

*The effect of pH on graphite wear in a chlorate cell process**

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An apparatus and a method for graphite wear investigation at constant pH values in a chlorate cell process have been developed and presented. The same set-up could also be used in a chlorine cell process. Experimental and compilative data show the existence of an optimal pH region providing minimal graphite consumption in electrolytic chlorate production. The latter also coincides with the same pH range which provides maximal rates of active chlorine chemical conversion into chlorate [1], and thereby maximal current yields as well. Therefore, by adjusting the pH, one simultaneously optimizes both the graphite wear and the whole electrolytic process.

1. Introduction

For more than eighty years, graphite has been a unique anode material in both chlorine and chlorate cell processes. A number of papers [3-37] have recently been published dealing with its wear, the study of the operational factors of production, such as current density, anode potential, temperature, concentration and composition of brine, its acidity and feed rate and their mutual effects on anode corrosion, as well as graphite structures, porosity and impregnation. These have had the aim of determining the optimum conditions governing its consumption. The continued increase in the number of chlorine and chlorate installations and the further improvement of cell designs and technologies have naturally been accompanied by the development of several methods [4-7, 9] for testing graphite loss during operation.

The aim of the present paper is to describe a method for graphite loss investigations under steady-state conditions, particularly of chlorate, but also of chlorine, production as well as to present experimental data of the effect of pH

on graphite wear. The main advantage of the present method is that it allows not only the usual operating parameters, but also the pH of the cell and the active chlorine content to be maintained constant over a long period.

Numerous recent papers [10-19, 22, 23] have presented investigations of graphite wear dependence on the pH value of brine. However, either the investigated pH ranges were narrow [12-19], or [10, 11] measurements were taken in phosphate and other electrolytes, hence the results cannot be related to chlorine and chlorate cell processes.

2. Apparatus and method of graphite wear investigation

The novel method of graphite wear investigation described uses a laboratory system providing operating conditions quite close to those found in the chlorate manufacture. The same apparatus could be used for anode wear testing in a chlorine cell process. It consists of the cell and a reaction vessel with facilities for brine recirculation, both of them being thermostatted (Fig. 1). Such a system provides for testing of total graphite wear under steady-state conditions of both chlorine and chlorate production. Not only can

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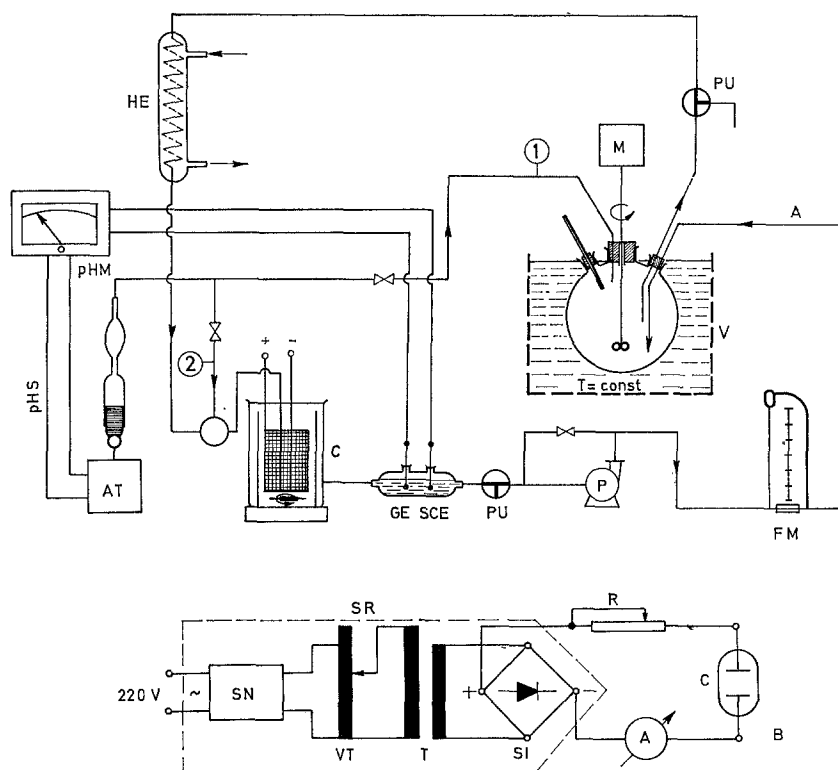


