

REACTIVITY TESTING OF ANODE CARBON MATERIALS

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Carbon samples representative of typical anode materials have been tested by conventional methods for their carboxyreactivity and airburn reactivity. The results indicate that when reactivities are measured by these means, and for otherwise similar carbons, the main detectable influence is that due to the presence of catalytic anode impurities. In further trials, the carboxyreactivity test was modified to examine the effects of internal CO₂ burning on the structure of the anode. It was indicated that when low levels of burning were confined to a small number of preferred sites, the break-down in anode structure could be very severe and led to pronounced strength reduction and much dusting.

Introduction

The laboratory-scale reactivity testing of anode carbon materials plays an essential role in the determination of factors which affect anode consumption and in the quality evaluation of prospective anode materials. Since the actual anode consumption is typically 25-45% greater than the theoretical electrolytic consumption (1), there is considerable scope for reducing the unwanted losses of this expensive raw material. Many factors have been found to influence the excess carbon consumption (2) but, in short, it may be said that non-uniform anode properties lead to uneven oxidation characteristics, often occurring preferentially within the binder phase, and increased excess consumption. The thermal history of the anode (e.g., calcining, baking), the type and distribution of metallic impurities (e.g., catalytic, neutral) and the accessible surface area are some of the leading factors which can contribute to anode heterogeneity. Both the internal C/CO₂ ("carboxy") reaction and the C/O₂ ("airburn") reaction are important reactions in the excess consumption process (3). The work presented below summarizes some results of our investigations of these two reactions and examines the usefulness of conventional testing procedures.

Experimental

The anode carbon materials used in this study were obtained from the Norwegian aluminium industry and are representative of the types typically employed in commercial reduction cells. The samples were obtained as drilled cores taken from either plant-scale or laboratory-scale prebaked anodes, and as petroleum coke aggregates.

CO₂ Susceptibility of Anodes

In the usual test procedure, core samples measuring 20 mm OD by 40 mm long were suspended in the hot zone of a "gold furnace" (Trans Temp. Corp., Chelsea, MA, USA) which was kept at 950±5°C. The gold furnace is transparent at the reaction temperature and permits visual monitoring of the progress of the reaction. The end of the samples were coated with alumina cement to limit the reaction to just the sides. A steady stream of CO₂ was blown through the furnace at a linear velocity of ca. 5 cm/sec for about 4-5 hours whilst the mass loss was continuously recorded against time with an electronic balance (LBP 1, BLH electronics, Waltham, MA, USA). The slope of the linear portion of the curve was taken as the carboxyreactivity of the sample and was expressed in units of mg/cm².hr.

CO₂ Susceptibility of Contaminated Petrol Coke

Impregnation of the filler cokes was carried out on 25-30 g batches of sized particles contained in a flask. To the system under vacuum was added about 200 cm³ of aqueous impregnant and the flask was then equilibrated with atmospheric pressure. The submerged particles were allowed to stand in the solution for ca. 20 hours before filtered, lightly rinsed, dried and, finally, sintered at 975°C in nitrogen. Aqueous solutions (5 and 10 wt%) of iron nitrate (Baker AR grade) and sodium nitrate (Merck PA grade) were used individually and in combination with each other as the impregnating agents.

The CO₂ reactivity was determined on 1 cm³ samples previously sized to -20+44 mesh (ca. -0.85+0.35 mm). A fixed volume of sample was chosen instead of a fixed mass to ensure essentially constant surface area. The

sample was placed in a platinum mesh basket (26 mm OD, mesh size ca. 0.25 mm) and suspended from an electronic microbalance (FTD-G-10, Schaevitz instruments, Berks., UK) in a vycor tube (30 mm ID) maintained at around 975°C. Carbon dioxide flowed past the sample at a rate of 50 cm³/min. Reactivity was taken from the slope of the mass loss versus time curve, as before, and expressed as mg/(gram particles)(hour). Reactivities were normalized to an arbitrary standard temperature of 975°C using the experimentally derived Arrhenius plot for the unimpregnated coke. An apparent activation energy of ca. 490 kJ/mole was obtained over the limited temperature range of 940-1000°C.

