

INFLUENCE OF HIGH-SULFUR COKES ON ANODE PERFORMANCE

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The characteristics of a variety of fluid and delayed cokes have been examined both in the laboratory and as fillers in statistically-significant numbers of full-size reduction cell anodes. Sulfur content varied from one to five percent and sulfur emission and anode performance indicated unique coke properties independent of sulfur level. Performance of high-sulfur filler anodes ranged from excellent to poor and is much more dependent on the amount of oxidant-accessible surface than on sulfur level. The significance of coke blend compatibility was investigated to improve anode performance with available fillers as coke quality changes.

Introduction

Anode carbon is consumed primarily by the aggressive electrolytic attack of nascent oxygen to form CO₂. Lesser amounts of carbon are also consumed by airburn of anode tops and from oxidation by primary CO₂ in pores just above the electrolytic face. These oxidation reactions also result in mechanical loss of anode carbon by dusting.

Earlier work on the variation of anode performance with binder and filler coke quality has already been reported (Ref 1). It was found that the prime requirement for good anode carbon is minimum surface accessible to oxidation. It is also desirable that this surface have as uniform carbon reactivity as possible. Anode surface of pores with diameters greater than one micron may be accessible to oxidation, and the surface of 1-10 μ diameter pores is particularly significant to anode carbon efficiency. Performance can be increased by reducing the extent of oxidant-accessible surface and specific surface reactivity for pores in the 1-10 μ range. Coke quality and anode fabrication practices are important factors affecting anode performance. Coke quality involves both physical and chemical properties of coke particles. Fabrication practices are designed to produce good binder-filler coke interactions which result in strong, dense anode carbon composites.

In this paper, we report results which substantially extend earlier work and are particularly concerned with the influence of sulfur on anode performance. Attention has also been given to the way in which certain blends of fluid and delayed cokes affect performance. Throughout this study, it has been important to consider the purity and structure of the cokes involved. Many impurities affect carbon oxidation rates by acting as catalysts, and coke microstructure determines the extent of oxidant-accessible surface available for reaction. The principal differences in pore spectra of various coke types, shown in Figure 1, are an important factor affecting both the available oxidation reaction surface and the ease with which thermal sulfur emissions can occur. The general structural change occurring between anisotropic low-sulfur needle coke and isotropic high-sulfur delayed coke is a decrease in open connected pores and increasing closed porosity. Representative microstructure for these two coke types are shown in Figure 2, for needle coke, and in Figure 3 for a high-sulfur delayed coke. Typical microstructure for high-sulfur fluid coke, shown in Figure 4, indicates still lower porosity, also shown in Figure 1, due to the nature of the fluid coking process. Maximum reduction of accessible porosity occurs for vitreous carbon (see Fig. 1) which, along with high purity, causes this carbon to give maximum performance as a laboratory anode (Ref 1).

The present work consists of a laboratory study of coke emissions during calcination and a pilot cell test of full-size prebake anodes containing 16 different cokes with sulfur levels from one to five percent. The pilot cell test involved 1203 20-in. anodes of 25 types which included 14 blends of delayed and fluid cokes. The results have been examined for various

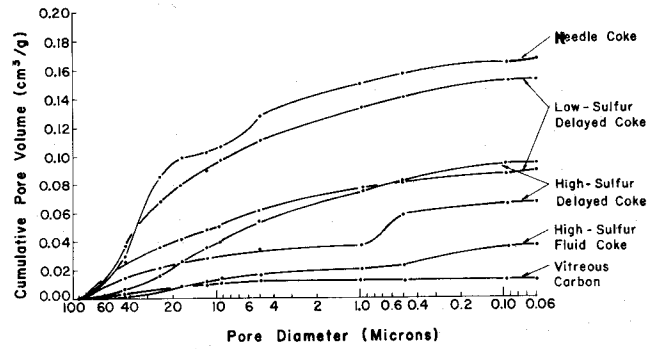


Figure 1. Pore Spectra of Various Coke Types

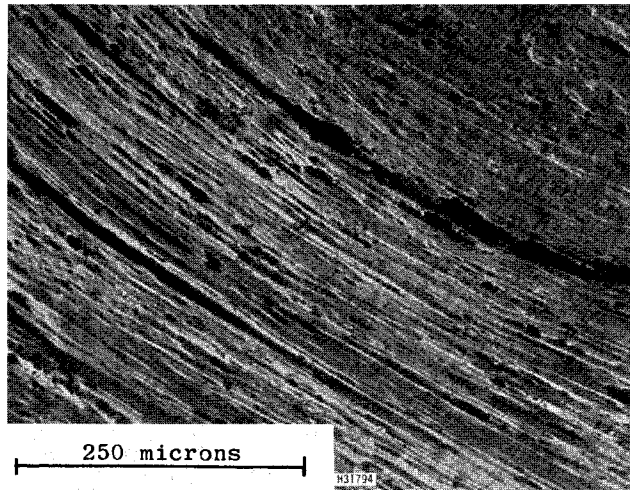


Figure 2. Microstructure of Calcined Needle Coke Produced from a Coker Feedstock of 100% Decant Oil

