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*Consumption of graphite anodes in chlorine manufacture by brine electrolysis**

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The anodic behaviour of carbon and graphite electrodes in aqueous electrolytes is described and the important reactions leading to the consumption of graphite during chlorine manufacture by brine electrolysis are discussed in detail. The present state of knowledge concerning the effects of chlorine cell electrolysis conditions on graphite consumption is also reviewed. A new investigation of the influence of graphite manufacturing variables and properties on consumption is also described. The variables studied were coke particle size, degree of pitch impregnation and the final heat treatment at the graphitization stage. Properties considered included electrical resistivity, apparent density, average crystallite size and unpaired electron spin density. The resistance of the graphite to anodic oxidation was found to increase with increasing coke particle size, increasing pitch impregnation and increasing final heat treatment temperature (up to 3000°C). Unpaired electron spin density was the property found best to correlate with this resistance.

1. Introduction

Electrographite has been used for anodes in chlorine manufacture ever since its discovery by Acheson in the latter part of the nineteenth century, and even with the advent of titanium anodes it is likely to play a continuing role. A major economic factor in the operation of cells with graphite anodes is that of anode consumption which normally amounts to 4–8 lb carbon per ton chlorine produced (2·4–4·7 g per kAh). The mechanism by which consumption occurs is complex and its rate depends not only upon the electrolysis conditions, but also upon the properties and manufacturing conditions of the graphite. This paper attempts to review the present state of knowledge concerning the factors affecting graphite consumption in aqueous electrolytes, and also presents some new information relating to the effects of graphite properties and manufacturing conditions. This new information was obtained in a study carried out by ICI in collaboration with UKAEA, Harwell during the period 1965–1970. The present review complements and extends the most recent previous reviews in this area by Finn [1], Vaaler [2], Potsch, Proft and Gotzmann [3], Ragoss [4] and Hine and Yasuda [5].

2. Anodic behaviour of graphite in electrolytes not containing chloride

It will be useful first to consider the anodic behaviour of graphite in aqueous electrolytes not containing chloride. The early work of Thiele [6, 7], Sihvonen [8] and more recently Krishtalik [9–17], Ubbelohde [18], Binder [19] and many others has shown that two general groups of reactions may be involved during the anodic treatment of graphite. The first group involves the electrochemical oxidation of water molecules (or of hydroxyl ions) according to the reactions

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e \; (E^0 = +0{\cdot}144 \text{ V})$$
$$C + H_2O \rightarrow CO + 2H^+ + 2e \; (E_0 = +0{\cdot}420 \text{ V})$$
$$2H_2O \rightarrow O_2 + 4H^+ + 4e \; (E_0 = +1{\cdot}23 \text{ V})$$

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and the second the formation of compounds. The formation of compounds is of two kinds. Various types of oxidic functional group such as $-C = O$, $-C-OH$, $-COOH$ can form on carbon and graphite surfaces [20] and, as in the oxidation of graphite by air [21], can be involved in the corrosion mechanism. The presence of these groups has frequently been indicated during voltammetric studies at graphite electrodes [22, 23]. Their formation may be favoured at particular imperfections in the graphite structure, e.g. edge atoms and defects. The formation of crystal compounds of graphite (intercalation, interlamellar compounds) such as graphite bisulphate may also occur in which the carbon appears to function as a macro-cation [18]. These reactions occur most readily in concentrated acids and involve penetration of the graphite lattice by anions. The effects are most readily observed with well-oriented graphites. Some acids (sulphuric, nitric, perchloric and others) have a strong tendency to form intercalation compounds whereas others (phosphoric, acetic, hydrochloric and others) have a weak tendency to intercalate [6]. The formation of crystal compounds generally causes an increase in the *c* spacing of the graphite lattice, swelling of the anode structure and exfoliation.

The direct loss of graphite as CO_2 and CO is always accompanied by mechanical loss. Electrographite has a complex structure and contains 20 to 30% pores. Owing to this high porosity, the carbon-consuming electrochemical reactions penetrate and widen the pores, promoting disintegration and mechanical loss. The balance between the chemical and mechanical loss has been studied by several workers e.g. Kubat and Rousar [24] and it is apparent that the extent of mechanical loss and the particle size of the debris formed increase as the anode potential increases. Where intercalation attack occurs then this can contribute appreciably to mechanical loss, as observed by Nystrom [25].