Fig. 1. Apparatus (A) and electrical circuit (B) for performing graphite wear testing. C, cell; V, holding vessel; P, pump; HE, heat exchanger; pHS, pH-stat; FM, flow meter; pHM, pH-meter; GE, glass electrode, SCE, saturated calomel electrode; PU, sample withdrawal for electrolyte control; AT, automatic titrator; M, electric motor and stirrer; SR, silicon rectifier; R, rheostat; A, ammeter.

temperature, current density, cell load, flow rate, brine composition and concentrations be maintained constant, but, most importantly, the pH and available chlorine* content.

A suitably modified automatic titrator was adapted as a pH-stat allowing the pH value to be maintained within ± 0.1 unit in the cell or the holding vessel, both operating as back-mix flow reactors. However, by combining certain flow rate values, temperature and a holding volume content (in other words by adjusting their mutual effect on the rate of chemical conversion of available chlorine to chlorate), one can also effectively maintain, at least within a transition pH region, a constant active chlorine concentration inside the cell (cf. [2]).

* 'Available chlorine' comprises the sum of concentrations of hypochlorous acid, hypochlorite ion and dissolved elemental chlorine. However, at the usual pH of electrolytic chlorate production the latter can be neglected and, hence, throughout this paper the more convenient term 'active chlorine' will be used for hypochlorous entities only.

Several graphite electrodes can be connected in parallel in the cell and several cells can be coupled in parallel for different brine recirculations, at different loads, pH or temperatures.

An identical auxiliary anode together with its Teflon holder can be easily and immediately replaced under load by an electrode for effective wear testing when the system reaches the given steady-state conditions. It is well known that only graphite previously used as an anode in the same electrode process under similar conditions can provide reliable comparative data of wear. The dimensions of the anode can be chosen to enable long-term investigations, whilst allowing measurements of corrosion depth.

The apparatus is similar to that described elsewhere [2] and used for steady-state measurements of the Faradaic efficiency of the chlorate cell process.

The cell was made of hard PVC (Fig. 2). In addition to uniform continuous flow of the electrolyte, a magnetic stirrer enables operation

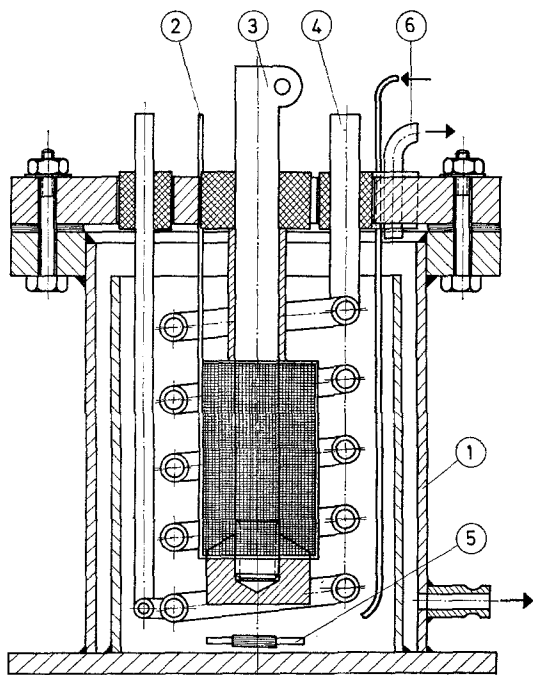


Fig. 2. Details of the electrolytic cell; 1, cell body; 2, platinum gauze cathode; 3, graphite anode with Teflon insulators; 4, glass cooling coil; 5, magnetic stirrer; 6, gas outflow.