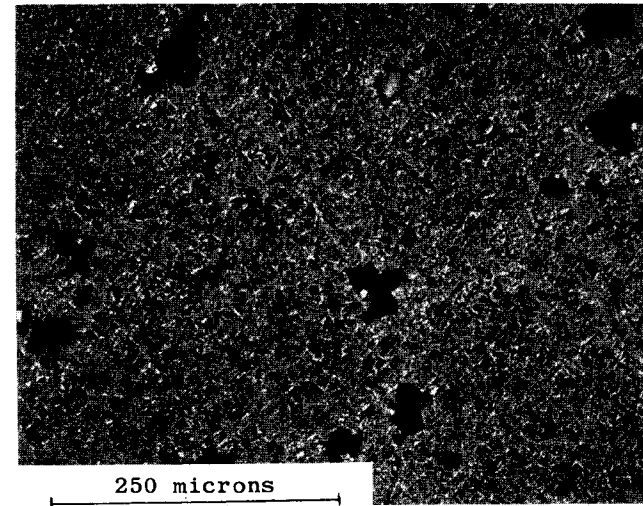


Figure 3. Microstructure of Calcined High-Sulfur Delayed Coke No. 13

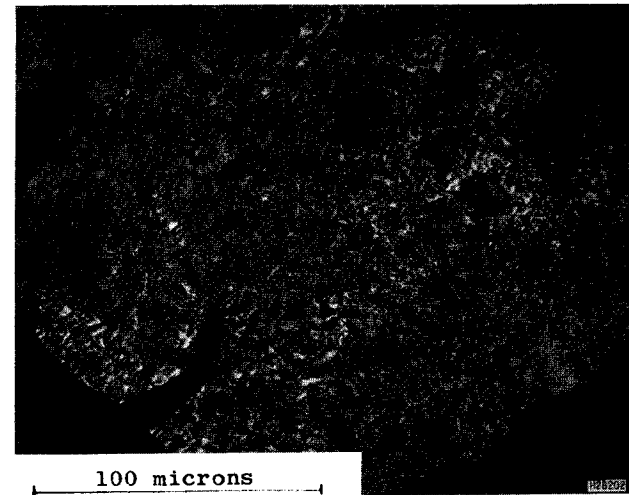


Figure 4. Microstructure of Calcined High-Sulfur Fluid Coke No. 16

correlations and subjected to linear regression analysis. Conclusions have been drawn about the influence of sulfur on anode performance and the degree of compatibility of various coke blends.

Experimental

All laboratory measurements of coke and anode carbon properties have been made as described previously (Refs 2, 3) and/or involved well-known carbon laboratory techniques.

For the pilot cell tests on full-size anodes, anode fabrication and testing procedures were the same as those described previously (Ref 1). All anodes were 20-in. tall and vibratory compacted from pastes of butts with selected coke fillers and filler blends with fluid coke. Standard prebake coal-tar pitch binder was used for all anodes with the exception of three test groups prepared with binders derived from fluid catalytic cracker bottoms, and from thermal and oxidation treatments of ethylene steam cracker tars. The properties of all four binders have been described previously (Ref 1).

Anode performance during cell operation was determined in the same way as for the earlier study (Ref 1). In final form, all net carbon consumption data were normalized to a common basis of (1) 90% current efficiency, (2) 5.70 amps/in² (0.884 amps/cm²) current density, (3) 970°C cell bath temperature, and (4) 1115°C anode bake finishing temperature. Performance normalization was done as described previously (Ref 1) and all normalized net carbon consumption values are believed to be accurate to ±0.005 lb C/lb Al.

Altogether, 1203 full-size prebake anodes have been tested involving 25 different compositions. Anode formulation involved the use of 16 different filler cokes and included 14 blends with fluid coke. Filler coke properties are described in Table I. The cokes have been arranged in approximate order of increasing sulfur content while also keeping similar coke types together. A wide range of coke types is shown with various combinations of property values. Generally, the less dense, more ordered (anisotropic), airburn-resistant cokes are listed first with more disordered (isotropic), airburn-sensitive types having higher coke numbers. However, Coke Nos. 4 and 5 are exceptions with low sulfur content but high ash, reactivity and density. All fillers in Table I are delayed cokes except No. 16 which is the fluid coke used for all coke blends.

Results and Discussion

Laboratory Investigations

Essentially all of the sulfur in anode carbon is organically bonded to the carbon polymer and no significant amounts of inorganic sulfides, sulfates etc. (Ref 4) are involved. However,

Table I. Properties of Calcined Filler Cokes Tested in Full-Size Prebake Anodes

Coke No.	1	2	3	4	5	6	7	8
VBD (lbs/ft ³)	53.4	45.2	49.0	58	57.6	51.8	40.3	49.8
RD _K (g/cc)	2.06	2.05	2.10	2.05	2.06	2.10	2.08	2.08
SR (Ω-in.)	0.040	0.047	0.036	0.036	0.034	0.035	0.040	0.033
HGI	32.8	37.1	36.8	22.8	27.1	36.4	41.5	36.6
550°C AB (mg/cm ² /hr)	21	92	73	155	178	53	46	86
650°C AB (mg/cm ² /hr)	169	228	271	370	236	221	227	241
970°C CO ₂ (mg/cm ² /hr)	9	20	41	122	67	28	22	37
Ash (%)	0.15	0.16	0.30	0.59	0.68	0.16	0.16	0.17
Fe (%)	0.014	0.017	0.018	0.032	0.019	0.017	0.016	0.016
V (%)	0.006	0.0093	0.005	0.043	0.028	0.008	0.0038	0.011
Ni (%)	0.006	0.0094	0.009	0.049	0.040	0.011	0.006	0.008
Ca (%)	-	0.0081	0.046	-	0.021	0.017	0.013	0.002
S (%)	1.33	1.53	1.71	1.20	1.06	2.00	2.10	2.51
N (%)	0.68	-	0.06	-	-	-	-	-

Table I. (Cont'd)