Airburn Susceptibility of Anodes

The airburn reactivity of anode core samples was determined in the same way as for the CO₂ reactivity, except that the test was carried out at ca. 495°C in flowing air. Temperature regulation was maintained with the furnace control thermocouple located inside the sample. Failure to take this precaution resulted in uncontrolled sample temperature increases of around 40°C, or more with highly reactive samples. Reactivities were normalized to a reaction temperature of 495°C using an apparent activation energy of ca. 165 kJ/mole determined for graphite samples (Union Carbide AGSR grade) over the temperature range 490-650°C. Limited results for the anode suggested that a similar value of activation energy could be used for the industrial carbons.

Anode Permeability

The air permeability of anode core samples (25 mm OD by 40 mm long) was determined as a single-point value using a commercial apparatus (Ruska Permeameter, Ruska Instrument Corp., Texas). After measuring the flow rate of air through the sample and knowing the pressure drop across it, the permeability in millidarcys is obtained using the appropriate relationship (4).

Internal CO₂ Burning of Anodes

In a further test method one end of an alumina tube (4 mm ID) was placed 10 mm into the top of a core sample (20 mm OD by 40 mm long) and cemented to it, as shown later in Figure 9. The whole arrangement was suspended within a 30 mm ID vycor reaction vessel closed to the atmosphere and located in a furnace held at 975±5°C. Carbon dioxide was blown through the alumina tube, and hence the sample, for 6 hours at a constant velocity which was in the range 13.5-150 cm³/min. The gas penetrating the sample was able to escape from any openings located on the sides or base of the anode core, but not from the cement-covered top. A nitrogen flow was maintained along the outside surface of the sample to prevent possible reaction with escaping CO₂ or residual air. Sectioning of the sample was carried out after the run to determine the extent of internal burning.

Results

CO₂ Susceptibility of Anodes

About 25 anode core samples were tested for their CO₂ reactivity. The samples tested represented a number of different anode manufacturers, petroleum coke sources and pitch binders, and the resulting carboxyreacti-

vity values (R_{CO_2}) ranged from about 10 to 50 mg/cm².hr. Despite the five-fold variation in reactivities, clear-cut relationships between the chemical and physical data from the average anode batch analyses (as supplied) and R_{CO_2} were difficult to find. This is probably due to a combination of the CO₂ large standard deviation that is inherent to such data and the relatively small size of the anode cores (compared with the size of the anodes). Consequently, about half of the tested samples, covering the extremes of the reactivities encountered, were sent for individual chemical analysis. The results of this analysis are presented in Table I, where the samples have been coded in the following manner: (X,y) = (Filler coke source, manufacturer). A re-appraisal of the data indicated that apparent relationships could be attributed to the presence of Na, Fe and Ca impurities, all of which are known catalysts for the C/CO₂ reaction (5). Previous workers have been able to establish correlations between the carboxyreactivity and the iron (6), sodium (7) or sulphur (8) levels. Sulphur has been suggested as an inhibitor for the C/CO₂ reaction (8), but only a poor inverse relationship was detected here ($r = -0.45$). However, the range of sulphur levels was rather restricted in the present study (1.66 to 3.51 wt%) and tended to be clustered around the 2 wt% level, so the result cannot be taken as conclusive.

Of the remaining impurities it was not easy to see just which single impurity was having the strongest influence on the reactivity since, generally, their concentrations in the samples tended to increase in parallel with each other. This can be seen in Table I. Some information is provided, however, by comparison of the iron contents for samples 1, 3 and 6: samples 3 and 6 have about the same carboxyreactivity, yet their respective iron contents differ by a factor of 2, whilst samples 1 and 3 also have iron contents differing by a factor of 2, yet their respective carboxyreactivities differ by a factor of 1.7 in the opposite direction. As for calcium, we see that there is a high relative error associated with its chemical analysis, so apparent trends must be viewed with caution.

Regression analysis tended to confirm these interpretations. Equations 1 to 3 in Table II list the correlations obtained for Na, Ca and Fe, respectively. The Table illustrates the stronger influence of Na, since any model not containing [Na] as a variable has a low correlation coefficient ($r < 0.8$) and a higher percentage error associated with the coefficient of the independent variable. Although not given here other models showed that, even when Na, Ca and Fe were taken together in different combinations to describe the R_{CO_2} , the correlation coefficient was always less than the value obtained for the simple linear regression employing Na as the lone variable. It can be concluded that, despite the presence of other catalytic metals, sodium had the strongest catalytic effect at the levels encountered in these samples.