as a back-mix-flow reactor. Stirring in the cell is further aided by cathodic evolution of hydrogen and appropriate positioning of both the platinum gauze cathode and the rod anode. Teflon isolating pieces confine the active anode surface to a space surrounded by the gauze part of the cathode. The cell temperature was maintained at 25°C. Higher operating temperatures could be used with other cell materials. The overflow mantle allows the efficient separation of gas bubbles from the brine. The cell assembly was gastight, enabling the evolution rate and composition of the evolved gases to be determined.

A PVC membrane pump was used for electrolyte circulation controlled by a differential manometer used as a flow meter. The flow rate was maintained at $8.2 \times 10^{-4} \text{ l s}^{-1}$, but could be varied within a wide range.

The holding vessel was 2.2 l in volume and was maintained at a temperature of 60°C. A stirrer was used to provide conditions for a back-mix-flow reactor.

The electrolyte was 300 g l^{-1} of NaCl and

4.0 g l^{-1} of sodium dichromate. Electrolysis was carried out to 60 g l^{-1} of sodium chlorate, whereupon the electrolyte was renewed. However, its composition could be maintained constant within very narrow limits. To provide operating conditions of a chlorine cell, a continuous isothermal brine flow is required rather than its recirculation through a holding vessel. The brine also needs further chlorine treatment and absorption. The graphite wear technique for testing under chlorine production conditions, recently developed by Vaaler *et al.* [7] seems more suitable for lower pH values.

Graphite wear was investigated by repeatedly measuring the anode weight during electrolysis under steady-state conditions. The rate of evolution and the composition of the anode gas could be used to follow the chemical part of the graphite corrosion (cf. [20]).

The principal advantage of the method of graphite wear testing described is the ability to maintain all operating and important process parameters at desired values, thus simulating cell conditions obtained in industrial practice.

Anode pieces were taken from plates (VEB Elektrokohle, Lichtenberg, DDR) of the standard type particularly prepared for chlorate cells. These were then impregnated with a linseed and tung oil composition in accordance with the method described elsewhere [3] and previously anodically conditioned in an identical way as during the testing itself.

The current density was, as is usual for unipolar chlorate cells, 3.0 A dm^{-2} .

Eberil' and Elina [8, 9] have found a certain critical anode potential above which graphite wear increases enormously. This is closely linked to the current density and, more particularly, with graphite impregnation (cf. [20, 26]). Similar observations [26, 27] have given rise to the terms 'transpassive' and 'subdiffusive' graphite behavior [8, 9]. Hence, in this investigation the current density (or anode potential) of the graphite electrodes was maintained well below its critical value (cf. [8, 9]).

3. Results and discussion

Graphite wear dependence on the pH value of brine under steady-state conditions in the

