

Introduction

The processes related to anode quality which contribute to the excess of carbon consumption in aluminium electrowinning are: air oxidation of exposed parts, CO<sub>2</sub> oxidation near anode-bath interface and "dusting". CO formation as a primary product of electrolysis is thought to be an important factor by some authors (1,2), but this has not been established definitively.

Although some evaluations are found in the literature (3), it is difficult to generalize about the relative importance of each mechanism, since they are related to details of design and operation of the pots, as well as to anode quality.

However, under no circumstances the importance of gaseous oxidation mechanisms can be overlooked. Even for "dusting" several authors have suggested a correlation between coke particle detachment and previous CO<sub>2</sub> oxidation near the anode-bath interface.

The papers by Paulin (4), who studied CO<sub>2</sub> permeation through anodes, and by Donrachey et al (5), who found an increase in laboratory measured electrolytic consumption after slight oxidation with CO<sub>2</sub>, are particularly relevant in this concern.

Accordingly, a careful study of factors that influence anode reactions with oxidant gases, has been considered convenient. Some of the results obtained will be discussed in this work.

Experimental section

The air reactivity of petroleum cokes was measured, after grinding and screening, by the use of a Rigaku-Denki Thermogravimetric analyzer. Samples weighing 20-50 mg and contained in small Pt crucibles were placed inside the balance furnace and a N<sub>2</sub> atmosphere was established. Temperature was raised to the desired value and then the N<sub>2</sub> was replaced by a 150 ml/min stream of dry air. Weight loss was continuously recorded, usually until consumptions higher than 50% were reached.

Temperature of the sample was recorded by means of a thermocouple welded to the base of the Pt crucible. It was kept constant ( $\pm 1^\circ\text{C}$ ) during each experiment. Most of them were performed on the 230/400 mesh fraction and at temperatures between 450 and 550°C. Three or more measurements at different temperatures were performed for each coke.

Baked carbon reactivity was measured by means of a thermobalance designed in our laboratory. Cylindrical samples (diameter=20mm, length=30 mm, weight=12 g) were suspended inside a vertical tube furnace. A system of spring and transducer allowed the measurement of weight, which was continuously recorded. A special sample holder allowed to introduce a type K thermocouple in a hole drilled along the axis of the sample. This thermocouple was used to control sample temperature by means of a Thermac R11C power controller connected to the furnace. Sample temperature was continuously recorded during each experiment and was kept constant ( $\pm 1^\circ\text{C}$ ) except in some very fast reactions.

The system was heated to the desired temperature while N<sub>2</sub> was flowing over the sample. Then the gas current was switched to dry air (about 3 l/min) and the weight loss recorded.

In most cases oxidation was performed at 530°C until a weight loss of 2 g was reached. Then the sample was allowed to cool under N<sub>2</sub> taken out from the furnace and weighed. After this, it was mechanically treated in a special

## STUDIES ON ANODE REACTIVITY TO OXIDANT GASES

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Anode oxidation by air or CO<sub>2</sub> causes excess of carbon consumption in aluminium electrowinning. It is shown that both oxidation processes are influenced by mass transport conditions inside the anode, but the transport mechanism and its relation with porous texture are not the same. As a first approximation, which disregards the existence of temperature gradients inside the anode, air oxidation is considered to occur under zone II reaction conditions. Then, the overall reaction rate is equally influenced by chemical reactivity and effective diffusivity. The existence of temperature gradients near the external surface could increase the influence of diffusivity.

A method for determining air chemical reactivity of coke was developed and used to study its correlation with chemical purity and thermal treatment. Also adequate procedures to measure anode air reactivity under zone II conditions are described and applied to the study of the influence of thermal treatment. It is found that overall reactivity varies slightly with temperature of treatment. As the variation in reactivity is confined to the more reactive phase, the binder coke, it causes an important change in oxidation selectivity and, then, in the anode behaviour.

ly designed drum which rotated at constant speed during a fixed time. Loose material was weighed and expressed as percentage of initial mass. Laboratory prepared carbon blocks were obtained using usual techniques and fired under an inert atmosphere. Properties of cokes and anode samples were measured by well known techniques ( $N_2$  or K absorption, mercury porosimetry, etc.)

The influence of mass transport on gaseous oxidation rates

Before proceeding to explain and discuss our experimental results we consider desirable a brief discussion of gaseous mass transport inside carbonaceous materials and its influence on the oxidation rate. In fact, although the influence of mass transport on reaction rate has been extensively discussed in the literature on carbon oxidation (6,7), the available information related to aluminium electrowinning anodes is very scarce.

In an anode, as well as in most carbonaceous materials, the surface able to react is mainly located inside the pores. In consequence, three major steps must be distinguished for the proper understanding of the reaction mechanism:

- a) transport of reactive gas and products between the external surface and the bulk of the gas.
- b) transport between the external surface and the reactive surface inside pores.
- c) reaction on pore surface.

Depending on the reaction conditions each of these steps will contribute differently to the overall process. In our case, step a) can be safely disregarded because external transport becomes important at temperatures well over 700°C for the C- $O_2$  reaction and over 1000°C for the C- $CO_2$  one. Conversely, as later discussed, transport inside pores is often a limiting factor on the oxidation rates.

Air oxidation.

