

## ANODE CARBON REACTIVITY

S. S. Jones, Sr. Staff Research Scientist  
R. D. Hildebrandt, Staff Research Engineer

Kaiser Aluminum & Chemical Corporation  
Pleasanton, California

Introduction

Anode carbon is consumed by four substantially different mechanisms as shown in Figure 1. About 79% of the carbon is removed by the electrolytic process in which atomic oxygen, as  $O^{-2}$ , is deposited with the primary formation of  $CO_2$ . Of this amount, about 12% represents excess carbon consumed due to metal current inefficiency from the oxidation by primary  $CO_2$  of reduced metal species in the bath. The third mechanism is airburn of the top part of the anode during cell operation, and accounts for about 17% of total carbon consumption. The fourth mechanism, responsible for about 4% of total carbon consumption, is the reduction of primary  $CO_2$  by carbon in the pores just above the electrolytic face of the anode, and by free carbon in the bath. Both  $CO_2$  and  $O_2$  oxidation reactions can cause mechanical loss of anode carbon and dusting in the cell bath. While it is very difficult to reduce carbon losses by the first two mechanisms, carbon oxidation by  $CO_2$  and  $O_2$  can be reduced significantly. This paper is devoted to this aspect of anode reactivity.

Carbon structure and impurities are factors which affect both  $CO_2$  and  $O_2$  thermal oxidation reactions. These reactions occur on exposed carbon surfaces and carbon structure affects the amount of such surface, while impurities which are oxidation catalysts affect specific surface reactivity. From a structural viewpoint, anode carbon may be considered as an array of graphite crystallites with various sizes, shapes, and orientations, permeated by voids and interspersed with foreign matter, some catalytic, some inactive. Graphitic carbon is physically and chemically very anisotropic, individual crystallites having the layer structure shown in Figure 2. Electrical and thermal conductivity are higher in the direction parallel to the layer planes than perpendicular to the planes. The layers also show great weakness to shear and cleavage. Reactivity of layer edges (A direction, Fig. 2) to thermal oxidation reactions is much greater than in the direction perpendicular to the basal planes (B direction, Fig. 2). Thus, carbon structures with much higher exposure of basal planes than layer edges, such as Types I and II in Figure 2, have lower reactivity than those, such as Type III, with high edge-to-plane surface area. In practice, crystallites are so small and disordered in arrangement that little use can be made of this fact to reduce carbon reactivity. Actually, such microstructural factors are of less practical importance than carbon macrostructure, or porosity, in affecting reactivity.

Significant reduction of carbon losses from airburn of anode tops and  $CO_2$  oxidation of anode bottoms can be achieved by optimizing composition and fabrication factors. Anodes consist of varying amounts of butts, delayed, fluid, and binder cokes, and voids. The reactivity of these constituents to  $O_2$  (air) and  $CO_2$  has been determined both separately and in anode composites. The influence of carbon structure and foreign matter (impurities and additives) on reactivity has been examined. The mechanisms of binder-filler oxidation bond failure have been considered.

Foreign matter is more important than normal carbon structure variation in affecting anode reactivity. Vanadium and iron impurities and reduction cell bath salts are some of the most active foreign materials which increase carbon reactivity. For this reason, binder cokes and butt particles usually are the least and most oxidation-sensitive, respectively, of all anode constituents. Binder-filler airburn bond failure occurs on the filler side of the interface for many fluid and delayed coke composites, but  $CO_2$  oxidation failure occurs on the binder side for fluid coke composites. Higher heat treatments generally reduce anode carbon reactivity even when extended well above the normal bake range. However, two high-baked full-size anodes did not benefit from this increased oxidation resistance due to higher thermal conductivity. The best sample anode carbon yet encountered in the laboratory is vitreous carbon.

In particular, pores with diameters greater than a micron appear to be the most important structural factor in carbon reactivity (1). While such pores greatly increase the carbon reaction surface, reactivity can be significantly reduced by accumulation of reaction products which inhibit oxidation.

While the carbon structural factor has been found to influence reactivity significantly, particularly in carbons heat-treated below 1000°C and above 1300°C, the catalytic effect of impurities has been found of even greater importance in the middle-temperature range where most anode carbon is conditioned. Reactivity is enhanced not only by certain impurities (particularly transition elements) present in the carbon, but also by some reduction cell bath constituents which are added to the carbon during fabrication. The overall effect of these noncarbon materials can produce a ten to hundredfold change in carbon reactivity as measured in the laboratory. While foreign materials may catalytically affect both CO<sub>2</sub> and O<sub>2</sub> oxidation reactions, the specific effects for the two reactions differ both qualitatively and quantitatively with the catalyst involved, and also with the chemical form and state of subdivision and distribution within the carbon (2).

During this study, carbon reactivity to CO<sub>2</sub> and O<sub>2</sub> (air) has been determined for a wide range of anode materials (delayed, fluid, and binder cokes, and butts) both separately and in composite form, in the laboratory, and full-size anodes were cell-tested in one case. The influence of structure and purity factors has been investigated, as well as certain variables related to the constitution and heat treatment of prebake and Soderberg composites. Mechanisms of binder-filler oxidation bond failure have also been considered.

#### Experimental

Carbon reactivity to CO<sub>2</sub> and air was determined by before-and-after weight-loss measurements on specimens of aggregate (-28/+200 mesh) and composite (10-20 grams) exposed to excess flowing air at 550°C and 650°C, and to flowing CO<sub>2</sub> at 970°C. In addition, continuous weight-loss measurements were made on half-gram samples of these materials by thermogravimetric analysis (TGA). Specimens were subjected to flowing oxidant gases while the temperature was increased, usually at 1°C/minute. Rate of weight loss (DTG) measurements were plotted against increasing time-temperature. Extensive use was

made of optical microscopy, with reflected polarized light, to examine the microstructure of polished, epoxy-mounted carbons. Scanning electron microscopy (SEM) with microanalysis by energy-dispersive x-ray (EDX) was also used on selected carbons to determine structure and the distribution of various foreign materials within the carbon. Transmission electron microscopy (TEM) was used to examine the structure of various carbon blacks used in this study. Laboratory Hall cell electrolysis tests were made on selected anode carbon specimens to determine anode carbon efficiency. Conventional analytical techniques were used to determine foreign materials in a variety of coke samples. Standard carbon laboratory procedures were used in coke and composite property measurement, and in the preparation of prebake and Soderberg composites.

#### Results

##### Oxidation of Cokes

A variety of cokes were examined for oxidation sensitivity, including delayed and fluid petroleum cokes, pitch cokes, metallurgical cokes, and vitreous carbon. Particular attention was given to relating specific impurities to coke oxidation catalysis. This proved to be difficult to do generally, but relatively clear association has been found for vanadium and iron catalysis. An example of this correlation is shown in Figure 3 for a coal-tar pitch coke (CTP) and a high-vanadium delayed coke (DPC(V)). By adding known impurities to pure graphite, McKee has found ignition temperatures (temperature of initial rapid oxidation) for vanadium, iron, and uncatalyzed reaction to be 490°C, 593°C, and 740°C respectively (3). In consideration of the differences in TGA technique (particularly heatup rate) and method of introducing impurities, these results agree substantially with those in Figure 3. While uncontaminated coal-tar pitch coke normally has slight impurity (0.11% ash), it appears that very little oxidation catalysis occurs. Similar results have been found with uncontaminated petroleum pitch coke which also has little native impurity (0.08% ash). These two cokes have substantially different microstructures (see Figures 16 & 17) and this fact, together with accumulated related data on other carbons, leads to the conclusion that the unusually low catalytic impurity content of these cokes is primarily responsible for their outstanding oxidation resistance.