The effect of sodium content on R_{CO_2} and on the dusting tendency of oxidised samples is shown in Figure 1. The dusting tendency was determined by weighing the loose dust that could be removed by gentle brushing at the end of a run and expressing this weight as a percentage of the total CO₂ burning loss. The dust consisted mainly of filler coke particles so most of the burning must have occurred preferentially within the binder phase or at the binder coke/filler coke interface. Since the dusting tendency increased with the Na-content, this would suggest that the sodium was largely contained within the binder phase. This situation is much more severe than if the catalytic impurity had been contained primarily within the petroleum coke because it will exaggerate any existing tendency towards dusting (9). In Figure 1 we have also included some points corresponding to the average batch anode data. The deviation between this data and that obtained from individual chemical analysis can

Table II. Comparison of Models to describe CO₂ Reactivity.

Model	r	Reliability of conc. coefficient
1. $R_{CO_2} = 12.3 + 297 [Na]$	0.86	± 19%
2. $R_{CO_2} = 7 + 1062 [Ca]$	0.78	± 26%
3. $R_{CO_2} = 8.6 + 387 [Fe]$	0.64	± 37%

R_{CO_2} in mg/cm².hr. [metal] in wt%.

Table I. Individual Chemical Analysis and Carboxyreactivity of Selected Anode Cores.

Number	S wt%	Si wt%	Fe wt%	Ti wt%	V wt%	Na wt%	Ca wt%	Ni wt%	Mn wt%	SBD ¹⁾ g/cm ³	R _{CO₂} ²⁾ mg/cm ² .hr	Dust %
1 (A,a)	2.06	0.004	0.034	0.0007	0.020	0.044	0.018	0.014	0.0009	1.56	31.5	8.4
2 (B,b)	2.67	0.024	0.04	0.0008	0.028	0.026	0.015	0.013	0.0009	1.50	15	8-9
3 (B,b)	1.80	0.029	0.068	0.0010	0.033	0.015	0.009	0.015	0.0017	1.65	18.5	6
4 (B,b)	3.51	0.041	0.046	0.0009 ³⁾	0.030 ³⁾	0.020 ³⁾	0.012 ³⁾	0.014 ³⁾	0.0011	1.49	12.5	7.5
5 graphite	0.11	0.013	0.014	0.0026	0.002	0.003	0.015	0.0008	0.0002	1.67	15	<1
6 (C,c)	1.80	0.009	0.029	0.0007	0.013	0.022	0.008	0.013	0.0005	1.45	18	13.3
7 (C,c)	1.94	0.10	0.037	0.0008	0.015	0.044	0.013	0.013	0.0006	1.42	15	11.3
8 (D,d)	2.12	0.021	0.082	0.0018	0.011	0.096	0.033	0.011	0.0014	1.39	38	17.1
9 (D,d)	2.10	0.017	0.072	0.0014	0.011	0.117	0.029	0.010	0.0014	1.42	45	21
10 (D,d)	2.06	0.022	0.086	0.0016	0.011	0.100	0.038	0.010	0.0016	1.36	40	19.3
11 (E,e)	1.66	0.024	0.060	0.0012	0.012	0.076	0.024	0.010	0.0011	1.44	48	23
Std. Dev. 4)	1-1.5	13	3	30	3	15	42	4	30	-	-	-

1) Sample Bulk Density.
 2) CO₂ reactivity.
 3) Not determined. Values are the average of samples 2 and 3.
 4) Standard Deviation of Chemical Analysis in Relative Percent.

