

## REFINERY FEEDSTOCKS, COKE STRUCTURES AND ALUMINUM CELL ANODES

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Selected commercial and experimental petroleum cokes derived from a variety of refinery feedstocks ranging from aromatic to asphaltic materials have been examined in the laboratory. A wide spectrum of coke structures has been observed resulting from the different types of feedstock and coking conditions used. In laboratory-scale anodes prepared by using conventional procedures sponge cokes derived from the residuals of paraffinic and several mixed crudes gave good results. When, however, the bulk density of these cokes was low, modification of the aggregate size distribution and adjustment in the binder content were necessary to obtain acceptable results. The use of anisotropic, needle-type, cokes from aromatic residuals did not result in a significant improvement of test electrode properties. Isotropic cokes including those derived from asphaltic feedstocks gave acceptable results in the laboratory when used alone or in a blend with anisotropic cokes. With this type of coke, however, the selection of the degree of grinding, the aggregate size distribution, and the binder content was more critical than with regular sponge cokes. Changes in coke structure have also been followed in production cell anodes. Observations in the laboratory and in the plants have been in general agreement.

Introduction

There are substantial differences in the physical structure of cokes derived from different petroleum refinery feedstocks. Aromatic charge materials yield anisotropic, needle-type coke, predominantly paraffinic and cycloparaffinic residues give coke with a variety of sponge-like structures, while asphaltic feedstocks usually yield dense, more isotropic cokes. The present study has been directed towards the effect of structure and resulting properties of the cokes on aluminium cell anodes prepared from them.

Materials and Procedures

Commercial and experimental petroleum cokes derived from aromatic, paraffinic, and asphaltic feedstocks have been selected. Several samples produced from intermediate feedstocks containing naphthenic (cycloparaffinic) components, or mixtures of paraffinic and aromatic residues have also been included. Only cokes produced by the delayed coking process have been considered. Calcination temperature of the cokes has been in the range of 1150 to 1250°C.

Coke structures were examined by optical microscopy on samples imbedded in resin and prepared for microscopic study by the usual polishing technique. Coke porosity was determined by an Aminco-Winslow mercury porosimeter on 20 x 35 Tyler mesh samples. The results reported represent the volume percentage of pores smaller than 100 microns in diameter. Bulk density was determined on the same mesh size sample vibrated to maximum density<sup>(1)</sup>. Coke hardness was measured by the ASTM Hardgrove Grindability method.

Laboratory-scale test anodes were prepared by using conventional procedures. In each case the calcined coke was ground, screened to seven size fractions and the fractions combined to give a standard aggregate size distribution. A commercial coal-tar pitch with usual properties was used as binder. The laboratory<sup>(2)</sup> baked test electrodes were evaluated by methods described earlier.

Results1. Coke StructuresCokes from Aromatic Feedstocks

Cokes derived from refinery thermal tars and decant oils of catalytic cracking units belong to the family of needle cokes. In most cases the needle-like structure is readily recognizable under the microscope, while in some instances the coke laminae are bent and curved to a degree which makes the identification of the striated structure more difficult. Figure 1 is a photomicrograph of typical straight-fibred needle coke particles derived from decant oil. Figure 2 shows the structure of a coke with bent laminae and fissure-like, elongated cavities, also produced from decant oil.

Cokes from Paraffinic and Intermediate Feedstocks

These feedstocks, normally the bottoms from atmospheric or

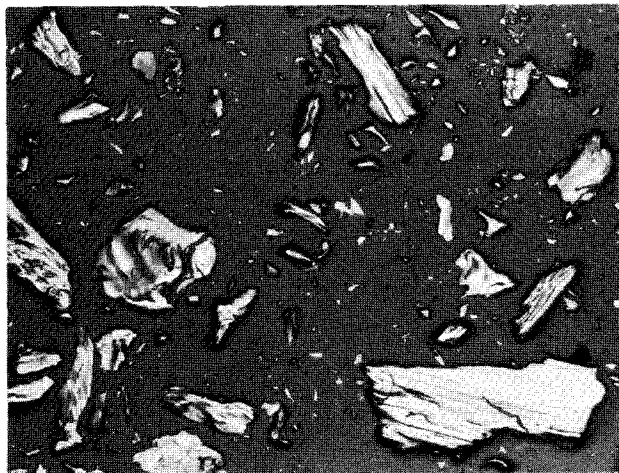


Figure 1. Needle coke from decant oil. Straight fibres (Mag. 100X)