In the present context, the highly irreversible reactions involving water oxidation are generally of the greatest importance in determining graphite consumption. There are numerous papers dealing with the kinetic aspects of these reactions, and the most recent by Kokhanov [26–29] and Krishtalik [11, 12, 16, 17] and their co-workers are perhaps the most relevant. Their studies were carried out mostly in phosphate electrolytes where intercalation effects are small and the water (or hydroxyl ion) oxidation reactions predominate. They examined the effects of factors such as pH, temperature, ionic strength and surface state on the kinetics using several techniques. A simple diagram showing the composition of the anodic products and anode potential as a function of pH at a fixed current density was first obtained by Kokhanov and Milova [26] and this is reproduced in Fig. 1. The product of reaction is mainly CO_2 in acid solution changing to oxygen in alkaline solution, the transition being accompanied by a sharp drop in anode potential. This transition probably represents a change from water molecules to hydroxyl ions as the oxidizing species. A more complex potential – pH diagram was obtained by Krishtalik and co-workers [16, 17] and this is shown in Fig. 2. The diagram shows contours of log current density ranging from $-1{\cdot}5$ to $-5{\cdot}0$ and also four different surface states, lettered A to D, defined from charging curves and denoted by different types of shading. Changes in the intensity of shading correspond qualitatively to changes in the amount of oxygen uptake. The numbers over the lines represent the CO_2 current efficiency. Three regions of characteristic kinetic behaviour, I to III, bounded by dashed lines, were also defined. In region I, potential is independent of pH but decreases with increasing ionic strength. Up to $+1{\cdot}9$ V the same type of oxidic film is present and it is most likely that the electroactive species is water molecules. Above $+ 1{\cdot}9$ V the surface changes to give a decrease in the CO_2 yield and a sharp increase in the crumbling of the graphite. In regions II and III, anode potential depends upon pH and more complex behaviour is observed. In region II the coincidence of shading intensity at identical current densities indicates that the reaction rate is directly connected with the quantitative features of oxygen adsorption. This may indicate that some step following the discharge of water molecules or hydroxyl ions plays an essential role in the overall mechanism. In region III potential increases with increasing ionic strength and hydroxyl ion appears to be the discharging species. At low potentials the oxygen current efficiency is high and the CO_2 efficiency low, but at high potentials a change in surface state occurs

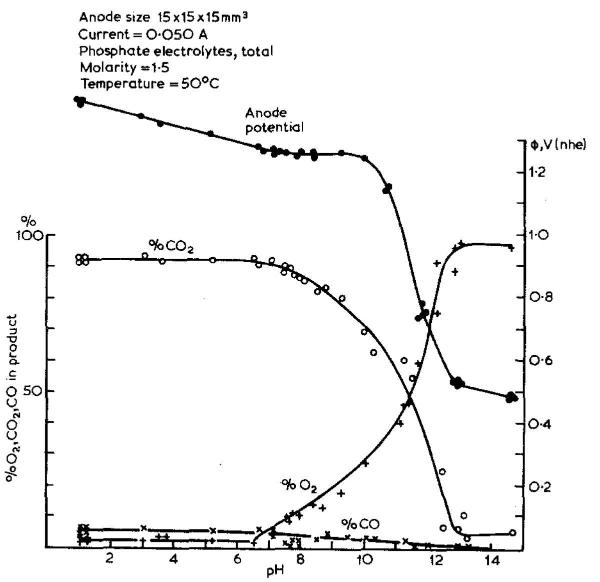

Fig. 1. Potential – pH kinetic diagram. (After Kokhanov and Milova, 1969).

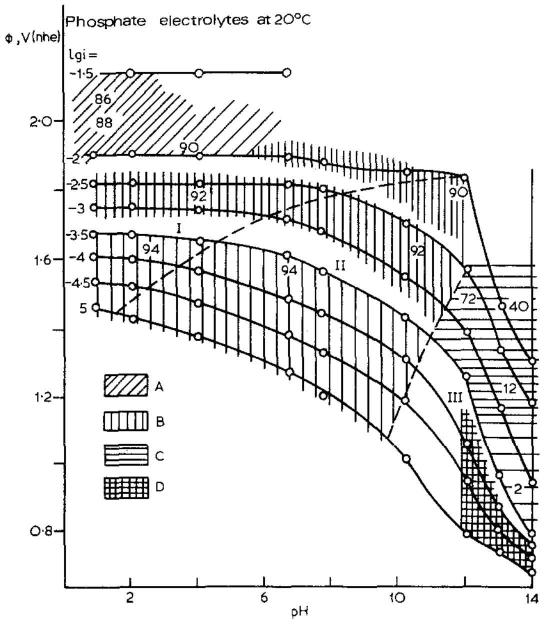

Fig. 2. Potential – pH kinetic diagram. (After Ngo Tai Piet, Kokoulina and Krishtalik, 1972).

