

## CARBON RAW MATERIAL EFFECTS ON ALUMINUM REDUCTION CELL ANODES

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In recent years significant variations have been experienced in carbon anode raw material properties, namely impurities and texture of petroleum coke, and in solvent insoluble contents of coal tar pitch. Impurities increase anode consumption mainly due to increased rates of carbon/gas-phase reactions. High porosity cokes impair the mechanical properties of the anodes; nevertheless they can be utilized either by pre-grinding or by altering the aggregate granulometry. Pitches with low levels of primary QI can be used with satisfactory results. High levels of primary QI in pitch are normally associated with increased impurity content, thus such a pitch may be objectionable for that reason. The beneficial effect of high pitch softening point was confirmed in bench-scale test electrodes with a pitch of 130°C (Mettler) softening point.

INTRODUCTION

Significant variations have been observed in carbon anode raw material properties over the past few years. As a result of the use of more and more heavy, sour crudes by refiners metallic impurities and sulphur content of petroleum cokes have generally increased. Variations in coke texture wider than before have been experienced, presumably due to the more frequent changes refineries had to make in crude slate, dictated by crude oil availability. Due to changes in metallurgical coke oven operating practices and fluctuations in productivity requirement, quinoline insoluble content of coal-tar pitch binders appreciably changed from time to time, or from one supplier to the other.

These changes in raw material properties can affect the anode manufacturing process and the performance of the anode in the electrolytic production of aluminum, to varying degrees. In the following it will be shown what the effects are and how the anode manufacturer might cope with changing raw material properties.

PETROLEUM COKE VARIABLESImpurities

Petroleum coke purity has been generally deteriorating over the past years. The trend towards more sour crudes for refining meant a

gradual increase in sulphur content although a substantial rise in sulphur level is not anticipated before the end of the decade (1). From the view point of aluminum producers more significant has been the increase in metallic impurities, particularly in the Western Region of North America, where relatively low sulphur but high metal content crudes have to be refined.

Table I illustrates the changes in coke purity observed by Alcan. The range of sulphur content specified ten years ago appears to be still attainable. Vanadium and nickel content of the cokes available in the West, however, appreciably exceed the specification of ten years ago.

Table I. Impurities In Green Petroleum Coke,  
Range/Typical

Element	Alcan Specification 1975	Available to Alcan 1985	
		Eastern North America	Western North America
Sulphur %	2 to 4	2 to 3.5	1.5 to 3.0
Vanadium ppm	200	220	350
Nickel ppm	150	140	380
Calcium ppm	N.S.	100	160
Iron ppm	300	260	260
Silicon ppm	200	220	140

N.S. = Not Specified

Using carbon reactivity rate equations published earlier (2) it is estimated that the higher metallic impurity level would result in an increase of 3.5% anode consumption due to air oxidation if the bare surface of a 60kA HS Soderberg anode is unprotected during electrolysis. The calculation is given in Table II.

Coke Texture

A trend towards more frequent appearance of shot coke has been observed over the recent years which is likely due to the more frequent use of asphaltic feedstocks by the refiners. Due to its high coefficient of thermal expansion and hardness, shot coke is not regarded suitable for anode manufacture, and when it

appears care is taken to limit its concentration in the coke to less than 5 to 10% by blending with shot-free sponge coke.

**Table II. Calculation of Excess Anode Consumption Due to Metallic Impurities in Coke**

Carbon Reactivity Regression Equation:(2)

$$R_{air} = 5.64 \times 10^{-2} + 1.422 \times 10^{-4}(V + Ni \text{ ppm})$$

g/cm<sup>2</sup>·h

V + Ni ppm	R <sub>air</sub> g/cm <sup>2</sup> ·h	Conversion Factor*	Excess Anode Consumption %
350	0.1061		
730	0.1601		
Difference: 0.0540 × 64.5 =			3.5

\*Derived from Table III. Reference (2):

$$\frac{\text{air oxidation as \% of theoretical consumption}}{\text{corrected air oxidation rate, g/cm}^2\cdot\text{h}} = 64.5$$

High porosity, low bulk density calcined coke is also undesirable, but can be used at the cost of increased binder level in the green anode mix. High calcined coke porosity results from high volatile content in the green coke, which in turn is caused by deviations from standard delayed coker operating practices. Low furnace outlet temperature, reduced coking cycle and incomplete drum filling will leave excess volatile matter in the green coke, leading to the development of high porosity in the coke during calcination.