Figure 2. Coke from decant oil. Bent and curved laminae. (Mag. 100X)

vacuum distillation units containing a relatively low amount of petroleum resins and asphaltenes, yield the well known sponge coke. This type of coke has been used almost exclusively for the production of aluminum cell anodes until recent years. Wide variations in the sponge-like coke structure have been observed due to changes in feedstock composition and coking practices. Coke microstructure and associated properties can be influenced by blending feedstocks and adjusting coking drum operating variables within practical limits<sup>(3)</sup>. Very generally, coke hardness and density increase with decreasing ratio of aromatic to paraffinic and naphthenic components in the feedstock. Similarly, higher coking drum temperature, pressure, and longer coking cycle favour the formation of harder coke<sup>(4)</sup>.

Figure 3 is a photomicrograph of a typical long-fibred sponge coke containing elongated and lenticular pores. The structure is sponge coke with short fibres and well distributed fine porosity is shown in Figure 4. Both the long and short-fibred sponge cokes derived from basically paraffinic or blended feedstocks have been known to give good quality aluminum cell anodes. Figure 5 is a photomicrograph of low bulk density sponge coke with elongated and spherical pores. This type of coke is also usually derived from paraffinic or blended feedstocks, but due to the relatively high volatile content in the green phase, the coke develops a high porosity during calcination. Anodes produced from this variety of sponge cokes will have an undesirably low apparent density and low strength.

Predominantly naphthenic feedstocks containing only small amounts of asphaltenes may yield a low-porosity, dense coke structure as shown in Figure 6. Usually the coke contains long-fibred grains with elongated pores and short-fibred grains with fine porosity in varying proportions. Anodes with high apparent density and good mechanical properties have been manufactured from this type of coke.

#### Cokes from Asphaltic Feedstocks

Reduced crudes containing a substantial amount of asphaltene fraction tend to give a more isotropic coke structure. Asphaltenes exist as well dispersed colloids in the feedstock, they are non-volatile and insoluble in organic solvents such as hexane or pentane. During the coking operation the colloidal suspension of asphaltenes forms a highly cross-linked, dense hard coke. The concentration of asphaltenes can usually be varied in the refinery and coking operation, thus the structure of the resulting coke can be modified.

Figure 7 is a photomicrograph of petroleum coke produced from asphaltic charge stock. The isotropic structure and low porosity are notable. The coke has a high bulk density and low grindability index. This material has been rejected in the past for aluminum cell anode manufacture primarily due to its hardness, poor bonding ability and impurities. It has found application, however, in recent years in blends with higher grade petroleum cokes.

Figure 8 shows the fused, finely fibrous texture occasionally found in commercial green petroleum cokes produced from asphaltic charge material. It is believed to be the result of rapid solidification of asphaltenes in the coking drum. The coke is very dense

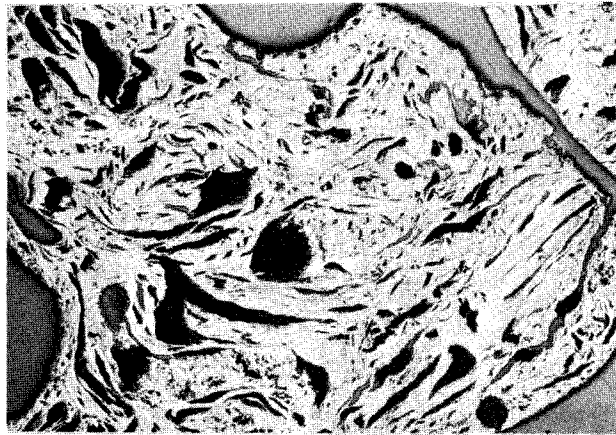


Figure 3. Typical sponge coke from intermediate feedstock. Long-fibred grains with lenticular porosity. (Mag. 50X)

