

Influence of the Sulfur Species on the Current Efficiency and Carbon Consumption in the Aluminum Electrolysis Process



MARTA AMBROVÁ, MICHAL KORENKO, and LÓRANT SZATMÁRY

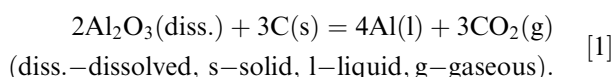
The influence of sulfur species on the current efficiency and carbon consumption in the aluminum electrolysis was investigated. Prebaked and graphite anodes with varying levels of sulfur were used. It was found that increasing the sulfur content in the anodes decreases the current efficiency and increases the carbon consumption of both types of anodes. The current efficiency decreased by 1.3 pct and the carbon consumption rose by 6.1 pct per 1 wt pct S in the prebaked anodes. The addition of sodium sulfate to the electrolyte during electrolysis with graphite anodes led to a decrease in current efficiency from 0.9 to 1.0 pct per 1 wt pct S, and to an increase in carbon consumption from 3.1 to 7.0 pct per 1 wt pct S. Electrolyte analysis showed the presence of sulfates, sulfides and polysulfides. Some link between sulfur content in the anodes and sulfur content in the electrolyte and outgoing gases was found. A comparison of the polarized and non-polarized conditions showed that the electrolysis increases the sulfur depletion from the cell and promotes the formation of soluble sulfides. Reactions of sulfur participation in redox processes have also been proposed.

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I. INTRODUCTION

ALUMINUM is industrially produced by the electrolysis of alumina dissolved in a mixture of molten fluorides (the main constituent is molten cryolite). The total reaction can be written as follows:^[1]



Aluminum production is an energy-intensive process associated with the significant release of CO₂ and other emissions. Therefore, the knowledge of any parameters to help to produce more climate- and energy-efficient primary aluminum is important. The main effort is to use low-energy resources, decrease the operating temperature, and impurities content in the electrolyte and raw materials, as well as to increase the current and energy efficiency of the process. Along with this, there is an effort to significantly reduce climate emissions.

Modern electrolysis cells can achieve current efficiency of up to 96 pct. This value was primarily attained by suppressing the back reaction of aluminum with CO₂ (Eq. [2]). Other sources of current efficiency loss include aluminum carbide formation, sodium uptake, anode electronic conductivity, the occurrence of anode effects, electrode short-circuiting (*e.g.* by metal fog formation), presence of impurities (*e.g.* in anodes, raw materials and production tools), the cell operation, and the corrosion of the different parts of the cell.^[1]



One of the impurities in the aluminum electrolysis process is sulfur. Sulfur can be present in the process in both organic and inorganic forms. Carbon anodes contain mainly organic sulfur, usually in the form of polycyclic aromatic hydrocarbons (*e.g.* thiophenes).^[2,3] Cryolite, aluminum fluoride and alumina usually contain an inorganic form of sulfur (mainly sulfates).^[1]

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Sulfur leaves the electrolysis process in the form of gaseous SO₂, COS, CS₂ and H₂S.^[2,4] Part of these gases are adsorbed on alumina and thus return to the cell. However, a considerable amount escape into the atmosphere as pollutants.

There are contradictory opinions on the effect of sulfur as an impurity in aluminum electrolysis process. Sulfur's negative impact is mainly related to the release of sulfur gaseous emission and, in terms of cell operation, it is usually classified as a less detrimental impurity with no effect on current efficiency.^[5,6] Some works have shown that a modest level of sulfur in the anode material can have a protective antioxidative effect on it (*e.g.* against air burn of the anodes or against oxidative reactivity of CO₂).^[6-16] Sulfur is also believed to depress the catalytic effect of sodium originating from the butts (recycled spent anodes).^[17] However, other authors claim that sulfur has a negative effect on the electrolysis process. Bullough *et al.*^[18] reported (5 ± 2) pct reduction in current efficiency per each pct increase of sulfur content in the anodes. Pietrzyk and Thonstad^[19] determined the current efficiency loss based on the aluminum weight and oxygen balance method. They found a 1.5 and 1.6 pct reduction in current efficiency per 1 wt pct sulfur in the anodes by aluminum weighing and oxygen balance method, respectively. In a similar way, the carbon consumption rise was determined based on anode weight and gas analysis. The corresponding values were 5.2 and 0.8 pct per 1 wt pct of sulfur in the anodes. Xiao *et al.*^[20] reported a strong catalytic activity of sulfur in terms of the air and CO₂ reactivity in the case of no other impurity interference. In addition to the sulfur present in the anodes, also the sulfur present in the electrolyte can affect the current efficiency of the electrolysis process. Burnakin *et al.*^[21] found that aluminum losses (Q_{Al}) linearly increase with the increasing content of sodium sulfate ($c(\text{Na}_2\text{SO}_4)$) in the electrolyte according to the equation:

$$\Delta Q_{Al} = 0.064 + 1.162 c(\text{Na}_2\text{SO}_4) \quad [3]$$

The current efficiency loss caused by sodium sulfate was estimated to be 0.2 to 0.3 pct. Ambrová^[22,23] reported on the loss of aluminum due to sulfur contained in the electrolyte and the formation of sulfides. These soluble sulfides were found to be able to react with metal oxides present in the electrolyte and precipitate as solid insoluble sulfides.^[22,24] They contaminate newly produced aluminum and negatively influence the current efficiency of the electrolysis process. Recently, Meirbekova *et al.*^[25] reported a 1.1 pct decrease in current efficiency per each 100 mg kg⁻¹ increase of sulfur concentration in the electrolyte.