The properties of anodes made from low bulk density coke can be somewhat improved by changing the aggregate size distribution. In a laboratory study, bench-scale test electrodes made with rotary kiln calcined low and high bulk density coke were evaluated. The properties of the two cokes are given in Table III and their granulometry and bulk density as a function of particle size range are illustrated in Figure 1. It is interesting to note that the run of kiln low bulk density calcined coke lacks the coarse sizes and its bulk density exhibits a minimum in the 4 to 14 Tyler mesh range. The latter observation has been utilized in the Alcan bulk density method where, in order to detect maximum differences in calcined coke bulk densities, a 4 × 14 Tyler mesh sample is taken and crushed to 20 × 35 Tyler mesh prior to bulk density determination.

Soderberg-type test electrodes were prepared with the two cokes by using the aggregate size distributions given in Table IV.

**Table III. Properties of Low and High Bulk Density Calcined Petroleum Coke**

Bulk density*	g/cm <sup>3</sup>	0.730	0.823
Real density,	g/cm <sup>3</sup>	2.04	2.06
Mean crystallite thickness, L <sub>c</sub> ,	Å	25.3	27.4
Carbon,	%	95.6	96.6
Sulphur,	%	3.5	2.1
Ash,	%	0.46	0.24
Porosity,	%	38.5	35.5
Electric resistivity,	μΩm	520	450
Iron,	ppm	260	390
Silicon,	ppm	590	190
Vanadium,	ppm	220	170
Nickel,	ppm	200	100
Calcium,	ppm	170	120

\*Vibrated Bulk Density by Alcan Method: 4 × 14 Tyler mesh fraction of coke crushed to 20 × 35 Tyler mesh prior to determination.

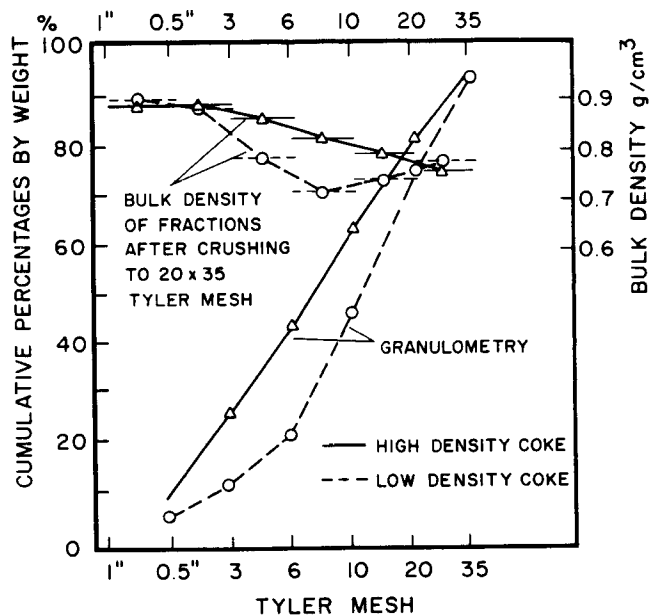


Figure 1. Density of coke fractions crushed to 20 × 35 Tyler mesh and granulometry of cokes as calcined.

The binder was a 100°C Mettler softening point commercial coal-tar pitch with 15.5% quinoline insolubles and 17% beta-resins. Mixing was done at 165°C for 1 hour using binder amounts giving a target paste elongation of 70 ± 15%. The test electrodes were baked at 970°C.

**Table IV. Aggregate Size Distributions Used in Test Electrodes Made With Low and High Bulk Density Coke**

Tyler Mesh	Wt. % of Aggregate			
	Straight-line Coarser		Aggregates Finer	
	A	B	C	D
+4	16	16	16	5
4x10	12	12	12	14
10x20	10	10	10	13
20x48	16	16	16	19
48x200	19	15	11	17
-200	27	31	35	32

Table V shows the green paste and baked test electrode properties. It can be seen that for identical paste elongations the 0.730 g/cm<sup>3</sup> bulk density coke requires 3% more binder than the 0.823 g/cm<sup>3</sup> bulk density coke. Thermal stability of the paste made with the low bulk density coke is inferior to that of the paste containing high bulk density coke. The baked electrodes show lower apparent density, higher electric resistivity and air permeability when the low bulk density coke is used. There is no significant difference in electrolytic anode consumption between the two cokes. Some improvement in apparent density, electric resistivity and air permeability is apparent with increasing minus 200 mesh fines in the aggregate. Of interest is to note that anode properties significantly improve when only the coarse,

plus 3 mesh, fraction of the low bulk density coke is used (aggregate D-1). This is explained by Figure 1 showing no difference in bulk density between the two cokes at the coarse end of the granulometry.

