaked cells. The anodes contained 2.4 mass % of sulphur and the main sulphur species in the gas was SO₂ (96 %), while 4 % of the sulphur was in the form of COS. The emission of CS₂ was 50 times lower than that of COS. *Tveito et al.* [2] found that the emission of COS from prebaked cells was 0.65 kg/tonne Al when the anodes contained 1.4 mass % S. *Utne et al.* [9, 10] carried out the measurements in the same plant and they found

that the specific emissions of COS were 0.28 kg/tonne Al.

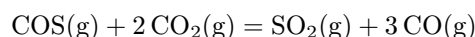
The chemistry of sulphur in carbon anodes is not fully understood. It has been assumed [11] that sulphur is mainly present in the form of thiophene and thiols. The primary composition of sulphur species in anode gases is influenced by chemical reactions, like disproportionation of COS according to the following equation



$$\Delta_r G_{1073 \text{ K}}^\circ = +19.510 \text{ kJ mol}^{-1}$$

$$\Delta_r G_{1273 \text{ K}}^\circ = -11.632 \text{ kJ mol}^{-1}$$

According to *Thonstad et al.* [10] the following reaction can proceed



$$\Delta_r G_{1233 \text{ K}}^\circ = +71.18 \text{ kJ mol}^{-1}$$

On the other hand, the Gibbs energy of the reaction of COS with oxygen is strongly negative. Also H₂S and CS₂ burn under the formation of H₂O, SO₂, and CO₂.

Gilmore and *Bullough* [12] reported that in the case of Söderberg cells the content of sulphur in the anode had no negative influence on the performance of the cell, while in the case of prebaked anodes [13–15] the sulphur had a negative influence on the electrolysis.

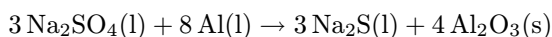
Burnakin et al. [16, 17] reported that a high content of sulphur in the anode mass resulted in increased content of sulphates in the bath. Electrochemical studies of sulphur-containing species in a cryolite-based electrolyte were carried out by *Burnakin et al.* [18, 19]. It was found that sulphates are reduced to sulphides by aluminium and/or graphite. It was also assumed that sulphur species can take part in the anode re-

actions. This opinion was supported by the work of *Gul'din* and *Buzhinskaya* [20].

In this paper we will present the results of a laboratory investigation of chemical reactions of sulphur species on a laboratory scale.

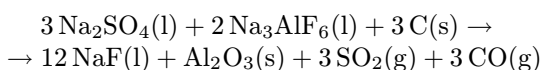
Chemical reactions of sulphates in cryolite-based melts have been discussed mainly by Russian authors. However, in most cases these considerations were not based on experimental data.

Baimakov and *Vetyukov* [21] reported that metallic aluminium dissolved in the electrolyte reduces sulphate to sulphide

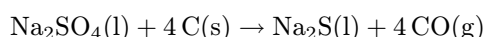


$$\Delta_r G_{1233 \text{ K}}^\circ \cong -3271 \text{ kJ mol}^{-1}$$

Shvartsberg [22] studied losses of sulphur from cryolite melts. He found that at a temperature of 1000 °C sulphate ions are reduced by graphite. He explained his observations by the following reactions



$$\Delta_r G_{1233 \text{ K}}^\circ = -173.057 \text{ kJ mol}^{-1}$$



$$\Delta_r G_{1233 \text{ K}}^\circ = -261.986 \text{ kJ mol}^{-1}$$

In most cases no experimental evidence has been given of the reactions mentioned above. The Gibbs energies of the reactions were calculated using the *JANAF Tables* [23].

EXPERIMENTAL

Handpicked Greenland cryolite and sublimated AlF_3 were used. NaF , Al_2O_3 , Na_2SO_4 , NaCl , and NiO were of anal. grade. Al_2S_3 (99.9 % metal basis, Acros Organics, New Jersey, USA), FeO (99.9 %, Aldrich, Germany), Al (99.996 % metal, HiChem s.r.o., Prague, Czech Republic) were used. Graphite crucibles were made by Elektrokarbon a.s. (Topolčany, Slovak Republic) from high-quality graphite (EK25). Sintered corundum crucibles were supplied by Elektroporcelán a.s. (Louny, Czech Republic). Pyrolytic boron nitride crucibles were supplied by International Ceramic Engineering (Worcester, USA).