Coke No.	9	10	11	12	13	14	15	16
VBD (lbs/ft ³)	52.5	51.6	48.0	52.0	59.5	55.7	45.2	70.1
RD _K (g/cc)	2.09	2.06	2.08	2.07	2.06	2.04	2.05	1.92
SR (Ω-in.)	0.041	0.038	0.042	0.045	0.043	0.044	0.047	0.037
HGI	36.2	40.8	37.7	38.3	16.1	32.3	43.2	20.8
550°C AB (mg/cm ² /hr)	127	129	94	66	180	113	166	189
650°C AB (mg/cm ² /hr)	221	288	258	313	390	226	310	351
970°C CO ₂ (mg/cm ² /hr)	34	15	18	16	10	18	9	16
Ash (%)	0.12	0.20	0.19	2.29*	0.55	0.17	0.18	0.19
Fe (%)	0.01	0.018	0.028	0.042	0.039	0.013	0.014	0.012
V (%)	0.003	0.010	0.003	0.006	0.10	0.040	0.019	0.049
Ni (%)	0.006	0.006	0.008	0.015	0.106	0.013	0.010	0.023
Ca (%)	0.019	0.017	0.012	0.040	0.001	0.016	0.006	0.015
S (%)	2.07	3.65	2.93	3.07	3.02	4.10	5.17	5.31
N (%)	0.55	0.40	-	-	1.16	0.56	0.53	0.46

*Coke contamination from refractory lining of rotary kiln calciner.

variation in sulfur-carbon bonding and carbon microstructure affect the ease of thermal desulfurization. Temperatures up to 1000°C remove relatively small amounts of sulfur and much higher temperatures are required for complete desulfurization (Refs 4, 5).

Thermogravimetric analysis (TGA) has been used to examine the volatiles emission spectrum of a series of cokes during heat treatment. 400 mg samples of -14/+28 mesh green coke were heated in flowing argon from room temperature to 1600°C at heatup rates of 10°C/min and 1°C/min. Weight loss rate (DTG) variation with temperature for various coke types is shown in Figures 5 through 8. While no analysis of volatiles was made, there are clear correlations with known coke property values. The upper numbers near the DTG curves on the right side of the figures identify either the specific coke from Table I or the sulfur content. The lower numbers indicate the total percent weight loss during the complete TGA experiment.

In Figure 5, low-sulfur delayed Coke No. 1 exhibits a water vapor emission peak near 100°C, and a large hydrocarbon-hydrogen emission peak with a maximum near 550°C which develops just above coker temperatures. The third peak near 1600°C is due mostly to sulfur emission, since bound oxygen and hydrogen have been substantially removed at temperatures near 1000°C. Coke No. 1 also has a significant (1.05%) nitrogen content which may produce additional emission at temperatures above 1000°C (Ref 6). High-sulfur fluid Coke No. 16 also shows considerable water vapor emission, but much less hydrocarbon-hydrogen emission than delayed Coke No. 1, reflecting higher fluid coker temperatures. Also, Coke No. 16 exhibits much sulfur emission above 1500°C which has not quite peaked at 1600°C. The apparent peak in Figure 5 is produced by additional soak time at 1600°C. Since Coke No. 16 also contains 1.82% nitrogen in the green state, significant, added emission from this source would be expected above 1000°C.

The emission characteristics of a delayed shot coke containing 5.08% sulfur (5.08S) is also shown in Figure 5. This coke shows no water vapor emission, but has a hydrocarbon-hydrogen peak at 580°C and a still higher sulfur emission peak at 1590°C. With about the same sulfur content as Coke No. 16, this shot coke releases sulfur somewhat more easily. Since shot coke has slightly more porosity than fluid coke, the difference in sulfur emission characteristics correlates well with microstructure differences if equal sulfur bonding is assumed.

The final DTG curve in Figure 5, 2D, is for low-sulfur anisotropic coke similar to No. 2 in Table I. However, 2D was made by high-temperature delayed coking of 100% decant oil, a very refractory feedstock used to make needle coke. This high-temperature coke is the only delayed coke in this study with a hydrocarbon-hydrogen peak near 700°C, and thus similar to that for fluid coke (No. 16). However, it can be seen that DTG curves for all the green delayed cokes in Figures 5, 6 and 7 have secondary peaks near 700°C. It thus is likely that this temperature is a significant emission point for many cokes, probably

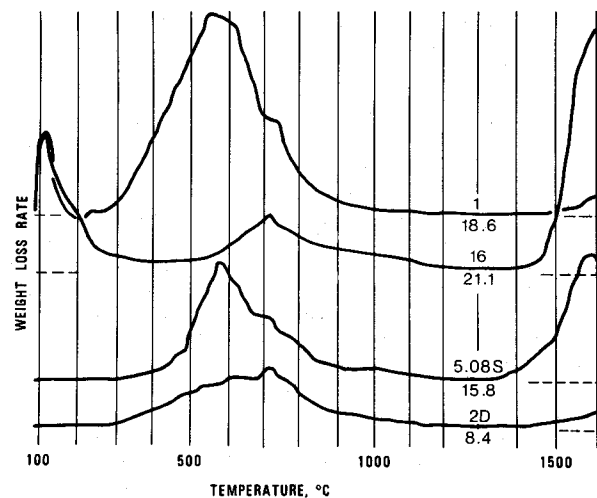


Figure 5. Thermogravimetric Analysis of Filler Coke Calcination-I (heatup rate = 10°C/min)

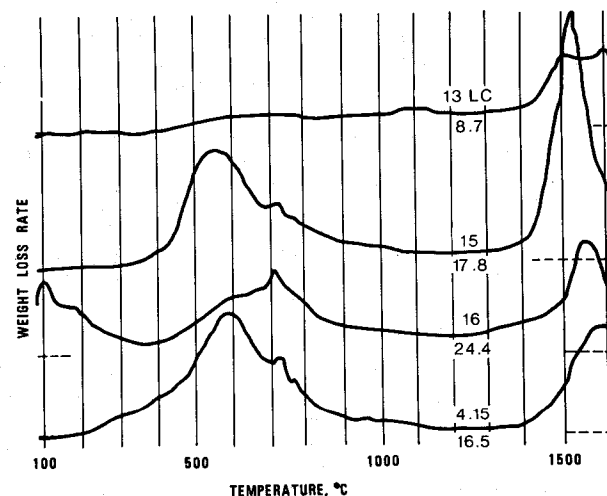


Figure 6. Thermogravimetric Analysis of Filler Coke Calcination-II (heatup rate = 10°C/min)