Another example of high porosity coke is undercalcined kiln dust. This material forms in rotary kilns where green coke fines are exposed to high heating rate and gas velocity. When the kiln is equipped with a waste heat boiler the material can be collected and utilized. It is also referred to as "swim coke" since the particles are so light, they float on water (3).

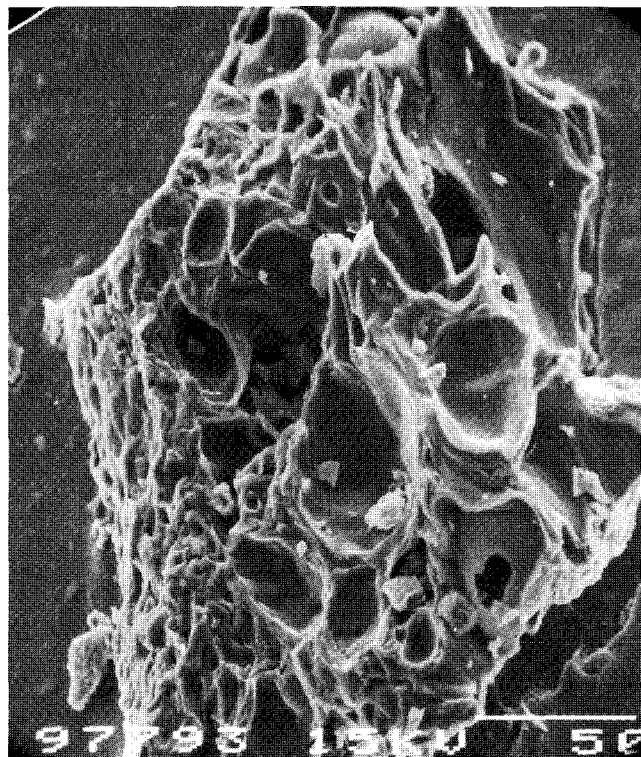
The range of properties of partially calcined fines is given in Table VI. The highly porous texture of the material in comparison to the texture of fines obtained by grinding fully calcined coke is illustrated by scanning electron microscope photographs in Figure 2.

Anode consumption was found to increase by 2.4% in a plant-scale HS Soderberg anode test when 8% undercalcined dust was added to the paste aggregate. A similar result was obtained in the laboratory. It was found, however, that if the high porosity of the material is destroyed by grinding in a ball mill, along with regular calcined coke of similar size range, an 8% addition to the paste aggregate would not have adverse effects on Soderberg anode performance. (4). This is illustrated by laboratory test electrode data in Table VII, where the results of a plant-scale test with 6% addition of ground partially calcined fines to the aggregate are also given.

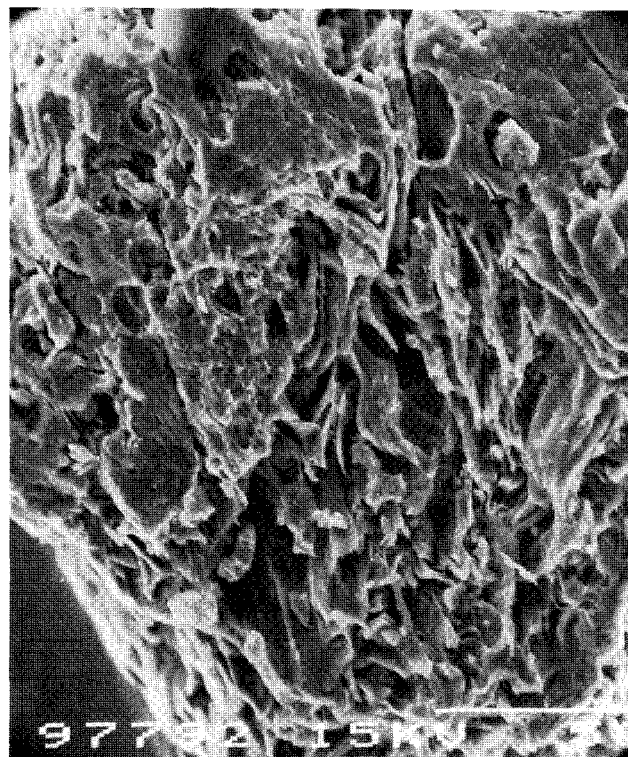
**Table V. Properties of Test Electrodes Made With Low and High Bulk Density Coke**

