CHARACTERIZATION OF GREEN AND CALCINED COKE PROPERTIES USED FOR ALUMINUM ANODE-GRADE CARBON

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ABSTRACT

Various properties of green (raw) and calcined petroleum cokes were analyzed and evaluated for use in aluminum anode-grade carbon. Petroleum cokes for this characterization study include different cokes produced from several refineries in U.S. and in other regions of the world such as China, Indonesia, Brazil, Argentine and Kuwait. Coke properties evaluated are: moisture, volatile carbon matter (VCM), ash, fixed carbon (FC) (by difference), sulfur, carbon, hydrogen, nitrogen, oxygen (by difference), metals (Si, Fe, V, Al, Ca, Na, Cr), calorific value, real density (RD), vibrated bulk density (VBD), size distribution, etc. Some of recent analysis results with these petroleum cokes are compared and presented.

INTRODUCTION

Export quality of petroleum cokes was evaluated and discussed at the ACS Las Vegas Meeting (September 7-11, 1997), based on recent analysis results from calcined petroleum coke produced for aluminum anode-grade and green (raw) coke used in calcination [1]. Production of petroleum cokes steadily increased by 51% during the past decade, expecting continuous increase in the coming years, primarily due to declining quality of crude oils. Exports to foreign countries are a major market for the U. S. coking industry and were 66% of the annual production (78,430 tons/cd) in 1993 . Green petroleum cokes are mostly used as utility fuels (about 73% for fuel grade), and as feedstocks (about 27%) for further upgrading calcination. The calcined petroleum cokes are used in production of specialty products: 71% for aluminum anode-grade, 9% for graphite electrodes, needle-grade, 8% for titanium dioxide pigments, 6% for recarburized ductile iron products, and 6% for others (chlorine, phosphorous, silicon carbide, calcium carbide, etc.).

Petroleum cokes are produced at refineries using three different types of coking processes: delayed, fluid, and flexicoking. The delayed coker is mostly used at forty-nine U.S. refineries processing total 1.57 mm b/sd [2]. The other fliud coker and flexicoker are less utilized at a relatively smaller capacity (seven refineries and 0.2 mm b/sd). Coke products from a delayed coker are classified as shot, sponge, (sometimes honeycomb), or needle coke depending on their chemical and physical characteristics. Shot coke (almost always sold as fuel) is hard, having spherical form, and physically produced through precipitating asphaltenes; sponge coke (mostly used for anode-grade) is dull and black, having porous, amorphous structure, and is considered as a mixture of shot and needle cokes; and needle coke (not used in anode production) is silver-gray, having crystalline broken needle structure, and chemically produced through cross linking of condensed aromatic hydrocarbons during coking reactions [3,4]. Most of fluid coke does not enter the anode pool and flexicoke has never been used in aluminum smelting.

The objective of this study is to evaluate various properties of green (raw) and calcined petroleum cokes used in aluminum anode-grade carbon, comparing different cokes produced from several refineries in U.S. and in other countries such as China, Indonesia, Brazil, Argentine and Kuwait.

COKE, ANODE PROPERTIES, AND CARBON CONSUMPTION

Rolle and Hoang [5] investigated the impact of metal impurities, vanadium and sodium, on the air reactivity of cokes and anodes. Vanadium has less impact on air reactivity than previously published and sodium is approximately five times more leveraging than vanadium on both coke and anode air reactivity.

Casada, Rolle, et. al. [6] reported the influence of nickel on reduction cell anodes. Nickel alone does not significantly effect anode air or CO_2 reactivity, but including anode butt material increased CO_2 reactivity.

Leach, et. al. [7] evaluated calcined coke and anode core properties to predict carbon consumption and anode performance in aluminum reduction cells. Calcined cokes having a range of properties can produce quality prebake anodes that yield low, stable carbon consumption. Their specific findings are:

- o Highly efficient modern prebake potlines can allow larger variability of carbon properties.
- o A strong correlation exists between the coke V content and anode air reactivity, while no correlation between coke air reactivity and anode air reactivity residue (ARR) was evident. To lower anode air reactivity (increase the ARR), reduce the coke V concentration.
- o A strong correlation exists between the anode Na content and anode carboxy reactivity residue (CRR), while a weaker correlation exists between the coke carboxy reactivity and anode CRR. The carboxy reactivity of the anode can be minimized by lowering the anode Na content through the use of cleaner butts and purer coke.
- o A strong correlation between coke grain stability and anode flexural strength was identified.

