High-temperature chlorine corrosion of technical carbons
Part II. Anodic corrosion in chloride melt*

H. WENDT, A. KHALIL, C. E. PADBERG

Institut für chemische Technologie der TH Darmstadt, Petersenstrasse 20, D6100 Darmstadt, Germany

Medium (200 to 400° C) to high (600 to 800° C) temperature corrosion of technical carbons (Acheson graphites) have been investigated in alkali chloride melts at chlorine evolving anodes. At low temperature in chloride melts containing free Lewis acid ($AlCl_3$) no chlorine is evolved — even at high current densities — because chlorine, together with aluminium chloride, instantaneously form intercalation compounds with graphite and, as a consequence, the carbon desintegrates very rapidly. At 200° C carbon is consumed anodically in a C/Cl of molar ratio $\sim 70/1$. With increasing temperature Acheson graphites become more stable so that at 700° C short term destruction cannot be observed in melts which contain free Lewis acid. Chlorine corrosion of carbon electrodes in purified basic alkali chloride melts, which are free of oxygen carriers and, in particular, free of water at temperatures between 600 and 800° C in basic chloride melts, is an electrochemical reaction proceeding at low current densities slower than anticipated from thermodynamic data for carbon chlorination equilibria. The anodic carbon corrosion reaction has an activation energy of only $50\,kJ\,mol^{-1}$ and its rate increases with increasing anode potential, or anodic current densities (rate: $\alpha \exp (i)$). At a technical current density of $0.4\,A\,cm^{-2}$ at 700° C the corrosion rate is estimated to be of the order of centimeters per year, rendering carbon anodes dimensionally unstable. Most important is to note that apart from CCl_4, chlorinated carbon compounds (olefins and arenes) are generated as side-products which are noxious and ecologically dangerous and must not be released from processes which use carbon anodes for chlorine evolution from salt melts.

1. Introduction

Little is known about the chemical stability of technical carbons and Acheson graphites in chlorine atmospheres. As has been discussed elsewhere [1] carbon should be completely converted to carbon tetrachloride in a chlorine atmosphere at ambient temperature but should become increasingly more stable as temperature increases. For instance at 700° C the equilibrium partial pressure of CCl_4 at 1 bar of chlorine has dropped to $\sim 10^{-3}$ bar. But since CCl_4 formation is a very slow and kinetically hindered reaction, technical carbons, which usually come as Acheson graphites, are practically stable in chlorine atmospheres up to 700° C. Since carbon anodes are used in chloride containing salt melts for anodic chlorine evolution ($MgCl_2$ and $AlCl_3$ electrolysis) it is of general interest to gather quantitative information on anodic chlorine corrosion of technical carbons in such melts, in addition to the knowledge which has been obtained on the corrosion of these materials in chlorine atmospheres [1].

This paper describes an investigation of anodic chlorine corrosion of technical carbons under two distinctly different conditions: 1. anodic medium temperature (200 to 300° C) corrosion of carbon in mixed alkali chloride (LiCl/NaCl, LiCl/KCl) melts to which aluminium chloride had been added in a ratio $AlCl_3/$MeCl greater than 1. Under the latter conditions, i.e. in acidic melts, carbon anodes are notoriously unstable [2], and 2. anodic high temperature chlorine corrosion (600 to 800° C) in dry, basic alkali chloride melts (MeCl), with and without the addition of 10 mol % aluminium chloride. The main issue is the investigation of the high temperature stability of chlorine evolving anodes.

2. Experimental details

Medium temperature chlorine corrosion of technical Acheson graphites in acidic alkali chloride/aluminium-chloride melts has been investigated on a semiquantitative basis by visual inspection of the consumption of carbon rod anodes which had been submerged in alkali chloride melts. At fixed currents the time was measured until the submersed part of the anode had decomposed completely and, as a consequence, the current suddenly dropped to zero. Attempts to measure