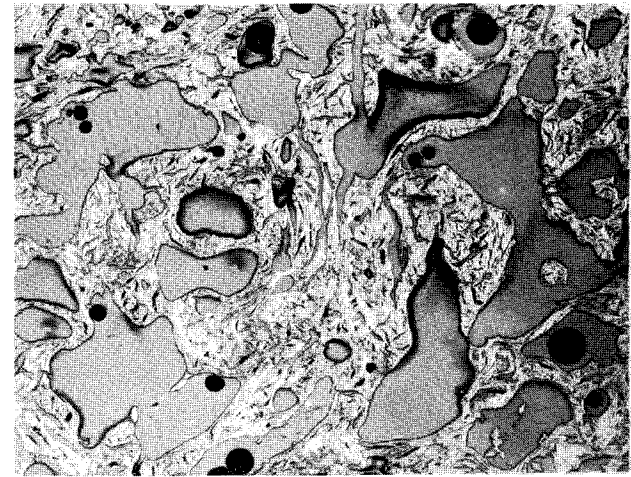


Figure 5. Low bulk density sponge coke from blended, intermediate feedstock. (Mag. 15X)

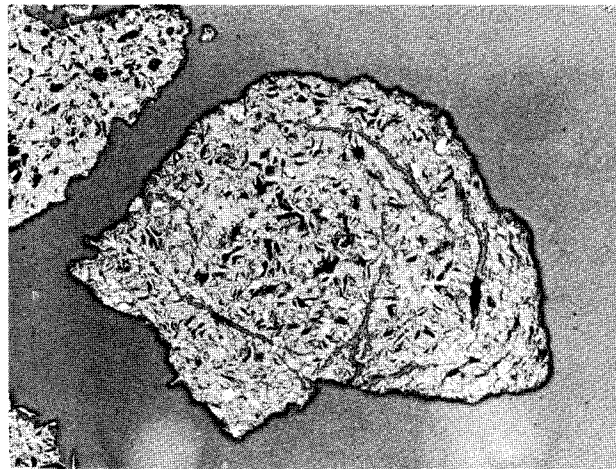


Figure 4. Sponge coke from intermediate predominantly paraffinic feedstock. Short-fibred grains with well distributed fine porosity. (Mag. 100X)

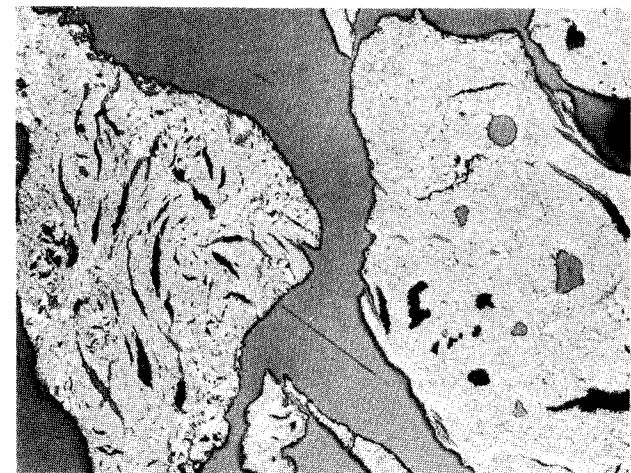


Figure 6. Sponge coke from predominantly naphthenic feedstock. Long-fibred grain on left, short-fibred grain on right. (Mag. 100X)

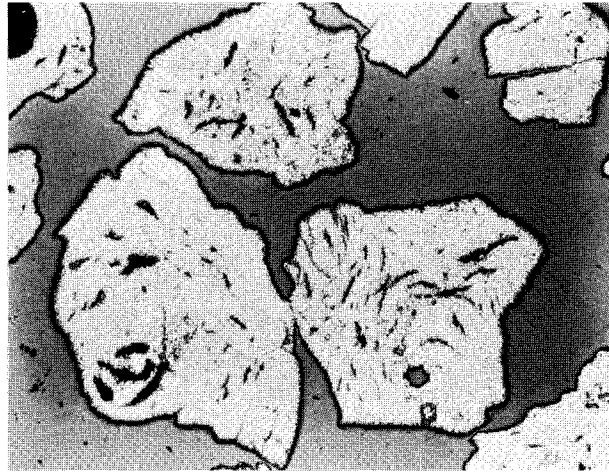


Figure 7. Structure of coke derived from asphaltic feedstock. (Mag. 50X)