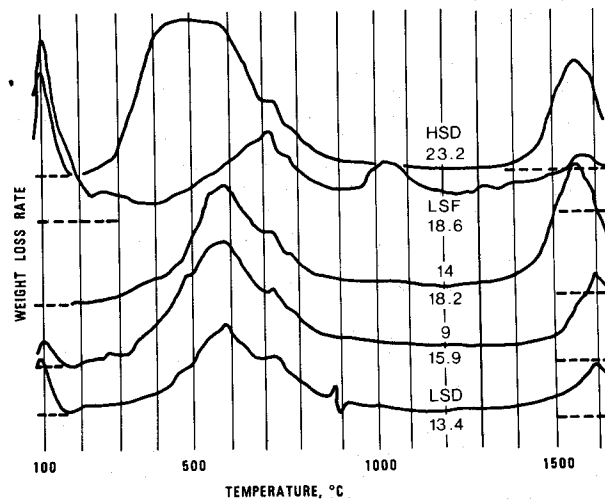


Figure 7. Thermogravimetric Analysis of Filler Coke Calcination-III (heatup rate = 10°C/min)

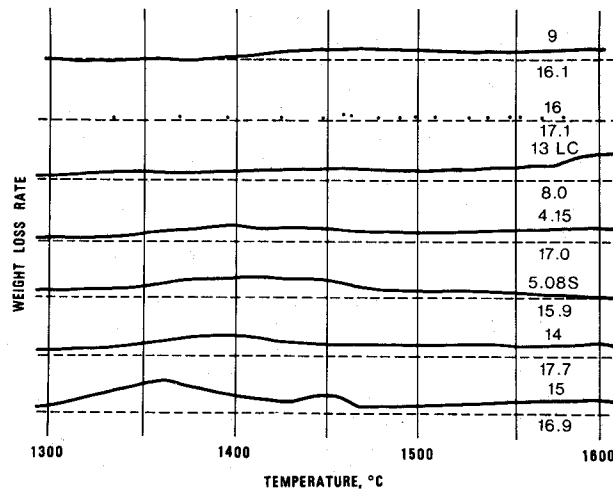


Figure 8. Thermogravimetric Analysis of Filler Coke Calcination-IV (heatup rate = 1°C/min)

associated with the release of very light hydrocarbons, hydrogen and/or bound oxides.

In Figure 6, Coke 13LC is a low-calcined form of Coke No. 13 in Table I. Prior heat treatment has removed most of the low-temperature volatility, and the unusual emission pattern above 1400°C may relate to the unusually high nitrogen content (2.37%) of the green coke. High sulfur Coke No. 15 in Figure 6 exhibits a relatively sharp low-temperature (baked) sulfur emission. The green coke has a sulfur content of 6.35% and this low density delayed coke shows the highest low-temperature (1000-1200°C) sulfur anode emission of all cokes involved in this study. The DTG curve for Coke No. 15 is in considerable contrast to that for Coke No. 14 in Figure 7, particularly above 1000°C. No. 14 exhibits much less low-temperature (1000-1200°C) sulfur emission and gave much better performance than No. 15 when the two cokes were used as fillers in full-size anodes.

The remaining DTG curves in Figures 6 and 7 give further examples of the volatile emission characteristics already discussed. Cokes not listed in Table I are a 4.15%S (4.15), another high-sulfur delayed (HSD), a low-sulfur fluid (LSF) and a low-sulfur delayed (LSD). The unusual peak for LSF near 1000°C is due to loss of coke particles from the sample crucible because of the pronounced tendency of fluid coke to become fluidized during heat treatment and sometimes to "dance" out of the container. The small DTG peak and depression for LSD near 900°C is due to a momentary emission increase from opening a small volatiles pocket as the coke shrinks with further heat treatment.

While all of the DTG curves in Figures 5, 6 and 7 were obtained at a heatup rate of 10°C/min, additional TGA calcinations were done at 1°C/min to examine sulfur emission at high temperatures. These two heatup rates relate to coke calcination and anode bake conditions closely enough to provide a basis for practical emission considerations. The DTG curves in Figure 8 were obtained at 1°C/min. When compared with curves in Figures 5-7 for the same cokes, it is seen that the lower heatup rate has resulted in significant sulfur emission at much lower temperatures. This is most evident for Coke No. 15 which gave poor performance in full-size anodes. However, there is less emission at lower temperatures for Coke No. 14 which gave good full-size anode performance. Other cokes in Figure 8, such as 13LC and 9, show still less low-temperature emission than that for No. 14. However, none exhibit so little emission as fluid Coke No. 16, now even at temperatures above 1500°C. The DTG curve for No. 16 in Figure 8 is represented by a series of points as average values over short temperature intervals due to the fluidization "dance" problem already mentioned. For sulfur emission, the most contrasting cokes in this study are Nos. 15 and 16. The 1°C/min heatup rate data for these two cokes were extended to a still lower heatup rate and temperature. Samples of these two cokes were pit baked with full-size anodes which received a standard prebake heat treatment with a finishing temperature of 1100°C. It was found that Coke No. 15 lost 20% of the initial sulfur content while fluid Coke No. 16 lost only 0.8%.