---

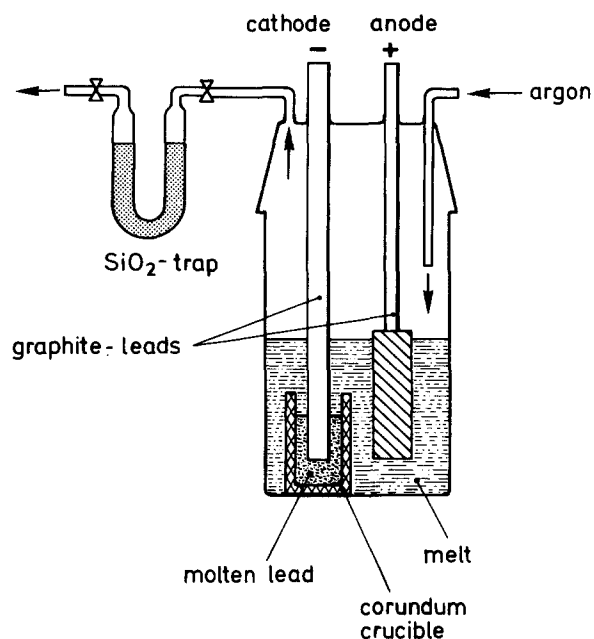* This paper is dedicated to Professor Dr Fritz Beck on the occasion of his 60th birthday.

Fig. 1. Schematic of the electrolysis cell for determination of the rate of anodic chlorine corrosion of technical carbons in chloride melt.

the weight loss of the carbon anodes gravimetrically *in situ* failed because, apart from the weight losses due to decomposition, there are uncontrolled weight gains superimposed due to penetration of the melt into the pores of the carbonaceous material. For the same reason the high temperature corrosion of chlorine-evolving carbon anodes in molten basic alkali chlorides was not measured gravimetrically but by determining the rate of release of chlorinated carbon compounds by gas chromatography. To what end the electrolysis vessel was continuously purged with argon. The argon/chlorine mixture leaving the vessel passed an adsorption trap filled with microporous silica granules (micropore diameter ~ 0.8 nm) which were exchanged every 2 h. After displacing the adsorbed chlorine in the adsorber tube by flushing the tube with pure argon the perchlorinated carbon compounds were desorbed by repeated digestion with liquid-pentane and the collected portions of pentane were analysed chromatographically using a fused silica column equipped with a layer for PCB-detection (SE-54-CB-0.5) and an EDC-system. Figure 1 shows the schematic of the experimental set-up. As expected from thermodynamic calculations [3] the most prominent corrosion product was carbon tetrachloride. But hexachloroethane and a number of chloro alkenes such as tetrachloroethene and hexachlorobutadiene and perchloroarenes such as hexachlorobenzene and octachlorostyrene were also found.

The carbon content of the different perchlorinated compounds was summed in order to determine the cumulative rate of carbon loss of the anode due to anodic formation of chlorocarbon compounds. At the cathode of the cell liquid alkali metal was electrodeposited. The cathodically generated alkali metal was dissolved in the cathode, which was molten lead. This prevented the alkali from ascending to the elec-

trolyte surface and reacting there with chlorine. Two different Acheson graphites were investigated: carbon-CE of Deutsche Carbone and carbon EK 78 of Sigri. Both are highly graphitised, have comparable densities (1.7 and 1.95 g cm^{-3}) but differ in grain size.

The alkali chlorides were thoroughly dried for 24 h as powders at 300° C. Aluminium chloride was double-sublimed. The salt mixtures were kept in a glove box, purged by thoroughly dried nitrogen.

3. Results

3.1. *Medium temperature corrosion of carbon anodes in acidic melts in the temperature range between 200 and 300° C*

The results of a comparative qualitative investigation of the behaviour of carbon anodes in acidic alkali/chloride/aluminium chloride melts containing 61 mol% $AlCl_3$ and 39 mol% NaCl [2] shows that carbon anodes decompose very readily at 200° C because intercalation compounds [4] are formed with sizeable volume expansion of the carbon-material so that the Acheson graphites disintegrate without any visible chlorine gas evolution. Increasing the temperature renders the intercalation compounds less stable and consequently slows down the disintegration of the material and relatively more and more gas is evolved as the temperature increases. Above 600° C carbon anodes are virtually stable and do not disintegrate even in highly acidic melts. Chlorine evolution in basic melts, which are completely free of added Lewis acids, does not effect the surface of carbon anodes to a detectable extent over periods of 1000 hours at low temperatures (200 to 300° C).