A desired range of calcined coke air reactivity based on the ignition temperature is 0.05-0.30 %/minute, and airburning increases near 0.30 %/minute [7]. A grain stability range of 75-85% is desirable with values below 75% causing substantially lower anode strength and thermal shock resistance. A substantial reduction in carbon consumption (a 12% decrease in eight years) was achieved and reported by de Mori by applying the correlation formula published by Fisher, et. al. that incorporates baked anode properties, potroom operations parameters, and a cell factor to predict carbon consumption.

$$PAC = C + 334/CE + 1.2\,(BT-960) - 1.5(ARR) - 1.7(CRR) + 9.3(AP) + 8(TC)$$

, where PAC is predicted anode consumption; C, cell factor; CE, current efficiency; BT, bath temperature; ARR, air reactivity residue; CRR, carboxy reactivity residue; AP, air permeability; and TC, thermal conductivity.

With 100% efficiency, the amount of carbon required would be 0.334 kg/kg of aluminum [4]. Actual net carbon consumption is in the range of 0.44 to 0.5 kg C/kg Al.

Eidet et. al. [8] studied effects of iron and sulfur on the air and CO_2 reactivity of calcined cokes. Excess carbon consumption (0.02 to 0.15 kg C/kg Al in prebake cells) in the aluminum electrolysis is caused by the oxidation of the anodes by air and CO_2, catalyzed by many different inorganic impurities present in the carbon anode materials. Iron catalyzes both O_2 combustion and CO_2 gasification of carbon. Sulfur is inactive in and do not have a significant effect on both reactions. Sulfur inhibits iron catalytic reactions.

Vogt and Ries [9] investigated the effect of anode desulfurization on baking by varying temperature and soak time. The best baking furnaces can achieve a uniform baking temperature (typically 1100-1150 deg C) with a variation of +/-25 deg C. Average anode baking temperature has been increased to near 1200 deg C with a soak time of 56 hours. Desulfurization during the baking can cause high air, CO_2 reactivities and permeability with abnormally low sulfur levels (<2.0% S as compared to >2.3% normal). Optimum baking temperature exists at a given soak time, and the porosity created by the loss of sulfur ultimately contributes to poorer reactivity behavior due to increased active sites available for oxidant molecules to attack carbon surface.

During calcining, green cokes with low sulfur less than 2% typically produce a calcined product having 90% of the green coke's sulfur level; cokes with high sulfur up to 5% calcine to about 85% of the original sulfur level. The remaining sulfur in the calcined coke is liberated during the smelting process. A critical temperature was identified in a laboratory calcining study investigating desulfurization, corresponding the initial release of sulfur and the creation of micropore volume (pore diameters <0.1 mm). The critical temperature was found to be coke specific and ranged from 1300 deg C for the high sulfur coke and 1500 deg C for the low sulfur coke.

TYPICAL PROPERTIES OF ALUMINUM ANODE-GRADE CALCINED COKE

Green (raw) petroleum coke is produced as a by-product in the refinery crude oil processing and primarily used in anode manufacture because of its low ash content. In general, coke is considered more valuable if it has low sulfur content, high bulk density, and metals content [4]. Sulfur emissions are an environmental liability in aluminum manufacturing. V and Ni (chemically bonded to hydrocarbons) and Na (dissolved as sodium chloride in water which is entrained with the crude oil) catalyze anode oxidation accelerating anode consumption and are ingot impurities. Two other variables affecting anode performance are density and sizing. Higher density cokes enhance anode properties and most coke users desire a product which is at least 30 wt % plus No. 4 Tyler mesh.