accompanied by an increasing CO_2 current efficiency.

3. Anodic behaviour in chloride electrolytes

In aqueous chloride electrolytes additional reactions occur and complicate the graphite consumption mechanisms. Water oxidation and graphite swelling still occur, but interact with the chlorine evolution reaction, which holds the anode potential within the range + 1·3 to + 1·8 V and electrolyte pH within the range 2 to 4. Under these conditions the carbon-consuming electrochemical reactions are inhibited, the general magnitude of the effect being shown in Fig. 3. This illustrates how the CO_2,O_2 and CO contents of chlorine vary with chloride concentration at a fixed current density under acidic conditions in a Hooker diaphragm chlorine cell [30]. As the sodium chloride concentration increases to the normal anolyte condition of ∿ 220 g NaCl l^{-1}, the formation of CO and O_2 becomes almost totally inhibited, whilst the formation of CO_2 is also low. The extent of inhibition varies with temperature [29, 31] and in the presence of specifically adsorbed impurity anions such as sulphate [9, 32 –35]. Chlorate ion may also promote graphite consumption [10] but the effect is less than that of sulphate. In addition to the main electrochemical reaction of chlorine evolution

$$2\,Cl^- \rightarrow Cl_2 + 2e \; (E_0 = +\,1{\cdot}36\ V)$$

important chemical reactions involving the oxidation of the graphite by hypochlorous acid and hypochlorite ions also occur.

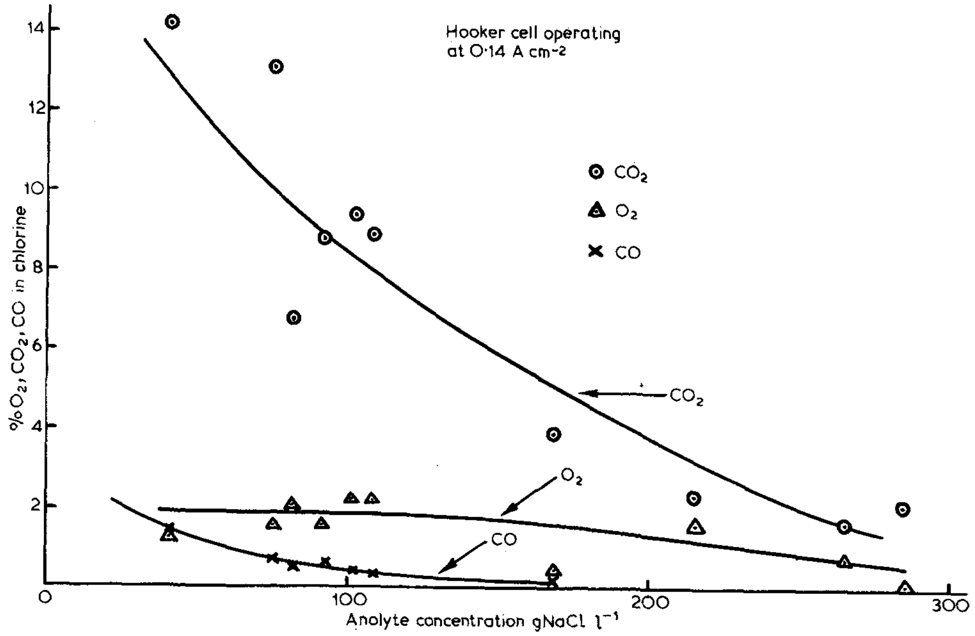

Fig. 3. Effect of chloride ion concentration on gaseous corrosion products during anodic consumption of graphite. (After BP 1,257,934).

$$C + 2\,HOCl \rightarrow CO_2 + 2HCl$$
$$C + 2\,OCl^- \rightarrow CO_2 + 2Cl^-$$

These oxidizing species form part of the 'active' or 'recoverable' chlorine present in the electrolyte and are produced and removed according to the following reactions:

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl$$
$$HOCl + OH^- \rightarrow OCl^- + H_2O$$
$$HOCl + 2OCl^- \rightarrow ClO_3^- + H^+ + 2Cl^-$$
$$6ClO^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 3/2\,O_2 + 6H^+ + 6e.$$

Chemical oxidation by this mechanism occurs particularly in the pores of the graphite and to reduce it graphite anodes are sometimes impregnated with oils.