The Faradaic efficiency of the rapid disintegration of the two graphitized technical carbons (SE from Deutsche Carbone and EK 78 from Ringsdorf) was investigated at 200° C by determining the amount of electricity consumed for the total disintegration of carbon rods. One obtains a consumption of 73 ± 7 carbon atoms per extracted electron for both carbon specimens. Allocating one intercalated chlorine atom per electron, and accounting for an unknown amount (x) of aluminium chloride which is incorporated into the intercalate, one arrives at a formal composition of the debris formed by anodic intercalation of $C_{10}(AlCl_3)_x Cl_{0.136}$. Data in the literature [4–14] on intercalate compositions relate to stoichiometries which range from $C_{10} AlCl_3 Cl_{0.3}$ to $C_{10} AlCl_{3.1} Cl_{0.33}$. It is evident, therefore, that the debris is not composed of fully chlorinated intercalates but that the degree to which the carbon is converted to intercalated carbon is close to 40%.

3.2. *Anodic chlorine corrosion of Acheson graphites in basic chloride melts at high temperatures*

3.2.1. Description of the Acheson graphites. For the investigation of the anodic chlorine corrosion well graphitized carbon qualities were selected; these were

Table 1. Characteristic data of two different Acheson graphites

Producer and signature	density $(g\,cm^{-3})$	grain size (mm)	porosity $(\%)$	ash content $(\%)$
Deutsche Carbone CE	1.7	1.5	18	0.5
Ringsdorf EK-78	1.85	0.03	8.5	0.2

expected to be particularly stable against anodic degradation by chlorine because of their high degree of crystallinity. They differed, strongly, however, with respect to their grain size. One of the carbons (CE of Deutsche Carbone) had a mean grain size of 1.5 mm whereas the second specimen (EK-78 of Ringsdorf) had a grain size of only 0.03 mm. Table 1 shows the relevant data for both carbons.

3.2.2. Corrosion in alkalichloride melts. The initial investigations were confined to a determination of the reproducibility and steady state behaviour of the anodic chlorine corrosion of the CE-carbon by collecting, over a period of 7 h, the chlorinated carbon compounds produced anodically at chlorine evolving CE-anodes at a current density of $0.1\,A\,cm^{-2}$ and at 700° C in $LiCl/NaCl/KCl$ (54.3/9.9/35.8 mol %) melts. Every hour the adsorber-U tube was changed and the adsorbed quantitites of the different chloro-carbon compounds were determined by gas chromatography.

Only six different compounds could be determined: carbon tetrachloride, the most abundant product, tetrachloroethylene and hexachloroethane, hexachlorobutadiene and two chloroarenes: hexachlorobenzene and octachlorostyrene. Steady state experiments demonstrated that over 7 h there existed a non systematic scatter of the analytical data which amounted to a mean uncertainty of $\pm 25\%$ but that the corrosion proceeds from the very beginning under steady state conditions. Table 2 summarizes these data.

The data of Table 2 sum up to an hourly loss of $3.26 \times 10^{-5}\,g$ of carbon or $3.26 \times 10^{-6}\,g\,cm^{-2}$ and a corrosion rate of approximately $1.3 \times 10^{-2}\,cm\,y^{-1}$ accounting for $8000\,h\,y^{-1}$ and a density of graphite of $1.98\,g\,cm^{-3}$).

Table 2. Mean hourly production of chlorocarbon compounds at 1 A and an anodic current density of $0.1\,A\,cm^{-2}$ at 700° C. Melt composition: 54.3 mol % LiCl/35.8 mol % KCl/9.9 mol % NaCl, CE-carbon.*

Composition/stoichiometry		Production rate $(mol\,h^{-1})$	Mass loss of carbon $(g\,h^{-1})$
carbon tetrachloride	CCl_4	1.6×10^{-6}	1.9×10^{-5}
tetrachloroethane	C_2Cl_4	2.0×10^{-7}	4.8×10^{-6}
hexachloroethane	C_2Cl_6	7.5×10^{-8}	1.8×10^{-6}
hexachlorobutadiene	C_4Cl_6	8.0×10^{-8}	3.8×10^{-6}
hexachlorobenzene	C_6Cl_6	4.0×10^{-8}	2.9×10^{-6}
octachlorostyrene	C_8Cl_8	3.0×10^{-9}	2.9×10^{-7}

* The data are certain to within 25%.