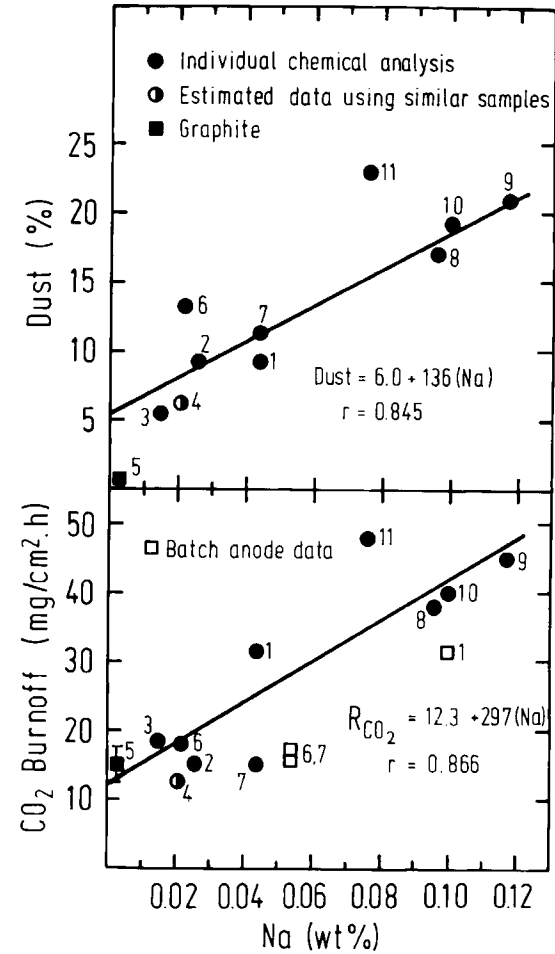


Figure 1. Carboxy-reactivity and dusting losses of anode samples as a function of the sodium content. Samples 4 and 5 were not included in the regression.

be quite large. It may be said that when employing a limited number of core samples of relatively small size, the average anode data may very well have little meaning. Much larger core sizes or an increased number of replicates would be needed before such data becomes useful.

Table I also suggests that there is a slight tendency towards lower reactivities as the sample bulk density increases, although a simple linear regression showed that the relationship on its own was poor. When taken together with the sodium content, however, the overall correlation is improved and a two-parameter relationship can be written as:

$$R_{CO_2} = 78.9 + 395 [Na] - 106 [BD]^{-1} \quad (4)$$

$$r = 0.88.$$

The goodness-of-fit of this model is illustrated in Figure 2. The very weak influence of bulk density is consistent with the tests being carried out under isobaric conditions and at relatively high temperatures where the reaction tends to be limited to the outside surface of the sample.

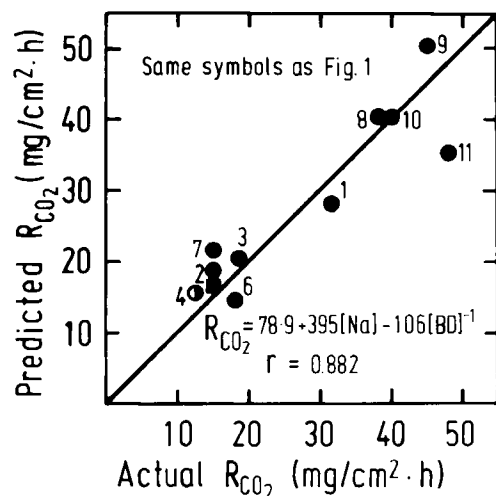


Figure 2. Goodness-of-fit for the two-parameter model involving Na-content and bulk density (Model 4). Same symbols as Figure 1.

CO₂ Susceptibility of Contaminated Filler Coke

It is known that both Fe and Na can occur as contaminants during the anode manufacturing process (9), so we examined their relative strengths when found occurring together in a petrol coke. For this purpose a standard coke was impregnated with the contaminating solutions and tested for its carboxyreactivity. The results have been presented in Figure 3 as normalized reactivity values to accentuate the increase in reactivity brought about by each of the respective contaminants. The normalized carboxy-reactivity was calculated as (Actual reactivity/Unimpregnated reactivity). Whilst there is some inconsistency in the values, probably due to non-uniform metal distribution during the impregnation stage, generally the

much stronger catalytic effect of sodium is demonstrated and sometimes overrides the presence of Fe altogether. The weaker, but never-the-less significant, influence of Fe is also shown and it must certainly be considered an impurity to avoid where possible. However, Na is a much more dangerous impurity and, qualitatively speaking, has an effect which is roughly 2.5 to 3.5 times stronger than the effect of Fe at similar contaminating levels.

