#### Investigation of Sodium Sulfate Additions into Cryolite-Alumina Melts

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# Abstract

In the Hall-Heroult process, sulfur impurities may not only emit harmful gases, but also reduce the current efficiency. To better understand this process, the behaviour of sulfur compounds in a cryolite-alumina melt (980°C) was investigated in a laboratory cell. Na2SO4 was added into the molten bath as a source of sulfur. The furnace off-gases were passed through a mass spectrometer for qualitative assessment. It was found that the stability of sodium sulfate in the cryolite melt was dependent on the presence of carbon (t1/2 = 116 min) and carbon-aluminium (t1/2 = 29 min), and was changed dramatically during electrolysis (t1/2 = 5-8 min). The sulfurous gases that were observed included SO2, COS, CS2 and H2S.

# Introduction

Sulfur enters the Hall-Héroult cell from various sources. Therefore it is important to study the behaviour of sulfur compounds in alumina-cryolite melts. Even small amounts of sulfur impurities in bath can impact the course of electrolysis [1]. The work presented in this paper includes experimental data obtained from a lab-scale cell and provides insight into the fundamental behaviour of sulphur in the cryolite bath during electrolysis, some of which may have practical implications.

## Background

In aluminium electrolysis, sulfur enters the cell mainly by the carbon anodes (80 %). The rest comes from alumina (20 %) and aluminium fluoride (1 %) [2]. The sulfur content in the anode can be in the range from 1-4 wt% depending on the type of coke [3]. Anodes are usually prepared by a mix of calcined petroleum coke (or pitch coke) and recycled butts, which are bound together with coal tar or petroleum pitch [4]. Petroleum coke is the main origin of sulfur in aluminium electrolysis cells [5]. Sulfur is an inevitable impurity in aluminium anodes both because petroleum coke inherits the sulfur from crude oil and the pitch which also inherits the sulfur from coal where sulfur is a part of the structure. Sulfur which originates from alumina and fluoride additions is considered to be in the form of sulfate [2].

Analysis of industrial bath samples showed that the bath contained both sulfate and sulfide [6]. Burnakin et al. [7] noted that sulfate was moderately stable in cryolite melts without aluminium. Several other researchers [8-12] have also studied the stability and phase diagrams of sulfates in cryolite melts.

Sulfur is known not to accumulate in the bath; instead it is readily released as sulfurous gas emissions. Sulfur emissions from an aluminium smelter with an annual production of 200000 tonnes can be as high as 1000 tonnes of sulfur per year [13]. The most important reported sulfurous gases from aluminium reduction cells are SO2, COS, H2S and CS2 [5, 13-15]. Sulfurous gases are known for their detrimental effect on local air pollution (particulate matter), acid rain, health and global climate. It has been reported that particulate matter is a key ingredient of polluted air and it has been estimated to kill more than 500000 people each year [16]. However, emissions of sodium sulfide and conversion into sulfate is also argued to be the most important factor in reducing the warming of the earth by backscattering solar radiation into space [17].

Earlier studies on current efficiency were contradictory [18-20]. However, recent work which motivated the work reported here was reported by Pietrzyk and Thonstad [21] who performed laboratory studies on anodes containing sulfur in the range of 0 to 3.8 wt% and claimed that sulfur has negative effect on current efficiency.

This work investigates the stability of the sodium sulfate in the cryolite-alumina melt under different conditions. The study suggests that sodium sulfate is not a stable compound in cryolite-alumina melts even though many phase diagrams exist. The results obtained here can be used to investigate the effect of sulfur on current efficiency, an important process parameter in aluminium electrolysis, and explain the possible mechanism that can contribute to current efficiency loss.

# Experimental

The bath mixture was composed of AlF3 (25.2 g), Na3AlF6 (319 g), CaF2 (18.92 g), Al2O3 (15.13 g). This corresponds to a cryolite ratio equal to 2.5, and with excess amounts of AlF3, Al2O3 and CaF2 of 6.75 wt%, 4 wt% and 5 wt%, respectively. The crucible with all mentioned contents was kept overnight inside the oven at 473 K (200 °C). The samples were melted in a gas tight furnace at 1253 K (980 °C). Argon was flushed to maintain inert conditions. The reaction vessels were made of sintered alumina and graphite. The carbon source was pieces of graphite which had approximate total surface area equal to 12 cm2. The total weight of aluminium was 12.9 grams. The electrolysis experiments were carried out in a laboratory cell shown in Fig 1. The graphite anode was lowered 2 cm into the melt before start of the experiment, giving a total surface area of 35.5 cm2. Sodium sulfate was added as a source of sulfur in the bath. Each experiment contained about 600-800 ppm of sulfur in the bath. These levels are common in industrial cells depending on the level of contamination of the bath with carbon dust [1].