3.2.3. Anodic chlorine corrosion in basic melts containing aluminium chloride. The anodic chlorine corrosion in basic alkali chloride melts containing $AlCl_3$ is of particular interest with respect to the electrowinning of aluminium from chloride melts [1]. A comparative investigation using three different melt compositions:

(i) 54.3 mol % LiCl; 35.8 mol % KCl; 9.9 mol % NaCl (m.p. = 400° C)

(ii) 47 mol % LiCl; 53 mol % NaCl (m.p. = 630° C)

(iii) 42 mol % LiCl; 53 mol % NaCl; 5 mol % $AlCl_3$ (Alcoa electrolyte; m.p. = 600° C)

was performed at 1 A and a current density of $0.1\,A\,cm^{-2}$. Table 3a, b and c show the results.

The data show that the exchange of potassium by sodium chloride does not influence the corrosion rate significantly. But the addition of 5 mol % of the Lewis acid aluminium chloride enhances the corrosion rate significantly although the melt is still basic, since the evolution rates of carbon tetrachloride and tetrachloroethane and tetrachloroethane increase by more than one order of magnitude. The evolution rates of hexachlorobutadiene, hexachlorobenzene and octachlorostyrene, however, are not significantly changed by aluminium chloride.

Table 3a. Anodic chlorine corrosion of CE-carbon at 700° C; 1 A; $0.1\,A\,cm^{-2}$; melt: 54.3 mol % LiCl, 35.8 mol % KCl, 9.9 mol % NaCl (m.p. = 400° C); anode area: 10 cm².

Compound	Rate $(mol\,h^{-1})$	Carbon loss $(g\,h^{-1})$	Wear rate $(cm\,y^{-1})$
CCl_4	1.5×10^{-6}	1.8×10^{-5}	
C_2Cl_4	2.2×10^{-7}	5.3×10^{-6}	
C_2Cl_6	7.4×10^{-8}	1.8×10^{-6}	
C_4Cl_8	8.8×10^{-8}	4.2×10^{-6}	0.013
C_6Cl_6	3.5×10^{-8}	2.5×10^{-6}	
C_8Cl_8	3.0×10^{-9}	2.9×10^{-7}	

Table 3b. Melt: 47 mol % LiCl, 53 mol % NaCl. (m.p. = 630°C)

	Rate $(mol\,h^{-1})$	Wear rate $(cm\,y^{-1})$
CCl_4	1.1×10^{-6}	
C_2Cl_4	2.1×10^{-7}	
C_2Cl_6	6.7×10^{-8}	
C_4Cl_8	7.0×10^{-8}	0.01
C_6Cl_6	4.0×10^{-8}	
C_8Cl_8	3.4×10^{-9}	

Table 3c. Melt: 42 mol % LiCl, 53 mol % NaCl, 5 mol % $AlCl_3$, (ALCOA, m.p. = 600° C)

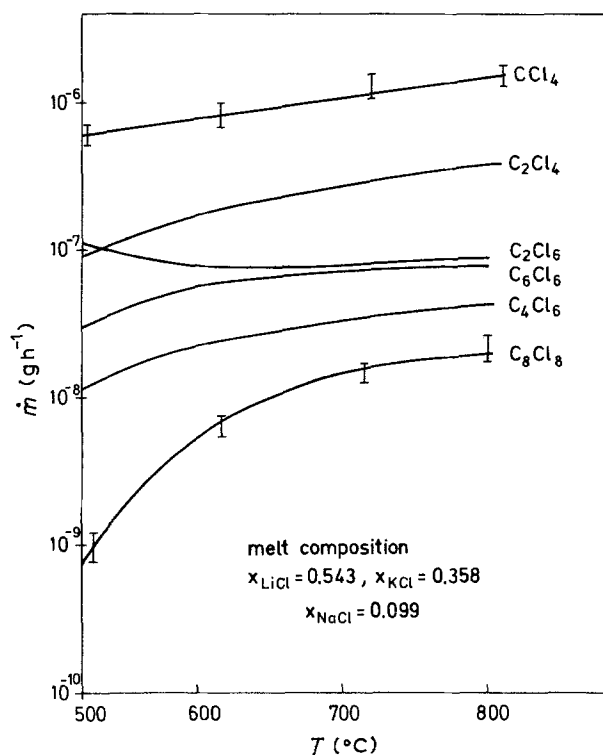| Rate $(mol\,h^{-1})$	Wear rate $(cm\,y^{-1})$
1.5×10^{-5}	
5.3×10^{-6}	
1.3×10^{-6}	
4.3×10^{-8}	0.14
3.5×10^{-8}	
6.9×10^{-9}	