Calcination process basically removes volatile matter, hydrogen and some of sulfur present in green cokes as a result increasing density and electrical conductivity suitable for use of carbon anodes in aluminum production. Typical ranges of calcined coke properties for aluminum anode-grade specifications are listed in the following [4,10-13]:

Property	Green	Calcined
wt% S	2.5	2.5 (1.7-3.0)
wt% ash	0.25	0.30 (0.1-0.3)
ppm V	150	200 (165-350)
ppm Ni	150	200(120-350)
wt% Si	0.02	0.02
wt% VM	10-12	<0.25
resistivity, microomega-m		950
real density, g/cu-cm		2.06
bulk density, g/cu-cm		0.80
coefficient of thermal expansion per deg C		2 x 10 to -6

SAMPLING AND PREPARATION

Representative samples of petroleum cokes for this study have been obtained from various refineries in U.S., China, Indonesia, Brazil, Argentine and Kuwait. Green (raw) cokes were produced in the delayed coking process and calcined using laboratory furnaces. Laboratory samples are prepared for coke properties analysis following the procedures and principles in handling listed in the ASTM Methods D 346, D 2013 and D 2234.

ANALYTICAL METHODS USED

Laboratory test methods using various advanced analytical instruments are described in the Quality Assurance Manual of the A. J. Edmond Company. Primary analytical methods used for this study are summarized as follows:

Purpose	ASTM Method		Instrument
metals	D5600	ICP-AES	PE Optima 3000
sulfur	D4239	LECO	LECO SC 432
CHN	D5373	LECO	LECO CHN-1000
Btu	D3286	PARR	PARR 1108, 1261, 1563
moisture	D3173		
volatile	ISO562		
ash	D4422,D3174		
VBD	D4292		
RD	D2638		Micrometrics AccuPyc 1330
sieve	D5709,D293		

RESULTS AND DISCUSSION

Table 1 summarizes analysis results of typical properties of green (raw) and calcined petroleum cokes used for aluminum anode-grade carbon. Export qualities of calcined cokes at U.S. West Coast ports are also included in the last two columns of Table 1 (Continued). Proximate, ultimate analysis, metals content, sizing, calorific value, RD and VBD were determined in this study and are compared.

Laboratory Calcination Results

Ratios of calcined to green coke property value as percentage are listed in Table 1 to evaluate laboratory calcination. Calcination basically removed VCM, hydrogen, and some of sulfur and nitrogen present in green cokes. As a result ash, FC and carbon contents increased, while calorific value decreased. Loss or gain of each coke property value after calcination are compared in the following.

Property	Loss, %	Gain, %
VCM	95.4-97.6	
Hydrogen	96.9-99.4	
Sulfur	8-13	(0-1% gain with three samples)
Nitrogen	25-46	
Ash		9-46 (0-10% loss with three samples)
FC		9-13
Carbon		5-6
Btu/lb	9-11	

Ash ratio of calcined to green coke significantly varies from 10% loss to 46% gain, showing analytical errors associated with low ash content of cokes studied (0.05-0.36 wt %).

Sulfur Content

Sulfur content of petroleum cokes analyzed for this study varies in the range of 0.46 to 3.21 wt %. Chinese, Brazilian and Indonesian cokes have a low sulfur content of 0.5 to 0.8 wt %, while cokes from Kuwait and several refineries in U.S. (USA1, USA3, USA4, LV and LB) have a high sulfur content of 2.2 to 3.2 wt %. Cokes from Argentine and a refinery in U.S. (USA2) have a medium sulfur content of 1.0 to 1.5 wt %. Aluminum smelter sulfur restrictions are regional, and locally regulated to meet environmental emission standards, depending upon industrial, urban or rural area [14]. In Europe and Scandinavia, a coke sulfur limit of 2% maximum is frequently imposed locally; and for new smelters in North America and Australia, the sulfur limit is 3% maximum. Latin America, South Asia and Africa generally have few restrictions on sulfur levels in calcined coke. To lower sulfur content of coke (which is projected to significantly increase to 5% in future), residual oil hydro-desulfurization or thermal desulfurization of petroleum coke may be become an important, viable process.

Ash and Metals Content

Ash content of petroleum cokes analyzed for this study ranges from 0.05 to 0.36 wt %. Calcined cokes from Kuwait, Brazil and several refineries in U.S. (USA1, LV and LB) show a low ash content of 0.07 to 0.13 wt %, while calcined cokes from Indonesia, USA2 and USA3 have a high ash content ranging from 0,29 to 0,35 wt %. A medium level of ash content, 0.17 to 0.19 wt %, is indicated with calcined cokes from China, Argentine and USA4.