A high cost and lack of low-sulfur anode materials increases the pressure to use high-sulfur coke. This can negatively affect not only the cell operation but also the amount of sulfur pollutants. It is therefore necessary to examine the effect of sulfur species on the key parameters of aluminum electrolysis. This, together with the contradictory results mentioned above, is the main motivation for this work. Unlike the foregoing works, that deal with either the effect of the anode sulfur

content or the effect of the electrolyte sulfur content on the electrolysis, this work attempts to explore the effect of both of these parameters simultaneously. This approach may better reflect the situation in the real industrial aluminum electrolysis process since both the carbon anodes and the electrolyte contain sulfur. Electrolysis experiments were performed with two types of anode materials since the form of sulfur species can significantly influence the reactivity of the anode.^[16] Prebaked anodes containing sulfur in organic form were used in the first series of experiments (P series). Graphite anodes containing sulfur in elemental form were used in the second series (G series). It should be noted that both forms might contain some amounts of each other. In the third series of experiments (GS series), the influence of added sulfur into the electrolyte (in the form of sodium sulfate) on the electrolysis process was investigated. Since industrial cokes (used in prebaked anodes) may contain a significant amount of S-S bound sulfur, (16 to 53 pct of total sulfur),^[16] the graphite anodes were used for this purpose rather than prebaked anodes. In addition to better control the composition of sulfur species, this type of anode was available in a wider sulfur content interval, and (unlike the prebaked anodes) also with zero-sulfur content. This allowed quantifying the background effect and the net influence of sulfate on the examined parameters. For this purpose, six runs with zero-sulfur content graphite anodes were performed: three runs without, and three runs with an addition of sodium sulfate into the electrolyte. In addition, three experiments were performed under non-polarized conditions (with 2.5 wt pct S in graphite anode) to evaluate the role of electrolysis.

II. EXPERIMENTAL SETUP

All electrolysis runs were performed in a closed laboratory furnace filled with argon (99.996 pct). The electrolysis cell (Figure 1) consisted of a graphite crucible inside which a lining made of sintered alumina was placed. The sides and top of the anode were shielded by boron nitride to avoid the reaction between CO₂ and the anode body. Electrolysis was carried out with the cathode formed by molten aluminum placed on a steel pad. The carbon anodes contained a known amount of sulfur, externally determined by suppliers using X-ray fluorescence analysis (XRF). The method meets the ISO 12980-2000 standard. The first type of anodes was prebaked anodes and contained sulfur mainly in organic form; the second type of anodes was made of graphite and contained sulfur in elemental form.

All electrolysis experiments were carried out for 4 hours at a constant temperature of (970 ± 2) °C. The phosphorus content in the anodes (which could also influence the current efficiency) ranged from 1 to 6 ppm. The anodic current density was approx. 0.705 A cm⁻²; the anode-cathode distance was maintained at 2.1 cm. All used chemicals (Merck, Germany) were analytical grade. They were dried in a closed furnace heated to 600 °C for 6 hours. Aluminum fluoride was cleaned by

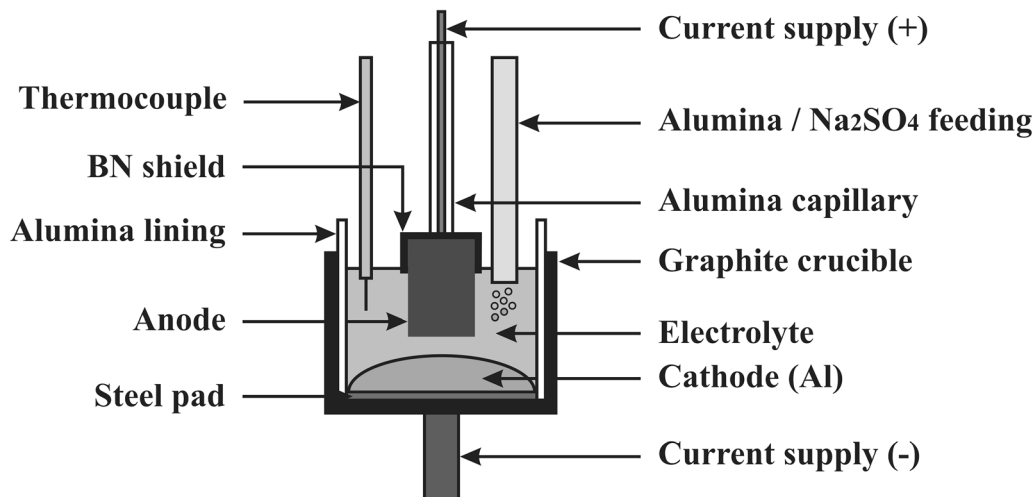


Fig. 1—A sketch of the electrolysis cell.

sublimation for 24 hours at 1300 °C in a platinum crucible. The electrolyte contained 81 wt pct cryolite, 10 wt pct AlF_3 , 5 wt pct CaF_2 , and 4 wt pct Al_2O_3 . Approximately 60 pct of the theoretical consumption of Al_2O_3 (alumina) was fed every 10 minutes (0.49 g Al_2O_3 /100 g electrolyte) to compensate for the amount consumed during the electrolysis (the rest of the alumina was dissolved from the alumina lining). In the third series (GS series), a constant amount of sodium sulfate (205 mg kg^{-1} S) was fed together with alumina every 10 minutes to sustain roughly constant sulfur concentrations in the electrolyte. The first addition was applied at the beginning of electrolysis, the last addition 10 minutes before the end of electrolysis. According to Meirbekova *et al.*,^[25] 1000 mg kg^{-1} S added into the electrolyte in the form of a sodium sulfate tablet dissolves within 5 minutes. Based on these results, we can expect that the applied amount (205 mg kg^{-1} S) in crystalline form (with a larger surface area for dissolution) will completely dissolve within 10 minutes.

The sulfur-containing gases (SO_2 , COS , H_2S) released during electrolysis were absorbed and oxidized to sulfuric acid by a 3 pct aqueous solution of H_2O_2 placed in three washing vessels. After the experiments, the solutions were analyzed for the content of sulfur by titration. The electrolyte was sampled three times (at the time 120, 180, and 240 min) just before feeding. Quenched samples of the electrolyte were analyzed for the content of sulfur (Benchtop Lab-X 3000 XRF Analyzer) and sulfides (classical iodometry). XRF thus reports the content of sulfur in the electrolyte in any valence $c(\text{S})_{\text{E}}$, while iodometry reports sulfur in the 2-valence state (*i.e.*, the content of soluble sulfides in the electrolyte $c(\text{S}^{2-})_{\text{E}}$ —it is not expected that the insoluble sulfides/polysulfides are present in the sample of electrolyte). Although the amount of soluble sulfides (determined by iodometry) is included in the amount of sulfur in the electrolyte (determined by XRF), it is not counted/considered twice in the calculations/discussions. A difference between the value reported by XRF and that reported by iodometry (denoted as $c(\text{S})_{\text{XE}}$) thus represents the sulfur content of