Fig. 2. Temperature dependence of the anodic evolution rate of six different perchlorinated compounds at $i = 0.1\,\mathrm{A\,cm^{-2}}$ of CE-carbon. Actually observed date are only indicated for the compounds CCl_4 and C_8Cl_8 in order to give a clear impression.

of CE-carbon determined for a current density of $0.1\,\mathrm{A\,cm^{-2}}$ by summing the carbon-consumption per unit area of the anode. Fig. 2 demonstrates the different kinetics for the different compounds. The rate of evolution of the main reaction product — carbon tetrachloride — increases linearly with temperature; so does the rate of C_2Cl_4 formation, whereas the rate of anodic C_2Cl_6 formation is nearly temperature independent. But the rates of formation of hexachlorobenzene, hexachlorobutadiene and of octachlorostyrene, which contribute little to anodic carbon corrosion at $500°\,C$, increase strongly with temperature, so that all three contribute substantially at temperatures between 700 and $800°\,C$. The highest activation energy of all compounds was determined for octachlorostyrene $(52 \pm 2\,\mathrm{kJ\,mol^{-1}})$. This value is much lower than the activation energy observed for gas phase chlorine corrosion of Acheson-graphites which amounts to approximately $150\,\mathrm{kJ\,mol^{-1}}$ [1]. The effective activation energy for anodic formation of carbon tetrachloride increases steadily with temperature from a value of between 10 anmd $15\,\mathrm{kJ\,mol^{-1}}$ at $500°\,C$ to $30 \pm 3\,\mathrm{kJ\,mol^{-1}}$ in the temperature range $700{-}800°\,C$. As shown in Fig. 3 the effective activation energy for the anodic corrosion of carbon CE is only approximately $10\,\mathrm{kJ\,mol^{-1}}$ at $500°\,C$ and increases to $52 \pm 5\,\mathrm{kJ\,mol^{-1}}$ between 700 and $800°\,C$.

3.2.4. Determination of the activation energy of the anodic chlorine corrosion.

The effective activation energy for the anodic generation of six corrosion products and the effective activation energy of anodic chlorine corrosion were investigated for CE-carbon in a melt containing 54.3 mol % LiCl, 35.8 mol % KCl, 9.9 mol % NaCl and no aluminium chloride at a current density of $0.1\,\mathrm{A\,cm^{-2}}$ (current: 1 A) by determining the evolution rate of the perchlorinated compounds. Figure 2 shows the temperature dependence of the evolution rates of different perchlorinated compounds and Fig. 3 demonstrates the determination of the effective activation energy of the corrosion rate
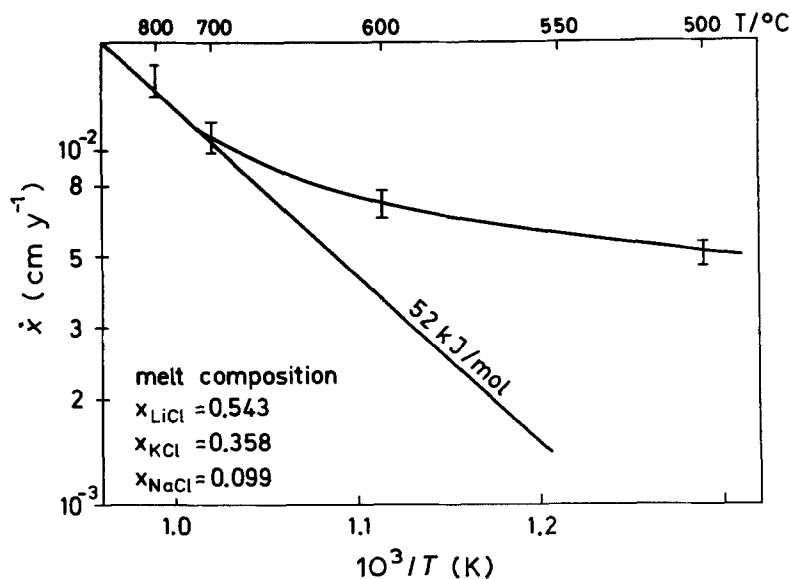
3.2.5. Current density dependence of the anodic chlorine corrosion of two different Acheson-graphites.