The content of sulphides samples of solidified melts was determined by classical iodometry. The samples were also analyzed by X-ray diffraction (XRD) (STOE automated theta/theta diffractometer). The gas leaving the reaction vessel (furnace) was bubbled through a 3 % H_2O_2 aqueous solution. In this medium SO_2 was oxidized to H_2SO_4 , which was determined in the next step by titration with sodium hydroxide.

Apparatus for Determination of High-Temperature Chemical Reactions

The samples (see Tables 1–3) were melted in a resistance-heated furnace. A sintered alumina tube (inner diameter 85 mm, length 600 mm) equipped with brass flanges formed the shaft of the furnace. Argon was used as the carrier gas. The reaction vessels were made of platinum, graphite, sintered alumina or boron nitride. The dimensions of the crucibles were as follows:

Platinum crucibles: bottom diameter 30 mm, upper diameter 45 mm, height 45 mm.

Graphite crucibles: inner diameter 55 mm, height 60 mm.

Corundum crucibles: inner diameter 45 mm, height 75 mm.

Boron nitride crucibles: inner diameter 26 mm, height 40 mm.

The temperature was measured by a Pt10Rh—Pt thermocouple and it was kept constant ± 3 K by means of an electronic regulator (Classic, Czech Republic) connected to an auxiliary thermocouple.

When the graphite crucibles were used, the reaction surface between the melt and carbon was about 65 cm². When the reaction between aluminium and the melt was investigated, the reaction surface of aluminium was about 7 cm². The reaction surface was estimated as the geometrical surface. In the case of graphite crucible, it was estimated as the surface of cylinder and in the case of aluminium as the surface of spheroid of liquid aluminium.

RESULTS AND DISCUSSION

The results of the investigation of chemical reactions of sulphates with aluminium and graphite are summarized in Tables 1 and 2. In addition to the chemical reactions of sulphates in cryolite-based melts, the chemical reactions of sulphates in molten sodium chloride and molten sodium fluoride were investigated. These model systems (NaF and NaCl) are simpler than the cryolite-based system and the determination of sulphates and sulphides by classical chemical analysis is also simpler for chloride samples.

In investigated samples we found SO_4^{2-} , S^{2-} , and polysulphide species in the solidified melts. Chemical analysis for determination of elemental sulphur was not carried out. In the gas phase we determined mainly SO_2 . In the presence of moisture H_2S was formed as well (determined by bubbling the gas through a solution of $\text{Cd}(\text{NO}_3)_2$).

In Tables 1 and 2 $w(\text{S}^{2-})$ denotes mass percent of sulphides in solidified melt. Mass loss of aluminium is reported as well.

In some cases (experiments 19, 20) two and three contents of sulphides in solidified samples are re-

Table 1. Investigation of the Chemical Reactions of Sodium Sulphate with Aluminium and Graphite in the Molten Systems NaCl—Na₂SO₄ and NaF—Na₂SO₄

Sample	Crucible	θ	t	Mass fraction/mass %			$w(S^{2-})$	$w(Al, \text{react.})$
		°C	min	NaCl	Na ₂ SO ₄	Al	mass %	mass %
1	corundum	850	90	79.87	10.00	10.13	0.145	0.23
2	corundum	850	90	79.82	10.00	10.18	0.224	2.42
3	corundum	1000	90	79.87	10.00	10.13	0.189	0.42
4	corundum	1000	90	81.72	9.08	9.20	0.210	3.27
5	corundum	850	180	79.87	10.00	10.13	0.160	2.49
6	corundum	850	180	79.87	10.00	10.13	0.081	0.24
7	graphite	1000	90	90.00	10.00	—	2.158	—
8	graphite	1000	90	81.72	9.08	9.20	2.216	1.43
9	graphite	850	180	79.87	10.00	10.13	1.796	19.91
				NaF	Na ₂ SO ₄	Al		
10	graphite	1000	90	90.00	10.00	—	2.111	—
11	graphite	1000	90	81.72	9.08	9.20	2.023	85.07

ported. These data are related to different layers in the samples. These layers differ also in colour.