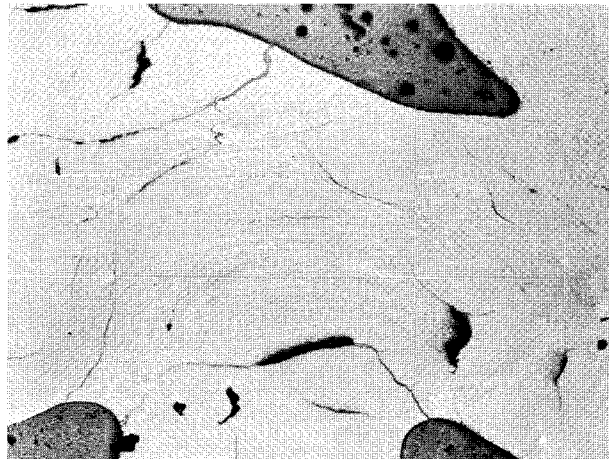


Figure 8. Fused, finely fibrous texture found in green coke made from asphaltic charge stock. (Mag. 50X)

with numerous curved cracks and virtually free of microporosity. It has an exceptionally low Hardgrove Grindability index indicating a very hard coke.

Under certain coking conditions refiners feeding asphaltic stock to the delayed coker may produce shot coke. Shot coke occurs in agglomerated spherical particles in the coke product. The size of the individual particles may range from 1 to 6 mm or more in diameter. Typical shot coke is shown in Figure 9 and its unique structure is magnified in Figure 10. This type of coke is generally considered unsuitable for manufacturing aluminum cell anodes due to its resistance to grinding.

## 2. Coke Physical Properties

It is known that the properties of petroleum coke are significantly affected by its structure which in turn is primarily determined by the composition of the petroleum feedstocks. Cokes from aromatic materials graphitize easily, have a low coefficient of thermal expansion, and are relatively soft. Cokes from asphaltic feedstocks are difficult to graphitize, have high coefficient of thermal expansion, and are dense and hard. It has also been observed that some cokes of asphaltic origin tend to decrepitate during calcination when heated rapidly. Cokes from intermediate reduced crudes exhibit a variety of properties depending on the history of coke formation and coke structure.

Table I summarizes the range of properties measured on calcined petroleum cokes of different structural characteristics and origin. Of particular significance is the variation in grindability which affects the efficiency of the milling operation and the variation in bulk density and porosity, which determines the amount of binder required for manufacturing aluminum cell anodes from the coke.

Table I. Typical Property Variations -  
Calcined Cokes Derived from a  
Range of Petroleum Feedstocks  
(Temperature of calcination 1200°C)

Type of Feedstock		Aromatic	Paraffinic	Naphthenic	Asphaltic
Coke Structure		Aniso- tropic needle	Sponge		Isotropic dense
Real Density	g/cm <sup>3</sup>	2.05	2.04	2.02	2.01
Bulk Density	g/cm <sup>3</sup>	0.860	0.880	0.920	0.980
Porosity*	%	24	22	20	14
Hardgrove Grindability Index		50	40	35	25
Mean Crystallite Thickness, L <sub>c</sub> , Å		27.5	26.0	25.0	24.0

\* Pore size range: 100 to 0.05 microns in diameter

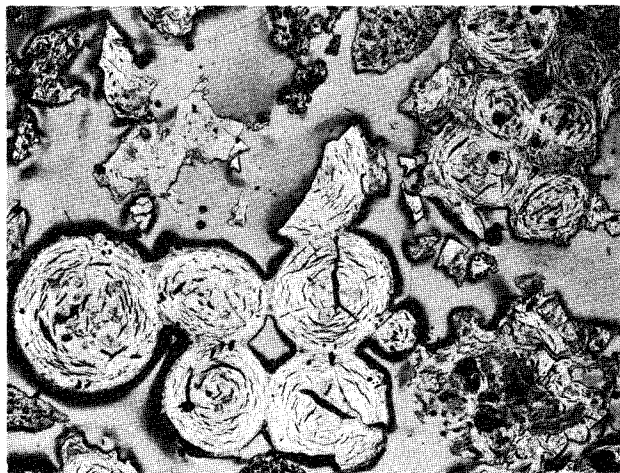


Figure 9. Shot coke produced from asphaltic feedstock. (Mag. 8X)