Let us consider, in the first place, the air oxidation of exposed parts of the anode. In this case, in-pore diffusion is responsible of mass transport.

A rigorous analysis of reaction conditions should include consideration of sample geometry, temperature distribution, anode properties and surface reaction kinetics. However, qualitatively correct discussions can be performed on the basis of simplified kinetics and disregarding the effect of sample geometry (8).

Let us consider the case of a reaction which is first order in oxidant concentration, and conditions such that diffusion does not influence the overall reaction rate. This means that mass transport is fast enough as to keep the concentration of oxidant gas essentially constant throughout the sample and equal to the external value in the gaseous phase. At the same time, the concentration of products will be very small over the sample. In that case:

$$v_o = k_o \text{ spc} \tag{1}$$

When the reaction proceeds free from diffusion limitations, i.e. chemically controlled, it is said that it occurs in zone I. It must be taken into account that as carbon is burnt off, the values of  $s, \rho$  and  $k_o$  can change so that, even in this simple case, the rate usually changes as the reaction proceeds. This is of great importance when the carbon reactivity is to be measured properly.

The rate constant varies with temperature according to an Arrhenius law

$$k_o = k_o^\circ \exp(-E_a/RT) \tag{2}$$

and activation energies of about 35-40 Kcal/mol are found for the C- $O_2$  reaction when impure carbons are used (7).

On the other hand, gaseous diffusion has a very low activation energy, (<3 Kcal/mol (8)). This means that, as higher temperatures are reached, reaction rate could increase to a point in which diffusion rates are not fast enough to keep the oxidant concentration uniform over the whole specimen. The reaction is then influenced by diffusional limitations and a concentration gradient develops in the specimen.

Let us consider a case in which oxidant concentration goes to zero at a certain distance from the external surface. Then, it is said that the reaction occurs in the zone II or under internal diffusion conditions. The overall reaction rate in the sample now is

$$v = (k_{o,sp}De)^{1/2} c \tag{3}$$

It is clear from equation 3 that the influence of the product  $k_{o,sp}$ , which can be considered the intrinsic or chemical reactivity of the material, is smaller than in the chemically controlled reaction (eq. 1). On the other hand, the overall reaction rate is now influenced by the porous texture of the material, through the presence of  $De$  in equation 3.

It can be shown that if  $3 |De/k_{o,sp}|^{1/2}$  is much smaller than the dimensions of the specimen, then the reaction is restricted to a relatively small region near the outer surface. Paulin (4) has measured gas compositions inside prebaked anodes during operation in the pot. He has found that  $O_2$  is effectively exhausted in the inner part of the anode. Then, reaction conditions are similar to those described above.

Further evidence comes from the study of specific surface gradients in anodes that were taken out of the pot after several days of use. As is shown in picture 1, specific surface is higher near the outer surface but falls to a normal value at a relatively small distance. This demonstrates that the anode is oxidized only in a zone near the external surface.

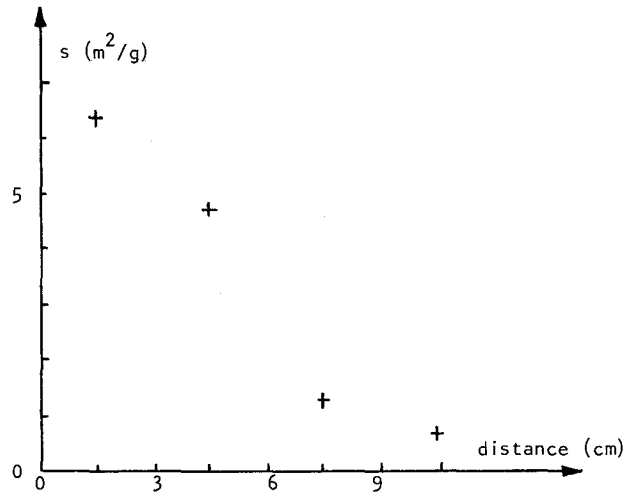


Fig. 1: Surface developed by air oxidation as a function of the distance from the outer surface.

In fact, the analysis of reaction conditions in an anode is more complex due to the existence of temperature gradients. However it can be shown that the reaction rate is controlled by the same factors than in the case of a zone II, isothermal reaction. The use of a simple model in which a linear temperature gradient near the surface was considered, allowed us to show that in a real case the influence of the chemical reactivity,  $k_0 s_p$ , is even lower than the one showed in eq. 3 (9). Conversely, the influence of  $De$  is greater.

CO<sub>2</sub> oxidation

It is a well known fact that a small upward flow of CO<sub>2</sub> exists through the anode, coming from the anode-bath interface where it is generated by the electrolytic reaction. According to Paulin (4) about 5% of the CO<sub>2</sub> formed in the pot escapes through the anodes.

As the CO<sub>2</sub> flows as described above, it reacts with C to form CO. Paulin (4) has found that this occurs over a small length near the anode-bath interface, and most of the CO<sub>2</sub> is transformed into CO.

Rhede (10) has estimated that the contribution of this reaction to the total carbon consumption is about 1,5% of the purely electrolytic one. A reasonable agreement between both estimations is observed. Now the relevant mechanism of mass transport is not diffusion. In fact, a pressure gradient exists between the lower and the upper face of the anode. Then, the flow is due to this pressure gradient and its magnitude is controlled by the permeability of the medium.