any sulfur compound except soluble sulfide/polysulfide. The sulfide (sulfur) contents (determined in samples collected at the time 120, 180, and 240 minutes) were averaged, and an arithmetic mean was calculated. An uncertainty was less than 3 pct. Some of the electrolytes were also analyzed for the content of (soluble) sulfates. The method of ion chromatography (Ion Chromatograph 761 Compact IC, Metrohm Ltd., Switzerland) was used for this purpose. A more detailed description of the method is given in the literature.^[23] The composition of the deposited aluminum and the electrolyte after the electrolysis experiments was determined by X-ray diffraction analysis (XRD, STOE Stadi, Germany). The aluminum cathodes were (before analysis) cleaned with a 10 pct aqueous solution of AlCl_3 for 1 hour and subsequently with ultrasound for 40 minutes. The cleaned cathodes were finally dried and weighed. Current efficiency (CE) was calculated according to Eq. [4]:

$$CE = m(\text{Al})_d / m(\text{Al})_t \cdot 100 \text{ pct}, \quad [4]$$

where $m(\text{Al})_d$ is the weight of the deposited aluminum (kg), and $m(\text{Al})_t$ is the weight of aluminum that should theoretically be deposited according to Faraday's law (kg):

$$m(\text{Al})_t = (M(\text{Al})/nF) \cdot It, \quad [5]$$

where $M(\text{Al})$ is the molar mass of aluminum (g mol^{-1}), I is current (A), n is a number of electrons involved in the electrode process, F is Faraday's constant (96485 C mol^{-1}), and t is a time of electrolysis (s).

Similarly, the cooled anodes were weighed before and after each electrolysis experiment and the carbon consumption (CC) was determined from the weight loss of the anodes.^[26] This parameter is usually expressed in kilograms of carbon consumed per 1 ton of aluminum produced. In this work, it is given (for fast orientation) in percent of CC , where one hundred percent represents the theoretical carbon consumption of 333 kg C per ton of deposited Al at 100 pct current efficiency.^[27]

III. RESULTS AND DISCUSSION

The results of current efficiency measurements are summarized in Figure 2 and Table I. It can be seen that the current efficiency decreases by 1.3 and 0.9 pct per 1 wt pct S in prebaked and graphite anodes, respectively. Our result is similar to the 1.5 pct loss in *CE* per 1 wt pct S in prebaked anodes reported by Pietrzyk and Thonstad.^[19] Their value was determined for the interval (0 to 3.82) pct S, including data obtained with graphite anodes (as zero sulfur material) and excluding butts.

As shown in Figure 2, the *CE* drop for prebaked anodes is, within the interval (1.91 to 2.90) wt pct S, larger than that for graphite anodes. Different behaviors were expected as two different anode materials are compared. They differ in not only impurity level, porosity and homogeneity but also in the type of carbon and sulfur containing compounds. As impurities (such as P, V, Fe, Na, Ni, Ca, Mg, Al) can also affect the current efficiency,^[1] the dependence *CE* vs (sulfur-free) overall impurity level was checked. No definite dependence was found. It looks, that the current efficiency (for actual impurity level, see Table I) is mainly influenced by sulfur content in the anodes and depends on the type of sulfur species. A rather narrow interval of compared sulfur content values does not allow any definitive conclusion to be drawn.

The addition of sodium sulfate to the electrolyte resulted in a very slight decrease in *CE*, if trends for graphite anodes are compared (*i.e.*, GS series compared with sulfate-free G series). Sodium ions can react with aluminum fluoride to form sodium fluoride. This leads to an increase of the cryolite ratio *CR* (the molar ratio of NaF and AlF₃). Since an increased cryolite ratio is correlated with the current efficiency loss by 4.2 pct per unit change of the ratio,^[28] it is of interest to ask if sodium ions (originating from sodium sulfate) would also contribute to an increase in *CR* and thus, the current efficiency loss. It was shown that the effect of sodium ions (originating from sodium sulfate) on the cryolite ratio can be neglected.^[25] Therefore, their effect on *CE* can also be neglected. As follows from Figure 2, a

constant amount of added sulfate leads to an approximately constant loss of *CE*. This finding supports the idea that *CE* loss is more influenced by anode sulfur than by added (sulfate) sulfur into the electrolyte that only contributes to the *CE* loss (from ca 92 to 91 pct).

Meirbekova *et al.*^[25] reported a loss in *CE* caused by sulfate ions added to the electrolyte. In this case, however, approx. the same loss in *CE* (1.1 pct) was found at about one order of magnitude lower electrolyte sulfur concentration compared to our results (experiments with zero-sulfur content in the anodes). Such large differences can be attributed to several factors: different quality and composition of the anodes, different electrolysis parameters, methods of analysis and sampling. In addition, an anode with a larger surface (contact area) was used, and the bubble generation was observed.^[25] Both of these facts contribute to the mixing of the electrolyte and support the formation and release of sulfur gasses. Bubble generation can favor back reactions and thus decrease *CE*. According to Ambrová,^[23] the obtained results may also be significantly influenced by the treatment of sample prior to analysis. Burnakin *et al.*^[21] and Ambrová *et al.*^[29] reported that sulfate may decrease *CE* and participate in both chemical and electrochemical reactions. Sulfates can be chemically reduced to sulfides by molten aluminum as well as by carbon.^[21,22,30,31] Possible redox reactions and the standard Gibbs free energy at 970 °C are listed below.

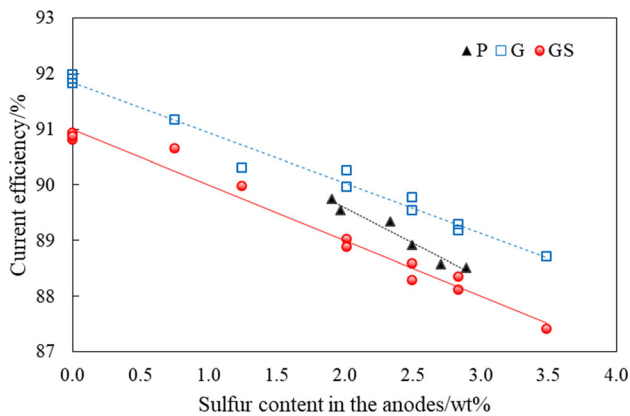
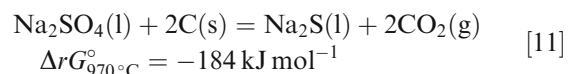
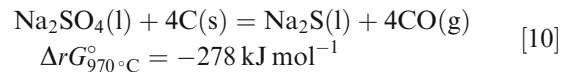
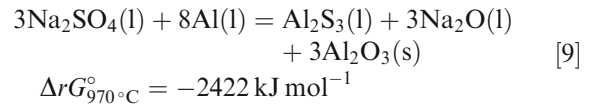
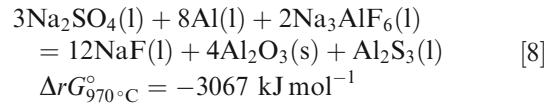
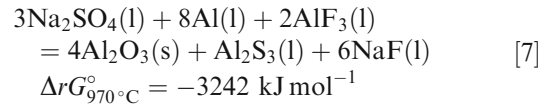
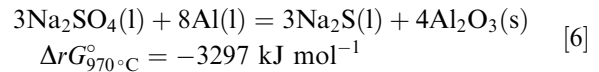


