QUALITY ANALYSIS OF PETROLEUM COKES AND COALS FOR EXPORT SPECIFICATIONS REQUIRED IN USE OF SPECIALTY PRODUCTS AND UTILITY FUELS

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ABSTRACT

Quality of petroleum cokes and coals has been evaluated for export specifications required in use of specialty products and utility fuels. Various green and calcined cokes, produced at refineries in California, and coals for shipment are sampled at California and national ports, and analyzed by using ASTM Methods. Quality analysis reports include: proximate and ultimate analyses, metals, Btu, density, size distribution, hardgrove grindability, and other physical, chemical and mechanical properties. Some of recent analysis results from calcined petroleum coke produced for aluminum anode grade, green (raw) coke used in calcination, petroleum coke for high- and low-Btu fuel grade, low- and high-rank coals are compared and presented. QC/QA/SQC programs have been utilized for good precision and accuracy of data generated with acceptable repeatability and reproducibility.

INTRODUCTION

The A. J. Edmond Co. bas over 30 years extensive experience specialized in analysis, testing and evaluation of petroleum cokes and coals for export specifications, which are used primarily as solid fuels in power plants and cement kilns and in other applications to produce specialty products, carbon anodes, metallurgical cokes, etc. Process development services currently provided include consulting, training, and process studies in production of calcined petroleum cokes for aluminum anode-grade. Quality of petroleum cokes was evaluated by Rolle, et. al. [1,2], investigating the effects of metal impurities (vanadium, nickel and sodium) on the properties of cokes and anodes.

The quality of petroleum cokes produced by U. S. refineries has been affected by several major governing factors during the past decade from 1984 to 1993: (1) declining quality of crude oils, (2) coke production increase, (3) market demand and supply in liquid/solid fuels and exports, (4) specifications for end-use products, and (5) coking processes and calcination technology [3]. The average API gravity of crude oils declined annually by 0.17 degree/yr from 33 to 31; and the average sulfur content of crude oils increased by 0.029 wt%/yr from 0.88 to 1.21. As a result the coke production steadily increased by 51 % expecting continuous increase in the coming years, and the sulfur content of cokes is projected to increase from current average, 4.5 wt% to 5.5 wt% in future.

The U. S. coking capacity was fully utilized in 1993 having more than 100% coke production factor. The annual production was 78,430 tons/cd, of which 66% was exports (a major market demand) to Japan, Turkey, Italy, and other countries (total 44). The price of petroleum coke varies highly dependent upon its quality estimating in the range of $19/ton for utility fuel-grade to $550/ton for calcined super-premium needle coke. Anode-grade coke can vary from $45/ton for green (raw) to $200/ton for calcined.

The objective of this study is to evaluate the petroleum coke quality for export primarily based on recent analysis results from calcined petroleum coke produced for aluminum anode grade, green (raw) coke used in calcination, petroleum coke for high- and low-Btu fuel grade, and in addition the quality of low- and high-rank coals is evaluated.

SAMPLING AND PREPARATION

Representative samples of petroleum cokes and coals have been obtained from various refineries in California and storage facilities at numerous national ports. The auto sampler installed at the Long Beach port is sometimes used upon client's request for periodic routine sampling of blends for shipment. Laboratory samples are prepared for quality analysis following the procedures and principles in handling listed in the ASTM Methods D 346, D 2013 and D 2234, which are documented in the Quality Assurance Manual. Analysis samples are designated as refinery daily, weekly, monthly, M/V ship, QC/QA round robin, special test, etc. and stored for additional week, three or six months before disposal.

QUALITY SPECIFICATIONS FOR EXPORT

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 [3]. The other fliud coker and flexicoker are less utilized at a relatively smaller capacity (seven refineries and 0.2 mm b/sd). Coke products are classified as shot, sponge, (sometimes honeycomb), or needle coke depending on their chemical and physical characteristics. Shot coke is hard, having spherical form, and physically produced through precipitating asphaltenes; sponge coke is dull and black, having porous, amorphous structure, and is considered as a mixture of shot and needle cokes; and needle coke is silver-gray, having crystalline broken needle structure, and chemically produced through cross linking of condensed aromatic hydrocarbons during coking reactions[4].

Product grades and uses of green (raw) and calcined petroleum cokes

Green petroleum cokes are mostly used as utility fuels (about 73% for fuel-grade) in power generation and cement production including future developing projects of gasification IGCC and COG, and as feedstock (about 27%) for further upgrading calcination [5]. Uses of calcined cokes are: 71% for aluminum anode-grade, 9% for graphite electrodes, needle-grade, 8% for titanium dioxide pigments, 6% for recarburization of ductile iron products, and 6% for others (chlorine, phosphorous, silicon carbide, calcium carbide, etc.). Needle-grade calcined coke has three types, super-premium (SP), premium (P) and intermediate (I) depending on properties. Calcined petroleum cokes are used as reducing agent in production of titanium dioxide pigments because of extremely low ash and volatile content (6), and are further thermally treated at 2500 deg C to lower sulfur content to 0.03 wt% to meet specifications for recarburization (7).