In this case, as pointed out by Barillon (2), specific surface and density gradients appear near the anode-bath interface due to oxidation by CO<sub>2</sub>.

The relation between mass transport properties and porous texture.

Gaseous diffusion inside a pore can follow quite different laws depending on the ratio between pore diameter,  $d$ , and the mean free path of molecules,  $\lambda$ . If  $\lambda/d \gg 1$ , the mass transport is controlled by collisions between the molecules and the pore walls. This is called "Knudsen diffusion" and the pore diffusion coefficient is proportional to  $d$  (8).

On the other hand, if  $\lambda/d \ll 1$ , diffusion is controlled by collisions between molecules (molecular or bulk diffusion) and the pore diffusion is independent of  $d$ .

Certainly, these are limit conditions and in other cases,  $d$  and  $\lambda$  are of the same order of magnitude.

In a porous medium, things are very complex as an extended range of pore dimensions exists and different diffusion mechanism can occur in different pores.

Let us consider some numerical values. The mean free path of air molecules at standard conditions is  $\lambda = 0,1$ . The value of  $\lambda$  at 500°C, a typical temperature in anode operation, is readily calculated to be 0,28. Fig. 2 shows mercury intrusion curves of typical samples.

It can be seen that most of the pore volume corresponds to pores with  $d \gg \lambda$ . In fact, when average diameters were evaluated from these and similar curves, values higher than 10 $\mu$  were always found.

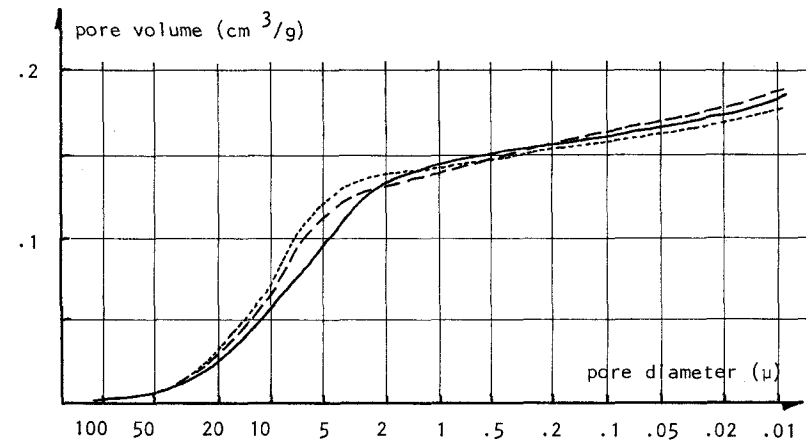


Fig. 2: typical porosimeter curves of anodes

According to this, it is clear that bulk diffusion is the predominant mechanism, in which case the diffusion coefficient is not dependent upon pore diameter. The effective diffusion coefficient  $De$  is related with total connected pore volume through the relation:

$$\frac{De}{Do} = \frac{\epsilon}{q} \tag{4}$$

where  $q$  is called the tortuosity factor.

Several authors have attempted to evaluate  $q$  using simplified models of the porous structure, but clear conclusions have not been reached. Walker et al (6) have experimentally found a relation between  $D_e$  and  $D_o$  as follows

$$D_e / D_o = \epsilon^2 \quad (5)$$

which means that

$$q = 1/\epsilon \quad (6)$$

This relationship, also finds some theoretical support when considering the model of porous diffusion developed by Wakao and Smith. This model leads to equation 5 when conditions are such that the predominant mechanism is bulk diffusion of molecules with not too different molecular weights (8). In consequence, this equation can reasonably be used to semiquantitatively consider the influence of porous texture on reaction rate.

In principle, only those pores connected to the outer surface are able to transport the reactive gas. The open porosity, usually different from the total one, must then be considered and the diffusivity must, in principle, be independent on pore size distribution.

When  $CO_2$  flow is considered and as it was mentioned previously, the relevant parameter is the permeability (11).

Also in this case two types of flow must be considered. In small pores, where  $\lambda \gg d$ , the flow occurs through a "Knudsen" mechanism, as it is controlled by collision between the molecules and the pore walls. On the other hand; in large pores, where  $d \gg \lambda$ , viscous flow is present. If  $d$  and  $\lambda$  are of the same order of magnitude, viscous flow with slip takes place, with contribution of both mechanisms. Consideration of pore distribution in anodes (Fig.2), as well as the experimental study of the relation between permeability and pressure allowed us to conclude that the slip contribution is small and a purely viscous flow can be considered (9).

The permeability constant  $B_o$ , which fully characterizes the properties of the medium when only viscous flow is relevant, can be expressed as (11):

$$B_o = \frac{\bar{\epsilon} \bar{d}^2}{40q_v^2} \quad (7)$$

where:  $q_v^2$  is a tortuosity factor which consider deviations from a straight path, as well as the additional resistance due to pore constrictions.

$\bar{d}^{-2}$  is a mean value defined by

$$\bar{d}^{-2} = \frac{1}{\epsilon} \int_0^\epsilon d^2 de$$

Comparing with expression 6, important differences between viscous flow and bulk diffusion are evident. In fact, while bulk diffusion is independent on pore dimensions, this is not the case for viscous flow. Then, in an anode  $CO_2$  flow will depend not only on connected pore volume but also on the pore size distribution. A coarser porosity will allow a greater  $CO_2$  flow through the anode.