If the observed degradation of chlorine evolving anodes and the formation of chlorinated compounds is an electrochemical rather than a chemical process, a sizeable dependence of the corrosion rate on the anode potential or the current density would be expected. Therefore the corrosion of carbons EC and EK 78 were investigated over a current density range from 0.05 to $0.2\,\mathrm{A\,cm^{-2}}$.

Figures 4 and 5 show the current density dependence of the formation rates of the six different carbonchloro compounds and Fig. 6 shows the effective corrosion rates of the two Acheson graphites.

Fig. 3. Determination of activation energy of anodic chlorine corrosion of carbon CE at $i = 0.1\,\mathrm{A\,cm^{-2}}$.
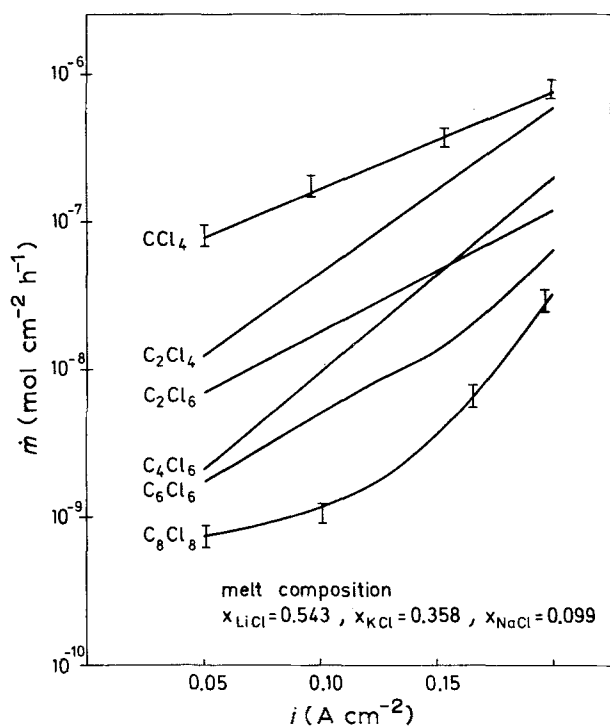
Fig. 4. Current density dependence of the anodic evolution rate of different perchlorinated compounds at 700°C at carbon CE. Actually observed data are only indicated for the most and least abundant compounds CCl_4 and C_8Cl_8.
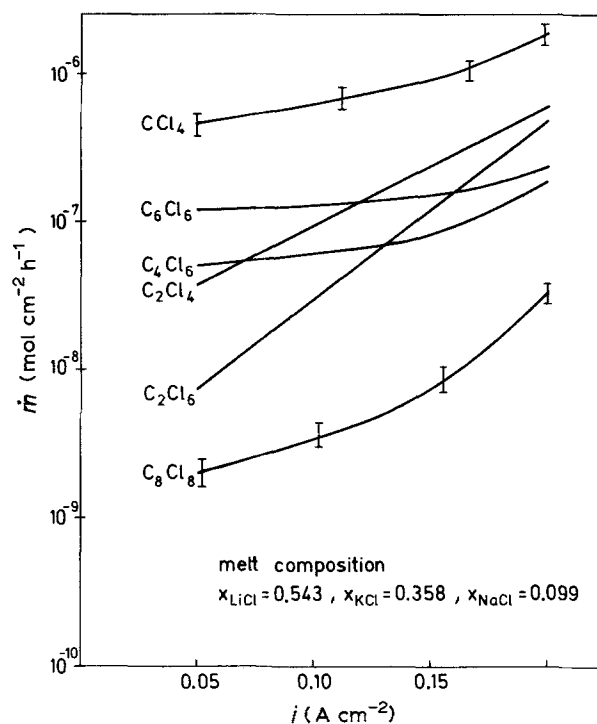
Fig. 5. Current density dependence of the anodic evolution rate of different perchlorinated compounds at 700°C at carbon EK-78. Actually observed data are only indicated for the most and least abundant compounds CCl_4 and C_8Cl_8.