Fig. 2—Current efficiency (*CE*) as a function of sulfur content in the anodes ($c(\text{S})_A$). P: series with prebaked anodes, G: series with graphite anodes, GS: series with graphite anodes and added sodium sulfate.

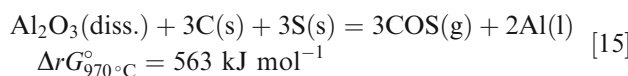
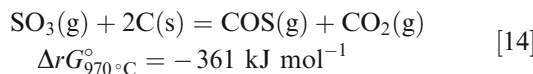
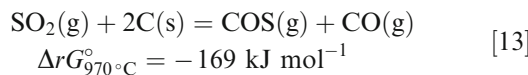
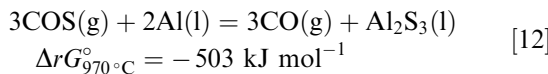
Table I. The Correlations for the CE Measurement and the Anode (Sulfur-Free) Impurity Level

Series	Correlation Parameters	Impurity Level/ppm
P	$CE = -1.2664c(S)_A + 92.124$ $R^2 = 0.9517$	1108 to 1701
G	$CE = -0.9048c(S)_A + 91.845$ $R^2 = 0.9789$	946 to 980
GS	$CE = -0.9950c(S)_A + 90.996$ $R^2 = 0.9783$	

CE: current efficiency (pct), $c(S)_A$: sulfur content in the anodes (wt pct).

The relatively negative values of the standard Gibbs free energy indicate, in terms of thermodynamics, there is a high probability of sulfide formation. However, the compounds in the real melt are not in the standard state, so their chemical potential is different from the chemical potential in the standard state. Therefore, based on the values of the standard Gibbs free energy, it is not possible to decide which of the reactions will take place in the system. Reactions [7] and [8] that produce sodium fluoride appears to be less likely as no increase in the cryolite ratio due to presence of sodium ions (originating from sodium sulfate) was observed.^[25] However, the reactions [6], [9], [10] and [11] can take place in the system. Both sulfides (Al_2S_3 and Na_2S) were identified in the electrolyte, and the reactions [10] and [11] can be pronounced because the gases formed can be released from the system.

Our ex-post analysis of the solidified electrolyte and the cathodes showed that sulfides are being formed regardless of the type of anode used (Table II). In the GS series, iron sulfides/polysulfides were also identified on the cathode surface. In this case, the wettability of the cathodes visibly decreased, which may be precisely due to a formation of iron sulfides/polysulfides. In addition, the intermetallic compound $Al_{13}Fe_4$ was identified as a reaction product between iron and molten aluminum cathode. The presence of sulfides in the sulfate-free electrolytes (P and G series) indicates that sulfur originating from the anodes is also involved in their chemical and/or electrochemical formation. For example, sulfides can form by the reduction of anode gases, or sulfur species present in the anode^[32,33]:



Reaction [15] producing aluminum is not thermodynamically favorable, but the reactions [12], [13], and [14] in which the gases are produced are possible. The reducing agent could be dissolved aluminum as well as carbon, as indicates the presence of Al_2S_3 and Na_2S , detected in the electrolyte. Since both sulfides are soluble in the electrolyte,^[24] a classical iodometry titration cannot distinguish between their quantities. However, it allows us to see to what extent the reduction to (soluble) sulfides takes place. Therefore, the sulfide content in the electrolyte ($c(S^{2-})_E$) was measured as a function of the sulfur content in the anodes. The results are shown in Figure 3 and Table III.

It is evident that while the sulfide content increases relatively linearly for the sulfate-free electrolytes (P and G series); this trend is more polynomial for electrolyte containing sulfate (GS series). The addition of sulfate does not appear to affect the level of sulfides in the electrolyte at higher anode sulfur content (above 2 wt pct). Similar behavior can be seen in Figure 4 for the sulfur content in the electrolyte ($c(S)_E$) determined by XRF. The corresponding linear regression parameters are therefore calculated only for the sulfur content interval (0 to 2.02) wt pct S (Table III). It should be noted that the sulfide (sulfur) contents represent an arithmetic mean of the values determined in samples collected at the time 120, 180 and 240 minutes. An uncertainty was less than 3 pct.

In all series, the sulfur (sulfide) content in the electrolyte did not vary with the time of sampling (120, 180, and 240 minutes). Since gaseous products can also be formed in the electrolyte, it cannot be expected that the equilibrium will be established in the system. However, it can be expected that a stationary state will be reached when the rate of sulfides' formation in the electrolyte and the rate of their vanishing from the system (by the formation of gaseous products) will equalize. The amount of sulfur (sulfide) in the electrolyte in the stationary state depends on several factors. There will be an infinite number of stationary states when the rates of sulfide formation and their vanishing equalize, depending on the possibilities of sulfur entering the system. However, there will probably be only one stationary state, when the sulfur content in the electrolyte will be maximum. If there is no additional source of sulfides (formed from added sulfate) in the electrolyte, the amount of sulfur coming from the consumed part of the anode is not sufficient to achieve this stationary state. However, at a certain amount of sulfate added to the electrolyte, the sulfide (sulfur) content in the electrolyte will be sufficient to reach this stationary state. The greater part of the sulfate is converted to

Table II. Composition of the Solidified Electrolytes and the Cathodes (XRD)