The chlorine evolution reaction on graphite has been studied by numerous workers [36–46]. The reaction proceeds with very high efficiency under normal chlorine cell conditions, and is classed as a moderately fast electrochemical reaction with Tafel parameters $i_0 \sim 10^{-4}$ Acm^{-2} and $\alpha \sim 0{\cdot}5$ at 25°C. Krishtalik, Kokhanov and co-workers [28, 29, 36, 37] showed that the kinetic behaviour changed in a stepwise manner reminiscent of platinum anodes as the chloride concentration in the electrolyte is lowered, or the pH and temperature raised. The change was attributed to an increase in the oxygen evolution reaction and to changes in surface state. Janssen and Hoogland have recently carried out a comprehensive study of the reaction in highly acidic brines [43–46]. They showed that the kinetics change as the electrode ages; on an aged electrode the Heyrovsky reaction (Cl^- + Cl adsorbed $\rightarrow Cl_2$ + e) is the rate-determining step while on a new electrode both the Heyrovsky reaction and the Volmer reaction ($Cl^- \rightarrow$ Cl adsorbed + e) determine the relationship between current and potential. Two types of surface state seem to occur. Apparently, a new electrode has an oxidic film which may originate during manufacture and is not readily reducible at –400 mV. On an aged electrode, this film has been removed by anodic treatment at sufficiently high potential (+1·72 V) and replaced by another film which is readily reducible at –400 mV.

Chemical attack on the graphite by hypochlorous acid and hypochlorite occurs to a substantial extent—for example 28% of the total consumption was reported in a study by Tasch, Vaaler and Finn [47]. It was noted previously that electrochemical loss of graphite in acidic solution varies little with pH and the observed variation of consumption with pH in chlorine cells is mainly due to the variation in the chemical attack and closely parallels the changes in the concentration of hypochlorous acid and hypochlorite in the electrolyte. Krishtalik [17] and Jaksic [48] have recently reviewed the effect of pH and Jaksic's summary of available literature data is reproduced in Fig. 4.

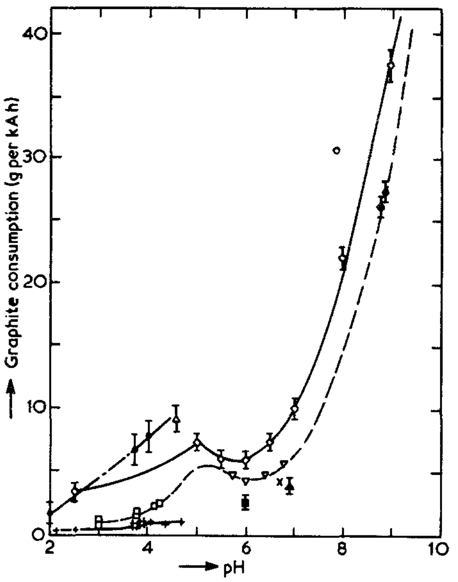

Fig. 4. Summary of data on the effect of electrolyte pH on graphite anode consumption during chlorine and chlorate manufacture. (After Jaksic, 1973).

The lines differ in detail but generally show the same pattern. As pH increases through the normal chlorine cell operating range of 2 to 4 and beyond, consumption first increases before falling and eventually rising again. This changing consumption pattern matches closely the formation and disappearance of hypochlorous acid and hypochlorite in the electrolyte by the reactions given above.

The penetration of electrochemical reaction and corrosion into the pores of the graphite and the consequent changes in structure have been studied by Bulygin [49–51], Krishtalik [14, 15], Ksenzhek [52], Flisskii and co-workers [53, 54] and Geise, Kallfelz and Vaaler [55]. The results of Vaaler and associates, who studied structural changes by means of resistivity measurements and also by radiography, are illustrated in Fig. 5.