Bulk Density g/cm <sup>3</sup> (1)	0.730					0.823			
	A	B	C	D	D-1(2)	A	B	C	D
Size distribution									
Binder %	35.0	34.7	34.7	35.0	31.2	31.7	31.7	31.3	32.0
Elongation %	56	80	69	59	67	79	87	68	65
Elongation after 72 hours %	31	35	37	26	68	57	61	50	58
Thermal stability(3)	0.55	0.44	0.53	0.44	1.0	0.72	0.70	0.73	0.89
Green apparent density g/cm <sup>3</sup>	1.562	1.556	1.538	1.547	1.639	1.632	1.634	1.637	1.616
Baked apparent density g/cm <sup>3</sup>	1.312	1.336	1.352	1.311	1.388	1.371	1.384	1.389	1.387
Electric resistivity μohm m	83	79	77	79	72	76	75	72	71
Compressive strength kg/cm <sup>2</sup>	321	323	335	359	299	261	264	288	303
Air oxidation rate g/cm <sup>2</sup> ·s	0.120	0.120	0.119	0.112	0.111	0.132	0.127	0.127	0.127
Air permeability cm <sup>2</sup> /s	116	117	82	108	55	73	60	62	51
Anode consumption %	124.9	125.4	125.7	125.6	124.6	124.1	126.0	126.0	123.0

1. Bulk density determined on 4 x 14 mesh coke crushed to 20 x 35 mesh.
2. Specimens made with +3 mesh coke, ground to the aggregate formulation "D".
3. Thermal stability is ratio of elongation after 72 hours at 225°C to initial elongation.



(a)



(b)

Figure 2. SEM photographs of rotary kiln coke fines: (a) partially calcined fine particle, (b) coke fine obtained by crushing fully calcined coarse coke. Magnification: 500X.

Table VI. Range of Properties of Partially Calcined Coke Fines From a Rotary Kiln

Property	Range
Volatile matter %	1.0-1.8
Hydrogen %	0.4-0.8
Mean crystallite thickness, $L_c$ Å	17-19
Real density $g/cm^3$	1.75-1.85
Bulk density $g/cm^3$	0.55-0.70
Porosity %	40-55
Ash %	0.4-0.6
Particle Size, Tyler Mesh:	
48 × 100 %	15-25
100 × 200 %	25-35
-200 %	45-55

Additional laboratory results not shown in Table VII indicated a deterioration in test electrode properties when ground partially calcined coke addition was increased above 10% in the aggregate. This is attributed to the presence of volatiles in the material leading to shrinkage cracks during anode baking.

Table VII. Use of Partially Calcined, Ground, Rotary Kiln Coke Fines in HS Soderberg Paste

Property	Wt. % in Aggregate		
	None	6	8
<b>Laboratory Study:</b>			
Binder content %	29	29	
Paste elongation %	40	75	
Green apparent density $g/cm^3$	1.62	1.64	
Baked apparent density $g/cm^3$	1.48	1.49	
Compressive strength $kg/cm^2$	316	350	
Electric resistivity $\mu\Omega m$	66	69	
Air permeability $cm^2/s$	14	36	
Air oxidation rate $g/cm^2 \cdot h$	0.140	0.126	
Anode consumption %	127.8	126.0	
Calculated paste consumption $kg/kAh$	0.160	0.158	
<b>Plant-scale Test:*</b>			
Binder content %	27.1	27.3	
Paste elongation %	72	75	
Measured paste consumption $kg/kAh$	0.163	0.164	

\*32 cells, 4 months

COAL-TAR PITCH VARIABLES

Solvent Insolubles

Primary quinoline insoluble content of electrode-grade binder pitches is usually between 10 and 16%. Toluene (or benzene) insolubles may range from 25 to 32% giving a beta-resin content (TI-QI) of about 16%. Significant deviations from these figures can occur, however, depending on coke oven design and operating practices (5). While it is generally accepted that increasing QI content improves the mechanical properties of the anode, it has also been suggested that high QI content is associated with increased amounts of ash forming constituents in the pitch (6). The latter can be detrimental to the air oxidation resistance and electrolytic consumption of the anode.