Series	Electrolyte Composition		Cathode Composition	
	Bulk	Vicinity of the Cathode	Surface	Bulk
P	Na ₃ AlF ₆ , Al ₂ O ₃	Na ₃ AlF ₆ , Na ₂ S, Al ₂ S ₃	Al	Al
G	Na ₃ AlF ₆	Na ₃ AlF ₆ , Na ₂ S, traces of Al ₂ S ₃	Al	Al
GS	Na ₃ AlF ₆ , traces of Al ₂ S ₃	Na ₃ AlF ₆ , Al ₂ S ₃ , Na ₂ S, polysulfides	Al, Al ₂ S ₃ , FeS, FeS ₂ , Fe ₇ S ₈ , Al ₁₃ Fe ₄	Al

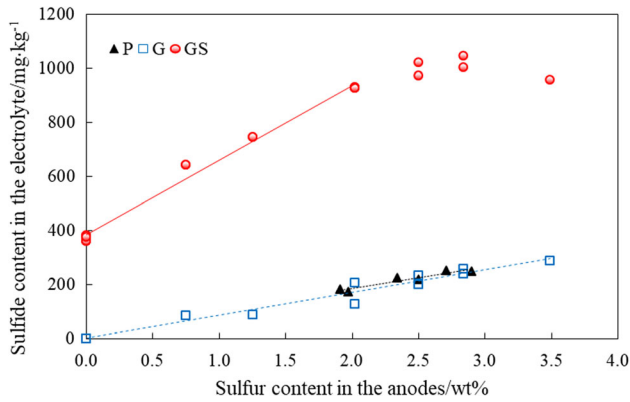


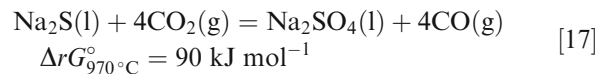
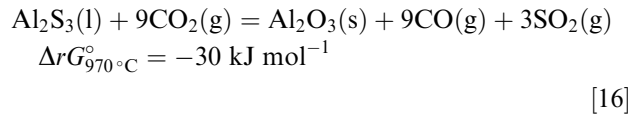
Fig. 3—Sulfide content in the electrolyte ($c(S^{2-})_E$) as a function of sulfur content in the anodes ($c(S)_A$). P: series with prebaked anodes, G: series with graphite anodes, GS: series with graphite anodes and added sodium sulfate.

gaseous products (either directly or *via* sulfides as an intermediate step) under this stationary state. The sulfur content in the stationary state then keeps the dissolution of sulfur from the anode at a constant value. This can be seen from Figures 3 and 4, where the sulfide (sulfur) content of the electrolyte no longer varies with the sulfur content of the anode, the sulfur from the anode dissolves only at a rate sufficient to replenish the sulfur escaped in the gaseous products. At lower sulfur contents in the anode (0.75 and 1.25 wt pct S), the sulfate addition to the electrolyte was not sufficient to achieve this particular stationary state. In this case, the stationary state was reached at lower sulfur contents in the electrolyte. This assumption is supported by fact that the sulfur (sulfide) content in the electrolyte did not vary with the sampling time, *i.e.*, the stationary states were also reached in the sulfate-free series (G and P series).

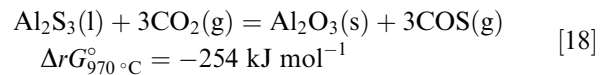
A comparison of the sulfur and sulfide amounts in the electrolyte showed that the sulfur amount is approx. 1.8 and 2.2 times higher than the sulfide amount for the P and G series, respectively. If the anode type did not change, this ratio remained approx. constant despite the addition of sulfate to the electrolyte (*i.e.*, 2.2 for G and GS series). The added sulfate appears to contribute only to the sulfide level in the electrolyte, which increased ca. five times. As follows from Figure 3, sulfide content for the P series is very similar to that for the G series. It indicates that the form of sulfur in the anodes does not significantly affect the soluble sulfide formation. Thus, approximately half of the sulfur detected in the electrolyte (by XRF) occurs in the form of any sulfur

compound except soluble sulfides/polysulfides. We assume that part of this sulfur (in text denoted as $c(S)_{XE}$) occurs in the insoluble sulfide/pyrite/polysulfide form (Table II), part in the soluble/insoluble sulfate form, and part can be present in carbon dust. Sulfur gases captured or adsorbed in alumina may also be present in the electrolyte, but iodometry is unlikely to detect them. Surprisingly, an approximately constant amount of soluble sulfate (1/5 of $c(S)_{XE}$) was detected by ion chromatography in three tested electrolytes (the samples collected during electrolysis with $c(S)_A = 2.5$ wt pct in GS series). It follows that some amount of sulfate can survive in the electrolyte under certain conditions.

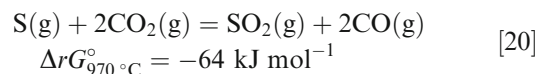
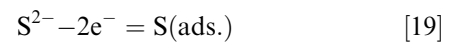
Up to now, it is not clear how the sulfide ions can oxidize, either by anode gases or directly at the anode. Some results in the chloride system^[34] showed that both SO₂ and sulfide could participate in the anode process. Sulfide can be oxidized in the vicinity of the anode, *e.g.*, according to the reactions:



Sulfide oxidation to form sodium sulfate (reaction [17]) appears not to be likely. Anodic oxidations of aluminum sulfide at a polarized carbon anode may be however thermodynamically possible. Aluminum sulfide can also react with anode gas to form carbonyl sulfide:



According to Baimakov and Vetyukov,^[30] part of the sulfides in the electrolyte dissolves and re-oxidizes at the anode:



Shvartsberg^[35] suggested that a higher amount of sodium sulfate, compared to aluminum, is consumed by its reactions with carbon under the formation of Na₂S and SO₂ by the reactions [10] and [21], respectively.

Table III. Correlations for the Electrolyte Sulfide and Sulfur Content Analyses

Series	Correlation Parameters	
P	$c(S^{2-})_E = 78.630c(S)_A + 27.313$ $R^2 = 0.9198$	$c(S)_E = 131.75c(S)_A + 60.254$ $R^2 = 0.9892$
G	$c(S^{2-})_E = 84.258c(S)_A + 1.3496$ $R^2 = 0.9603$	$c(S)_E = 187.87c(S)_A + 1.0363$ $R^2 = 0.9692$
GS	$c(S^{2-})_E = 276.090c(S)_A + 383.99$ $R^2 = 0.9904$	$c(S)_E = 473.51c(S)_A + 1039.5$ $R^2 = 0.9634$

$c(S^{2-})_E$: sulfide content in the electrolyte (mg kg⁻¹), $c(S)_A$: sulfur content in the anode (wt pct), $c(S)_E$: sulfur content in the electrolyte (mg kg⁻¹).