Further evidence of the great influence of catalytic impurities on coke oxidation resistance has been obtained by comparing the resistance of the original coke with that after various purification treatments. Several efforts were made to remove significant amounts of the original impurities with a minimum of disturbance of the carbon microstructure. Acid extractions did not remove most of the impurities, but still reduced oxidation sensitivity as much as 50-80%. Coke treatment with chlorine at 1200°C removed over 90% of the impurities and produced greatly-increased coke oxidation resistance. While chlorination at higher temperatures was even more effective, the treatment at 1200°C was below the normal coke-calcination temperature and produced less carbon structure perturbation. An example of the great improvement in resistance of a low-purity low-sulfur coke produced by this 1200°C purification is shown in Fig. 4. The original coke was changed from an inferior oxidation-sensitive material to one with the oxidation resistance of pure graphite. The purified coke is clearly more resistant than a standard high-purity low-sulfur coke already used in anode carbon, shown for comparison in Figure 4.

Further efforts have been made to relate specific impurities, as they occur in various cokes, to oxidation catalysis. It has already been determined that nickel, calcium, lead, manganese, copper, and chromium, in addition to iron and vanadium, are important catalysts and also occur frequently in cokes (3). A series of cokes was analyzed for these eight elements, and the ash level and airburn sensitivity (550 & 650°C) to distinguish vanadium and iron catalysis were also determined. The collected data are shown in Figure 5. A computer multiple regression analysis was made to determine meaningful relationships between elemental analysis and airburn, but strong correlations were not found beyond those already established for iron and vanadium. For example, even though lead is known to be one of the strongest catalysts under certain circumstances, this is not at all apparent from the data in Figure 5. The absence of further strong correlations between airburn and suspected catalysts, on the basis of impurity concentration alone, is evidence of the complexity of this phenomenon.

Carbon oxidation catalysis is known to vary not only with the specific cation involved, and its concentration, but also with the chemical form of the cation-anion association and the physical distribution of the catalyst throughout the carbon. For example, carbonates tend to

show highest catalytic activity while phosphates are least catalytic, and can often act as inhibitors of oxidation (4). Also, the more finely distributed the catalyst the greater its influence. While highly-purified carbons are most resistant to oxidation, impure carbons with ash levels below about 0.5% appear most sensitive to catalysis if active elements are present. As the ash level increases above one percent, even strong catalysts tend to become less effective, and with ash levels above 5% strong catalysts can become ineffective so that the highly-impure carbon is as oxidation-resistant as the slightly-impure carbon. For example, one metallurgical coke with 9% ash is almost as resistant as the most oxidation-resistant delayed coke yet encountered, which has 0.1% ash. This disparity cannot be explained on the basis of porosity differences, but appears due to ineffective distribution of catalytic impurities in the metallurgical coke and the oxidant-screening effect of high ash levels.

The technique of scanning electron microscopy with x-ray microanalysis (SEM-EDX) has been used to examine oxidized specimens of selected cokes to determine the detailed structural association of specific insitu impurities with surrounding carbon microstructures. Localized areas with high levels of oxidation were often found to contain large (greater than 10 microns) clusters of impurity ash which had several catalytic (Fe, V, Ni, Ca) and non-catalytic (Al, Si, S) elements present. In less heavily oxidized areas, impurity-ash clusters tended to become smaller, with fewer elements per cluster. Examination was continued to the point where submicron particles of ash were found to contain only one impurity per particle, and appeared to be the precursors of the large clusters. In some cases, the submicron particles were discovered in what appeared to be the original location in the preoxidized state of the carbon. However, it was also apparent that many still-smaller catalyst particles were present which are below the level of resolution and identification of the instrument.

Airburn data have been collected on a wide variety of carbon particles as well as the standard cokes used for anode carbons. Examples of the great range in oxidation resistance and diversity of carbon types investigated are shown in the Arrhenius diagram in Fig. 6. This type of plot permits comparison of airburn rate variation with temperature for different carbons. The diagonal lines represent earlier data by Cowlard and Lewis for baked carbon (BC), close-grained graphite (CGG),

and vitreous carbon with 200 and 20 ppm impurities (VC200 & VC20) (5). While slow-coked, (10-20°C/hr) high-baked (1150°C) pitch cokes (PPS & CTPS, petroleum and coal-tar, respectively) are the most airburn-resistant cokes normally used in anode carbon, fast-coked (Conradson), low-baked (700°C) pitch cokes (PPF & CTPF) are the opposite extreme. The fast-coked pitch cokes are considerably more resistant when baked to 1200°C (1200-PPF & 1200-CTPF), but are still quite inferior to the slow-coked pitch cokes at the same bake temperature. Addition of 20% thermal black or lampblack to the slow-coked, high-baked pitch cokes also increases oxidation resistance (PPS+20T, CTP+20LB, etc.). Resistance of delayed coke increases substantially with increasing bulk density from 39 to 44 to 49 lbs/cu ft (DC-39, 44, & 49). Type M fluid coke (MFC) is less resistant than some delayed cokes and not quite as resistant at low temperatures as the corresponding green fluid coke (GMFC) probably due to porosity differences. However, this coke has more airburn resistance after thermal treatment at 2000°C (MFCTP), and much more resistance after chlorine-purification treatment at 2000°C (MFCCP). Generally, we have found that impure cokes, fluid and delayed, show only 10-20% improvement in airburn resistance after calcination of the green coke. In contrast, relatively pure cokes exhibit 90% or more improvement in oxidation resistance after calcination. This disparity between pure and impure cokes is apparently due to impurity catalysis of oxidation.

Type M acetylene black (MAB) and lampblack (LB) are two of the most oxidation-sensitive carbons in Figure 6, but thermal treatment of the lampblack to 2000°C produces a marked increase in resistance (2000-LB). The most oxidation-resistant particles in Figure 6 are Type C fluid coke with anisotropic pyrocarbon shells produced by deposition of coke from gas-phase hydrocarbon pyrolysis. This coke structure, shown in Figure 7, is in striking contrast to the less-ordered shell structure of ordinary fluid coke (from liquid-phase pyrolysis) shown in Figure 8. While the onion-like shells in ordinary fluid coke have the general orientation of crystallite layers to provide maximum oxidation resistance, the shell structures are too imperfect to be effective and the overriding factor which determines the resistance of such fluid coke is the high impurity level, particularly vanadium, which is found in many such cokes. In contrast, the higher perfection of the pyrocarbon shells in Type C fluid coke gives this material substantially greater oxidation resistance than all known fluid and most delayed cokes, even with

a considerably higher impurity level (0.5% ash) than most cokes. The milled pyrocarbon (CPC) is not quite as resistant as the unmilled spheres (BCPC), but becomes more resistant after 2000°C chlorine purification (CPCCP). The chlorine-purified unmilled pyrocarbon spheres (BCPCCP) have the greatest airburn resistance of any coke particles yet considered for electrode composites.

While CO<sub>2</sub> and O<sub>2</sub> oxidation of cokes are affected by the same carbon structure and purity factors, the relative ranking of cokes by oxidation sensitivity to these two oxidants shows great variation. Some examples of this are given in Table I, where the oxidation rates shown represent typical values for our experience with the various coke types.

TABLE I  
CO<sub>2</sub> and Air Oxidation Rates of Carbon Aggregate

Carbon Type	Weight-loss Rate (mg/cm <sup>2</sup> -hr)		
	CO <sub>2</sub>	Air	
	970°C	550°C	650°C
Fluid Coke	4	150	360
Coal-Tar Pitch	14	5	82
Petroleum Pitch	8	3	107
Delayed Hi-S	6	72	371
Delayed Low-S	19	6	221
Metallurgical	10	12	82
Uintaitite	16	42	321
Graphite	32	5	47
Butts	39	191	410
Needle	19	21	258

While coal-tar and petroleum pitch cokes are very airburn-resistant and fairly resistant to CO<sub>2</sub> oxidation, we have found only one coke which is quite resistant to both oxidants. In the other extreme, butt particles are the most oxidation-sensitive (CO<sub>2</sub> & O<sub>2</sub>) of all anode filler materials. Fluid coke, while very airburn-sensitive, is extremely resistant to CO<sub>2</sub> oxidation. In the opposite sense, we found graphite quite airburn-resistant and sensitive to CO<sub>2</sub> oxidation. While it is not true of all high-sulfur cokes, we tend to find higher catalytic impurity levels with high-sulfur than with low-sulfur cokes. For this reason, high-sulfur cokes usually have higher airburns than low-sulfur cokes.