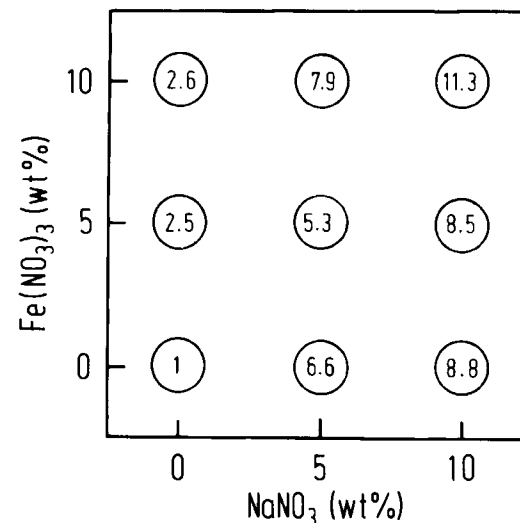


Figure 3. Normalized carboxyreactivity of impregnated filler coke as function of Na and Fe concentration in impregnating solution. Unit reactivity = 25 mg/(gram particles)(hour).

Airburn Susceptibility of Anodes

The results from airburn reactivity trials have been compared with either the average batch anode specifications, or with values estimated from the individual chemical analysis of similar samples. In most cases data was available for the following: Fe, Si, V, Ni, Na and ash. Since the batch anode specification was the data usually available, and in view of its limitations encountered earlier with the CO₂ testing, many more replicates were employed in the program in order to obtain the "average" reactivity at the nominally quoted impurity levels.

Several trends were apparent: Fe (0.01 to 0.08 wt%), Si (0.003 to 0.050 wt%) and ash content (0.1 to 1.25 wt%) had no influence on the reactivity. Iron is a catalyst for the C/O₂ reaction (5) but it was not effective in this case. It was thought that both the silicon and ash contents may have had an inhibiting effect at the higher levels, by acting as a barrier to the oxidizing gas, but this was not the case. Both Ca (0.01 to 0.025 wt%) and Na (0.04 to 0.09 wt%) appeared to have a positive effect on the reactivity, but the concentration ranges were too narrow to permit good correlations. Much of the data for Ni was given as (V+Ni) so its individual effect could not be determined. V (0.0 to 0.31 wt%),

(V+Ni) (0.0002 to 0.45 wt%) and S (0.5 to 2.5 wt%) all showed fairly good correlations with airburn, as shown in Figures 4-6. Note, however, the large standard deviation in the replicates: $\pm 30\%$ is not unusual in many cases. Had individual chemical analyses been carried out on the samples, the standard deviation would probably have been much smaller.

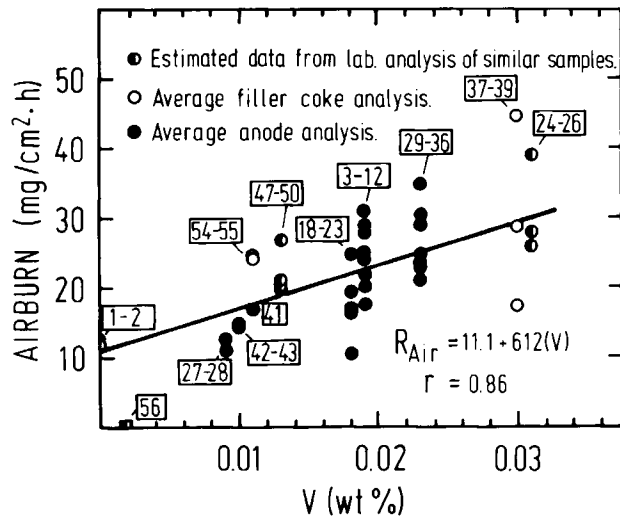


Figure 4. Airburn as function of the vanadium content.

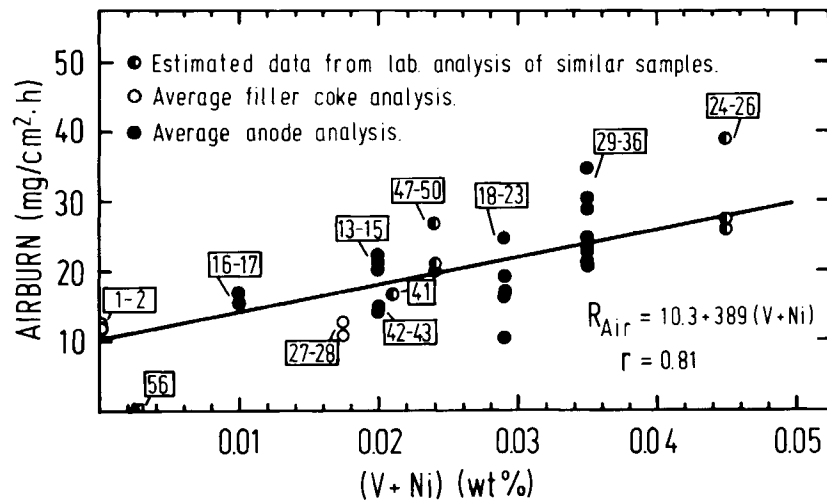


Figure 5. The combined effect of vanadium and nickel on airburn.