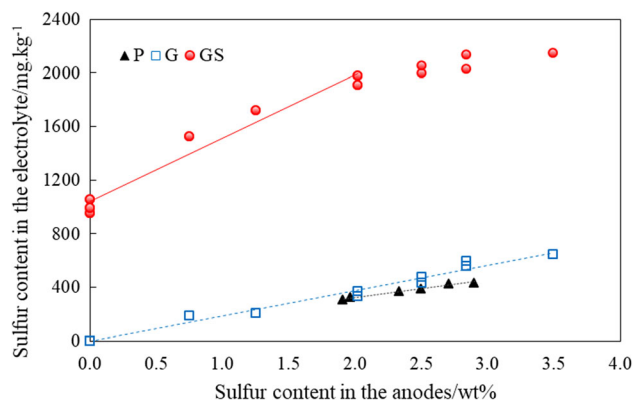
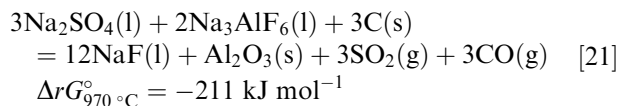
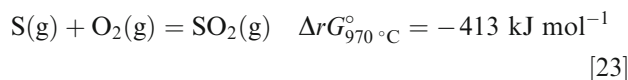
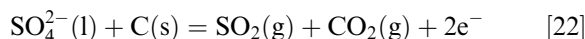


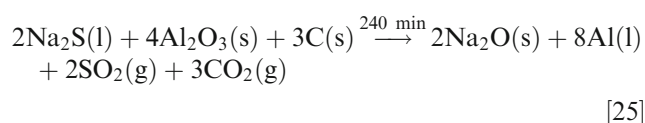
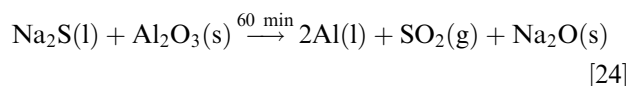
Fig. 4—Sulfur content in the electrolyte ($c(S)_E$) as a function of sulfur content in the anodes ($c(S)_A$). P: series with prebaked anodes, G: series with graphite anodes, GS: series with graphite anodes and added sodium sulfate.



Author^[35] explained it by a much higher sulfate loss and the amount of formed Na_2S in the presence of carbon, compared to sulfate loss and the amount of Al_2S_3 formed in the presence of aluminum. Shvartsberg^[35] suggested that sulfates and sulfides may also be oxidized electrochemically according to reactions [19] and [22], followed by oxidation of sulfur by oxygen [23] evolved at the anode.



In connection with the above, Burnakin *et al.*^[21] proposed that Na_2S oxidizes according to the overall reactions:

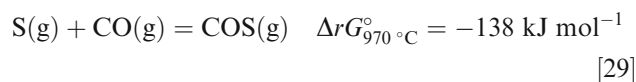
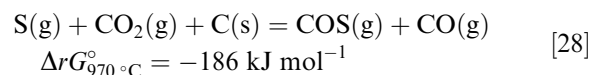


Minh and Yao^[36] electrolyzed Al_2S_3 dissolved in the LiF–NaF eutectic mixture at 1023 K. Gaseous sulfur was formed at the graphite anode and aluminum at the cathode. The anodic reaction was treated as a two-step reaction:



The sulfur formed by the reaction [26] dissolved in the melt and subsequently reacted according to the reaction [27].

As shown in Figure 5 and Table IV, the anode gases contain different amounts of sulfur depending on the used anode material. Therefore, the further results can also differ depending on the composition of the anode. Although the sulfur amount in the gases represents ca 61 to 68 wt pct S (relative to the consumed part of the anode), a relatively high amount of sulfur released from the anodes ends in the electrolyte. It can remain in its original form (in carbon dust), change to a gaseous form and absorb on alumina, as well as react according to some of the above-mentioned reactions or according to reactions:



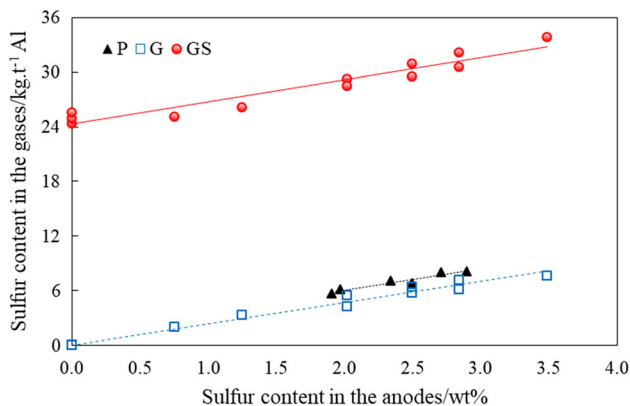


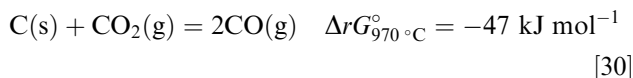
Fig. 5—Sulfur content in the gases ($c(S)_G$) as a function of sulfur content in the anodes ($c(S)_A$). P: series with prebaked anodes, G: series with graphite anodes, GS: series with graphite anodes and added sodium sulfate.

Sillinger and Horwath^[37] found that the ratio $S_{\text{foam}}/S_{\text{bath}}$ (0.062 wt pct/0.020 wt pct) increases linearly with the ratio $C_{\text{foam}}/C_{\text{bath}}$, *i.e.*, the more carbon dust is floating on the bath (electrolyte), the higher the content of sulfur in the bath. Also, according to Meirbekova *et al.*^[38] the sulfur concentration in the bath depends significantly on the concentration of carbon dust in the bath. The black spot area (representing carbon dust) identified in the bath sample by SEM contained 1.41 wt pct S. The sulfur concentration in the bath varied from ca 0.011 to 0.048 wt pct S.^[38] These findings indicate that the carbon particles can attach (bound) the sulfur present in the electrolyte. Thus, a relatively high sulfur (sulfide) content in the electrolyte may be partly related to the presence of carbon particles, which can serve as a center for the capture of sulfur species (sulfate reduction products). This can allow a slow accumulation of sulfur in the electrolyte until a stationary state is reached at the maximum sulfur content in the electrolyte. Stagnant conditions in the laboratory cell, sulfur gases captured or adsorbed in the alumina as well as the properties of the sulfate reduction products may also contribute to the value of sulfur content in the electrolyte.