## Results and discussion

### Measurements of coke reactivity

The problems found in the measurement of the reactivity of carbonaceous materials are well known. Particularly, Guerin (12) has pointed out several of them, including the possible influence of in-pore diffusion and the change in reaction rate with burn off. Improper consideration of these and other factors have led to some confusion and, sometimes, to contradictory results.

Walker et al (13) have recently studied the reactivity of coal chars under chemically controlled conditions. They have found that thermogravimetric data for all materials and even for different oxidant gases can be represented by a single curve,  $x$  vs  $\tau$ ,  $\tau$  being a reduced time defined by

$$\tau = t/t_{1/2} \quad (9)$$

In this case, it is obvious that reactivities can be compared by using a single value such as the initial reaction rate, the maximum reaction rate developed, the time required to get a certain burn-off, etc. In fact, the existence of a unique  $x$  vs  $\tau$  curve, means that the evolution of reaction rate with burn-off is always the same.

If this is not so, the measurement of a single reactivity value can not be accepted without critical examination. In those cases, Guerin (12) has correctly suggested the use of one of the following parameters

$$\text{medium reactivity index } R_m = \frac{1}{x} \int_0^x \frac{1}{m_o - m} \frac{dm}{dt} \cdot dx \quad (10)$$

$$\text{or integral reactivity index } R_i = \frac{1}{x} \int_0^x \frac{dm}{dt} \cdot dt \quad (11)$$

We have studied the oxidation of a large number of petroleum cokes with air under chemically controlled conditions. Only some results and conclusions will be quoted here. A more detailed report will be published elsewhere.

Basically, it was found that different materials give different  $x$  vs  $\tau$  curves, as shown in Fig.3. Slightly different curves were found even for different particle sizes of the same coke.

On the other hand, a unique curve was found for each coke and particle size when different temperatures were used. This allows us to develop a simple method to measure activation energies and to compare values obtained at different temperatures for different materials.

Looking for the most convenient index to compare the reactivities, several parameters were measured and correlated. The results shown in table I, point out that  $R_i$  and  $R_m$  are, in this case, equivalent (table II)

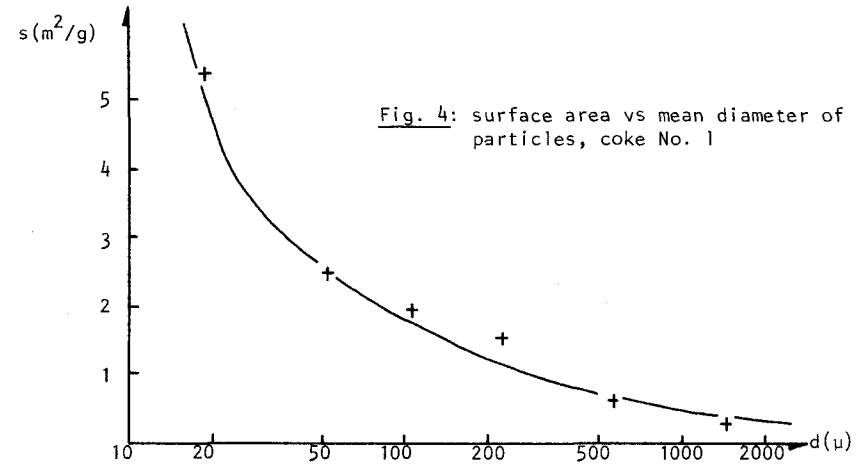
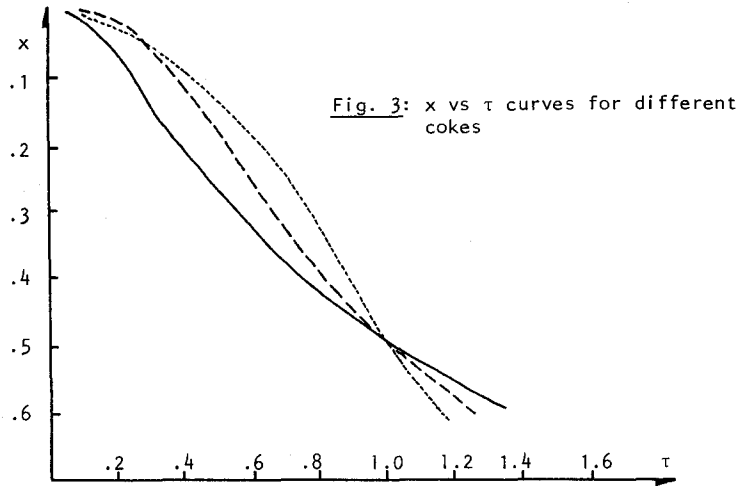