We believe carbon structural (porosity) differences and the fact that vanadium is not a catalyst for CO<sub>2</sub> oxidation account for the lower oxidation sensitivity of high-sulfur coke to CO<sub>2</sub> than occurs for low-sulfur coke.

While it is often difficult to separate the influence of purity and porosity factors on oxidation sensitivity, it appears desirable for anode filler coke to be low in catalytic impurities, low in coarse porosity (above micron size), and relatively disordered (for strength). Our experience with the porosity of various carbon types is given in Figure 9. The lower porosity of high-sulfur fluid and delayed cokes appears desirable, as well as the strength of these materials. However, these advantages are offset by the presence of sulfur and often high levels of catalytic impurities. Here the low-sulfur sponge cokes are preferred with lower impurity levels and airburn sensitivity. And so the practical choice becomes a compromise of good and bad characteristics of each coke type. While it is not useful other than for research purposes, because of cost and fabrication problems, vitreous carbon incorporates many of the characteristics of an ideal anode carbon (5). It has approximately the same density, and conductivity (thermal and electrical) as anode carbon. It can be prepared as a nonporous single phase, without binder, by slow-coking of certain thermosetting resins of relatively high purity. Our laboratory tests (oxidation and Hall cell anode) of this carbon show it to be of such high quality as to be approached only remotely by existing practical anode fillers. But vitreous carbon serves to demonstrate the desirable properties possessed by a carbon with this unusual structure.

Coke sensitivity to oxidation by CO<sub>2</sub> and O<sub>2</sub> is so varied that no correlation has been found. An example of the scatter in such data is shown in Figure 10, where 550°C airburn has been plotted against 970°C CO<sub>2</sub> oxidation. A similar spread in the data was also found for airburn results at 650°C.

Oxidation of Composites

The composites used for anode carbons involve varying amounts of butts, delayed and fluid cokes, as fillers, with 10-20% binder coke which coats the filler and forms physical and chemical bonds to provide the necessary anode strength. Since the green pitch binder is baked in contact with calcined filler, a complex stress pattern develops as the bonds form. When

localized stresses become excessive some bonds have been found to rupture, but adequate overall anode carbon strength is achieved. This is, however, a relatively heterogeneous material from the viewpoint of reactivity, and does not oxidize uniformly from point to point within the microstructure. Factors which influence anode carbon reactivity include binder and filler coke quality, noncarbon materials, binder level, fabrication techniques, and calcination and bake history. Examples of the oxidation sensitivity of some prebake and Soderberg composites representative of our experience are shown in Table II together with results for vitreous carbon.

TABLE II  
CO<sub>2</sub> and Air Oxidation Rates of Carbon Composites

Composite Type	Wt-loss Rate (mg/cm <sup>2</sup> -hr)		
	CO <sub>2</sub>	Air	
	970°C	550°C	650°C
Vitreous Carbon	0.2	0.3	2.1
CTP-CTP (P)	2	2.6	109
PP-PP (P)	5	3.7	145
LSDC-CTP (S)	12	1.1	14.5
LSDC-CTP (P)	8	4.2	183
HSDFC-CTP (P)	8	16	233
(35 HSFC-65 LSDC) - CTP (S)	5	2.6	144
(35 HSFC-65 LSDC) - CTP (S) + 0.5 Li <sub>2</sub> CO <sub>3</sub>	15	22	245

- CTP = Coal-tar Pitch
- PP = Petroleum Pitch
- LSDC = Low-sulfur Delayed Coke
- HSDFC = High-sulfur Delayed & Fluid Cokes
- HSFC = High-sulfur Fluid Coke
- P = Prebake
- S = Soderberg

Among standard materials for anode use, pitch coke-bound pitch coke is most oxidation resistant probably due to the high purity of this carbon. The quality of pitch-coke binder is again evident by comparison of the airburn resistance of prebake and Soderberg composites made with the same materials. The increased binder-coke content in the Soderberg anode substantially reduces airburn sensitivity. The comparison between prebake anodes with low-sulfur pure coke and high-sulfur impure cokes shows the adverse effect of impurity catalysis on oxidation resistance. The additional adverse effect of butt fines (-4/+48 mesh) instead of normal butt

aggregate (-5/8"/+4 mesh) in the same high-sulfur coke composite increased 550°C airburn more than tenfold. For Soderberg composites, even with the higher pitch-coke content oxidation sensitivity is greatly increased by the addition of  $\text{Li}_2\text{CO}_3$  which is an extremely low-temperature ignition catalyst.

The influence of various filler calcination and composite bake treatments on airburn resistance of pre-bake anodes made with iron-contaminated low-sulfur coke is shown in Figure 11. Here, thermogravimetric analysis shows the significant increases in composite airburn resistance with increasing heat treatment. The high-calcination, high-bake sample has a temperature of maximum oxidation rate about 125°C higher than that for the low-calcination, low-bake sample. For the intermediate heat treatments, intermediate oxidation resistance was produced with the high-calcination, low-bake sample exhibiting more airburn resistance than the low-calcination, high-bake sample.

The influence of bake and purity factors on Soderberg composite reactivity is shown in Figure 12. Results are given for thermogravimetric analysis of airburn of two different Soderberg pastes at heat treatment temperatures of 1000°C and 1180°C. The composition of the pastes is essentially the same except for the presence of impurities and/or additives. Paste P has no additives, but is made from coke with substantially more impurities (particularly vanadium) than Paste I. Paste I contains about 1/2%  $\text{Li}_2\text{CO}_3$  and has been contaminated with iron rust. The influence of these foreign materials is quite evident from the observed airburn rates. Lithium carbonate is well known as a low-ignition catalyst and has initiated oxidation of Paste I near 425°C. The iron rust contaminant is not very highly dispersed and so exhibits hot-spot localized catalysis at 630°C which affects only a small fraction of the carbon and quickly burns out. While the higher temperature heat treatment of Paste I has removed much of the lithium carbonate catalysis, probably by decomposition of the catalyst, there has been essentially no effect on the iron catalysis. Paste P has a higher peak at 560°C than occurs for Paste I for the 1000°C heat treatment, due mostly to the higher impurity level, and probably vanadium catalysis, for Paste P coke. This disparity is substantially removed at the higher heat treatment, probably because of the greater ability of high-baked binder coke to protect the underlying sensitive filler from oxidation. When airburning Soderberg and prebake

composites with the same filler composition and heat treatment, and differing only in amount of binder, the Soderberg composite will usually exhibit the lower peak burn rate and generally lower rates at the same temperature, due to the moderating effect of the higher fraction of resistant binder coke.

All other variables remaining constant, the oxidation sensitivity of a baked composite can vary with the manner in which the green paste is compacted. If mold pressure is too low, a low-density composite results which has poor binder-filler interaction and inadequate bonding. The high void fraction of such a composite tends to increase the surface exposed to the oxidant, and relatively poor oxidation resistance results. On the other hand, if mold pressure is excessive and coke strength is inadequate, it is possible, particularly in all-coke composites without a coarse butt aggregate fraction, to incur significant press-crushing of the filler and thereby increased airburn. Newly exposed coke-fracture surfaces and fracture dust, particularly for an impure filler, will tend to increase the exposed oxidation surface and decrease airburn resistance. An example of the above conditions of underpressing and overpressing, together with a pressing at intermediate mold pressure, is shown in Figure 13 for an impure low-sulfur all-coke composite. It is important to emphasize that this phenomenon may not play a significant role in the airburn sensitivity of standard prebake anodes which use a coarse butt fraction instead of coke.