V, Ni and Na metal impurities catalyze oxidation and gasification reactions of carbon in the aluminum smelting process resulting in a higher carbon consumption. Studies performed with various V and Na concentrations indicated a strong correlation with air and carboxy reactivity, but with Ni results were less conclusive. Other metals most likely stay with aluminum ingot as impurities and may affect coke quality parameters.

Chinese, Argentina and Indonesian calcined cokes have a low V content of 24 to 81 ppm; 228-257 ppm with Brazilian, Kuwait and USA4; and a high V content of 300 to 607 ppm is observed with calcined cokes from several refineries in U.S. (USA1, USA2, USA3, LV and LB).

A Ni content less than 200 ppm (ranging from 118 to 194 ppm) is shown with Argentina, Kuwait, USA1, USA4, LV and LB calcined cokes. Other calcined cokes have a high Ni content of 215 to 592 ppm.

Na content of calcined cokes studied varies less in the range of 21 to 140 ppm compared to V and Ni content.

Real Density and Vibrated Bulk Density

Real density of calcined cokes is in the range of 2.057 to 2.076, and all are acceptable for aluminum smelting. Vibrated bulk density of calcined cokes varies in the range of 0.672 to 0.922 g/cu-cm, indicating significant differences in size distribution among calcined cokes studied.

Size Distribution

Larger than 4 mesh size fraction of calcined cokes varies ranging from 22.9 to 53.7 wt %. Depending on buyer and producing refinery, as listed in Table 1 (Continued), export specification for this fraction can be >32% or >55%. Less than 200 mesh size fraction of these cokes is in the range of 0.2 to 0.6 wt %, meeting export specification.

SUMMARY

Various green (raw) and calcined cokes were analyzed and evaluated for application in production of aluminum anode-grade carbon. Typical coke property data are obtained from nine green and

eleven calcined cokes produced in several different regions of the world (U.S., China, Argentine, Indonesia, Brazil and Kuwait). Important coke quality parameters for these cokes are tabulated and compared, primarily focused on sulfur content, ash and metals (V, Ni, Na) content, density and size distribution. Coke quality significantly varies and is regional in nature depending upon quality specifications dictated by buyer and/or producing refinery.

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Table 1. TYPICAL PROPERTIES OF GREEN AND CALCINED COKES USED FOR ALUMINUM ANODE-GRADE CARBON

Origin	China		Argentine		Indonesia		Brazil		Kuwait	
Type	*Green*	*Calcine*	*Green*	*Calcine*	*Green*	*Calcine*	*Green*	*Calcine*	*Green*	*Calcine*
(as-received)										
Moisture, wt%	1.2		7.2		5.7		5.1		0.9	
(dry-basis)										
Proximate, wt%										
VCM	9.90	0.27	11.74	0.28	11.07	0.28	10.09	0.29	8.46	0.28
Ash	0.15	0.17	0.21	0.19	0.36	0.33	0.11	0.11	0.05	0.07
FC	89.95	99.56	88.05	99.53	88.57	99.39	89.80	99.60	91.37	99.65
Ultimate, wt%										
Sulfur	0.68	0.66	1.45	1.46	0.53	0.46	0.79	0.73	3.21	3.14
Carbon	92.10	97.52	91.09	96.89	92.22	97.87	91.95	97.46	91.55	96.05
Hydrogen	3.73	0.10	3.61	0.09	3.94	0.11	3.63	0.05	3.43	0.08
Nitrogen	2.30	1.55	2.08	1.37	1.63	1.23	2.63	1.65	1.05	0.66
Oxygen	1.04	0.00	1.56	0.00	1.32	0.00	0.89	0.00	0.59	0.00
Metals, ppm										
Silicon	87	124	98	73	472	579	42	20	7	9
Iron	98	106	256	268	93	184	197	99	18	51
Vanadium	31	34	91	81	5	24	201	257	184	257
Nickel	256	279	117	134	144	238	176	215	86	118
Aluminum	88	85	43	83	48	95	13	9	3	15
Calcium	87	95	123	130	48	73	8	9	5	3
Sodium	63	59	110	96	91	124	51	61	15	21
Chromium	1.1	1.2	0.5	1.4	0	0.8	1.5	1.5	0.3	0.3
Btu/lb	15603	14089	15660	13997	15666	14156	15454	14087	15664	13889
RD, g/cm3		2.066		2.068		2.070		2.071		2.075
VBD, g/cm3		0.823		0.765		0.672		0.810		0.792
Size, wt%										
+20 mm	21.2		10.3		10.3		13.7		38.0	
-6 mm	51.1		70.6		72.5		65.7		24.7	
+4 mesh		37.7		28.2		31.8		22.9		53.7
+8 mesh		52.6		44.7		49.8		35.7		68.0
-50 mesh		6.4		6.5		3.4		11.8		5.3
-70 mesh		1.4		3.9		1.7		7.3		3.1
-200 mesh		0.3		0.5		0.3		0.6		0.3
Ratio of Calcine to Green, %										
VCM		2.7		2.4		2.5		2.9		3.3
Ash		109		90		92		100		140
FC		109		113		112		111		109
Sulfur		100		101		87		92		98
Carbon		105		106		106		106		105
Hydrogen		0.6		2.5		2.8		1.4		2.3
Nitrogen		60		66		75		63		64
Btu/lb		90		89		90		91		89