The principal factors responsible for the observed differences in sulfur emission with heat treatment are type of sulfur bonding, coke particle microstructure, and particle size (Ref 4). We do not yet know the details of organic sulfur bonding in coke. However, it appears that a dense disordered (isotropic) low-porosity microstructure hinders sulfur removal. In addition, larger coke particles of whatever microstructure reduce sulfur emission. The approximately millimeter size (-14/+28 mesh) particles used in this laboratory study thus tend to enhance sulfur emission in contrast to some of the larger aggregate sizes which are calcined and used as anode fillers. Since these experiments indicate rapid sulfur emission does not occur until temperatures near 1500°C are maintained for periods of the order of an hour, thermal calcination desulfurization appears unlikely. 1500°C is near the working limit of present rotary calciners and this temperature is experienced by the coke for only a few minutes at most. Hence, calcination sulfur removal is expected to remain small and additional sulfur will then "bleed" from baking anodes as affected by bonding and structural consideration already mentioned. It further appears that if thermal calcination were upgraded to accomplish coke desulfurization, the product would otherwise be over calcined for optimum anode and energy usage.

Pilot Cell Studies with Full-Size Anodes

This evaluation of full-size anode performance has involved a total of 1203 20-in. prebake anodes of 25 types, including 14 blends with fluid coke, and using a total of 16 different filler cokes. Filler coke property values have been given in Table I and the data on anode composition, properties and performance are shown in Table II. In order to determine the degree of correlation among the important variables involved, a series of linear regression analyses has been applied to the data.

The sulfur content of the cokes used in anode fabrication has an important influence on property differences between green and baked anode carbon. In particular, with increasing sulfur level the green anode loses more weight, due to thermal sulfur emissions, and exhibits less dimensional shrinkage, due to reduction in coke apparent density from sulfur emission puffing. The single exception to these changes with increasing sulfur content is high-sulfur fluid coke, where thermal sulfur emissions are so small that baked weight loss and anode dimensional change are essentially the same as for low-sulfur coke. Unrelated to its sulfur content, fluid coke does have a high elastic modulus and rounded particle shape, even when milled, which causes some reduction in anode green density for fluid coke blends as discussed previously (Ref 1). This green density reduction is less severe when fluid coke is blended with high-modulus isotropic coke than with low-modulus anisotropic filler.

For cokes other than fluid Coke No. 16, variation of property differences between green and baked anode carbon with green anode sulfur content is shown in Figures 9, 10 and 11. Variation of the density difference, ΔD , between green and baked density is

Table II. Full-Size Prebake Anode Composition, Properties and Performance

Anode Filler Coke Nos.	No. of Anodes Tested	Filler Coke Content (%)	Anode Sulfur Content (%)	Baked Anode Density (g/cc)	Baked Anode Properties		Normalized ⁽¹⁾ Net Carbon (lbs C/lb Al)
					550°C Ab (mg/cm ² /hr)	970°C CO ₂ (mg/cm ² /hr)	
1	74	75	1.40	1.53	32	-	0.423
1-16	39	35	2.81	1.47	88	-	0.485
4	22	75	1.32	1.55	38	-	0.435
4-16	46	35	2.77	1.51	64	-	0.445
5-16	66	40	2.68	1.52	80	23	0.447
14	24	75	3.17	1.53	72	-	0.429
14-16	37	35	3.61	1.49	80	-	0.462
8	65	80	2.13	1.54	41	28	0.448
8-16	27	40	3.12	2.60	88	34	0.475
6	63	80	1.79	1.76	58	38	0.443
6-16	41	45	2.83	2.99	90	32	0.470
9-16	17	40	2.97	2.78	92	29	0.465
9	49	80	1.84	1.81	43	36	0.460
10	58	80	2.94	3.02	86	24	0.457
11	58	80	2.41	2.61	72	31	0.461
12-16	53	40	3.33	2.82	85	24	0.463
13-16	83	20	3.69 ^(*)	1.47	85	24	0.467
13-16	37	20	3.74 ^(*)	1.51	76	-	0.452
13-16	27	20	~3.78 ^(*)	1.50	83	-	0.455
13-16	45	20	~4.24 ^(*)	1.49	83	-	0.457
13-16	45	20	3.14	1.45	68	-	0.471
2	59	80	1.49	1.42	87	20	0.465
3	75	80	1.65	1.48	41	27	0.448
15	44	80	3.89	1.75	38	34	0.444
				2.72	76	36	0.458

(1) Calculated assuming 2.25% S in butts (except 2.59% S for Anode Filler Coke Nos. 10 and 3) and 0.58% S in coal-tar pitch binder.
 (2) Measured values.
 (3) All performance net carbon values normalized to 90% current efficiency, 5.70 amps/in² current density, 970°C cell bath temperature, and 1115°C anode bake finishing temperature.
 (4) Estimate based on approximate filler coke composition and the sulfur content of binders A, D, B, and C (Ref 1) from top to bottom, respectively, used in anode fabrication.

shown in Figure 9. All points represent single (unblended) delayed filler coke compositions, with butts, and the number code refers to coke numbers from Table I. Correlation of ΔD with % S is quite good, but the correlation coefficient, R, is reduced, for reasons already given, from 0.91 to 0.52 if fluid coke blends are included. Correlation of average linear anode shrinkage, ALS, with % S is still satisfactory for the unblended delayed coke compositions in Figure 10. However, if fluid coke blends are included, R is changed from -0.74 to -0.32. In Figure 11, percent anode baked weight loss correlates well with % S for unblended delayed coke fillers. However, introduction of fluid coke blends reduces R from 0.86 to 0.62.