If the binder coke fraction of a composite is high and of high quality, it is possible to make a rather airburn-resistant carbon from very impure coke. A rather unusual example of this condition is shown in Figure 14, which gives TGA airburn results for a pyrolytic carbon-bonded composite of impure high-sulfur fluid and delayed cokes. Airburn results are also given for the better of the two filler cokes, thus showing, on a somewhat understated basis, the contrast in oxidation resistance that exists between fillers and composite. The microstructure of this composite is shown in Fig. 15. The composite was produced by deposition of pyrocarbon from the gas-phase coking of pitch. Gas deposition of binder coke permitted filling many voids in and around filler particles which would not be filled if liquid pitch binder were coked in the normal manner for anode carbons. The composite contains 22% anisotropic pyrocarbon binder, somewhat more than Soderberg binder coke level. While it demonstrates the role of binder coke in

reducing composite airburn, the compressive strength of this composite is low (~700 psi) due to the inherent weakness of anisotropic carbon to shear and cleavage of the layered structure. It is also not practical to make full-size anodes in this manner.

Anode carbon is normally made by slowly coking green coal-tar pitch binder around calcined coke filler to give pitch-coke bonds with the structure shown in Figure 16. This bond coke is a rather heterogeneous array of ordered and disordered carbon interspersed with shrinkage cracks. In spite of structural deficiencies, it functions quite well to impart strength, electrical conductivity, and oxidation resistance to the anode composite. In recent years, anticipated shortages of coal-tar pitch has led to expanding use of petroleum pitch binders. In contrast to the rather uniform quality which has been experienced for coal-tar pitch in the past, petroleum pitch has been found to be quite variable in quality, depending on the source and method of production. In contrast to coal-tar pitch, most petroleum pitches are less-condensed aromatic structures and have little or no quinoline-insoluble phase. This means that they undergo greater shrinkage when pyrolyzed and are converted to relatively well-ordered binder coke such as shown for the bonds between fluid coke particles in Figure 17. Such petroleum pitch coke bonds have been found to be weaker than coal-tar pitch coke bonds, and do not provide as much oxidation protection for fluid coke filler. In order to reduce petroleum pitch-coke shrinkage, increase bond strength, and provide more oxidation protection for the filler, we have investigated the influence of carbon black additions on bond improvement. The result of adding 20% carbon black (34 m<sup>2</sup>/g) to petroleum pitch binder for fluid coke fillers was a greatly-changed bond structure as shown in Figure 18. While small areas (light spots in Fig. 18) of anisotropic carbon remain, the bond has substantially the characteristics of low-density isotropic carbon. Bond coke shrinkage has been reduced, and shrinkage cracks now have the pattern of a dried mud flat instead of the larger interlaminar cracks observed for anisotropic carbon. The compressive strength of such fluid coke composites has been doubled by carbon black addition, and airburn has been greatly reduced. Most of this work has been done with fluid coke fillers to date, and great airburn reduction has not yet been observed for similar delayed coke composites, apparently because the coke used was already quite airburn-resistant.

Binder coke quality has been found to depend on the type as well as the amount of carbon black added to the pitch. Lampblack-type carbons, with surface areas of 20-70 m<sup>2</sup>/g interact more favorably with the pitch than thermal blacks with areas near 7 m<sup>2</sup>/g. The higher-surface blacks produce isotropic binder coke which is more homogeneous with much smaller pores and greater strength and airburn resistance. Typical microstructures of pitch coke modified by added thermal black and lampblack are shown in Figures 19 and 20. The large difference in the amount of anisotropic carbon in the two cokes easily accounts for the greater strength of the coke containing lampblack. The airburn superiority of fluid coke composites made with lampblack-modified pitch coke is shown in Table III in comparison with composites made using other related binder coke types.

TABLE III

Airburn of Fluid Coke Composites

Binder	Airburn at 550°C (mg/cm <sup>2</sup> -hr)
CTP (10% QI)	20
CTP (0% QI)	79
PP (0% QI)	58
PP (15% TB)	53
PP (10% LB)	26
PP (20% LB)	5

CTP = Coal-tar Pitch  
 PP = Petroleum Pitch  
 QI = Quinoline Insolubles  
 TB = Thermal Black  
 LB = Lampblack

It can be seen that quinoline-insolubles considerably improve the airburn quality of coal-tar pitch coke, and lampblack is much more effective than thermal black in improving petroleum pitch coke quality. Composite airburn resistance is improved because (1) binder coke itself is more resistant with lampblack, and (2) the fine texture of the modified coke protects the oxidation-sensitive filler to a higher degree than the original binder coke.

Mechanism of Binder-Filler Oxidation Bond Failure

For a long time, published information has indicated that binder coke is the weak element in oxidation bond failure of carbon composites (6,7). However, the present work has shown quite clearly that slow-coked pitch coke is equal or superior to almost all known filler cokes with respect to airburn resistance. While this airburn disparity might conceivably change in going from separate coke specimens to baked filler-binder composites, examination of the microstructure of oxidized composites has shown that this airburn difference is still present qualitatively. It is also clear from TGA oxidation experiments that the overall oxidation resistance of the composite increases as the binder-coke fraction is increased. While much of the microscopic examination of composites was done with fluid coke fillers, where it is particularly easy to distinguish binder and filler, some work has also been done with delayed coke fillers, and with similar results. An example of airburn failure of a bond between fluid coke and coal-tar pitch coke is shown in Figure 21. A similar example for failure of a bond between delayed coke and coal-tar pitch coke is shown in Figure 22. In both cases, it is clear that failure has occurred on the filler side of the binder-filler interface. It thus appears that in many cases of practical interest, similar results can be expected. Of course, this oxidation disparity would be smaller (or even rarely, to be reversed) as the relative airburn resistance of filler and binder cokes become more equal (or very rarely, filler coke resistance exceeds that of the binder).

While the same principles apply, the results are somewhat different for CO<sub>2</sub> oxidation of composites than for airburn. This condition exists because some fillers, such as fluid coke, are considerably more resistant to CO<sub>2</sub> oxidation than pitch-coke binder. Microscopic examination of CO<sub>2</sub> oxidized fluid coke-filled composites has revealed, contrary to the airburn results, that bond failure occurs on the binder-side of the bond. An example of this condition is shown in Figure 23. However, in many cases, the disparity of CO<sub>2</sub>-oxidation resistance between filler and binder cokes is not as great as for airburn, and bond failure can be expected to occur on either side of the binder-filler interface, depending on the specific coke involved, and on composite preparation history.

Airburn of Full-size High-baked Anodes

Thermal treatments of most filler and composite carbons above 1200°C tend to produce more ordered (graphitic) carbon, to remove sulfur (with accompanying loss of density and strength), and to remove many other impurities in varying degrees. Since impurity removal by reaction with sodium fluoride is sometimes used to purify carbons, the presence of bath salts in anode carbon may enhance thermal purification (8). Laboratory thermal treatments of a variety of filler aggregate and baked composites have been done to temperatures from 1400°C to 2000°C, at heating rates of 5 to 40°C/minute. Airburn was reduced as much as 90% with a 1400°C treatment in some cases. Heat-treating electrode samples gave better results than heat-treating aggregate.

In order to scale up the laboratory experiments for pilot cell tests, two full-size anodes (25% butts, 21% delayed coke, 54% fluid coke, with coal-tar pitch binder), previously baked to about 1150°C, were heat-treated to temperatures between 1500°C and 2000°C. The anodes were high-baked by resistance heating in a small rectangular furnace with anodes placed end-to-end in a series circuit and thermally insulated with alumina.