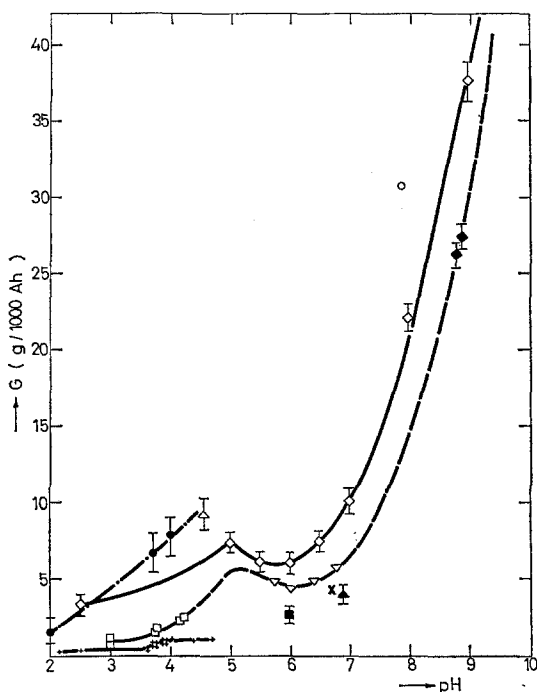


Fig. 3. Experimental and compilative plot of graphite wear G versus pH value of sodium chloride solution both in chlorine and chlorate electrolysis at 3–5 A dm⁻². \diamond , experimental data; ∇ , according to Eberil' and Filippov [17, 18]; \square , Vaaler [12]; \circ , Sjödin and Wranglén [26]; \blacksquare , Shlyapnikov and Filippov [53]; \times , Baner [54]; \triangle , Lenon and Vaaler [36]; \bullet , Krishtalik *et al.* [19, 33]; \blacklozenge , estimated according to Janes [27] and Kubát and Roušar [25]; $+$, Kohanov and Hanova [16].

chlorine and chlorate cell processes is shown in Fig. 3, which summarizes the available data.

In the strongly acid region, the anode consumption rate of plain graphite increases slowly with pH and, as was found earlier, it corresponds to the rate of oxygen evolution in the electrode process [19].

The first maximum of graphite wear is found at about pH 5 and coincides well with the pH region of maximum hypochlorous acid content [44]. pH 5 also represents the region of the highest positive potential values of the solution relating to available chlorine existence [55]. However, the potential is even more positive at the pH values where elemental chlorine exists, but graphite wear decreases at lower pH values of the brine. This would imply that active chlorine is essential for graphite corrosion. Janes [5], has pointed out that total graphite wear can be divided into two parts, chemical corrosion

depending on direct oxidation by hypochlorous acid, and electrochemical removal due to the anodic oxidation processes. Ksenzhek and Solovei [21] have shown that direct graphite oxidation by hypochlorous acid represents a heterogeneous reaction of the first order (cf. [24]). Hence, a direct relationship is found between graphite wear and hypochlorous acid concentration at higher values of the plotted pH function.

Graphite wear decreases to a well-defined minimum at about pH 6, after which it exhibits a very steep increase.

It has been pointed out [1, 52] that in concentrated solutions of neutral salts, such as are employed in chlorine and chlorate production, an increase in hydronium ion activity of about one order of magnitude compared to dilute solutions (cf. [45]), causes a shift in the optimal pH region for active chlorine chemical conversion to chlorate from 7.0 to 6.0[†] as defined by the equation

$$\text{pH}_M = \text{p}K^* - \log 2. \quad (1)$$

K^* denotes some practical rearranged dissociation constant of hypochlorous acid [1, 2]. Hence, the pH 6.0 for the chlorate cell brine also defines the region of minimum steady-state active chlorine content (cf. Fig. 4) and thereby of maximum overall current efficiency [1]. In other words, it could be concluded that graphite wear in chlorate cells is a direct function of the active chlorine content as approximately is the current yield.

The further rapid increase in graphite wear at pH values larger than 6.0 might also be related to the accumulating active chlorine content of the brine. The higher the pH, the higher is the bulk active chlorine concentration, but this also implies an even higher content within the anode diffusion layer (cf. [40]). This originates with the decrease of the rate of bulk

[†] It has earlier been shown [1] that the relevant equilibrium constant for calculating the actual concentrations of the hypochlorous species at the ionic strength of the brine is

$$K^* = \frac{a_{\text{H}_3\text{O}^+} \cdot C_{\text{ClO}^-}}{C_{\text{HClO}}} = K_a \cdot \frac{f_{\text{HClO}} \cdot a_{\text{H}_2\text{O}}}{f_{\text{ClO}^-}} \approx 10 K_a \quad (1a)$$

where K_a denotes the thermodynamic dissociation constant of hypochlorous acid.