Laboratory results obtained on Soderberg-type test electrodes prepared with pitches from the same source but containing different levels of QI are shown in Table VIII. The results indicate an increase of 0.3% in paste binder requirement per 1% increase in QI, an increase in the apparent density and strength of the baked anode, a moderate increase in air oxidation rate, and a significant increase in electrolytic anode consumption with increasing QI content of the pitch binder. Table IX compares two pitches in prebaked-type test electrodes with 5.1 and 12.0 QI content, respectively. These pitches are not from the same source, but have identical softening points (110°C, Mettler). Here the increase in binder demand is only 0.1% per 1% increase in QI, there is a noticeable increase in anode strength with the higher QI content, while the other properties of the anode are not significantly affected.

Table VIII. Properties of Soderberg-type Test Electrodes Made with Pitches Containing Different Amounts of QI

QI in pitch	%	15.7	19.1	21.1
TI in pitch	%	32.6	33.2	42.3
Beta resins	%	16.9	14.1	21.2
Pitch ash	%	0.09	0.25	0.24
Binder content	wt %	31.0	31.9	32.7
Paste elongation	%	90	52	66
Green apparent density	g/cm <sup>3</sup>	1.602	1.581	1.576
Baked apparent density	g/cm <sup>3</sup>	1.370	1.395	1.406
Compressive strength	kg/cm <sup>2</sup>	295	376	322
Electric resistivity	μΩm	77	75	76
Air oxidation rate	g/cm <sup>2</sup> ·h	0.105	0.107	0.133
Anode consumption	%	122.5	123.6	125.6

Table IX. Properties of Prebaked-type Test Electrodes Made With Pitches of Different Solvent Insolubles

QI in pitch	%	5.1	12.0
TI in pitch	%	21.2	30.5
Beta resins	%	16.1	18.5
Binder content	wt %	15.9	16.5
Green apparent density	g/cm <sup>3</sup>	1.56	1.56
Baked apparent density	g/cm <sup>3</sup>	1.46	1.46
Compressive strength	kg/cm <sup>2</sup>	286	320
Electric resistivity	μΩm	65	61
Air permeability	cm <sup>2</sup> /s	20	20
Air oxidation rate	g/cm <sup>2</sup> ·h	0.119	0.122
Anode consumption	%	116.3	115.7

Pitch Softening Point

Most tar distillers can increase the softening point of the pitch produced at the customer's request. The advantage of the use of high softening point pitch in anodes is the increased binder coke yield and if it is used in Soderberg paste, the reduced tar fume emission. An experimental high softening point pitch was evaluated in prebaked-type test electrodes. The results of the evaluation given in Table X show that increasing the pitch softening point from 100 to 135°C results in a significant increase of the apparent density, strength, and electric conductivity of the anode, due to the higher coke yield. Resistance to air oxidation and electrolytic consumption of the anode remain unchanged. The net gain is an increase in anode life brought about by the 10% higher binder coke yield. In the case of Soderberg anodes a corresponding decrease in paste consumption would be realized.

CONCLUSIONS

Increasing vanadium and nickel content in petroleum coke increases electrolytic anode consumption by promoting anode air oxidation. High porosity, low bulk density coke adversely affects the physical properties of anodes, but can be utilized after pregrinding or by increasing the ground fine fraction in the aggregate. Quinoline insoluble contents above 16% in coal-tar pitch binder result in an increase of electrolytic anode consumption. The use of high softening point pitch binders is advantageous, because due to the higher coke yield, prebake anode life is increased or Soderberg paste consumption is decreased.

Table X. Effect of Pitch Softening Point on  
Prebaked-type Test Electrode Properties

Pitch:			
Softening Point (Mettler)	°C	100	135
Coking Value (Alcan)	%	59	69
Quinoline Insoluble	%	15.8	16.5
Toluene Insoluble	%	32.9	35.2
Beta Resin	%	17.1	18.7
Green apparent density	g/cm <sup>3</sup>	1.522	1.532
Baked apparent density	g/cm <sup>3</sup>	1.465	1.484
Weight loss upon baking	%	4.8	3.5
Compressive strength	kg/cm <sup>2</sup>	256	298
Electric resistivity	μΩm	72	67
Air permeability	cm <sup>2</sup> /s	23	16
Air oxidation rate	g/cm <sup>2</sup> ·h	0.148	0.143
Anode consumption	%	117.9	117.4

ACKNOWLEDGEMENT

The authors are grateful to Lise Castonguay of the Arvida Research and Development Centre for supervising most of the laboratory investigative work.

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