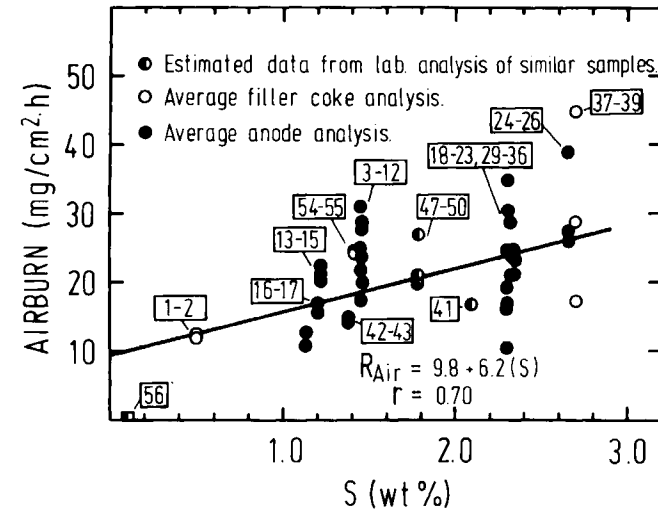


Figure 6. Airburn as function of the sulphur content.

Both V and Ni are known catalysts for the C/O₂ reaction, with V considered the stronger of the two (5), but S presents a conundrum. Since there were no high S/low V or low S/high V sample combinations, the direct effect of S could not be obtained. But from the literature describing the production of petrol coke, it is known that the coking process tends to concentrate the sulphur and metallic impurities together (10). We therefore suspect, like others (8), that the correlation between R_{AIR} and S is coincidental and the apparent influence is probably due to the copresence of catalytic metals. This idea is supported by reference to Figure 7 where the increase in S content is plotted against the increase in V content: there is a direct proportionality. Now, whilst the apparent correlation between airburn and S content is thought to be coincidental, it is relatively easier to determine sulphur levels in the percentage range than it is to accurately determine vanadium levels in the ppm range. The sulphur-content might, then, be usefully employed as a secondary standard for indicating those carbon materials with an increased susceptibility for airburn. This is also depicted in Figure 7 where a known, easily determined S-level is used to imply a catalytic metal content (in this case, V) and, hence, an expected value for R_{AIR}.

Comparison of Test Methods

Controlled laboratory consumption tests employing gas-phase oxidation have highlighted the important role played by particular catalytic impurities in accelerating the respective excess carbon reactions, namely, Na for the C/CO₂ reaction and V for the C/O₂ reaction. Such test clearly serve useful purposes and have been successfully used in the past to determine the influence of these and many other process variables (e.g. pitch content, baking temperature). In terms of convenience, however, there are several reasons that make an airburn reactivity test less attractive for use on a routine basis:

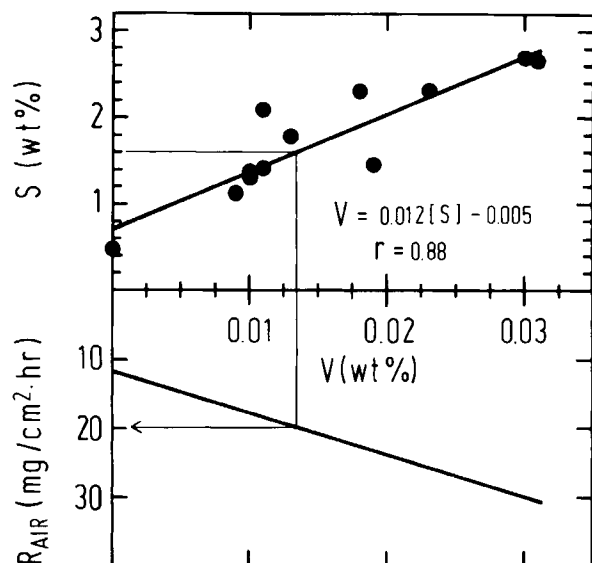


Figure 7. Correlation between S content and V content (upper half) and the implied relationship with airburn (lower half).