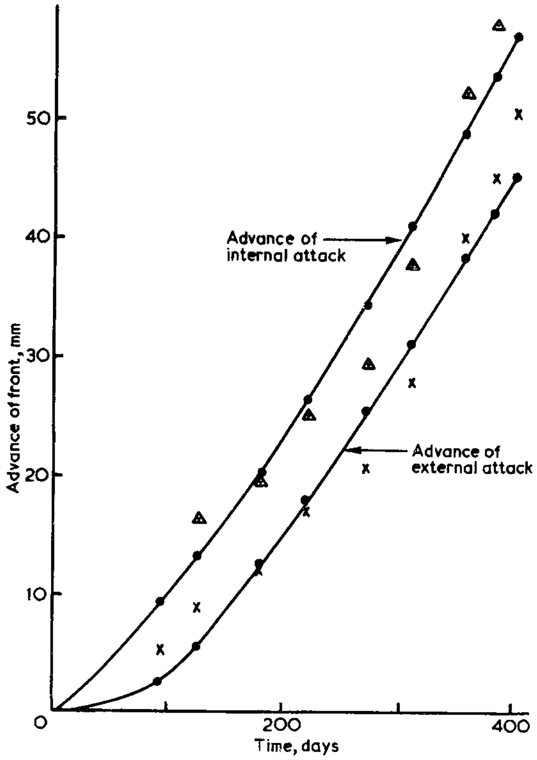

Fig. 5. Pattern of internal and external attack for graphite anodes. (After Geise, Kallfelz and Vaaler, 1964).

As attack on the graphite proceeds, the pores widen and the penetration of chlorine formation and of corrosion increase. A corrosion front moving with time develops and advances within the graphite structure, and behind this the density of the graphite falls until the external layer eventually crumbles. Finally, the rate of crumbling approximately matches the rate of advancement of the corrosion front. The movement of the internal corrosion front as the electrode ages is given by the upper line in the figure and the changes in the external dimensions by the lower line. The difference between the ordinates of the two graphs at any point in time thus represents the thickness of the disintegrating layer, which slowly increases from zero to about 12 mm as the electrode ages. Janssen and Hoogland [43] also studied the development of roughness of graphite electrodes with ageing by means of double layer capacitance measurements using three techniques—galvanostatic charging, potential pulse and AC impedance. These all showed an increase in roughness with ageing, but the roughness factors obtained varied with the method used. The galvanostatic method probably gave a measure of the ratio between the electrochemically-active area and the geometric area, and the potential pulse method, the ratio between the total wetted and the geometric areas.

Lennon and Vaaler [56] studied the influence of current density on anode consumption using both plain graphite and graphite impregnated with oil to reduce porosity and internal attack. Their results are illustrated in Fig. 6.

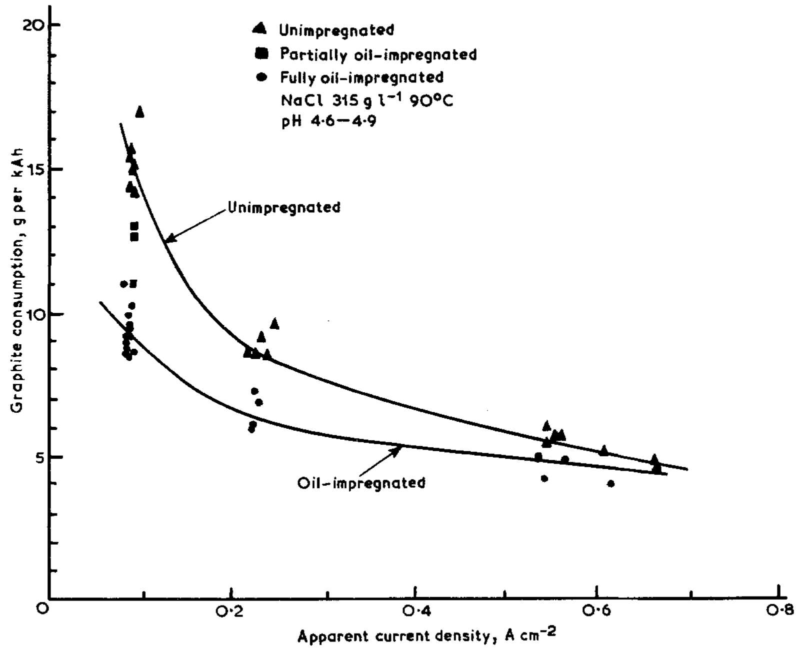

Fig. 6. Effect of apparent current density on the consumption rate of graphite anodes. (After Lennon and Vaaler, 1963).