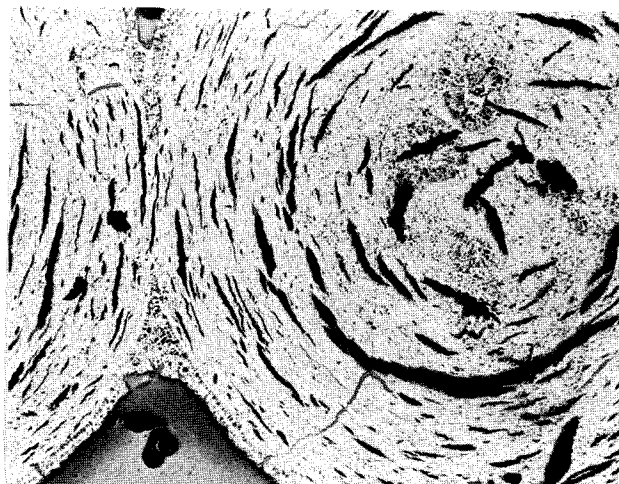


Figure 10. Typical structure of shot coke. (Mag. 50X)

### 3. Effect of Coke Structure on Test Anodes

Table II shows the properties of laboratory scale H.S. Soderberg test electrodes prepared with cokes produced from different feedstocks. Soderberg paste binder requirement for a given paste elongation significantly decreases with increasing isotropicity of the coke. This is due to the decreasing porosity from the aromatic to the asphaltic coke. Acceptable green and baked apparent densities have been obtained with all four types of coke used. The isotropic coke gave the highest electrical resistivity. Compressive strength was the lowest for the anisotropic and highest for the isotropic coke. The increase in air oxidation rate from aromatic to asphaltic feedstocks is attributed to the increasing concentration of metallic impurities in the cokes rather than to their structure. A significant correlation was found between the sum of vanadium and nickel content of the cokes and the test electrode air oxidation rates shown in Table II. The laboratory baked anode consumption for the coke of paraffinic and naphthenic origin is within the range normally found for sponge cokes. It is significantly lower for the coke derived from aromatic feedstock and it is the lowest for the isotropic coke derived from asphaltic feedstock.

Table III gives the results of analysis of two selected calcined petroleum cokes, one obtained from paraffinic and one from asphaltic feedstock. The two cokes and a 50 to 50 percent blend of them have been evaluated in laboratory V.S. Soderberg test electrodes. The results are shown in Table IV. They are in general agreement with those obtained on H.S. Soderberg test electrodes shown in Table II. Again, the coke from asphaltic feedstock gave a substantially lower baked anode consumption in the laboratory test cell than the coke of paraffinic origin. The blend of the two cokes gave intermediate results. There was no indication of selective oxidation or electrolytic consumption of either component.

Table V compares the properties of prebaked-type test electrodes prepared with two cokes of distinctly different structure. The feedstock for the first coke can be characterized as predominantly paraffinic containing aromatic components. The second coke was derived from a basically naphthenic charge material with a substantial amount of asphaltic components. The optimum binder content, determined by a laboratory method, was significantly lower for the coke from the asphaltic feedstock than for the paraffinic-aromatic coke. The former gave higher apparent densities, higher electrical resistivity, higher compressive and bending strength. Thermal conductivity and the coefficient of thermal expansion were also higher for the asphaltic coke, but the ratio of these two properties, which contributes to the characterization of the resistance to thermal stresses of carbon<sup>(5)</sup>, was not significantly different for the two cokes. Again, the higher air oxidation rate of the test electrode made with coke from asphaltic feedstock is attributed to the catalytic effect of the metallic impurities in the coke, principally vanadium and nickel. The electrolytic anode consumption for the isotropic, asphaltic coke electrode is essentially the same as for the sponge, paraffinic coke electrode. The difference in the results shown in Table V is not statistically significant.

Table III. Results of Analysis of Calcined Petroleum Cokes Derived from Paraffinic and Asphaltic Feedstock

Type of Feedstock	Paraffinic	Asphaltic
Coke Structure Observed	Typical sponge coke structure as shown by Figure 3	Isotropic structure, low porosity, similar to coke shown by Figure 7
Hydrogen	% 0.06	0.08
Carbon	% 95.8	94.0
Sulphur	% 2.2	4.6
Ash	% 0.15	0.25
Real Density	g/cm <sup>3</sup> 2.08	2.04
Mean Crystallite Thickness L <sub>c</sub> , Å	30.2	26.5
Electrical Resistivity	μΩcm 435	480
Reactivity to CO <sub>2</sub>	cm <sup>3</sup> /g sec 0.15	0.90
Porosity	% 24.0	14.0
Bulk Density	g/cm <sup>3</sup> 0.850	1.015
Hardgrove Grindability Index	40	24
Iron	% 0.020	0.030
Silicon	% 0.028	0.020
Vanadium	% 0.024	0.055
Nickel	% 0.015	0.035
Calcium	% 0.010	0.010