At higher current densities the evolution rate of almost any chlorocarbon compound increases exponentially with current density. Exceptions are chlorobutadiene and octachlorostyrene.

Evidently the rate of anodic chlorine corrosion is different for the two different carbon qualities, in particular at low current densities. There the EK-78-carbon corrodes appreciably faster than CE-carbon, mainly due to formation of CCl_4, C_4Cl_8 and C_6Cl_6. But as the current density approaches $0.2\,A\,cm^{-2}$ the evolution rates of the different carbon-chloro compounds, and the effective wear rates calculated from them, approach each other for both carbon specimens.

For both carbons wear rates of $0.6\,cm\,y^{-1}$ and $5\,cm\,y^{-1}$ for current densities of 0.3 and $0.4\,A\,cm^{-2}$ are obtained by extrapolation. $5\,cm\,y^{-1}$ is also the limiting wear rate predicted if one assumes that in the evolved chlorine the formation equilibrium of carbon tetrachloride is fully established ($K_p = 1.3 \times 10^{-2}\,bar^{-1}$ at 1000 K).

4. Discussion

The data of Fig. 6 clearly demonstrate that at current densities, above $0.05\,A\,cm^{-2}$, anodic chlorine corrosion of Acheson graphites is faster than gas-phase chlorine corrosion.

The previously observed CCl_4 and C_2Cl_4 concentrations in the carbon corrosion experiments with gaseous chlorine are lower than anticipated from equilibria data [1]. The anodic chlorine corrosion of EC-carbon, however, leads, at a current density of

$0.2\,A\,cm^2$, to C_2Cl_4 concentrations is evolved chlorine exceeding the equilibrium value by a factor of approximately 2. Chlorine corrosion of EC-carbon, as well as EK-78-carbon, produces, at current densities of $0.05\,A\,cm^{-2}$ C_2Cl_6 and C_6Cl_6 concentrations which are by at least one (C_2Cl_6) and 3 (C_6Cl_6) orders of magnitude higher than the equilibrium values and these factors increase with current density (Compare equilibrium data in [1]). All chlorinated compounds except CCl_4 may be assumed to be typical transition products of graphite chlorination with CCl_4 as the stable end
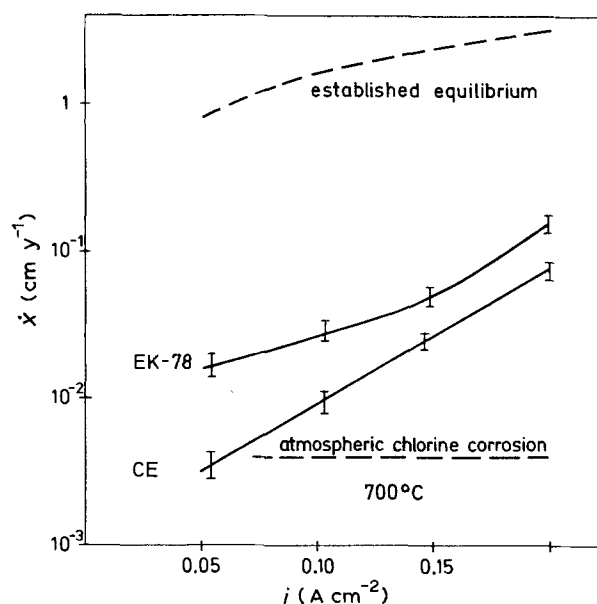

Fig. 6. Current density dependence of effective anodic chlorine corrosion rates of technical carbons CE and EK 78 at 700°C.

product. It is obvious that the formation of these compounds is kinetically controlled — resulting in an effective wear rate above the rate calculated with the assumption of completely established equilibrium.