The Systems NaCl—Na₂SO₄ + (C, Al) and NaF—Na₂SO₄ + (C, Al)

Chemical reactions of sodium sulphate in sodium chloride and sodium fluoride melts were studied at 850°C and 1000°C, respectively, and the results are presented in Table 1. The mass of the samples was *ca.* 80 g when graphite or corundum crucibles were used and 30 g in the case of platinum crucibles. The extent of reaction was determined quantitatively both by the determination of sulphide and by the mass loss of aluminium. The colour of the solidified melt, which was originally white, changed to grey, yellow or pink. This may be considered as qualitative evidence of the presence of sulphide and polysulphides in the solidified melt. When solidified samples were leached in water the solution was alkaline. The higher was the content of sulphides in the sample, the higher was pH of the solution.

The results show that the sulphate was reduced both by graphite and by aluminium. The surface area of the aluminium spheroid on the bottom of the crucible was about 10 times smaller than the surface area of graphite in contact with the melt. When the reduction of sulphate to sulphide was related to the same surface area, the kinetics of the reduction was approximately the same in both cases. The same also holds when both carbon and aluminium were used as reducing agents.

When aluminium was used as the reducing agent, only a small amount of SO₂ was recorded in the gas leaving the furnace. When both aluminium and graphite were used as reducing agents (molten aluminium in graphite crucible), the amount of SO₂ was 50 times higher in comparison with experiments in a

corundum crucible and 10 times higher in comparison with the graphite crucible itself, and the mass of SO₂ counted as S, escaping from the furnace was the same as the mass of sulphides detected in the solidified melt. As can be seen from Table 1, the experiments carried out in the system NaF—Na₂SO₄ gave approximately the same results as those in the chloride system. However, because of the reaction of aluminium with NaF [1], the losses of aluminium were rather high.

The System Na₃AlF₆—Na₂SO₄ + (C, Al)

The results obtained in cryolite-based melts are summarized in Table 2. When a sample of cryolite with 10 mass % Na₂SO₄ was kept at 1000°C in a platinum crucible (experiment 13), small amounts of SO₂ (SO₃) were detected in the gas (the analytical method based on oxidation of SO₂ to SO₃ cannot distinguish between these two compounds). This can be caused by thermal decomposition of sodium sulphate. No sulphide was detected in the solidified samples. This might be considered as a blank test for determination of sulphides.

When aluminium was added to molten sodium sulphate (experiment 12) Na₂S should be formed, according to *Baimakov* and *Vetyukov* [21]. Our experiments confirmed the reduction of sulphate to sulphide by aluminium. However, the amount of sulphide was too small for detection by X-ray analysis. A similar reaction was observed (*i.e.* the formation of sulphide) when sodium sulphate was added to cryolite in the presence of aluminium. In experiment 18, X-ray diffraction lines corresponding to the formation of Al₂S₃ were detected. It should be stressed that the system NaF, AlF₃ // Na₂S, Al₂S₃ is a reciprocal system. Thus, investigation of solidified samples cannot give a direct answer about the composition of the liquid system.

Table 2. Investigation of the Chemical Reactions of Sodium Sulphate with Aluminium or Graphite in the Molten Na₃AlF₆—Na₂SO₄—Al₂O₃ System