After high-baking, samples from the anodes were found to have from one-fourth to one-hundredth the airburn of the original baked anode, reduction being greatest for parts of the anode heated to the highest temperatures. Other changes included 75% reduction of sulfur content, 50% reduction of compressive strength, 400% increase in thermal conductivity, and little or no change in electrical resistivity. When installed in the pilot reduction cell, it became clear that the substantially higher thermal conductivity of these anodes was a serious deterrent to their use. In normal operation, the average anode temperature was 75-100°C higher than regular baked anodes. This condition greatly offset the increased airburn resistance gained by the treatment. One of the anodes was in operation only four days when airburn in the center trench region had removed enough carbon to expose the metal stubs as shown in Fig. 24.

Additional data related to the above experience were collected by measuring the appropriate properties of suitable anode composites as a function of bake temperature. The collected data are shown in Fig. 25. It can be seen that while resistivity and airburn decrease sharply to low values at high bake temperatures, along with a moderate decline in baked density, thermal



conductivity increases rather rapidly and thus accounts qualitatively for the observed behavior of the high-baked pilot cell anodes.

#### Conclusions

1. While both carbon structure and purity are important factors affecting anode reactivity, the catalytic effect of foreign matter appears more important between 1000°C and 1300°C where most anode carbon is conditioned.

2. Regarding the structural factor, porosity above one micron is much more important than submicron features of size, shape, and arrangement of graphite crystallites.

3. There is great variation in reactivity among the constituents of anode carbon, from highly-reactive butt particles to highly-resistant binder coke.

4. In contrast to previous reports of the greater sensitivity of binder coke to oxidation failure in carbon composites, we find the filler to be the weaker element in airburn bond failure for many cokes of interest.

5. While heat treatment of anode carbons is generally beneficial up to temperatures of 1200-1300°C, higher baking may upset the balance of property values required for good anodes and produce an overall negative result even though airburn sensitivity is reduced.

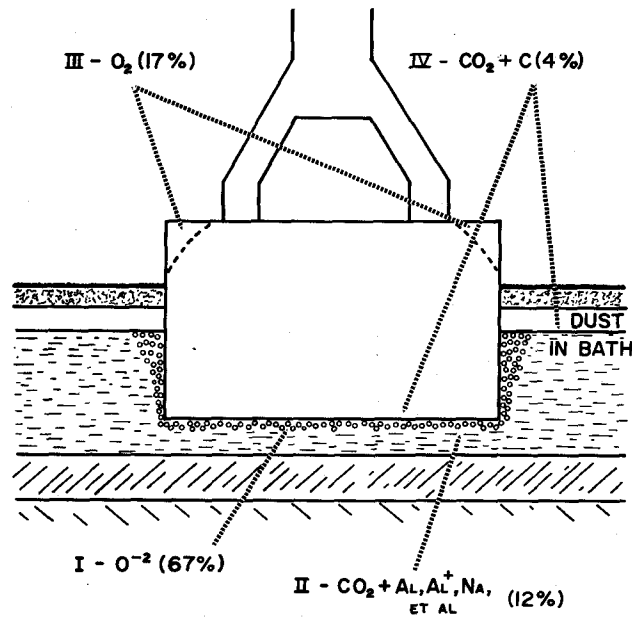
6. While useful only for research purposes, vitreous carbon has been found to have many characteristics of the ideal anode carbon. It combines adequate density and a suitable balance of electrical and thermal characteristics with a single-phase (instead of binder and filler) of essentially nonporous carbon having great strength and oxidation resistance.

#### References

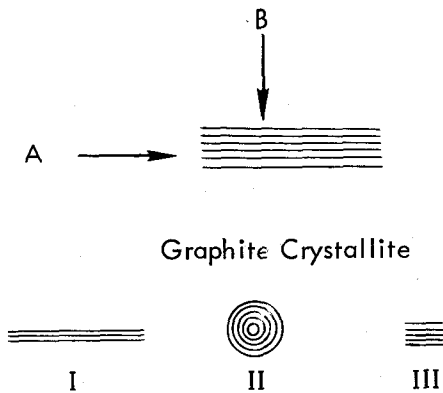
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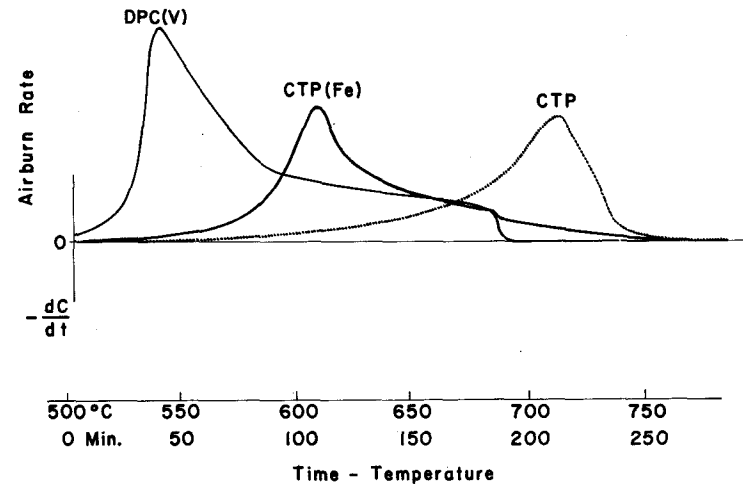
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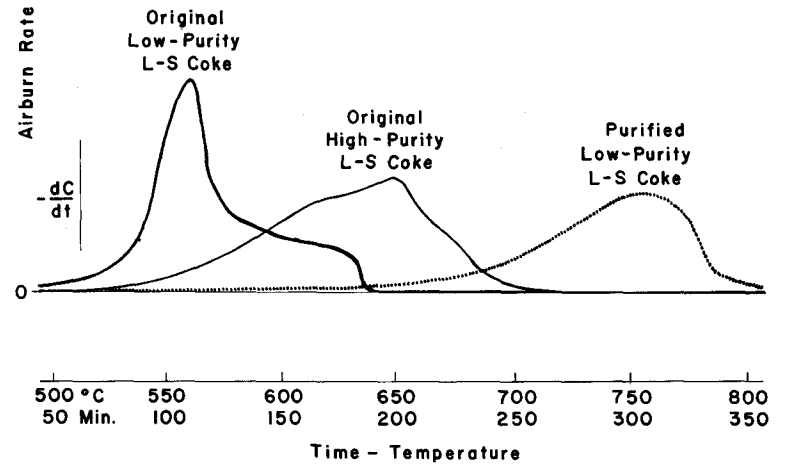
1. How Anode Carbon is Consumed