Table IV. Properties of V.S. Soderberg Test Electrodes Prepared with Coke Derived from a Paraffinic and from an Asphaltic Feedstock

Coke Structure and Analysis		As Described in Table III		
Coke Origin		Paraffinic Feedstock	Asphaltic Feedstock	50 to 50% Coke Blend
Binder Content	wt %	33.2	28.8	31.8
Paste Elongation	%	190	115	140
Green Apparent Density	g/cm <sup>3</sup>	1.606	1.645	1.630
Baked Apparent Density	g/cm <sup>3</sup>	1.380	1.465	1.445
Electrical Resistivity	μΩcm	80	90	86
Compressive Strength	kg/cm <sup>2</sup>	205	250	220
Air Permeability	cm <sup>2</sup> /sec	78	85	65
Air Oxidation Rate	g/cm <sup>2</sup> hr	0.080	0.135	0.115
Baked Anode Consumption	%	128.4	118.6	124.3
*Calculated Paste Consumption kg/kAh		0.156	0.143	0.151

\* See footnote in Table II.

Table II. Properties of H.S. Soderberg Test Electrodes Prepared with Petroleum Cokes of Different Origin

Type of Feedstock Coke Structure	Aromatic Anisotropic	Paraffinic Sponge	Naphthenic Sponge	Asphaltic Isotropic
Binder Content	% 31	29	28	26
Paste Elongation	% 45	50	55	55
Green Apparent Density	g/cm <sup>3</sup> 1.62	1.62	1.63	1.64
Baked Apparent Density	g/cm <sup>3</sup> 1.43	1.45	1.45	1.45
Electrical Resistivity	μΩcm 65	75	75	80
Compressive Strength	kg/cm <sup>2</sup> 220	260	260	320
Air Permeability	cm <sup>2</sup> /sec 20	45	50	70
Air Oxidation Rate	g/cm <sup>2</sup> hr 0.090	0.120	0.140	0.200
Baked Anode Consumption	% 122.0	126.5	126.5	119.5
*Calculated Paste Consumption kg/kAh	0.154	0.158	0.158	0.147

\* Calculated on the assumption that the loss on baking is 0.6 (1-CV)/B, where CV is the coking value and B the binder content, both expressed as a decimal fraction.

Table V. Properties of Prebaked-type Test Electrodes Made with a Typical Sponge Coke and Low Porosity, Isotropic Coke  
(Baking Temperature, 1100°C)

Type of Feedstock		Paraffinic with Aromatics	Naphthenic with Asphaltenes
Coke Structure		Sponge with anisotropic grains	Dense, isotropic low porosity
Coke Bulk Density	g/cm <sup>3</sup>	0.800 - 0.860	0.950 - 1.050
Binder Content	%	16.2	14.8
Green Apparent Density	g/cm <sup>3</sup>	1.546	1.620
Baked Apparent Density	g/cm <sup>3</sup>	1.457	1.529
Electrical Resistivity	μΩ m	68	80
Compressive Strength	kg/cm <sup>2</sup>	362	400
Bending Strength	kg/cm <sup>2</sup>	62	85
Air Permeability	cm <sup>3</sup> /sec	20	18
Thermal Conductivity	W/m °C	4.0	5.4
*Coefficient of Thermal Expansion	10 <sup>-6</sup> /°C	4.8	6.1
Air Oxidation Rate	g/cm <sup>2</sup> h	0.085	0.180
Baked Anode Consumption	%	114.5	116.0

\* 25 to 900°C

Of particular interest is the finding that in Soderberg electrodes isotropic cokes give significantly lower electrolytic anode consumption than sponge cokes, while in prebaked electrodes the two types of coke give nearly equal consumption rates. This may be explained by the hypothesis that excess anode consumption is due to the preferential oxidation of the binder coke in the anode leading to subsequent release of coke particles into the electrolyte. (6) The higher reactivity of the isotropic coke as shown by the carbon dioxide reactivity figures in Table III reduces the difference in reactivity between the coal-tar pitch binder coke and petroleum coke aggregate resulting in a decrease in preferential oxidation of binder coke. The effect is significant in Soderberg electrodes where binder coke is abundant, but becomes hardly detectable in low-binder prebaked electrodes. It is of interest to note that similar results were obtained with several isotropic cokes including those derived from tar-sand bitumen.