chemical active chlorine conversion to chlorate with increasing pH of the brine (cf. [1, 2]). On the other hand, due to subsequent chlorine hydrolysis, which prevails inside the diffusion layer, hypochlorous species diffuse in both directions from and towards the generating electrode, thus creating a certain concentration maximum inside the boundary layer [40]. As a result of both chlorine hydrolysis and the Foerster reaction of anodic chlorate formation, the anode diffusion layer of a chlorate cell could be considered as strongly acidic (cf. [42]). This has been experimentally confirmed [46] by investigating the structure of the boundary layer with a micro-glass electrode and occurs even in the presence of the strongly buffering system of hydrochromic and hypochlorous acids. On the other hand the Foerster reaction equation for anodic chlorate formation in the interpretation of De Valera [47] also indicates that the concentration of hypochlorous acid is high inside the diffusion layer.

[1, 2]) from the experimental data using equation (1a) are also shown. The values of K_a at different temperatures were calculated from the data of Morris [48].

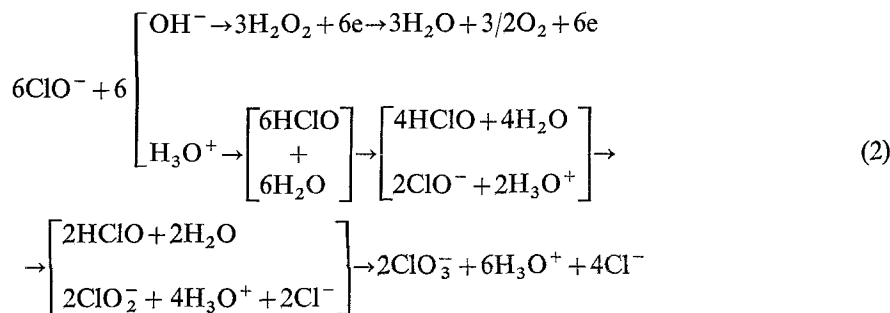
$$pK_a = \frac{3000 \cdot 00}{T} - 10 \cdot 0686 + 0 \cdot 0253 \cdot T, \quad (3)$$

and Caramazza [49]:

$$pK_a = \frac{800}{T} + 4 \cdot 892. \quad (4)$$

The two experimentally found pH dependencies (Figs. 3 and 4) agree well, thus providing convincing support for the correlation between graphite wear and active chlorine content of the brine. (Also cf. [18, 38].)

In the entire pH region investigated, oxygen evolution increases with pH in accordance with the Foerster equation for electrochemical chlorate formation or otherwise with active chlorine content (cf. [2, 40, 50, 51]). The oxygen content



One can therefore conclude that graphite wear in all cases will be a function of the effective hypochlorous acid concentration of the brine in close proximity to the anode and also a function of the total available chlorine concentration in the bulk both of which are mutually connected.

Kokoulina and Krishtalik [38] obtained a similar pH dependence of the steady-state active chlorine concentration in a chlorate production system to that found for graphite wear (Fig. 3). The same conclusion results for the strongly acid region from the data of Yokota [39].

Fig. 4 shows experimental values of steady-state available chlorine concentrations as a function of the pH of the holding vessel at 60°C (cf. [41, 42]). The separate concentrations of both hypochlorous species as calculated (cf.

of the gas is, however, always much larger than the carbon dioxide content, which is produced as a result of chemisorption of the former at a rather slow rate. Therefore, in neutral and alkaline pH regions, graphite is mainly lost as a sludge.