The above anode property variations with % S between green and baked carbon composites indicate that anode baked density (BD) should decrease with increasing % S. This conclusion is supported by the data shown in Figure 12 for unblended delayed coke compositions. While correlation between BD and % S in the baked anode is good, R is changed from -0.83 to -0.61 if fluid coke blends are included. While addition of fluid coke to anode composites does reduce anode baked density (Ref 1), this density reduction is related to the mechanical properties of fluid coke and mechanical interaction with other coke types, as discussed earlier, and not to sulfur content.

Increasing sulfur content of anode carbon is also associated with changes in carbon oxidation sensitivity to O₂ (air) and CO₂. However, the result is to increase airburn and decrease CO₂ oxidation with increasing baked anode sulfur content. Rather good correlation is shown in Figure 13 between 550°C airburn (550 AB) and % S. This is due primarily to the tendency of coke impurity content to increase with sulfur content, and often such impurities are oxidation catalysts for O₂ oxidation. However, a carbon structure and porosity factor is also present which affects the extent of oxidant-accessible surface. Figure 13 contains data on both unblended composites (circles) and blended compositions of delayed and fluid cokes (triangles). At high sulfur content, both compositions produce lower density anodes with more porosity. However, the unblended anodes tend to have much submicron porosity from sulfur puffing emissions (Ref 7), while the blended anodes have more coarse porosity above the micron level. It is known (Ref 8) that submicron pores are essentially inaccessible for gas oxidation because of diffusion limitation. While structured differently, both blended and unblended anode carbons have such combinations of accessible surface and specific reactivity that measured reactivity increases in good correlation with sulfur content.

The degree of correlation between CO₂ oxidation of anode carbon and sulfur content, shown in Figure 14, is much less than that for airburn. However, critical examination of the data indicate that the probability of a real correlation is approximately 19 out of 20 times. While the same general principles of gas-surface reactions in porous solids apply to both O₂ and CO₂ carbon oxidation, the specific reaction mechanisms are quite different and involve different oxidant-accessible surfaces, specific oxidation

Figure 9. Linear Regression Analysis of Correlation Between Green-Baked Density Difference and Percent Sulfur in the Green Anode

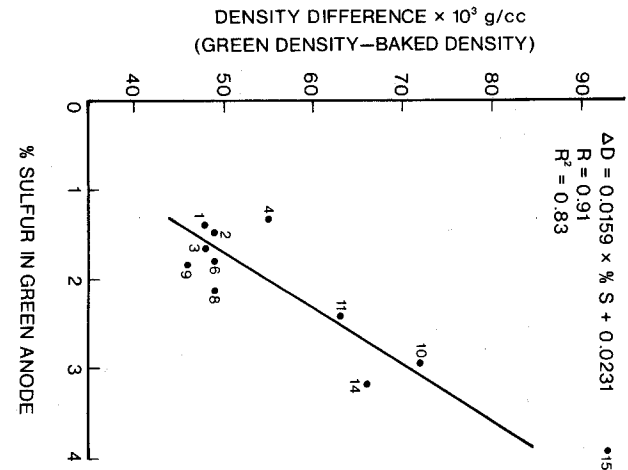
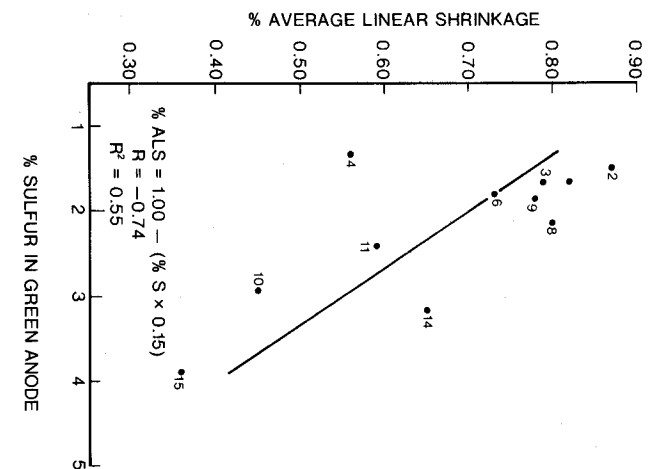


Figure 10. Linear Regression Analysis of Correlation Between Percent Average Linear Anode Shrinkage and Percent Sulfur in the Green Anode



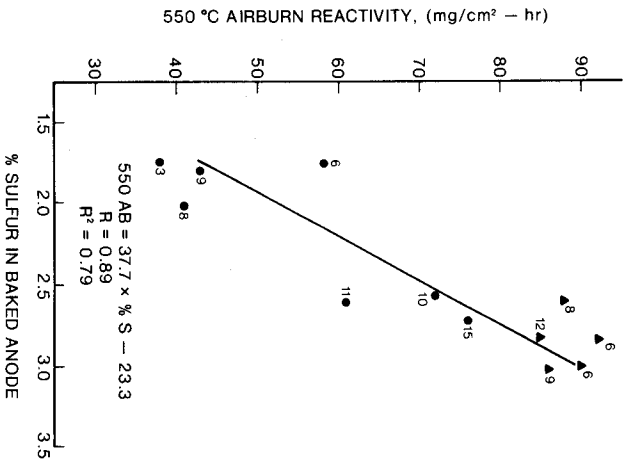


Figure 13. Linear Regression Analysis of Correlation Between 550°C Anode Airburn Reactivity and Percent Sulfur in the Baked Anode

