

INVESTIGATION OF THE EFFECT OF ELECTROLYSIS CONDITIONS ON THE STABILITY OF GRAPHITE ELECTRODES IN THE CHLORINE CELL*

L. I. Krishtalik, G. L. Melikova and E. G. Kalinina

Translated from Zhurnal Prikladnoi Khimii, Vol. 34, No. 7,
pp. 1543-1547, July, 1961

Original article submitted April 19, 1960

In the preceding communication [1] we considered the effect of anolyte acidity on the wear of graphite anodes. The present investigation is concerned with the effects of certain other factors, including the sulfate content.

Various opinions have been expressed in the literature concerning the effect of sulfate. Some writers [2, 3] consider that the anodic liberation of oxygen and graphite wear are increased to a small extent in presence of the $\text{SO}_4^{=}$ ion, but their experimental data are very meager (one to three determinations) and in some instances refer to conditions which differ considerably from those of industrial electrolysis [2]. Moreover, Filippov et al. [4] concluded that $\text{SO}_4^{=}$ does not influence the anode process of graphite although, in our view, their data suggest that anodic liberation of oxygen is intensified in presence of sulfate.

Industrial experience with the diaphragm process for production of chlorine and alkalis does not indicate that the effect of sulfate is considerable [5], while a small effect is difficult to detect against the background of inevitable fluctuations in the operating conditions in industrial cells. An increase of wear with increasing Na_2SO_4 concentration has been observed during electrolysis by the mercury process; although the effect of sulfate is small, it is quite distinct against the small value of total wear [6]. It should be pointed out, however, that the data in [6] do not make it possible to decide conclusively whether they refer to the influence of sulfate itself on the anode process or whether there is a secondary effect, perhaps due to a decrease of the brine concentration in presence of Na_2SO_4 .

We therefore undertook a more detailed study of this problem. Concurrently with our work, the effect of sulfate on the anode process was also investigated by Flisskii, Veselovskaya, and Dzhagatspanyan [7], who determined the balance of the anodic products. Their main results are in good agreement with our data on the influence of the $\text{SO}_4^{=}$ ion on the chemical wear of graphite anodes.

The method of investigation was similar to that described earlier [1]. In both investigations the brine concentration was 300 g NaCl per liter, so that large amounts of sodium sulfate could be added to the solution without risk of salt precipitation.

Brines with various Na_2SO_4 contents were electrolyzed. A steady sulfate concentration was attained in the anolyte, about 1.3₃ times the average concentration in the brine. Accumulation of sulfate in the anolyte was caused by migration of $\text{SO}_4^{=}$ ions to the anode.

The amount of sulfate entering the anode compartment with the brine is $I_S(\text{SO}_4^{=})_S$ moles per second [I_S is the volume of brine per second, and $(\text{SO}_4^{=})_S$ is its $\text{SO}_4^{=}$ content]. Under the influence of the electric field the amount of $\text{SO}_4^{=}$ reaching the anode is $n_{\text{SO}_4^{=}} = \frac{I}{2F}$ moles, where I is the current strength, F is the Faraday number, and $n_{\text{SO}_4^{=}}$ is the transference number of the $\text{SO}_4^{=}$ ion in the anolyte of the given composition. It may be expressed in terms of the mobility of $\text{SO}_4^{=}$ l_1 the equivalent conductances Na_2SO_4 $\left(\lambda_{\frac{1}{2} \text{Na}_2\text{SO}_4}\right)$ and NaCl (λ_{NaCl})

and the chloride (Cl^-) and sulfate ($\text{SO}_4^{=}$) concentrations in the anolyte:

* Communication II.

$$n_{\text{SO}_4}^{\text{..}} = \frac{2l_{\frac{1}{2}\text{SO}_4}(\text{SO}_4^=)}{(\text{Cl}^-)\lambda_{\text{NaCl}} + 2(\text{SO}_4^=)\lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4}}.$$

The loss of $\text{SO}_4^=$ ions from the anolyte is $L_a(\text{SO}_4^=)$, where L_a is the volume of anolyte per second. From the balance equation

$$L_a(\text{SO}_4^=) = L_s(\text{SO}_4^=)_s + n_{\text{SO}_4} \frac{I}{2F},$$

substituting the expression for n_{SO_4} and $\frac{I}{F} = \frac{L_c C_{\text{NaOH}}}{A}$ (L_c is the catholyte volume, C_{NaOH} is the NaOH concentration in the catholyte, and A is the current efficiency as a fraction of unity), and introducing the relative volumes of the catholyte $K_c = \frac{L_c}{L_s}$ and anolyte $K_a = \frac{L_a}{L_s}$, we have

$$(\text{SO}_4^=) = \frac{(\text{SO}_4^=)_s}{K_a - \frac{K_c C_{\text{NaOH}}}{A} \frac{l_{\frac{1}{2}\text{SO}_4}}{(\text{Cl}^-)\lambda_{\text{NaCl}}}}.$$