1. Experimental Difficulties. It is inconvenient and sometimes difficult to control the sample temperature at a known level, yet this is critical for obtaining correct and reproducible reactivity values.

2. Realism. The act of closely controlling the sample temperature is an unrealistic restriction to impose on the test since the top surface of new anodes undergo a continuous and rapid rise in temperature to ca. 700-800°C over 7-10 days (11,12). In this temperature range mass transfer control limits the rate of reaction such that the differences in chemical reactivity become less recognizable.

3. Importance. It is believed by many (2) that the carboxyreaction is more important than the airburn reaction because: (a) airburn can be greatly minimized by appropriate anode protection; (b) carbon dioxide has a greater potential for inflicting damage since it is an internal reaction; and (c) the reaction with CO₂ is most often used as a tool for predicting dusting tendencies.

Thus, the carboxyreaction is frequently the test of convenience employed in the laboratory. However, it would be useful to extract more information from the test. For instance, it is known that the related properties of permeability, porosity and bulk density can influence the reactivity (13), so a test utilizing the anode permeability would be an advantage.

Anode Permeability

The results from air permeability measurements conducted on anode core samples are shown in Figure 8. The data have been coded as before using the classification: (Filler coke, manufacturer). The general shape of the

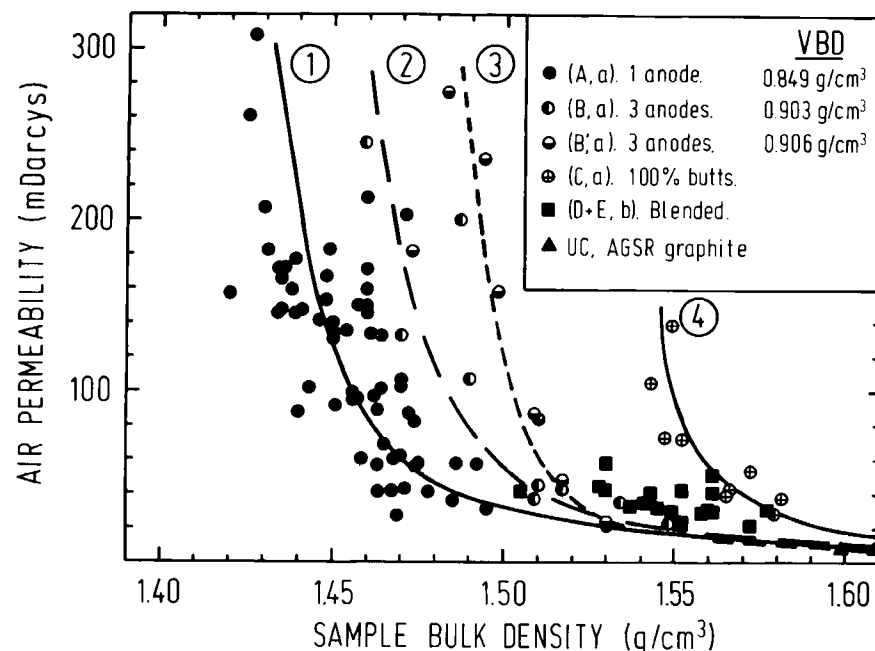


Figure 8. The relationships between air permeability, bulk density and vibrated bulk density (VBD) of anode samples.

curves is qualitatively similar to that presented recently by Alusuisse (13), but on the slightly expanded scale used here a single line does not adequately represent all the data. Rather, a series of curves can be drawn through the separate sets of points with each curve in the series separated from its neighbour by the vibrated bulk density of the aggregate coke. Only the results from a single manufacturer have been used for this comparison, so they are internally consistent.