A quite different situation arises in the absence of chloride ions and thereby hypochlorous species [10, 11]. In such cases, graphite appears even more stable in the alkaline region. This arises as a result of passivation of the carbon surfaces due to the formation of a layer of chemisorbed oxygen and its inhibiting effect (cf. [14, 15]). This is also the case in aqueous electrolysis using alkaline (KOH) solutions, where oxygen evolution at an extremely high pH value proceeds with negligible carbon dioxide formation

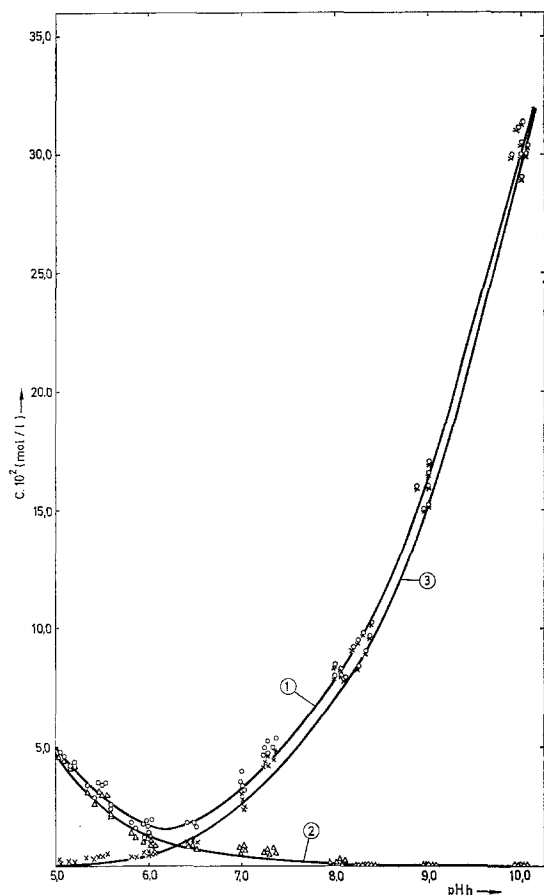


Fig. 4. Steady-state concentrations of active chlorine (○, 1), hypochlorous acid (△, 2) and hypochlorite ion (×, 3) as a function of pH of concentrated NaCl solution for holding vessel of the chlorate producing system (see Fig. 1). Concentrations of two hypochlorous species were calculated [1, 2] from corresponding values of active chlorine contents by means of the rearranged dissociation constant (K^*).

and highly decreased graphite corrosion compared to the chlorate cell process.

The nature of graphite and carbon corrosion has been considered in more detail elsewhere [28] (cf. [29]). It was found that acids and salts of the so-called 'phosphoric acid group' mainly attack edge carbon atoms, while more aggressive interplanar intrusion takes place in solutions of the 'sulphuric acid group', to which chloric and perchloric acid and their salts belong [28], and probably the hypochlorous species also. It is well known [28] that certain ions, such as OH^- , support and aid oxide formation at graphite surfaces. Also, they are self-inhibiting if they are stable. Some other ions such as Cl^- ,

SO_4^{2-} , ClO_4^- , ClO^- , also lead to the decomposition and dispersion of the oxide.

It should also be noted that even in the presence of hypochlorous species, a markedly different dependence of graphite wear on pH is found in the range 5–7 [13].

The experimental, as well as published data from quite different sources, agree well with each other (cf. Fig. 3) although they relate to different kinds of graphite, often very different temperatures of investigation and usually to values obtained under unsteady-state and also different operating cell conditions.

It can be stated that besides the anode potential (or otherwise the current density as a less convenient and reliable parameter), temperature and the brine concentration, the pH value, as a measure of the active chlorine content, represents in itself the essential factor for graphite wear in a chlorate electrolytic system. Therefore, the data and conclusions presented seem to be of importance for optimization of current efficiency and graphite consumption in the chlorate cell process.

It might also be added that the impregnation method described elsewhere [3] has been developed still further, and the improvements obtained with diacyl peroxides, and, particularly, with dilauroyl peroxide [3], were advanced with the use of pinan hydroperoxide [43]. The latter is stable to higher temperatures thereby providing the benefits described elsewhere [3], that result from keeping the anode potential close to the value for plain graphite and from increasing the life-times of electrodes in a chlorate cell process.

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