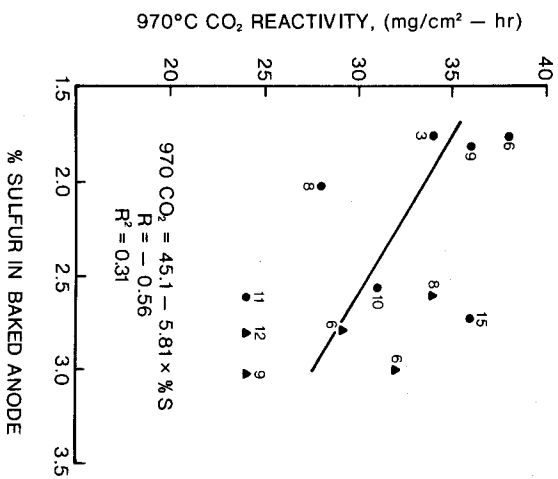


Figure 14. Linear Regression Analysis of Correlation Between 970°C Anode CO₂ Reactivity and Percent Sulfur in the Baked Anode

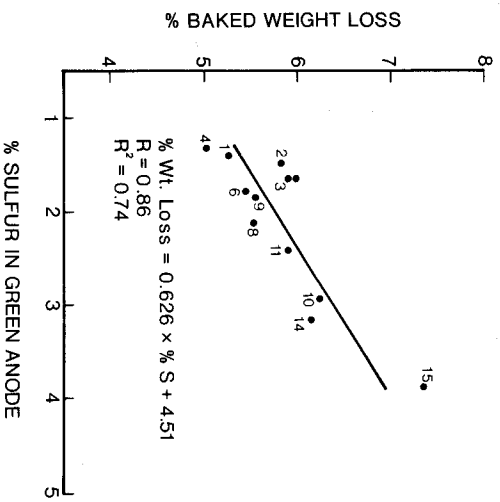


Figure 11. Linear Regression Analysis of Correlation Between Percent Anode Baked Weight Loss and Percent Sulfur in the Green Anode

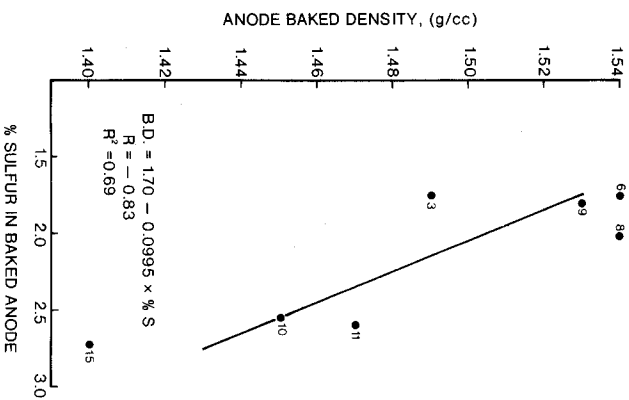


Figure 12. Linear Regression Analysis of Correlation Between Anode Baked Density and Percent Sulfur in the Baked Anode

rates and catalytic factors. CO_2 oxidation is endothermic, occurs here at lower rates, involves penetration to smaller pore diameters and is affected differently by various oxidation catalysts than exothermic airburn reactions (Ref 9). For example, vanadium is one of the most important catalysts for O_2 -carbon oxidation, while it is neutral or an inhibitor for CO_2 -carbon oxidation. This may be an important reason, along with reduced porosity, why fluid coke blends in Figure 14 exhibit less CO_2 reactivity. However, it is not now possible to account in detail for the data scatter in this figure.

The presence of sulfur in anode carbon should reduce anode performance. Pechiney has reported (Ref 10) 5-10% increased consumption with high-sulfur cokes, the upper limit being associated with additional catalytic oxidation from impurities which often increase with sulfur content. Reynolds has also reported (Ref 11) reduced anode performance with increased sulfur content, including reduction in current efficiency. Other work (Ref 12) has shown that COS is the major compound of sulfur identified in the primary anode gases before contact with air. Since CO_2 is the principal if not the only primary anode product in industrial cells (Ref 13), the increased anode consumption rate (per oxygen atom) for COS formation is $44/6 = 7.3$ times that for CO_2 formation. This amounts to $44-6/32 = 1.2\%$ increased consumption for each additional percent sulfur.

This investigation has indicated considerable diversity in the variation of anode performance with sulfur content. Anodes containing 3% S, made with Coke No. 14, performed as well as some anodes with only 1% S and better than most of the 25 anode types tested. Other anode types also containing 3% S, particularly fluid coke blends, gave some of the poorest performance. However, the best correlation of net carbon consumption with percent sulfur in the baked anode was obtained for anodes with ~2-3% S. These data are shown in Figure 15, and indicate normalized net carbon increased about 3% for 1% increased sulfur content between 2 and 3%. Only slightly less correlation, for the number of data points involved, was found from a linear regression analysis of correlation between normalized net carbon consumption and percent sulfur in 25 green anode types with 1-4% S. The correlation coefficient is 0.51, and indicates ~2% increased consumption per 1% increased sulfur content. We thus find a significantly greater increase in consumption with sulfur content than might have been expected. It appears that additional impurity catalysis of airburn is primarily responsible for this result.

In this study there was also no significant correlation of cell current efficiency with anode sulfur content. The evidence suggests that most of the sulfur impurity in the anode escapes in the gas phase and only trace amounts of sulfides have been detected in the electrolyte. While sulfates present in bath materials introduced directly into the electrolyte may affect current efficiency, such contaminants do not appear to come from sulfur in the anode.