Bath samples were taken every 5 min over a time span of 30 min, then the samples were taken every 10 min for another 30 min and after that the sampling frequency was 20 min for each experiment. The total sulfur amount in the bath was measured by ICP-MS (Inductive Coupled Plasma - Mass Spectrometry).

The furnace off-gases were passed through a mass spectrometer (MS) for qualitative assessment. MS was the only available gas analysis equipment during the time experiments were performed. The drawback of the equipment was that it was not possible to get quantitative analysis; therefore no mass balance of the sulfur was performed. The gas analysis results were used only to support and explain the gas products formed during reactions.

C:\Users\rauan\Desktop\experimental.eps Figure 1: Schematic of laboratory cell used for experiments

# Results and Discussions

A summary of results of the tests with brief experimental details are shown in Table I. The results show that sodium sulfate is relatively stable in cryolite-alumina melts when no electrolysis is taking place and in the absence of the reducing agents, carbon and aluminium. The total sulfur half-life is equal to 231 min. The gas analysis showed very limited release of gases when there were no reducing agents present.

|  |  |  |  |
| --- | --- | --- | --- |
| Table I. Half-life of sodium sulfate at different conditions. | | | |
| C | Al | El | T1/2 (min) |
| - | - | - | 231 |
| + | - | - | 116 |
| + | + | - | 24 |
| + | + | + | 6.9 |

As can be seen from Table I, the half-life of the sodium sulfate is reduced by half in the presence of the carbon in the bath. After the addition of carbon, the signals for CO2, SO2 and CS2 increased. The intensity of the H2S was not much affected. The gas analysis results indicated that CS2 is formed when there is a source of sulfur and carbon in the bath. It was observed that COS was also formed even in the absence of electrolysis. It was found that COS was increased when signal intensities of CO2 increased.

The possible reactions between sodium sulfate and carbon are as follows [7, 22-24]:

|  |  |
| --- | --- |
| 3Na2SO4 + 12C = 3Na2S + 12CO | (1) |
| ∆rG° at 1253 K = -877 kJ/mol |  |
| 3Na2SO4+3C = 3Na2S+6CO2 | (2) |
| ∆rG° at 1253 K =- -581 kJ/mol |  |
| 3Na2SO4 + 2Na3AlF6 + 3C =  12NaF + Al2O3 + 3SO2 + 3CO | (3) |
| ∆rG° at 1253 K = -209 kJ/mol |  |
| 3Na2SO4 + 2Na3AlF6 + 3/2C =  12NaF +3/2CO2 +Al2O3 +3SO2 | (4) |
| ∆rG° at 1253 K = -135 kJ/mol |  |

where ∆rG° is the standard Gibbs energy of the reaction. In the presence of both reducing agents the half-life of the sodium sulfate is reduced to one tenth of the half-life in the absence of both aluminium and carbon. After addition of aluminium, the signals for all gases remained in a similar range as in the case of only carbon presence. The possible chemical reactions between sodium sulfate and aluminium are [7, 22-24]:

|  |  |
| --- | --- |
| 3Na2SO4 + 8Al = 4Al2O3 + 3Na2S | (5) |
| ∆rG° at 1253 K = -3315 kJ/mol |  |
| 3Na2SO4 + 8Al = 3Na2O + 3Al2O3 + Al2S3 | (6) |
| ∆rG° at 1253 K = -2431 kJ/mol |  |
| 3Na2SO4 + 2AlF3 + 8Al = 6NaF + 4Al2O3 + Al2S3 | (7) |
| ∆rG° at 1253 K = -3286 kJ/mol |  |
| 3Na2SO4 +2Na3AlF6 +8Al = 12 NaF + 4 Al2O3 +Al2S3 | (8) |
| ∆rG° at 1253 K = -3059 kJ/mol |  |

where ∆rG° is the standard Gibbs energy of the reaction. Ambrova et al. [24] reported the formation of Al2S3 and Na2S, identified by XRD from a solidified bath, in the presence of aluminium when a graphite crucible was used.

The substantial decrease (33 times) of sodium sulfate half-life is observed during electrolysis. The intensity of the COS signal was considerably increased (4.4 times higher than in other experiments). The magnitude of the other gases was in the same range as in experiments without electrolysis. The sulfur concentration as a function of time is shown in Fig. 2. Based on Fig. 2, a linear regression of the data results in the following relationship for the decay of 800 ppm of sulfur, with:

|  |  |
| --- | --- |
|  | (9) |
|  | (10) |

where *Cs*is the concentration of sulfur, *t* is the time addition of sulfur, *t1/2* is the half life time.