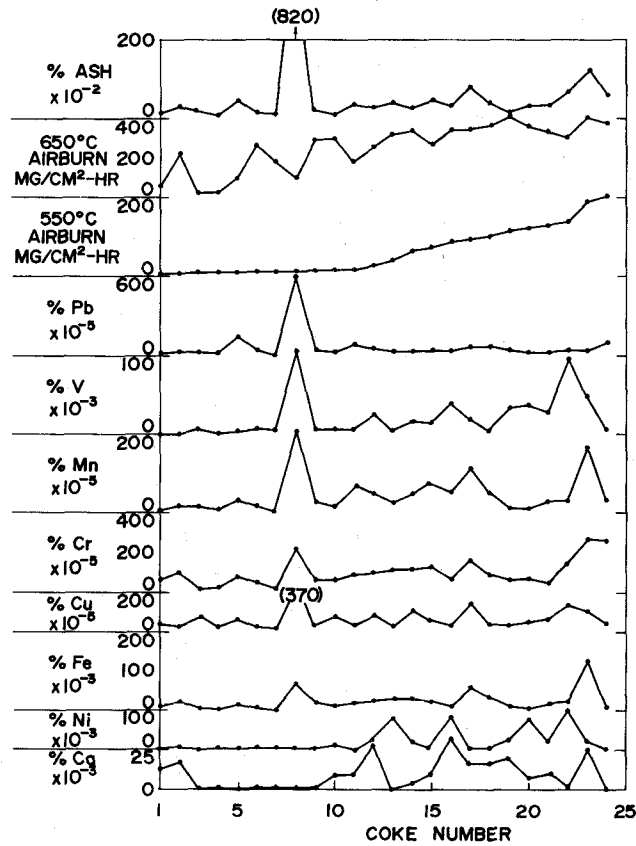
2. Carbon Microstructure



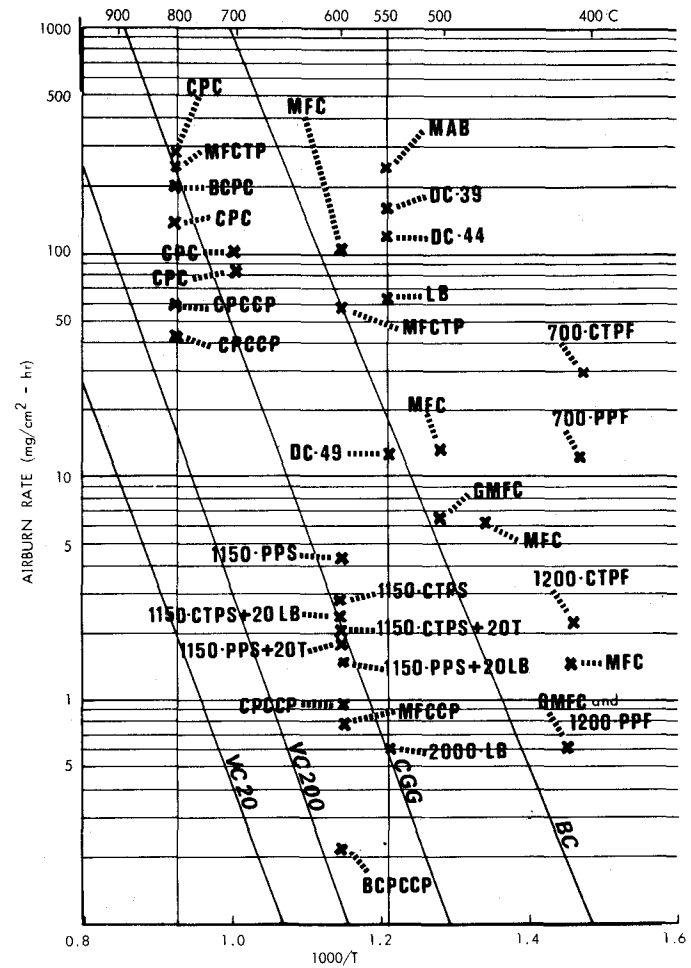
3. Impurity-Catalyzed Air-Oxidation of Coke



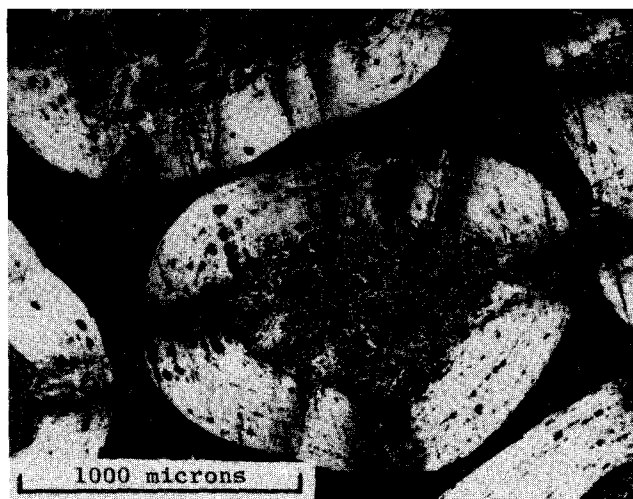
4. Purity Factor in Coke Reactivity



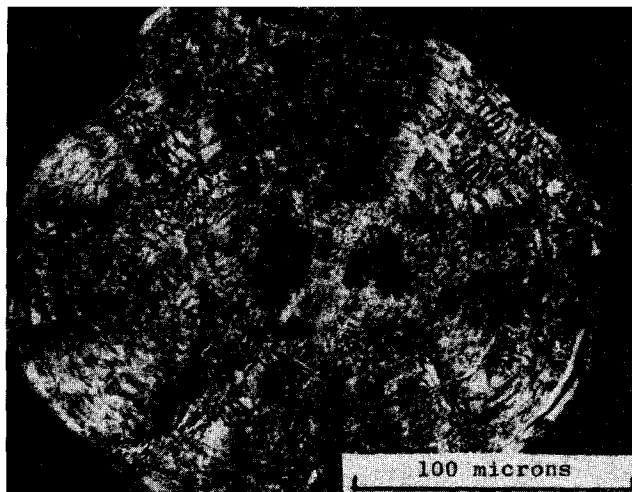
5. Airburn-Impurity Relationships for Various Cokes



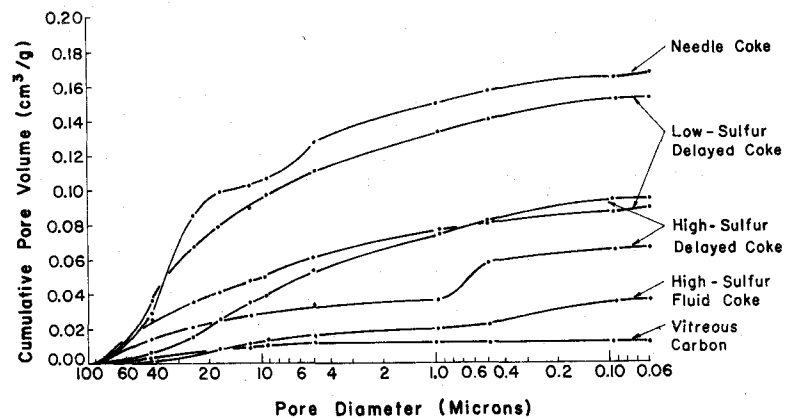
6. Airburn Rates for Various Carbon Types



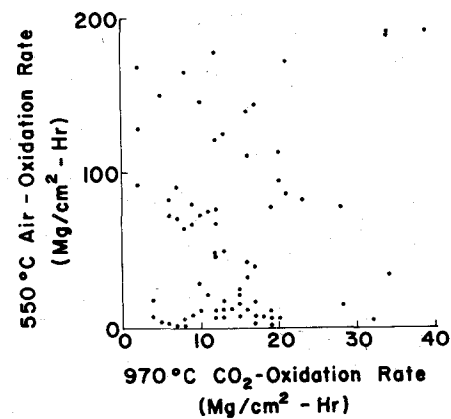
7. Cross-section of Type C Fluid Coke Showing Central Substrate on which Anisotropic Pyrocarbon is Deposited



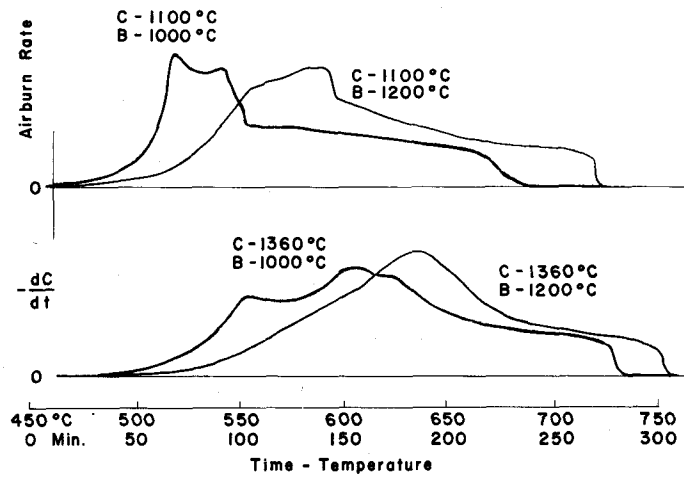
8. Cross-section of Typical Fluid Coke Particle Showing Central Substrate and Shells of Moderately-ordered Carbon