Sample	Crucible	θ	t	Mass fraction/mass %				$w(\text{S}^{2-})$	$w(\text{Al, react.})$	Composition of the sample (XRD)
		°C	min	Na ₃ AlF ₆	Na ₂ SO ₄	Al ₂ O ₃	Al	mass %	mass %	
12	corundum	960	90	—	66.38	—	33.62	0.265	0.06	Na ₂ SO ₄ , traces of Al, Na ₂ S ₅ O ₁₆ , S
13	platinum	1000	90	90.00	10.00	—	—	0.000	—	Na ₃ AlF ₆
14	corundum	960	90	85.17	2.00	12.83	—	0.000	—	Na ₃ AlF ₆ , Al ₂ O ₃
15	corundum	960	90	84.73	2.00	12.76	0.51	0.130	100.00	Na ₃ AlF ₆ , Al ₂ O ₃
16	corundum	960	90	84.29	2.00	12.70	1.01	0.138	100.00	Na ₃ AlF ₆ , Al ₂ O ₃
17	corundum	1000	90	81.72	9.08	—	9.20	0.178	48.96	NaF, Na ₃ AlF ₆ , NaAl ₁₁ O ₁₇
18	corundum	1000	90	69.41	10.00	10.45	10.14	0.421	50.35	Na ₃ AlF ₆ , Al ₂ O ₃ , traces of Al ₂ S ₃
19	graphite	1000	90	—	100.00	—	—	19.984 14.490	—	Na ₂ S, polysulphides
20	graphite	1000	90	—	64.22	—	35.78	22.781 13.637 14.347	18.87	—
21	graphite	1000	90	90.00	10.00	—	—	0.162	—	Na ₃ AlF ₆ , NaF, Al ₂ O ₃
22	graphite	1000	90	90.00	10.00	—	—	0.178	—	Na ₃ AlF ₆
23	graphite	1000	90	90.00	10.00	—	—	0.162	—	Na ₃ AlF ₆ , NaF, Al ₂ O ₃
24	graphite	1000	90	90.00	10.00	—	—	0.163	—	Na ₃ AlF ₆ , NaF, Al ₂ O ₃
25	graphite	1000	180	90.00	10.00	—	—	0.146	—	NaF, Na ₃ AlF ₆ , Na ₂ SO ₄ , Na ₂ S, C
26	graphite	1000	90	81.72	9.01	—	9.20	0.556	57.83	Al ₂ (SO ₄) ₃ , NaF, Na ₃ AlF ₆ , NaAl ₁₁ O ₁₇

Table 3. Phases in the Solidified Melt of the Na₃AlF₆—Al₂S₃ Determined by X-Ray Analysis

Sample	Crucible	θ	t	Mass fraction/mass %		Composition of the sample (XRD)
		°C	min	Na ₃ AlF ₆	Al ₂ S ₃	
27	boron nitride	650	60	80.75	19.25	Na ₃ AlF ₆ , Na ₅ Al ₃ F ₁₄ , Al ₂ S ₃
28	boron nitride	700	60	80.75	19.25	Na ₃ AlF ₆ , Na ₂ S, Al ₂ S ₃ , Na ₅ Al ₃ F ₁₄

When graphite was used as reducing agent for sodium sulphate, Na₂S and polysulphides were identified by X-ray analysis of solidified samples. The kinetics of the reduction of sulphates to sulphides was similar to that observed in sodium fluoride and

sodium chloride. However, because of dissolution of aluminium, the losses of aluminium were rather high.

It can be concluded that the chemical reduction of sulphate to sulphide proceeds in a similar way as in sodium chloride or sodium fluoride melts. The impor-

tant difference is the formation of Al_2S_3 in the cryolite-based system. Also in this case the amount of SO_2 in the gas phase was remarkably higher when aluminium was used as reducing agent in a graphite crucible.

Table 3 shows X-ray analysis of samples prepared by melting mixtures of Na_3AlF_6 and Al_2S_3 in boron nitride crucibles. In addition to cryolite and Al_2S_3 , the solidified samples also contained Na_2S and chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$). Chiolite originates from the reaction of AlF_3 with cryolite [1]. These experiments show that the system Na_3AlF_6 — Al_2S_3 is not a simple binary eutectic system. One has to take this fact into consideration when chemical reactions are discussed on the basis of the composition of solidified samples.

From the presented results it follows that the chemical reactions of sulphur species in cryolite-based melt are rather complex. The situation is even more complicated because besides the chemical reactions, the sulphur species take part also in electrochemical reactions. The research of this topic is under the progress.

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