A kinetic interpretation is straight foward: obviously the anodic oxidation of graphite in chloride melts proceeds by simultaneous formation of CCl_4 and of thermodynamically less stable chlorinated C_2-compounds, the latter being unstable intermediates, forming gas mixtures with too high a content of these C_2-compounds. The chlorinated arenes — hexachlorobenzene and octachlorostyrene — may be formed directly or, as reported by Maier [15], due to association reactions from hexachloroethane or tetrachloroethane.

Most unexpected is the observed high rate of anodic wear. Extrapolating the data of Fig. 6 to current densities of 0.5 or even $1\,A\,cm^{-2}$ results in wear rates exceeding $1\,cm\,y^{-1}$. The wear rates observed for carbon anodes in the ALCOA process at $1\,A\,cm^{-2}$ and in magnesium electrowinning cells are much lower [16, 17]. The electrolytes, used in these processes, however, are never free of oxygen anions or oxygen donors like traces of water, whereas this investigation was performed in carefully dried melts. It is known that the reaction of carbon with oxygen is strongly hindered in chlorine atmosphere because chlorine displaces adsorbed oxygen from carbon surfaces [1]. It may, therefore, also be anticipated that adsorbed oxygen species, generated anodically from oxygenanion or other oxygen donors contained in chloride melts, hamper the attack of anodically generated chlorine on graphite. This would explain the observed stability of carbon anodes in the ALCOA cell or Mg-electrowinning cells.

5. Conclusion

The relatively rapid consumption of chlorine evolving carbon anodes observed in dry chloride melts, which is accelerated in the presence of tetrachloroaluminate anions, i.e. in basic mixed melts of alkalichlorides and aluminium chloride, would render Acheson graphite anodes dimensionally unstable at current densities exceeding $0.2\,A\,cm^{-2}$.

In impure, oxygen ion containing chloride melts the wear rate of chlorine evolving electrodes is, however, reported to be much slower so that, under technical conditions, chlorine evolving anodes are rather consumed by oxygen attack than by anodic chlorine corrosion. But the most important finding, that non negligible amounts of noxious chlorinated products are formed by chlorine corrosion of graphite anodes in dry melts should be reason enough to investigate the actual emission of such compounds by Mg-electrowinning plants and of other processes working with chlorine evolving carbon anodes in chloride melts very thoroughly.

References

[1]   H. Wendt, S. Dermeik and A. Ziogas, *Werkstoffe und Korrosion* **41** (1990) 457.
[2]   H. Wendt and K. Reuhl, *Aluminium* **61** (1985) 518.
[3]   D. R. Stull and E. E. Westrum, 'The Chemical Thermodynamic properties of organic compounds' (1969).
[4]   R. Schlögel, A. Baiker and E. Habegger, *Ber. Bunsenges. Phys. Chem.* **89** (1985) 530.
[5]   V. Avdeev and V. A. Mukhanov, *Vestn. Moskow Univ., Ser. 2, Khim* **25** (4) (1984) 409.
[6]   A. Baiker, E. Habegger, V. K. Sharma and W. Richarz *Carbon* **19** (1981) 329.
[7]   M. Fouletier and M. Armand, *ibid.* **17** (1979) 427.
[8]   J. Hooley and P. T. Hough, *ibid.* **16** (1978) 221.
[9]   E. Stumpp, *Mat. Sci. and Eng.* **31** (1977) 53.
[10]   J. Hooley, *Carbon* **11** (1973) 225.
[11]   *Idem, ibid.* **10** (1972) 155.
[12]   B. Bach and A. R. Ubbelobbe, *Proc. Royal Soc., Lond. A.* **325** (1971) 437.
[13]   R. C. Croft, *Quart. Rev.* **14** (1960) 1.
[14]   M. L. Dzurus, G. R. Henning, *J. Amer. Chem.* **79** (1957) 1051.
[15]   K. Maier, *Giesserei* **75** (1988) 149.
[16]   K. Haupin, private communication.
[17]   H. Øye, private communication.