These show that oil impregnation gives rise to a reduction in the rate of consumption which diminishes with increasing current density. This suggests that electrolysis takes place increasingly on the outer surface of the electrode as current density increases. The lower end of the current range shown in this figure corresponds approximately to diaphragm cell conditions and the upper end to mercury cell conditions. Oil impregnation is, therefore, likely to be most effective in the case of diaphragm cell anodes.

In addition to the above information there is also a considerable number of papers relating to the effects of electrolysis conditions on graphite consumption during chlorate manufacture [57–64] which in some cases are also relevant to chlorine manufacture.

4. Relationship between the manufacturing conditions and properties of electrographite and its consumption during chlorine manufacture

The relationship between the manufacturing conditions of electrographite and its performance in brine electrolysis has been little investigated, and there is not much to guide the chlorine manufacturer on the quality he should choose. To provide more information in this area, a study was carried out by ICI in collaboration with the UKAEA using the experimental graphite plant at Harwell. This plant has been described in the literature [65] and was set up to develop a specification for nuclear graphite. In the study, samples of graphite were made on the plant under different conditions from common stocks of material. The physical properties of the samples were then determined and their rates of consumption measured, in laboratory mercury cells. The method of preparing the samples followed the procedures normally used in the large-scale manufacture of electrographite [21] which are briefly as follows. The starting materials are normally petroleum coke as filler and coal tar pitch as binder. The coke is first calcined and ground. In an appropriate size distribution it is then mixed with pitch in heated vessels at 140 – 175°C in the ratio of about 30 parts of binder to 100 parts of filler. The mixture is then cooled to 95–105°C prior to being formed by extrusion in a mechanical press. The die of the press is designed carefully in order to permit the correct shrinkage to occur during the subsequent heat treatment stages. Extrusion is completed by cutting and rapid cooling of the product which is now at what is termed the 'green' stage. It is then subjected to a critical baking operation at about 1000°C, at which stage considerable chemical and physical changes occur. The carbon prepared in the baking operation is then often impregnated with pitch and rebaked to give improvement in the properties of the graphite. This procedure may be carried out one or more times. Finally, the carbon is graphitized in special furnaces by gradual heating up to about 3000°C. Crystallite growth and impurity removal commence around 2000°C and the potential for growth is latent within the filler and the green carbon structure–the greater the crystallite alignment, the greater the growth during graphitization. The graphite is then machined to the required shape. In general the shapes used are simple rods or blocks for diaphragm cells [31, 66], slotted and holed blocks for mercury cells [66–68]. As mentioned, the graphite may also be impregnated with oils or antioxidants to reduce internal corrosion and several techniques and materials have been evaluated for this purpose by Mulina, Krishtalik and Kolotukhin [68–71], Wasilewski *et al.* [72], and others.

The product of the graphitizing process is a polycrystalline material of surface area about 1 $m^2 g^{-1}$. Typical properties of commercial anode electrographite have been described by Ragoss [4]. The high porosity of 20–30% has already been mentioned and is of both the open and closed pore types. The complex pore structure of electrographite has in fact been related by some workers [53, 54] to its rate of consumption during chlorine manufacture. The properties frequently vary according to the direction of extrusion as a result of the alignment of the long dimension of the graphitized coke particles in this direction. In general, pitch impregnation of the baked material tends to increase density and strength and to lower electrical resistivity. Microscopically, the structure consists of graphitized coke particles, usually termed grains, surrounded by the graphitized binder [21]. During electrolysis, the binder phase appears to be more readily attacked than the grains [25].

In the present investigation a study was made of three of the manufacturing variables–the particle size of the coke filler, the degree of pitch impregnation and the final heat treatment temperature. The results of the consumption tests on the experimental Harwell samples are shown in Table 1. In all cases, petroleum coke and coal tar pitch were used.