Taking $C_{\text{NaOH}} \approx 3$ mole/L, substituting the values of (Cl^-) , K_a , K_c and A corresponding to this alkali concentration [5], and taking on the basis of data on conductances and ionic mobilities at the corresponding ionic strength that $l_{\frac{1}{2}\text{SO}_4} \approx 0.6 \lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4}$ and $\lambda_{\text{NaCl}} \approx 1.5 \lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4}$, we have $(\text{SO}_4^=) / (\text{SO}_4^=)_s \approx 1.3$, which is close to the experimental value.

The influence of sulfate concentration on the wear of new anodes is shown in the figure (curve 1).

These data show that anode wear increases roughly linearly with Na_2SO_4 concentration. The average increase of wear is about 0.8 g/1000 amp-hr per 10 g of Na_2SO_4 per liter of anolyte, which corresponds to about 1.1 g/1000 amp-hr per 10 g of Na_2SO_4 per liter of brine.

The increase of anode wear in presence of sulfate is due primarily to intensification of chemical wear. This is shown by the appreciable increase of the CO_2 content and the consequent increase of anolyte acidity. The anolyte acidity was above 0.01 N in all experiments with addition of Na_2SO_4 , and when the sulfate content was considerable it remained at the level of 0.02 N. In electrolysis of brine without sulfate this acidity was reached only by acidification of the brine. The increase of CO_2 concentration corresponds by order of magnitude, in the first approximation, to the increase of wear of new (unused) anodes.

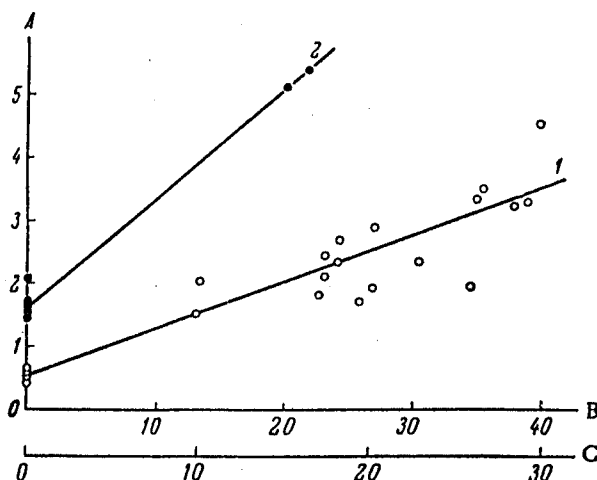
The influence of sulfate on the breakdown of very worn anodes is represented by an increase of wear amounting to 1.6 g/1000 amp-hr per 10 g of Na_2SO_4 per liter of anolyte (2.2 g/1000 amp-hr per liter of brine; upper curve (2) in the figure). The ratio of chemical to mechanical wear remains almost the same as in absence of sulfate if values for the same degree of chemical wear are compared [1].

Therefore sulfate does not appear to have any appreciable specific influence on mechanical crumbling of graphite; i.e., the swelling of graphite which is observed in sulfuric acid at higher anode potentials [8] does not occur.

* Subsequently the term $2(\text{SO}_4^=) \lambda_{\frac{1}{2}\text{Na}_2\text{SO}_4}$ is omitted from the denominator, because the sulfate concentration

is considerably lower than the chloride concentration, and its equivalent conductance is also somewhat lower.

The data in this and the preceding communication show that sulfate has much less effect than anolyte acidity on the stability of anodes in the chlorine cell. The opposite conclusion drawn by Bulygin [9] was based on the results of experiments conducted under conditions which were very far from those used in electrolysis of NaCl.



Effect of sulfate content on anode wear. A) Anode wear G (g/1000 amp-hr); B) sulfate concentration in anolyte (g/liter); C) sulfate concentration in brine (g/liter).