Table 1: Properties of petroleum cokes

N°	[Fe]	[Si]	%S	[V]	[H]	[Na]	[Ti]	s*
1	350	320	1.28	110	1000		13	2.43
2	300	200	1.13	86	860		6	
3	230	240	1.18	114	800	250	8	
4	310	260	1.28	134	660	210	8	0.93
5	300	190	2.20	230	680	180	8	
6	310	160	2.50	156	750		8	
7	290	530	2.4	134	800		10	
8	320	260	1.8	132	810	180	6	9.3
9	400	310	1.6	100	600		14	
10	280	200	1.4	59	600		7	
11	370	300	2.8	210	1270		11	3.2
12	220	180	0.92	66	770		6	4.2
13				145	1550			
14				207	1700			
15				416	960			9.3
16				400	1300			
17	220	250		40		360	4	
18	270			14		190	3	
19	240	160	1.8	162	700	220	4	
20	280	280	1.5	85	900	180	4	
21	320	350	2.5	112	400		6	
22	220	180	1.0	123	1100	300	6	
23	270	130	2.7	129	580		5	
24	280	320	1.8	153	920	280	8	

\* specific surface measured on 230/400 fraction

Of all the other possible indexes of reactivity considered, the best correlation, which is a very good one, was found with  $1/t_{1/2}$  and, for this reason, we have adopted this index to measure and compare the reactivity of petroleum cokes. According to our results, we feel that those methods based on the measurement of total weight loss after a given time, should not be considered as fully reliable.

It was found that although the oxidation rate by unit mass can vary with particle size, this is not due to the presence of in-pore diffusion limitations in our experiments. In fact, when the rate is expressed by unit of surface area, it is independent on particle size. This fact, together with the activation energy values obtained, clearly show zone I conditions for the air oxidation reaction in our experiments. The change in reaction rate with particle size is due to a change in accessible surface area caused by the opening of closed porosity when the coke is ground (Fig. 4).

The activation energy values obtained ranged between 37 and 41 Kcal/mol in perfect agreement with those usually found for impure carbons (7).

Reactivity of carbonaceous materials is influenced by several factors of which chemical purity, specific surface and thermal treatment seem to be the most important ones.

The initial surface area of several cokes was measured. Although large differences in initial specific surface were found (table 1), it is not easy to ascertain its influence on overall reactivity as done by  $t_{1/2}$ . In fact, different cokes can show a quite different evolution of surface area with burn-off.

Correlations between reactivity, as measured by  $t_{1/2}$ , and impurity content were looked for. Those impurities that are currently measured on as received coke shipments were considered (table 1). Significant correlations

were found with Vanadium and Hydrogen content. No other impurity considered gives a significant correlation. The regression equation obtained is

$$10^3/t_{1/2} = 1,198 + 0,0227 [V] + 0,0363 [H] \quad (12)$$

Fig. 5 shows the relation between calculated and experimental values. It can be seen that equation 12 gives a reasonable estimation of reactivity although differences as high as 20% can be expected. These differences reflect the effect of other impurities, structural factors, etc.

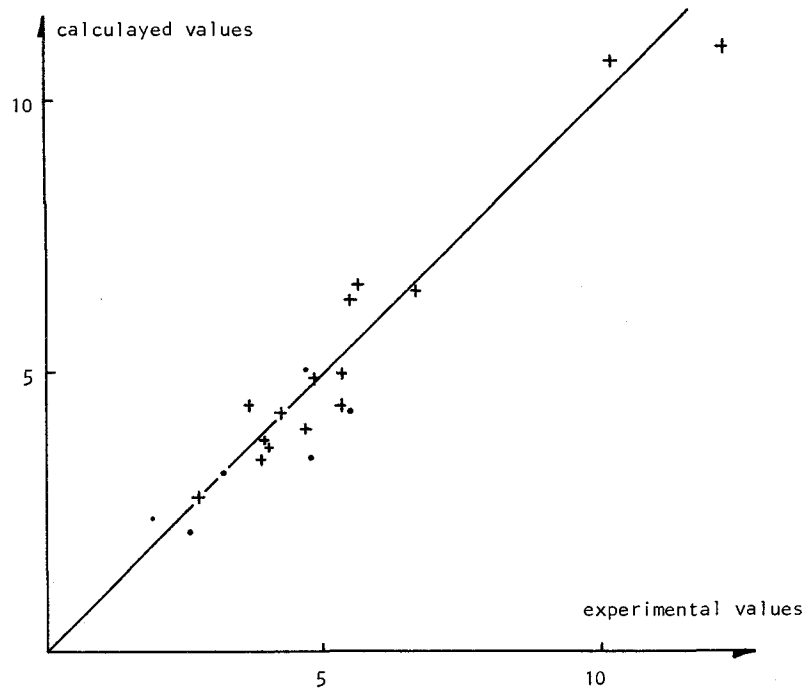


Fig. 5: Equation 12. calculated values vs experimental values  
 + cokes used to determine regression equation  
 o cokes not used to determine regression equation

Most of the cokes were studied as received from the calciner, so it is not possible to ascertain its previous thermal treatment. In order to establish limitations of equation 12 due to this fact, several cokes were further calcined in the laboratory (1200°C, 24 hs, N<sub>2</sub> atmosphere). Remarkable changes in reactivity were observed (Table II). The changes were much greater than those expected from the mere contribution of H in equation 11. This observation indicates that H content itself does not suffice to take into account previous thermal history effects on reactivity.