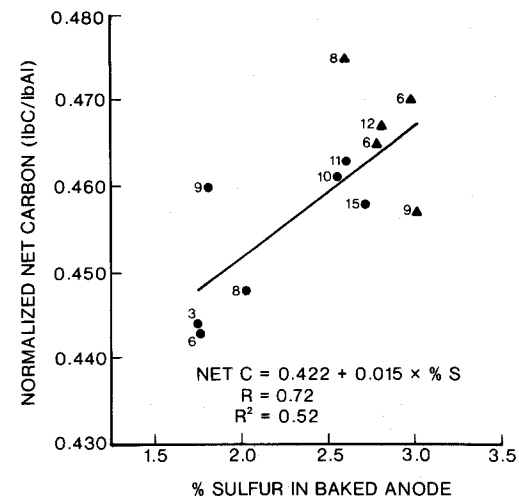


Figure 15. Linear Regression Analysis of Correlation Between Normalized Anode Net Carbon Consumption and Percent Sulfur in the Baked Anode

Properties of the 25 anode carbons used in this study were examined further for correlations. It was found that $R = 0.65$ for correlation between 550°C airburn and net carbon consumption. For correlation between baked density (BD) and net carbon consumption, $R = -0.57$. By adding the second variable, BD, the multiple linear regression analysis equation in Figure 16 was obtained with R increased from 0.65 to 0.72. However, it should be noted that these two variables are not independent as indicated by $R = 0.46$ for 25 data points. The data in Figure 16 show a comparison of actual normalized net carbon consumption with that predicted by this multiple linear regression analysis equation for net carbon as a function of 550°C airburn and baked density. As used previously, circles indicate unblended delayed coke fillers and triangles indicate blended compositions of delayed coke with Fluid Coke No. 16. However, for the point number code, the first digit indicates anode sulfur content to the nearest percent while the last one or two digits indicate the appropriate delayed coke number from Table I.

The data points in Figure 16 fall mostly between the dashed side lines at ± 0.01 lb C/lb Al about the solid center line determined by the multiple regression equation. Anode compositions above the diagonal lines performed better than predicted while those below the lines had lower performance than predicted. Good performers are near the lower left, poor performers are near the upper right. The best performer, 11, was converted to the worst performer, 31, by blending the oxidation-resistant, low-sulfur, anisotropic delayed coke with fluid coke. This case

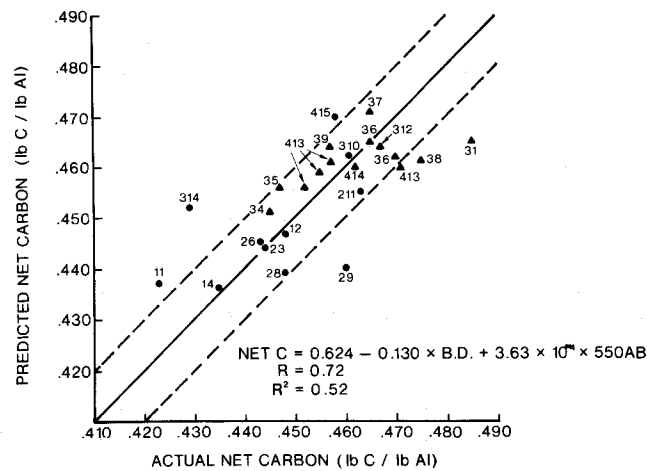


Figure 16. Comparison of Actual Normalized Anode Net Carbon Consumption with that Predicted by Multiple Linear Regression Analysis Equation for Net Carbon as a Function of Anode Baked Density and 550°C Airburn

of maximum coke incompatibility involves both physical and chemical coke properties. When low-modulus interlocking coke particles are blended with high-modulus low interlocking particles of greatly different oxidation sensitivity, the result is more springback during paste compaction to produce a lower density more porous anode with more oxidant-accessible surface of uneven specific reactivity.

It can be seen that most of the fluid coke blends are in the lower performance part of Figure 16. However, anode density reduction and uneven specific reactivity can be reduced by blending fluid coke with other dense high-modulus reactive cokes. The high performance of dense high-sulfur 314 anodes have already been mentioned. However, even low-density high-sulfur 415 anodes performed better than predicted because the submicron porosity produced by sulfur emission does not add oxidant-accessible surface even though apparent anode density is reduced. Other deviations from predicted performance such as 29 anodes are due to high CO₂ reactivity not considered by the multiple regression equation.

Conclusions

1. Thermal desulfurization of coke by calcination is not practical. However, except for fluid coke, appreciable sulfur

loss during anode baking may occur for many delayed cokes.

2. Anode net carbon consumption increases 2-3% per percent sulfur in the anode between 1 and 4% total sulfur.
3. This is about twice the increased consumption expected for primary COS as the principal anode sulfur emission. Additional impurity-catalyzed airburn is probably primarily responsible for the increased consumption difference.
4. Some high-sulfur cokes show excellent performance as anode fillers with carbon consumption as low or lower than low-sulfur cokes.
5. While our experience is limited to fluid coke blends, it suggests that the important coke properties for blend considerations are particle shape, density, strength, elastic modulus, pore structure and impurity content.
6. Work with coke blends involving high-sulfur, airburn-sensitive fluid coke shows that baked anode density is substantially reduced with fluid coke addition, often with significant reduction in anode performance (increased net carbon consumption). The substantially lower cost of fluid coke is an important factor offsetting reduced performance.
7. Fluid coke gives best results when blended with dense isotropic, high-modulus cokes which have much closed porosity.
8. The most incompatible fluid coke blend yet encountered, increasing net carbon consumption 15%, is that with anisotropic (ordered), oxidation-resistant Coke No. 1.
9. Many variations in anode performance can be encountered with fluid coke blends, depending on the extent to which porosity and reactivity to O₂ and CO₂ tend to interact to produce differing degrees of reinforcement or counteraction.
10. While net carbon consumption has been used in this discussion as the standard for anode performance, relative carbon dusting levels in the reduction cell may significantly affect overall performance evaluation.
11. Since incompatible blends are quite possible, with significant adverse influence on anode performance, there is considerable incentive for more extensive investigation of this increasingly important factor in anode usage.

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