Of further interest is curve 1 which shows the results of many core samples taken from a single anode. The degree of internal variation in both bulk density and permeability (especially) is quite marked, i.e., the anode was measurably non-uniform in its physical properties. Anode inhomogeneity may have serious consequences for consumption, as discussed elsewhere (2). In this case relatively small decreases in bulk density often produced large excursions in the anode permeability (200-400%), the consequence of which would be more CO₂ flow through the anode. By contrast, the samples taken from the blended coke anode (manufacturer "b") are much more uniform and there is virtually no change in the (low) permeability for similar changes in the bulk density.

Intuitively it can be said that the CO₂ flow through the anode will always occur along the path of least resistance, i.e., the larger pores, cracks and/or other macroscopic flaws. Thus, whilst the small pore sizes generate most of the internal pore volume and surface area, it is the larger pores, representing a small percentage of the total pore volume which will carry most of the penetrating gas. It can be speculated, then,

that the internal CO₂ burn becomes confined to a small number of preferred pathways, thereby creating localized weakness. Some evidence for this is presented below.

Internal CO₂ Burn of Anodes

A series of core samples taken from a single anode and covering a range of permeabilities, were subjected to internal CO₂ burning. At high flow rates (150 cm³/min) severe channelling of the penetrating CO₂ occurred to such an extent that a hole was burnt through the side of the sample. At lower flow rates (50 cm³/min) such extreme behaviour was not observed. Nevertheless, the pathway taken by the penetrating gas always took the form of a single preferred direction along which most of the gas flowed. The site of this pathway could be easily detected by probing the surface with a pointed stylus. At the site of preferred flow the carbon matrix, whilst superficially unchanged in appearance, was found to be very soft and crumbled easily. The structural integrity of the matrix was completely destroyed, having very little strength, and could best be described as "rotten". The interparticle bonds had apparently been selectively removed so that loosened filler coke grains were easily dislodged from the region and produced a great deal of dust (e.g., 0.2-0.5 g dust at 6-7% burn off). The remainder of the carbon matrix was quite unaffected and retained its strength, illustrating that the damage had been completely localized to a small region of the sample. Figure 9 is a sectioned core sample showing the location of the burning.

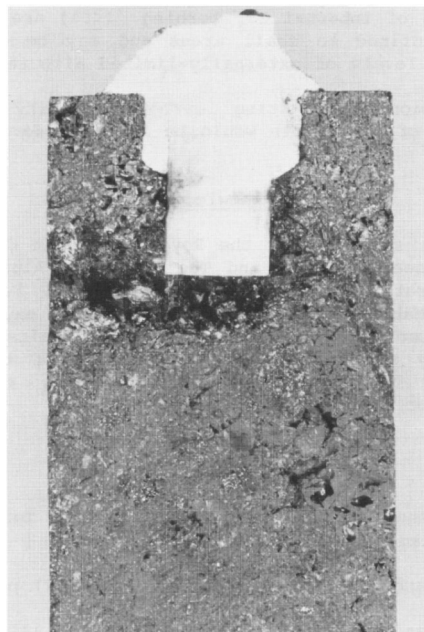


Figure 9. Internal carboxyreactivity specimen: Sectioned view showing extent of the internal "rotten" area.

Whilst the amount of carbon lost by burning alone was typically just a few percent (3-8%) the structural damage incurred, when localized to a small area, was very severe. These results have consequences not only for the structural integrity of the anode, but possibly also for adverse changes in its resistivity and current distribution. Currently we are trying to improve the testing procedure so that the systematic changes in the anode properties at low levels of internal burning may be monitored.

Conclusions

1. Gaseous oxydation tests based on the carboxy and airburn reactions, respectively, can be usefully employed to differentiate between the reactive natures of anode carbons.
2. Controlled laboratory testing by these methods has highlighted the important role played by specific catalytic metals in describing the essential difference between otherwise similar carbons.
3. For the C/CO₂ (carboxy) reaction the most dangerous impurity is Na, whilst for the C/O₂ (airburn) reaction the most dangerous impurity is probably V.
4. The airburn reactivity is a less convenient test to employ on a routine basis because of inherent experimental difficulties. Further, the airburn reactivity ratings of carbons obtained under carefully controlled laboratory conditions may not necessarily apply in the plant where quite different circumstances exist.
5. Low levels of internal CO₂ burning (<8%) are potentially very destructive when confined to small areas and may be more damaging to the anode than higher levels of externally-limited airburn.
6. The extension of existing carboxyreactivity tests to include the internal porosity of the sample would be a useful development to pursue.

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