#### 4. Observations on Production Anodes

Historically, good results have been obtained in both the Soderberg and Prebaked-type aluminum cells with anodes manufactured from sponge cokes derived from paraffinic and naphthenic feedstocks containing aromatic components in varying amounts and having low concentrations of asphaltenes. Concerning the physical properties of the coke after calcination the following range of values has been preferred by Alcan:

Real Density	g/cm <sup>3</sup> :	2.02 - 2.08
Bulk Density	g/cm <sup>3</sup> :	0.820 - 0.960
Porosity	%:	20.0 - 26.0
Hardgrove Grindability	Index :	35 - 45

Different refiners may feed a variety of single-source of blend charge stocks to the delayed coker unit depending on crude oil availability and may use different coking practices. In many instances this results in a considerable variation of the properties listed above.

Green sponge coke of high volatile matter content from a predominantly paraffinic feedstock gave a bulk density of 0.740 to 0.780 g/cm<sup>3</sup> after calcination in rotary kilns. It had a structure similar to that shown in Figure 5. During anode manufacture the coke aggregate required a significantly higher amount of binder than normally used with sponge cokes. The anodes appeared fragile and sensitive to potroom operating variables. Excessive dusting, and anode side oxidation were noted in the potrooms. To increase anode density and strength it was necessary to modify the aggregate size distribution by increasing the amount of fine fraction in the aggregate composition when this type of coke had to be processed. Alternatively it was blended with a denser coke prior to being fed to the rotary kiln calciner.

Needle coke from such aromatic feedstocks as decant oil or thermal tar, the typical raw material for graphite production, has not been used for aluminum cell anode manufacture because of the high price it demands. Sponge cokes from reduced crudes containing up to 30% needle-type coke, however, have been used routinely by Alcan and found to give good results. The coke excelled by its purity and ease of handling during calcination and subsequent grinding, but in terms of anode quality and consumption it did not give anodes clearly superior to those produced from paraffin-base sponge cokes.

Isotropic coke structures have been observed from time to time in cokes received from refineries normally producing sponge coke. On occasions cokes with predominantly dense, isotropic structure have been used for substantial lengths of time at various smelters. While a quantitative production scale evaluation has not been undertaken, a number of observations have been made which are believed to be conclusive and significant. They are discussed below.

During calcination the larger particles of isotropic cokes tend to break down more easily than particles of regular sponge cokes. This may result in a shortage of the coarse (plus 4 mm) fraction of the aggregate for anode manufacture. On the other hand the calcine coke product has a lower grindability which makes the production of fine (minus 200 mesh) fraction for the aggregate more difficult. The binder requirement of the final aggregate is lower than for sponge coke aggregates and binder control is more critical because of the decreased availability of surface accessible pores to the binder in the coke of isotropic structure. With optimum binder content no adverse effects have been observed on Soderberg anode behaviour or consumption in the potroom.

Shot coke is generally considered unsuitable for aluminum cell anode manufacture. While it gives acceptable results in the laboratory when adequately ground and combined with the correct amount of binder, its commercial use so far has given highly controversial results<sup>(7)</sup>. This is attributed to the fact that the concentration of shot coke in commercial cokes often shows a considerable variation which poses a problem in grinding the mixture of hard shot coke and softer sponge-like coke to a uniform end product. It is of significance that fluid coke having a structure somewhat similar to shot coke has given good results in Soderberg anodes when ground and used in controlled quantities in the aggregate.

Prebaked anodes made with a relatively high bulk density coke containing 10% shot coke have been used on production scale without apparent operating difficulties. The use of a basically isotropic coke containing up to 30% shot coke, however, caused considerable dusting and operating problems in H.S. Soderberg cells, when the shot coke particles were not adequately ground.

#### Conclusions

Petroleum cokes derived from different feedstocks exhibit a wide range of structural characteristics varying from anisotropic through sponge-like to isotropic nature as the feedstock changes from aromatic through paraffinic to asphaltic composition. Cokes from aromatic, paraffinic, or cycloparaffinic feedstocks and from blends of a variety of charge materials give aluminum cell anodes with good structural properties. Those derived from highly asphaltic feedstocks having various isotropic structures, are in some instances problem-cokes requiring special attention in grinding for anode manufacture.

#### Acknowledgement

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