It is seen that the final heat treatment temperature has a marked effect on the rate of consumption. The rate is also less with the coke particles of greater size. One pitch impregnation and rebaking prior to graphitization significantly reduces the consumption rate, but subsequent impregnations have little or no effect. The benefit of a single impregnation is also apparent with the material of lower particle size.

Measurements of various properties were also made on these graphites in order to define a specification. These are shown in Table 2 and include physical properties such as density, resistivity, Young's modulus and also structure-related properties such as average crystallite size and unpaired electron spin density.

It had been anticipated from comments in the literature that the growth of crystallinity would be a fundamental factor affecting the consumption rate. Fig. 7 shows both consumption rate and crystallite size, as a function of the final heat treatment temperature. While the drop in consumption rate occurs at a heat treatment temperature well below that at which the crystallites have developed appreciably, there is good accord between the consumption rate and the reciprocal of the crystallite size.

Table 1. Effect of the manufacturing variables of electrographite on its consumption rate during brine electrolysis

Graphite sample reference number	*Final heat treatment temperature, °C*	*No. of pitch impregnations*	*Coke particle size*	*Consumption rate mm per day*
1200	1200	0	Up to 1 mm	5
1500	1500	0	Up to 1 mm	1·44
1800	1800	0	Up to 1 mm	0·47
2100	2100	0	Up to 1 mm	0·36
2700	2700	0	Up to 1 mm	0·24
3000	3000	0	Up to 1 mm	0·19
G20	2700	0	Up to 1 mm	0·31
D9	2700	1	Up to 1 mm	0·23
F3	2700	2	Up to 1 mm	0·25
F16	2700	3	Up to 1 mm	0·22
893/B/1/2	2700	0	Up to 70 μm	0·39
875/B/3/2	2700	1	Up to 70 μm	0·30

Consumption rates are for 18% brine of pH 2–3 at 70°C and 0·6 A cm^{-2}. 0·1 mm per day ∿ 1·2 g kAh^{-1}

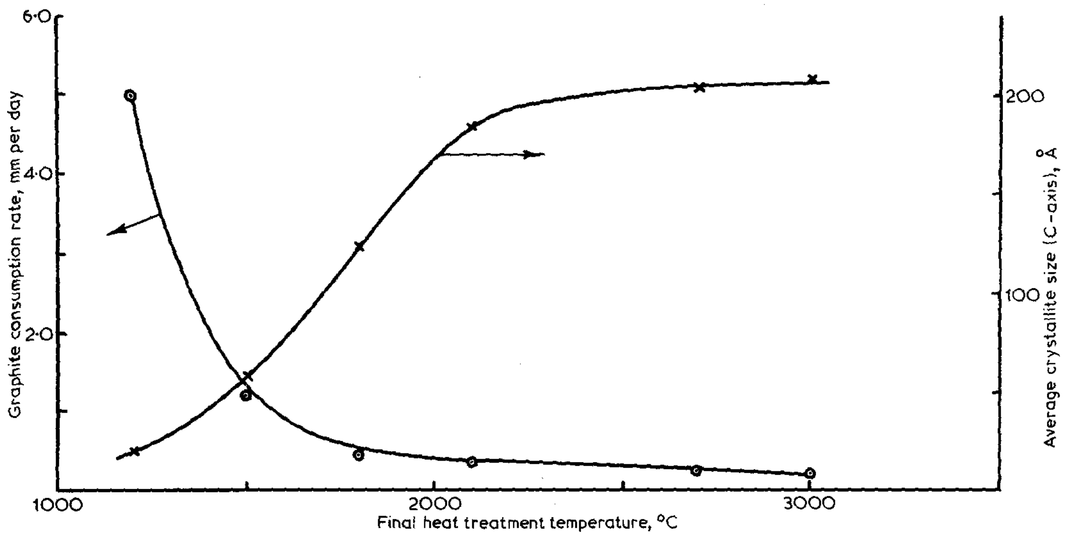

Fig. 7. Relationships between consumption rate, average crystallite size and final heat treatment temperature for Harwell graphites.

An equally good correlation exists between the consumption rate and the unpaired electron spin density (Fig. 8). The relationship between the unpaired spin density of carbons and graphite and their structural features is not fully understood [73] but the sudden changes in spin density and consumption rate seem to coincide with the change from a disordered structure to a turbostratic structure as the heat treatment temperature increases [74]. It seems probable, in view of the above results, that this change occurs while the crystallites are still quite small.