As was pointed out, a correlation between reactivity and impurities such as Fe, Ti or Na was not found despite the fact that these impurities are

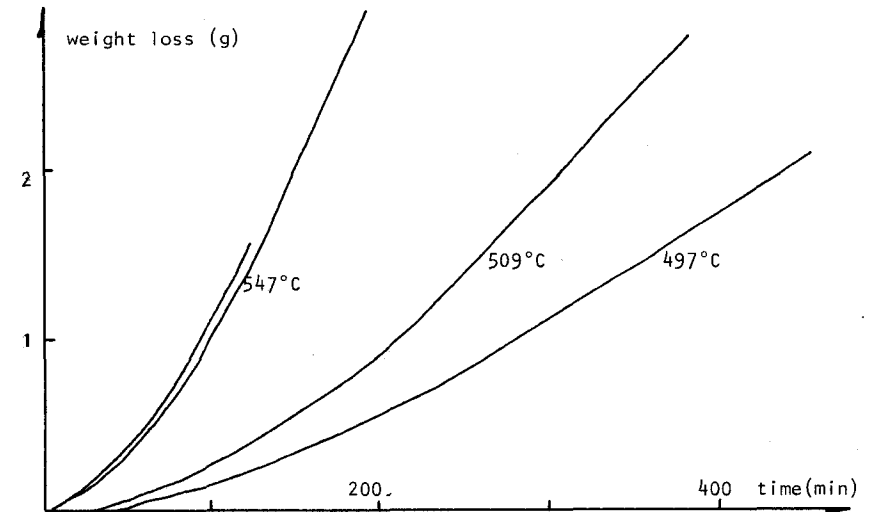


Fig. 6: Weight loss vs time for samples taken from the same anode

Table II: Air reactivity data of petroleum cokes, correlation between different parameters (500°C, 230/400 mesh fraction)

N°	$R_i \times 10^3$	$R_m \times 10^3$	$\frac{10^3}{t_{1/2}}$	$\frac{10^3}{t_{0.1}}$	$r_o \times 10^{-3}$	$r_m \times 10^{-3}$	$x_{100}$	$x_{50}$	$\frac{10^3}{t_{1/2}}$ #
1	1.17	1.63	4.67	19.5	1.45	3.92	0.222	0.095	0.57
2	0.99	1.37	3.83	15.6	1.23		0.187	0.076	0.73
4	0.95	1.31	3.67	14.7	0.95	3.16	0.167	0.090	
5	1.33	1.80	5.61	19.7	1.17	5.13	0.265	0.067	2.68
6	1.09	1.53	4.16	14.7	0.62	3.87	0.170	0.062	
7	1.42	1.99	5.35	17.5	0.91		0.232	0.082	
11	1.44	2.03	5.40	18.0	0.81	5.24	0.232	0.083	
13	1.36	1.86	5.29	24.0	1.64	4.07	0.285	0.127	1.19
14	1.76	2.48	6.62	22.0	1.39	6.49	0.330	0.118	3.52
15	3.22	4.49	12.3	45.5	1.22	11.1	0.582	0.310	
16	2.65	3.68	10.2	40.0	2.87	9.02	0.520	0.246	
17	0.49	0.67	1.94	9.7	0.68		0.095	0.040	
18	0.55	0.75	2.18	11.5	1.22	1.74	0.112	0.058	
19			4.67						
20			4.75						
21			3.92						
22			5.49						
23			4.26						
24			4.82						
$r^2$	---	.997	.997	.947	.249	.985	.976	.900	

# after laboratory calcination (1200°C, 24 hours, N<sub>2</sub> atmosphere)

well-known oxidation catalyst. This is due to the relatively constant level of this impurities in most of the cokes studied.

Although only preliminary measurements were done, it is thought that similar procedures could be developed to study coke reactivity with CO<sub>2</sub>.

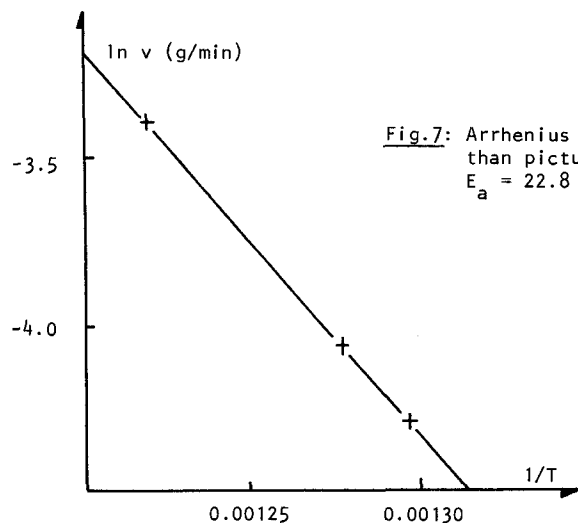
The measurement of reactivity of anode samples.

As it was pointed out in paragraph 3, in-pore diffusion plays a relevant role in the air oxidation of anodes. This fact must be taken into account if a useful procedure to measure reactivity is desired.

We have mentioned that the presence of temperature gradients in the anode tends to increase the relative importance of porous texture as a factor that determines anode burning. At the same time the influence of chemical reactivity can be smaller than the one showed by equation 3.

As these effects are difficult to assess quantitatively, the most reasonable method to characterize anode reactivity is the oxidation of a sample under zone II conditions. To reach this conditions, it is necessary to use relatively large samples and fast reaction rates.