If some of the sulfur species will be able to reduce and subsequently to re-oxidize, the formed redox pairs between the anodes and the cathode may cause significant *CE* loss. In addition, the interfacial tension at the electrolyte/aluminum interface can be unfavorably affected, causing the metallic aluminum to disperse in the electrolyte, where it can be more easily oxidized. This can then result in a further decrease in *CE*. Soluble sulfides present in the electrolyte are also able to react with metal oxides and precipitate as solid insoluble sulfides. In this way, they can contaminate the aluminum produced and reduce current efficiency. From this point of view, it is advisable to monitor their presence in the electrolyte. Based on our results we assume that sulfide may form according to reactions [6], [9], [10], or [12] and oxidize according to reactions [16] or [18].

Circa 68 wt pct of the sulfur released from prebaked anodes ends in the gas phase (P series in Figure 6). This amount is approx. 7 wt pct higher in comparison to the sulfur amount released from graphite anodes (G series). The addition of sulfate to the electrolyte led to a significant increase in the sulfur amount in the gases (ca. sixfold), but the distribution of sulfur remained more or less constant (G vs GS series in Figures 5 and 6). Similar trends can also be seen in the amounts of sulfur/sulfide: the amounts of sulfur and sulfide increase ca. five times, but their distribution remains almost constant, although conditions in the system changed by the addition of sulfate (G vs GS series in Figures 3, 4 and 6). It should be noted that the input sulfur in Figures 6 and 8 represents the sum of the mass of sulfur from the consumed part of anode, the mass of sulfur originated from Na_2SO_4 and the mass of background sulfur.

Although the given values are only semi-quantitative (ca. 5 wt pct of sulfur has not been detected most probably due to feeding and sampling), we can assume that the form of sulfur in the anodes affects what type of sulfur compound will form (P vs G series in Figure 6). This may be related to the type of bond by which the sulfur is bound in the anode material. According to Jahrsengene *et al.*,^[16] CO_2 reactivity decreases with increasing content of S–S bound sulfur, thus it is involved in inhibiting the reaction of CO_2 with coke:



The reduction in reactivity was also found to be more dependent on the amount of S–S type of sulfur compound rather than the total amount of sulfur. These findings are in agreement with the foregoing and the *CC* measurements (Figures 6, 7 and Table IV). The *CC* and sulfur content in the gases are higher for prebaked anodes (organic sulfur) than for graphite anodes (S–S bound sulfur). Also, the *CC* values for the GS series are only slightly higher than for the P series (Figure 7).

As can be seen in Figure 7 and Table IV, the measured *CC* is higher than the theoretical. Typical reasons are the excess carbon gasification and the formation of carbon dust.^[27] Excess carbon gasification is caused mainly by the Boudouard reaction^[30] when CO_2 can react with non-polarized carbon inside the anode pores, or with carbon dust present in the electrolyte. However, unlike in the case of *CE*, the increase in *CC* is not constant over the entire range of $c(S)_A$. It increases more at higher sulfur content in the anodes. According to Pietrzyk and Thonstad,^[19] the total carbon consumption can be increased due to electrochemically produced carbonyl sulfide (COS). As shown in our results, the distribution of sulfur under polarized and non-polarized conditions differs (Figure 6 vs Figure 8).

Under non-polarized conditions (Figure 8), we can see a very similar distribution of sulfur between the electrolyte and gas phase for all series. But, the amounts of sulfur and sulfide in the electrolyte are higher and the amounts of sulfur gases are lower compared to polarized conditions (Figure 6). It indicates that the electrolysis increases the sulfur depletion from the cell. Similar to

Table IV. Correlations for the Gas Sulfur Content Analysis and CC Measurements

Series	Correlation Parameters	
P	$c(S)_G = 2.3678c(S)_A + 1.2849$ $R^2 = 0.9327$	$CC = 6.1241c(S)_A + 111.32$ $R^2 = 0.9696$
G	$c(S)_G = 2.2895c(S)_A + 0.1420$ $R^2 = 0.9787$	$CC = 3.1296c(S)_A + 110.20$ $R^2 = 0.936$
GS	$c(S)_G = 2.4298c(S)_A + 24.296$ $R^2 = 0.9223$	$CC = 7.0179c(S)_A + 111.99$ $R^2 = 0.971$

$c(S)_G$: sulfur content in the gas (kg t^{-1} Al), $c(S)_A$: sulfur content in the anode (wt pct), CC : carbon consumption (pct).

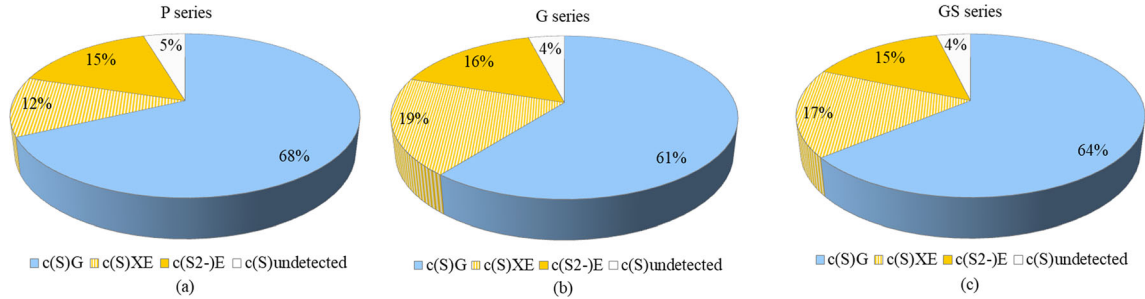


Fig. 6—Distribution of sulfur after electrolysis calculated with respect to input sulfur (wt pct). (a) P series with prebaked anodes; (b) G series with graphite anodes; (c) GS series with graphite anodes and added sodium sulfate. $c(S)_G$: sulfur in the gas, $c(S)_{XE}$: sulfur in the electrolyte after subtracting sulfides, $c(S^{2-})_E$: sulfides in the electrolyte, $c(S)_{undetected}$: undetected amount of sulfur.