Table 1 (Continued). TYPICAL PROPERTIES OF GREEN AND CALCINED COKES USED FOR ALUMINUM ANODE-GRADE CARBON

Origin	USA1-CA		USA2-CA		USA3-CA		USA4-LA		LV-WA	LB-CA
Type	*Green*	*Calcine*	*Green*	*Calcine*	*Green*	*Calcine*	*Green*	*Calcine*	*Calcine*	*Calcine*
(as-received)										
Moisture, wt%	4.2		2.6		9.2		6.4		0.03	0.1
(dry-basis)										
Proximate, wt%										
VCM	8.90	0.26	11.02	0.29	11.18	0.51	10.54	0.27	0.1	0.1
Ash	0.11	0.12	0.28	0.35	0.22	0.29	0.13	0.19	0.1	0.13
FC	90.99	99.62	88.70	99.36	88.60	99.20	89.33	99.54	99.8	99.77
Ultimate, wt%										
Sulfur	2.96	2.95	1.10	1.02	2.42	2.20	2.81	2.65	2.8	2.85
Carbon	91.20	96.03	91.27	96.59	90.68	96.32	91.02	96.22		
Hydrogen	3.56	0.02	3.83	0.12	3.79	0.04	3.70	0.04		
Nitrogen	1.47	0.88	3.39	1.92	1.80	1.15	1.67	0.90		
Oxygen	0.70	0.00	0.13	0.00	1.09	0.00	0.67	0.00		
Metals, ppm										
Silicon	23	22	60	87	156	130	22	20	30	20
Iron	28	45	202	272	211	291	83	105	50	75
Vanadium	321	365	504	607	264	338	229	228	300	385
Nickel	137	158	488	592	238	300	190	194	125	160
Aluminum	10	18	28	61	131	211	14	27		
Calcium	18	13	127	140	44	52	89	156	15	30
Sodium	32	31	133	140	37	67	79	89	30	35
Chromium	0.5	0.5	1.9	1.9	0.7	0.7	0.1	0.1		
Btu/lb	15600	13991	15539	13929	15612	14030	15633	13946		
RD, g/cm3		2.068		2.065		2.057		2.076	2.07	2.07
VBD, g/cm3		0.823		0.922		0.758		0.744	0.89	0.87
Size, wt%										
+20 mm	20.5		33.0		19.2		6.2			
-6 mm	50.1		34.3		53.7		65.5			
+4 mesh		44.7		29.1		32.0		33.4	32	55
+8 mesh		58.2		46.3		50.0		47.9	-	70
-50 mesh		8.0		1.8		5.1		10.9	8	-
-70 mesh		4.8		0.9		2.7		7.1	-	3.3
-200 mesh		0.3		0.2		0.4		0.6	0.6	0.3
Ratio of Calcine to Green, %										
VCM		2.9		2.6		4.6		2.6		
Ash		109		125		132		146		
FC		109		112		112		111		
Sulfur		100		93		91		94		
Carbon		105		106		106		106		
Hydrogen		0.6		3.1		1.1		1.1		
Nitrogen		60		57		64		54		
Btu/lb		90		90		90		89		