Preliminary experiments (9) made clear that a very good control of sample temperature was necessary. Otherwise, uncontrolled sample heating becomes a serious source of error. Provided that the sample temperature remains constant during the experiment, the thermogravimetric curves are similar to those reported by Walker et al (6) and other authors for the gaseous oxidation of baked carbons. In all cases, an initial period in which the slope of the curve increases progressively is followed by an extended zone where it remains constant (Fig. 6). It was then considered convenient to measure the reactivity of the sample by this constant slope, which is usually reached after a weight loss of about 10%. Several samples taken from the same anode were measured at different temperatures, allowing an apparent activation energy of 22,8 Kcal/mol to be determined. (Fig. 7)



Most of the measurements were performed at temperatures near 530°C and, by using the activation energy value indicated above, they were referred to a reference temperature of 527°C.

Using effective diffusivities and rate constant values as well as the usual criteria for diffusion controlled reactions (6,8) it can be shown that the oxidation takes place in the in-pore diffusion regime or in conditions close to it. This is further confirmed by the properties of oxidized samples which show a hard and unreacted core as well as by the activation energy value quoted above. Measurements of air reactivity were applied to the study of the influence of baking temperature on anode properties. For instance, let us consider the data quoted in table III. Several samples were drilled from a low temperature baked anode (HTM 950-1000°C).

Table III: Air reactivity of samples from the same anode.

Type	Treatment	1	2	3	4	5	6	$\bar{R}$	$\sigma$	sign level
1		15,9	15,6	14,9	15,7	15,3	14,7	15,35	0,47	95%
2	1100°C	14,7	13,9	15,4	14,4	14,4		14,36	0,55	
3	1200°C	13,1	12,3	11,8	11,8	12,0		12,20	0,54	99%

Air reactivities were measured after a previous heat treatment in the laboratory (12 hs at stated temperature). As is shown only small, although statistically significant, differences were observed between the different group of samples. Similar figures were obtained through extensive measurement on plant and laboratory baked specimens. Then, it is clear that the influence of HTT on overall reactivity is relatively small. In spite of this as discussed later HTT is quite important in deciding anode behaviour in reaction with oxidant gases.

Oxidation selectivity

As it is well known, differences in the reactivity between filler and binder cokes in an anode, result in selective oxidation of one of the phases. This selective oxidation is responsible of the eventual detachment of carbon particles during electrolysis. This fact in addition to increasing carbon consumption, causes important interferences with normal pot operation.

Selective oxidation has been studied specially in connection with CO<sub>2</sub>, as some authors consider that it is related with dust formation in anode-bath interface. However this selectivity is also present in air oxidation.

Several procedures have been reported in the literature in order to evaluate oxidation selectivity with CO<sub>2</sub> (14,19). We have adopted a mechanical treatment after controlled air oxidation, as described in the experimental section.

Considering the data listed in table IV, it can be seen that loose carbon diminishes quite markedly as HTT is increased, indicating a much more uniform reactivity of both carbonaceous phases.

Table IV: Loose carbon after oxidation - samples from table III

Type	1	2	3	4	$\bar{Lc}$	$\sigma$	sign level
1	21	14,8	18,2		18,0	3,1	99,9
2	8,5	8,2	8,7	10,4	8,9	1,0	99,9
3	4,8	3,6	3,4		3,9	0,7	

This is further evidenced by the surface texture of the samples after testing (Fig. 8). Low temperature samples show an extremely irregular surface with protruding coke particles, while those calcined at 1200°C show an uniform surface.

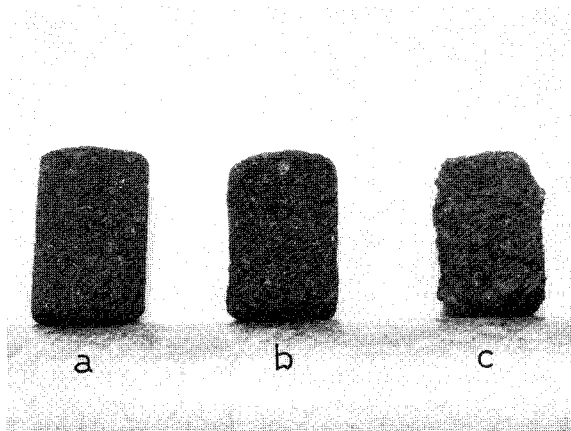


Fig. 8: Aspect of samples after air oxidation and mechanical treatment. a) 1200°C sample b) 1100°C sample c) original sample

The calcination temperature of petroleum coke was, in this case, about 1150°C. Then, it is thought that its reactivity is only slightly modified by heat treatment at 1100°C or lower temperatures. Accordingly, most of the variation in reactivity between the first and second row in table II must be due to changes in the reactivity of pitch coke. Since it represents a small part in the mass of the sample (about 10%) a small change in overall reactivity is probably due to a larger change in pitch coke reactivity.

Calcination at 1200°C is surely accompanied by variations in reactivity of both carbonaceous phases, as the petroleum coke was originally calcined at a lower temperature. This is evidenced by H content of samples (original petroleum coke: 0,089%; original baked carbon 0,104%; 1200°C sample: 0,053%) and explains the much more important variation in overall reactivity found after calcination at 1200°C.