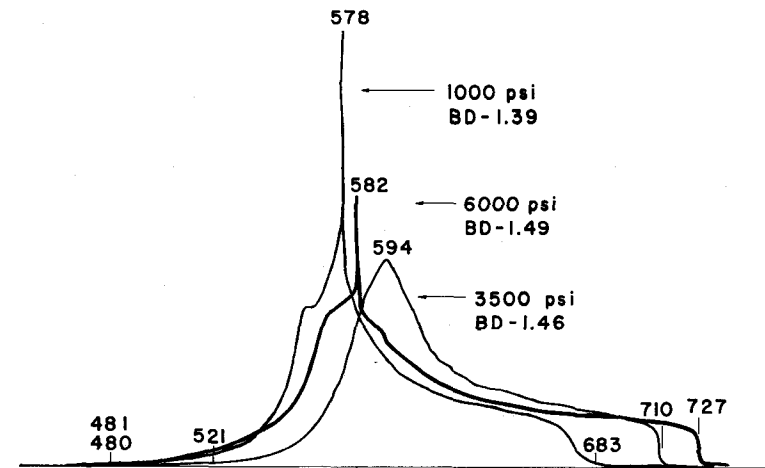
9. Porosity of Various Carbons



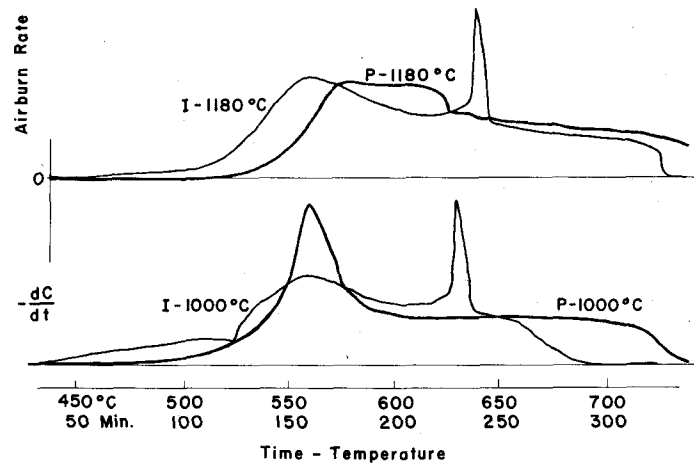
10. Carbon Reactivity to Air and Carbon Dioxide



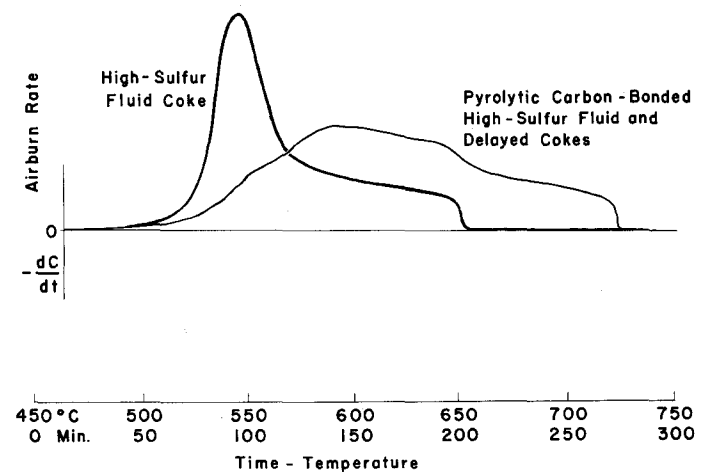
11. Bake and Calcination Factors in Prebake Composite Reactivity



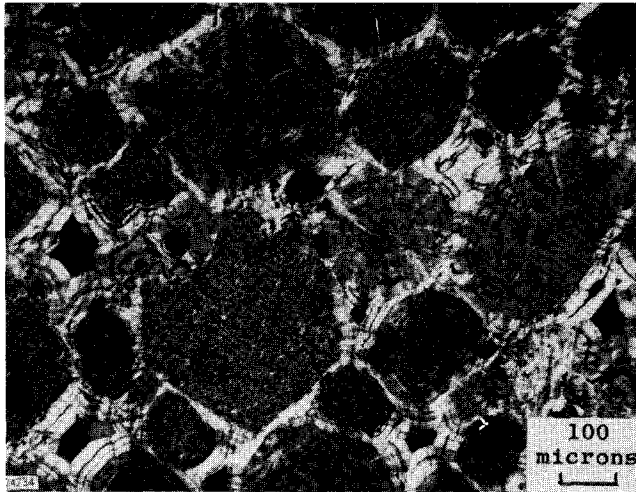
13. Compaction-Pressure Factor in Prebake Composite Reactivity (Temperature in °C)



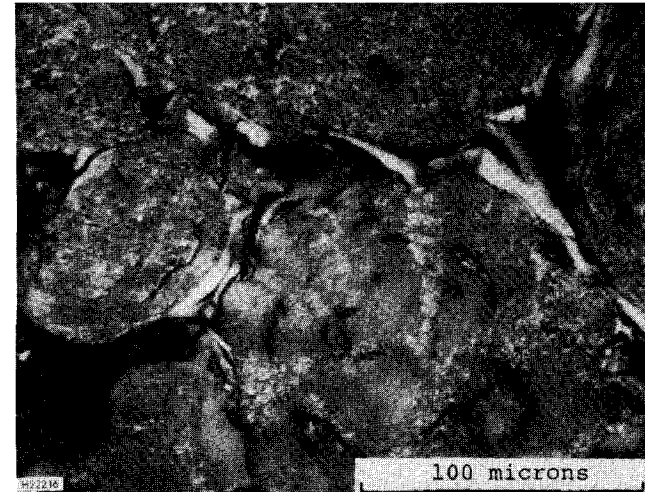
12. Bake and Purity Factors in Soderberg Composite Reactivity



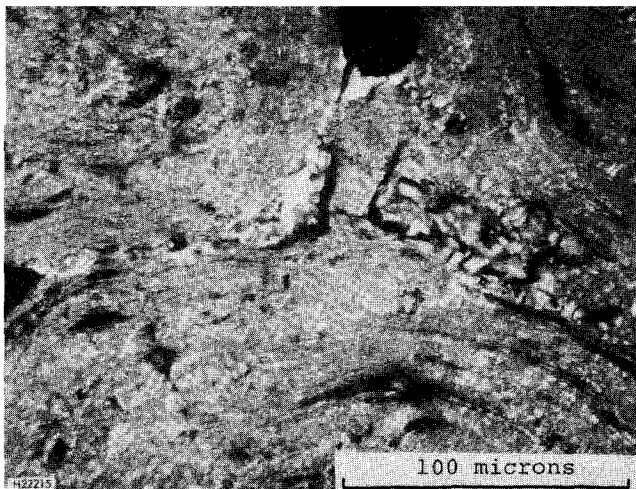
14. Binder-Coke Factor in Composite Reactivity