The fast depletion of sodium sulfate can be attributed to either a chemical or an electrochemical reaction or both simultaneously.

Sodium sulfate can be reduced to sulfides by both carbon and aluminium according to equations (1-8) given above.

Both Burnakin et al. [7] and Ambrova et al. [24] reported increased loss of aluminium in presence of aluminium and carbon. The sulfides can be oxidized electrochemically at the anode according to following reaction [25]:

S2- = S + 2e- (11)

Probable sequential reactions, which result in the formation of CS2 and S2, were proposed by the same authors [31]:

S = S(ad) (12)

followed by

S(ad) = S2(ad) (13)

and/or

S(ad) +xC = CxS(ad) (14)

2CxS = CS2(ad) + (2x-1)C (15)

It should be noted that gas measurements were done during electrolysis and CS2 was among the detected gas species (SO2, COS, CS2 and H2S).

Other successive electrochemical reactions were proposed by Hajasova [12] based on her electrochemical studies of sodium sulfate:

2SO42- + 3e- = S2O42- + 4O2- (16)

S2O42- + 2e- = S2O +3O2- (17)

Figure 2: Sulfur concentration development over time.

Further experiments were performed to keep the sulfur concentration in the bath constant. Sulfur addition was made after 10 minutes. In order to check if the assumption was accurate, samples were taken 5 and 10 minutes after the addition of sodium sulfate tablets. Samples taken 5 minutes after addition should give an indication of the maximum concentration after addition, and the 10 minutes samples should show the lowest concentration. Analysis of these two samples should give an indication whether overfeeding or underfeeding of sulfur was occurring. Bath samples taken earlier than 5 minutes after addition contained undissolved tablets and the obtained concentrations from the ICP analyses were then much higher than expected (eg. 5000 ppm). Therefore the sulfur measurements taken within the first 5 minutes after tablet addition cannot be assumed to be representative of the average sulfur concentration in the bath. Sampling was done every 15 minutes at the same time as the alumina additions. Fig. 3 and 4 show results of experiments where the target levels of sulfur were 1000 ppm and 500 ppm respectively. It can be concluded that the assumption works reasonably well, because if the assumed total time was overestimated we would observe underfeeding in Fig. 3 and 4, and reverse, overfeeding in the case of an underestimate of half-life.

The effect of sulfur on current efficiency can be studied by either using anodes with different sulfur contents or by adding sodium sulfate directly into the bath, supplementing for the depletion as indicated above. In order to investigate the sulfur effect on CE, the sodium sulfate concentration in cryolite should be stable. The industrial cells have steady supply of sulfur from anodes and using anodes with different sulfur contents will probably make the control of sulfur concentration easier, but it also has its own disadvantages. High sulfur in the anodes is correlated with other trace impurities [26] and moreover, anodes with different sulfur levels differ not only by structure, but also in wetting properties and electrochemical behaviour [27, 28]. Therefore, in order to isolate the effect, introducing sulfur directly into the system can be an attractive alternative; nevertheless both approaches should be helpful in determining the overall effects.

Figure 3: Sulfur concentrations in the bath analyzed by ICP analysis (1000 ppm target). The cs(max) is the values sampled after 5 minutes addition and the cs(min) is the values sampled after 10 minutes respectively.

Figure 4: Sulfur concentrations in the bath analyzed by ICP analysis (500 ppm target). The cs(max) is the values sampled after 5 minutes addition and the cs(min) is the values sampled after 10 minutes respectively.

# Conclusion

Results indicate that stability of sodium sulfate in the cryolite melt depends on the presence of carbon (t1/2 = 116 min) and carbon-aluminium (t1/2 = 29 min), and changed dramatically during electrolysis (t1/2 = 5-8 min) as compared to t1/2 = 231 min in the absence of electrolysis, carbon or aluminium. It was clear that electrolysis had the strongest influence on the depletion rate. The sulfur removal from the bath increased during electrolysis most likely due to the increased stirring and enhanced mass transport as well as aseous sulfur compounds being prodused at the electrodes. Sulfur additions were made after 10 minutes based on the depletion curve and half-life of sodium sulfate in cryolite-alumina melt during electrolysis. The results are important for running accurate measurements and understanding the value of the verifying of the concentrations by taking frequent samples.

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