The described data led us to conclude, in agreement with Guerin (12) and other authors, that, except perhaps in the 1200°C samples, the most reactive phase in air oxidation is pitch coke. Jones et al (3) do not coincide

with this idea and think that it is the less reactive one.

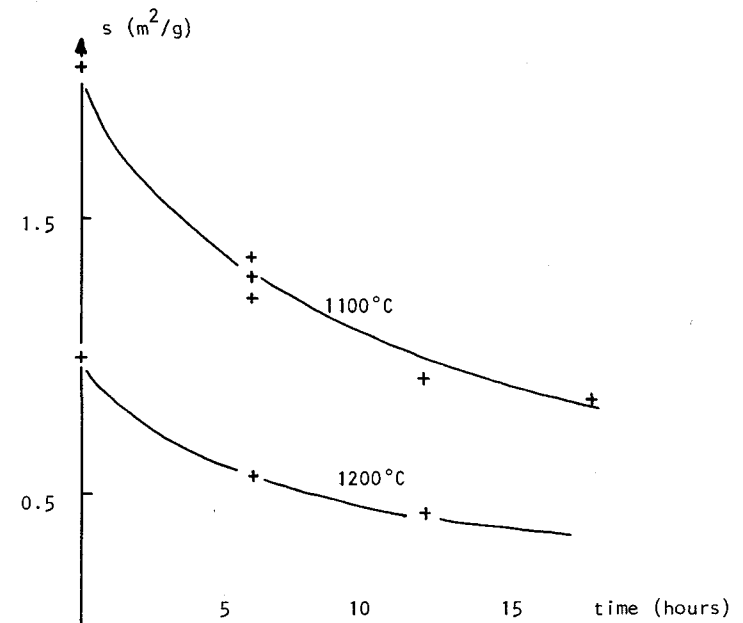


Fig. 9: Influence of thermal treatment on surface area.  
Calcination program: 0-200°C 2 hs  
200-600°C 22 hs  
600-1100°C 7 hs  
Time at highest temperature of treatment variable

Fig. 9 shows the influence of calcination history on surface area of laboratory prepared carbons. Specific surface of original coke aggregate was 2,24 m²/g. It can be seen that in all cases surface area of baked samples is smaller than that of the dry mix. It is also shown that the surface area in the low temperature baked carbons decreases considerably after a more severe calcination treatment. This facts suggests that a great proportion of the original area of the coke is blocked and that most of the accessible area in the baked carbon is contributed by the binder coke. This, in turn, explains why the binder phase is the most reactive one, except perhaps at the higher temperatures of calcination.



## Nomenclature

$v_o$  = reaction rate expressed by unit volume in the absence of any diffusional limitation (mol/cm<sup>3</sup> sec)  
 $v$  = reaction rate expressed by unit of external surface under in-pore diffusion conditions (mol/cm<sup>2</sup> sec)  
 $k_o$  = rate constant expressed by unit of surface area (cm<sup>3</sup>/m<sup>2</sup> sec)  
 $k_o^o$  = preexponential factor in Arrhenius relation (cm<sup>3</sup>/m<sup>2</sup> sec)  
 $s$  = specific surface (m<sup>2</sup>/g)  
 $\rho$  = apparent density (g/cm<sup>3</sup>)  
 $c$  = oxidant gas concentration in bulk gaseous phase (mol/cm<sup>3</sup>)  
 $E_a$  = activation energy (Kcal/mol)  
 $De$  = effective diffusivity in porous medium (cm<sup>2</sup>/sec)  
 $D_o$  = diffusion coefficient in bulk gaseous phase (cm<sup>2</sup>/sec)  
 $\epsilon$  = porosity  
 $Bo$  = permeability constant  
 $d$  = pore diameter (cm)  
 $\bar{d}^2$  = quadratic mean diameter of pores (cm)  
 $\lambda$  = mean free path of molecules in gaseous phase (cm)  
 $q$  = tortuosity factor for bulk diffusion  
 $q_v$  = tortuosity factor for viscous flow  
 $t$  = time (min)  
 $t_{1/2}$  = time needed to reach a 5,0 % consumption (min)  
 $t_{0,1}$  = " " " " " 10 % " (min)  
 $\tau$  =  $t/t_{1/2}$  reduced time  
 $m_o$  = initial mass (g)  
 $m$  = mass consumed at time  $t$  (g)  
 $x$  =  $m/m_o$  fraction consumed at time  $t$   
 $x_{50}$  = fraction consumed at  $t = 50$  min  
 $x_{100}$  = " " " " = 100 min  
 $r$  =  $\frac{1}{m-m_o} \frac{dm}{dt}$  weight loss rate of coke by unit mass (min<sup>-1</sup>)  
 $r_o$  = initial value of  $r$  (min<sup>-1</sup>)  
 $r_m$  = maximum value of  $r$  (min<sup>-1</sup>)  
 $R_m$  = medium reactivity index  
 $R_i$  = integral reactivity index  
 $[x]$  = concentration of  $x$  in coke (ppm)  
 $\% x$  = weight percentage of  $x$

$r^2$  = correlation coefficient  
 $R$  = weight loss rate of anode sample (mg/min)  
 $Lc$  = loose carbon after oxidation and mechanical treatment (%)

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