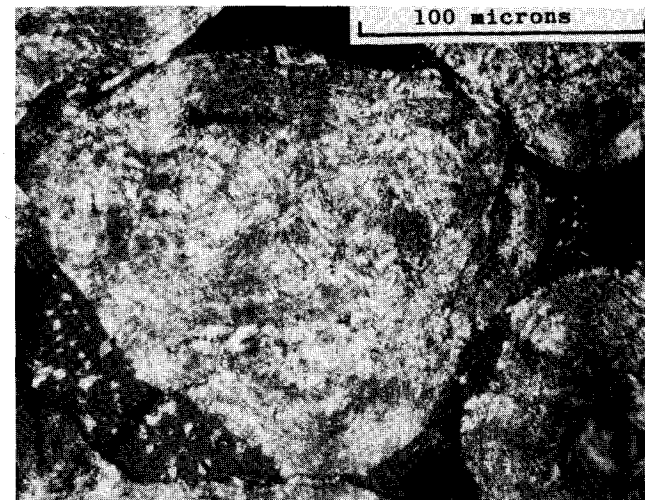
15. Pyrolytic Carbon-bonded Composite of High-sulfur Fluid and Delayed Cokes



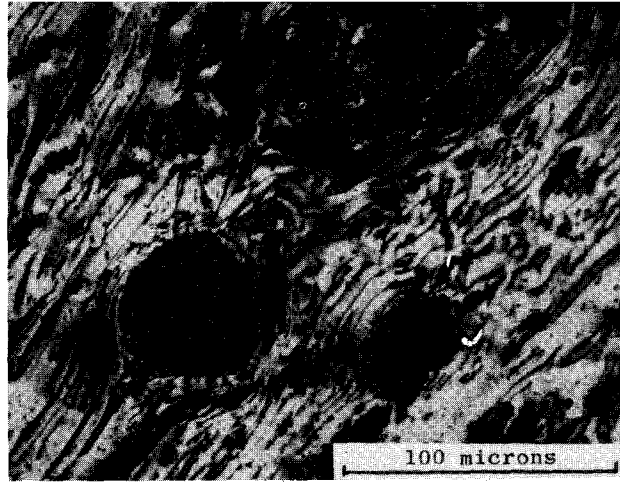
17. Petroleum Pitch Coke Bond Structure in Baked Composite with Fluid Coke



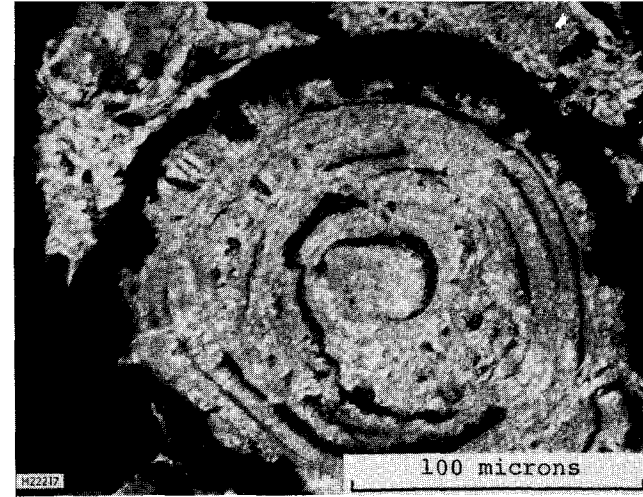
16. Coal-tar Pitch Coke Bond Structure in Baked Composite with Fluid Coke



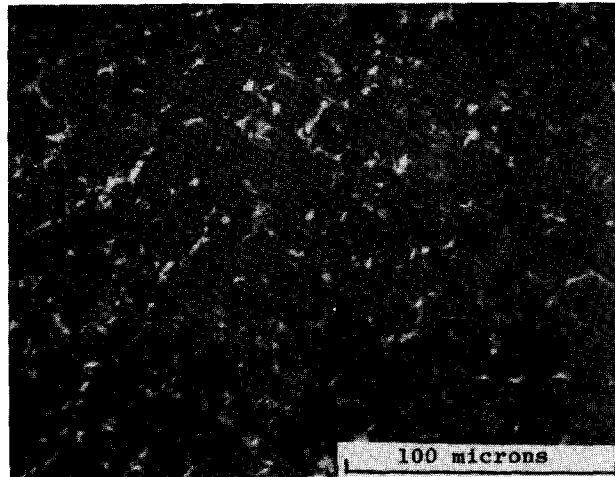
18. Baked Composite of Fluid Coke and Petroleum Pitch Containing 20% Carbon Black ( $34 \text{ m}^2/\text{g}$ )



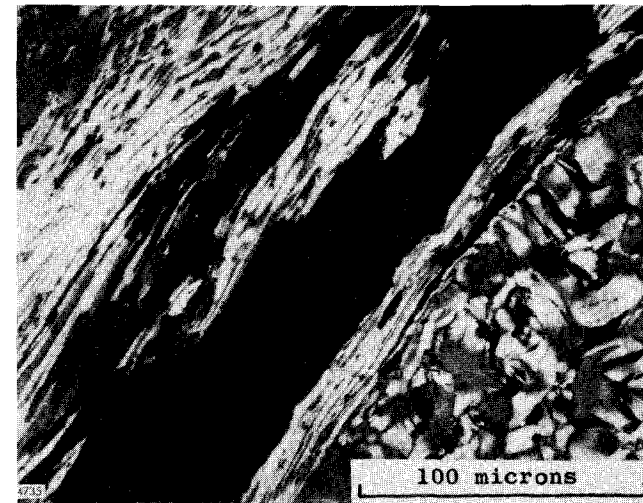
19. Structure of Petroleum Pitch Coke Containing 20% Thermal Black



21. Airburn Failure on Filler Side of Bond Between Fluid Coke and Coal-tar Pitch Coke



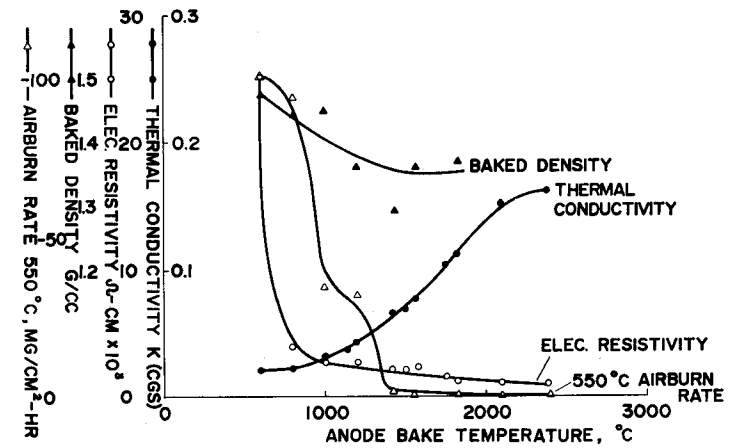
20. Structure of Petroleum Pitch Coke Containing 20% Lampblack



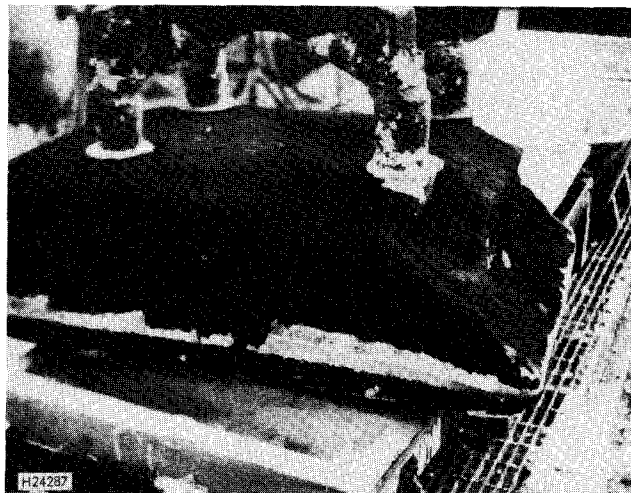
22. Airburn Failure on Filler Side of Bond Between Delayed Petroleum Coke and Coal-tar Pitch Coke



23. CO<sub>2</sub>-Oxidation Failure on Binder Side of Bond Between Fluid Coke and Coal-tar Pitch Coke



25. Anode Property Variation with Bake Temperature



24. High-baked Anode after Four Days' Cell Operation