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The author would like to thank colleagues in the UKAEA and ICI for their contributions to the work described, and ICI for permission to publish this paper.

Table 2. Physical properties of Harwell graphite samples

Sample reference number	*Corrosion rate mm per day*	*Electrical resistivity at 20° C, Ω cm × 10^{-3}*	*Thermal conductivity at 30° C, cal cm^{-1} s^{-1}*	*Apparent density g cm^{-3}*	*Surface area by B.E.T. (single point method), m^2 g^{-1}*	*Thermal expansion at 20° C, °C^{-1} × 10^{-6}*	*Young's modulus at 20° C, dynes cm^{-2} × 10^{11}*	*Average Crystallite size, Å*		*Unpaired electron spin density, spins per cm^3 × 10^{18}*
								In 'a' direction	*In 'c' direction*	
1200	5	4·4/6·8	0·01/0·006	1·6	0·72	1·7/4·3	1·2/0·4	<25	25	38
1500	1·44			1·6				<50	58	16
1800	0·47	3·8/6·3	0·04/0·03	1·6	0·71	2·0/4·9	0·8/0·4	88	126	6·8
2100	0·36	3·4/5·7	0·09/0·04	1·6		2·0/4·7	0·6/0·3	133	184	7·2
2700	0·24	0·9/1·7	0·30/0·22	1·6	0·81	1·5/3·2	0·7/0·3	261	204	4·9
3000	0·19	0·9/	0·35/	1·6	0·76	1·3/	0·6/	387	208	3·0
G20	0·31	0·9/1·7	0·30/0·22	1·60	0·89	1·5/3·2	0·7/0·3	375	208	3·3
D9	0·23	0·8/1·3	0·34/0·27	1·72	0·96	1·7/4·1	1·1/0·5	449	200	4·5
F3	0·25	0·7/1·2	0·36/0·28	1·78	1·03	1·6/4·2	1·2/0·6	300	208	6·0
F16	0·22	0·7/1·3	0·40/0·30	1·82	0·93	1·4/4·2	1·1/0·5	280	220	7·8
893/B/1/2	0·39	0·7/1·6	0·50/	1·69	1·11	0·9/5·1		300	200	7·2
875/B/3/2	0·30	0·6/1·4	0·53/	1·79	1·10	1·0/5·2		292	163	7·8

Where two figures are given, these refer to values parallel to and perpendicular to the direction of extrusion respectively.

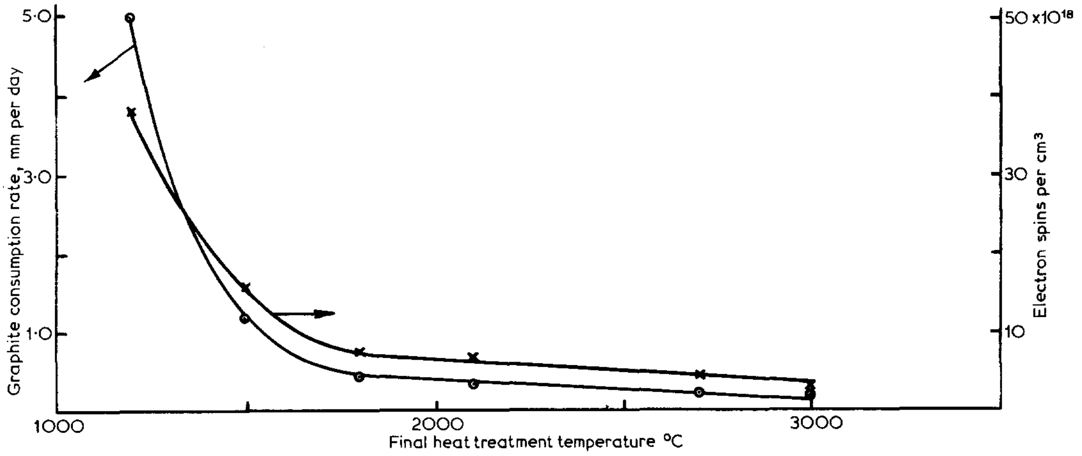

Fig. 8. Relationships between consumption rate, electron spin density and final heat treatment temperature for Harwell graphites

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