The effect of sulfate in industrial cells can be estimated from the above value (2.2 g/1000 amp-hr) with the assumptions that about 40% of the anode weight is waste material and that the current efficiency is 94-95%. It follows that anode wear is increased by approximately 2.5 kg per ton of 100% NaOH by each 10 g of Na_2SO_4 present in the brine. This estimate may be somewhat too high, because mechanical wear is relatively less in industrial cells and because of the influence of $\text{SO}_4^{=}$ on the acid balance in the anolyte.

According to Gardiner [6], the corresponding value in mercury cells is about 1.4 kg. It should be taken into account that anolyte exchange is more rapid in mercury cells than in diaphragm cells, so that the difference between the sulfate concentrations in the anolyte and brine is less (calculations show that the ratio of these concentrations should be about 1.07). If Gardiner's data are reduced to the same sulfate concentration in the anolyte the effect increases to 1.7 kg per ton of alkali. The somewhat lower effect of sulfate in mercury cells is to be expected, because anode wear is generally lower at high current densities (over 3000 amp/m² in this case).*

We also determined the influence of sulfate on the stability of graphite anodes impregnated with linseed oil. In this case only the wear of previously used anodes can be measured reliably, because the very low value of the initial wear is distorted owing to some leaching of the impregnant from new anodes. The wear of impregnated anodes at high anolyte acidity (above 0.01 N) in absence of sulfate was found to be 1.19 g/1000 amp-hr (average from three experiments). The wear of an unimpregnated anode under the same conditions is 1.34 times this value.

It is interesting to note the change in the composition of the anode gas when impregnated anodes are used. Whereas with unimpregnated anodes the CO_2 content was 0.2% and the free oxygen content (after deduction of atmospheric oxygen) was not higher than 0.01-0.02%, with impregnated anodes the CO_2 content fell to 0.1 % and the free oxygen concentration rose to 0.07%. Quantitative comparison of these results is impossible because of the inadequate precision in the determination of such small amounts of impurities, but the qualitative change in the nature of anode oxidation as the result of impregnation is quite distinct.

The wear of impregnated anodes in presence of sulfate (with 27.4 g of Na_2SO_4 per liter in the anolyte) was 3.91 g/1000 amp-hr (mean of six determinations). The increase of wear for each 10 g/liter was 1.0 g/1000 amp-hr,

* See also the comments made above concerning the possibility of a somewhat lower effect in industrial cells.

which is less by a factor of 1.6 than with unimpregnated anodes. However, the effect is fairly considerable even in this case, so that in industrial electrolysis the sulfate concentration of the brine must be kept to a minimum.

The most rational procedure is to remove sulfate at the evaporation stage. It is then possible, at minimum cost, to maintain the sulfate concentration of the brine at a low level (5-6 g/liter) which results in only a small decrease of anode stability. Total purification of the brine with the use of barium salts would be much more costly.

Two views have been put forward in the literature concerning the possible causes of the influence of sulfate: direct discharge of $\text{SO}_4^{=}$ ions (e.g., see [3]), and intensification of the harmful effect of electrolysis in anode pores as the result of sulfate accumulation in the pores and a corresponding increase in the conductance of the solution [10]. However, the anode potential in the chlorine cell is not high enough for direct discharge of $\text{SO}_4^{=}$ ions, while accumulation of sulfate in the pores is not sufficient [11] to produce any significant changes in the properties of the solution.

Flisskii, Veselovskaya and Dzhagatspanyan [7] found that $\text{SO}_4^{=}$ ions are strongly adsorbed on graphite anodes. If this adsorption is superequivalent than accumulation of $\text{SO}_4^{=}$ may cause a shift of the ψ_1 potential in the negative direction and, in consequence, to approximately equal retardation of the discharge of Cl^- and OH^- ions and acceleration of the discharge of water molecules. The final result is an increase in the proportion of current consumed for liberation of oxygen. Similar effects (retarded liberation of chlorine and accelerated liberation of oxygen) could be produced by inclusion of sulfate in the chemically adsorbed layer on the graphite surface.

In addition to studies of the effect of sulfate, we also investigated anode wear in presence of chlorate. With 20 g of NaClO_3 per liter of anolyte the wear of previously used anodes was 1.9 g/1000 amp-hr (average from five experiments). The influence of this anion is therefore very small, 0.15 g/1000 amp-hr per 10 g of NaClO_3 per liter.

SUMMARY

Investigations of the influence of sulfate on the wear of graphite anodes in the chlorine cell showed that the wear of both unimpregnated and impregnated anodes increases appreciably in presence of $\text{SO}_4^{=}$. Removal of sulfate from recycled brine is advisable under industrial electrolysis conditions. Anode wear is increased a little in presence of chlorate.

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