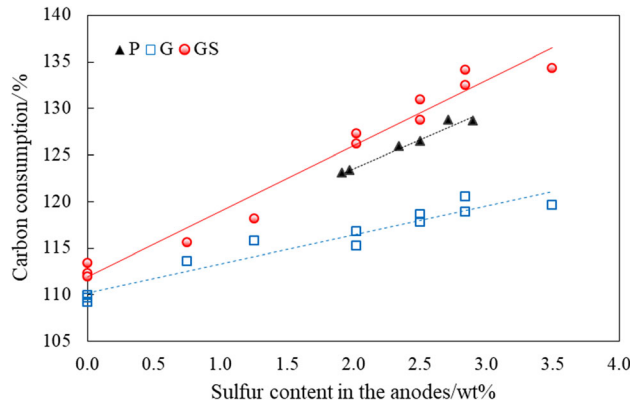


Fig. 7—Carbon consumption (CC) as a function of sulfur content in the anodes ($c(S)_A$). P: series with prebaked anodes, G: series with graphite anodes, GS: series with graphite anodes and added sodium sulfate.

polarized conditions, the ratio between the amounts of sulfur and sulfide remained approx. constant (2.3) despite sulfate was being added to the electrolyte (the ratio for G and GS series under polarized conditions was 2.2). This means that the added sulfate only increases sulfide concentration in the electrolyte when the anode type (in this case also a reducing agent) does not change. However, when comparing polarized and non-polarized conditions for the P series, the sulfur to sulfide ratio increased from 1.8 to 2.0. Thus, the electrolysis promotes the formation of soluble sulfides in this case.

It should be noted that the experimental results are interfered with by many factors (homogeneity of the anode, calcination level, chemical state and form of sulfur, porosity, initial impurity level, *etc.*) to some extent. Therefore, they should not be generalized for whatever type of anode.

IV. CONCLUSION

Based on our knowledge this is the first study where the simultaneous effect of sulfur in the anode material and the sulfur in the electrolyte on CE and CC was measured and evaluated. The results are extended and compared with the results obtained for both these effects individually. Prebaked and graphite anodes with varying levels of sulfur were used. It was found that CE lowers by 1.3 pct per 1 wt pct S, and CC increases by 6.1 pct per 1 wt pct S for prebaked anodes. The addition of sulfate to the electrolyte led to the CE decrease from 0.9 to 1.0 pct per 1 wt pct S, and to the increase in CC from 3.1 to 7.0 pct per 1 wt pct S for graphite anodes. The addition of sulfate into the electrolyte was found to increase the sulfur level in the electrolyte and gas phase, but the distribution of sulfur between the liquid and gas phases was almost the same. It indicates that sulfur distribution (calculated with respect to input sulfur) is more influenced by anode sulfur than by sulfate sulfur added into the electrolyte.

Sulfides and polysulfides were detected in the solidified electrolyte after electrolysis. Their content increased up to approx. 2 wt pct of S in the anode and then became constant. Similar behavior was observed for the

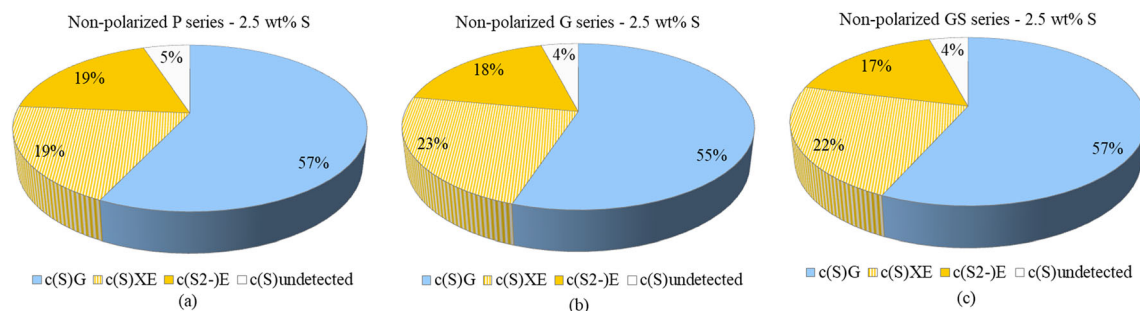


Fig. 8—Distribution of sulfur under non-polarized conditions calculated with respect to input sulfur (wt pct). (a) P series with prebaked anodes; (b) G series with graphite anodes; (c) GS series with graphite anodes and added sodium sulfate. $c(S)_G$: sulfur in the gas, $c(S)_{XE}$: sulfur in the electrolyte after subtracting sulfides, $c(S^{2-})_E$: sulfides in the electrolyte, $c(S)_{undetected}$: undetected amount of sulfur. Distribution includes only experiments with $c(S)_A = 2.5$ wt pct S.

sulfur content in the electrolyte. We assume that a stationary state is reached at this stage. The greater part of the sulfate is converted to gaseous products (either directly or *via* sulfides as an intermediate step) under this stationary state. The sulfur content in the stationary state then keeps the dissolution of sulfur from the anode at a constant value. The sulfur to sulfide ratio was revealed to be approx. constant (for the same type of anodes) within the entire interval of sulfur content in the anodes. Surprisingly, it was also found that a certain amount of sulfate remains in the electrolyte despite the electrolyte's reductive environment. Analysis of the gases and electrolytes showed that a relatively large amount of sulfur is being released from electrolysis in the form of sulfur emissions (including very powerful greenhouse gases like COS and CS₂). A significant amount of sulfur from the consumed part of anodes remained in the electrolyte where sulfur species may form redox pairs. These continually generated redox pairs could reduce the CE of the electrolysis process, similar to those known for phosphorus.

A comparison of the polarized and non-polarized conditions showed that the electrolysis increases the sulfur depletion from the cell and (in the system with prebaked anodes) promotes the formation of soluble sulfides. Soluble sulfides are able to react with metal oxides and precipitate as solid insoluble sulfides. In this way, they can contaminate the aluminum produced and reduce current efficiency.

It can be concluded that the sulfur species can negatively influence key parameters of aluminum electrolysis and increase sulfur emissions.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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