Fuel-grade green coke

Depending on the location of refineries in the U. S. sulfur content of fuel-grade cokes varies; 2.25-2.60 wt% produced in Kansas and Oklahoma and 4.30-4.95 wt% in California, Louisiana Gulf Coast and Texas Gulf Coast. Typical ranges of coke properties for fuel-grade specifications are listed as follows:

13,000-15,000 Btu/lb
2.5-5.5+ wt% sulfur
200-400+ ppm vanadium
9-12 wt% volatile matter
0.1-0.3 wt% ash
100 HGI

Normally cokes are blended with coals at 10-20 % before burning in boilers because of their low volatile matter and high sulfur content. In use of cement kilns the addition of cokes can constitute up to 50 % of the fuel mixture and is carefully controlled conducting test burn due to detrimental effects of high sulfur and vanadium content to concrete quality [8]. Sulfur contamination can cause cement cracking and preheater plugging, and high vanadium content above 500 ppm can cause cement to lose strength.

Aluminum anode-grade calcined coke

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 as follows [5,7-9]:

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

Graphite needle-grade calcined coke

Feedstocks, needle coke precursors, are characterized by low API gravity, low asphaltene content, and a high degree of aromaticity [8]. Generally hydrocarbon streams are used with low sulfur content catalytic cracker slurry oils, tars derived from the thermal cracking of refinery gas oils, hydrodesulfurized catalytic cracker slurry oils, and coal tar pitches. Operating pressure and temperature of a coker are higher than other coking operations. The most important specification has been the coefficient of thermal expansion (CTE) as an indicator of the coke's structural alignment, which is related to the current-carrying capacity and mechanical integrity of resultant graphite electrodes. Typical ranges of calcined coke properties for graphite needle-grade specifications are listed as follows [7-9]:

Property	Green	Calcined (SP/P/I)
wt% S	0.8	0.8 (0.3-0.8)
wt% ash	0.10	0.15 (0.03-0.2)
ppm V	10	10
ppm Ni		20-40
wt% Si	0.04	0.04
wt% VM	8	<0.25
resistivity, microomega-m		1100
real density, g/cu-cm		2.12 (2.12-2.15)
bulk density, g/cu-cm		0.88
coefficient of thermal expansion per deg C		0.3 x 10 to -6 (0.2-0.4 x 10 to -6)

Coal quality specifications

On-line coal quality analyzers are available for power plant monitoring and optimization resulting in lower operating costs [10]. Electric Power Research Institute (EPRI) developed coal quality impact model (CQIM) and coal quality evaluation system (C-QUEL). Coal quality is based on various complex properties such as heating value, ultimate analysis, ash content, moisture content, sulfur content, and mineral analysis. Key properties correlated for EPRI cause and effect relationships are ash, moisture, sulfur, silica, alumina, heating value, volatile matter, etc.

Typical ranges of coal properties analyzed at the A. J. Edmond Co. are listed in the following. Bituminous coal properties are obtained from M/V ship samples, and subbituminous coal properties are from western coal round robin samples.

Property	Bituminous	Subbituminous
(As-received)		
wt% moisture	6-10 (max. 10)	25-30
wt% ash	8-10	4-8
wt% volatile	36-41	30-35
wt% fixed carbon	42-47	30-35
Btu/lb	11,450-11,750	8,000-9,000
wt% sulfur	0.3-0.5	0.3-0.5
(Ultimate, dry, wt%)		
carbon	71-72.5	66-68
hydrogen	4.5-5.5	4.6-5.1
nitrogen	1.2-1.5	0.9-1.1
chlorine	0.01-0.03	
sulfur	0.4-0.5 (max. 0.7)	0.4-0.6
oxygen	10-12.5	17-20
(Mineral, wt% ash)		
silica	52-62	30-40
alumina	12-17	15-20
ferric oxide	3-7	3-6
titania	0.6-0.8	1-2
phosphorous pentoxide	0.2-0.8	
lime	7-14	15-25
manganese oxide	0.02-0.03	0.01-0.03
magnesia	1-3	3-6
barium oxide	0.04-0.11	
sodium oxide	0.5-4	1-3
potassium oxide	0.4-0.9	0.5-2

Property	Bituminous	Subbituminous
(Mineral, wt% ash)		
sulfur trioxide	5-7	10-15
Hardgrove Grindability Index	45-49	
ash fusion temperature, deg C		
IDT	+1,220	
HT	+1275	
FT	+1,340	
size 50 mm x 0	100%	
2 mm x 0	30% max.	

ANALYTICAL METHODS USED

Laboratory test methods using various advanced analytical instruments are described in the Quality Assurance Manual of A. J. Edmond Co. Primary analytical methods are summarized in the following.

Purpose	ASTM Method		Instrument
metals	D5600	ICP-AES	PE Optima 3000
	D3682	ICP-AES, AA	
	D5056	AA	
sulfur	D4239	LECO	LECO SC 432
	D3177	PARR	PARR 1760
	D1552	Dietert/LECO	
	D5016	LECO	
CHN	D5373	LECO	LECO CHN-1000
N	D3179	KJELDAHL	
	ISO333	KJELDAHL	
Btu	D3286	PARR	PARR 1108, 1261, 1563
moisture	D3173		
ADL/RM	D3302,D4931		
volatile	ISO562,D3175,D4421		
ash	D4422,D3174		
VBD	D4292		
RD	D5004		
HGI	D5003,D409		
sieve	D5709,D293		

QC/QA/SQC PROGRAMS

Laboratory quality control (QC) program includes sample tracking and identification, sample preparation and analysis. Analytical tests are generally run within 24 hour period, however, some analyses of samples, i.e. moisture, sulfur, volatile, shot, etc. are completed in an hour, two hour or eight hour intervals in order to meet customer's requests and respond to any process changes. Information of analysis results is transferred through a Computer Data Base or simply by hand-written daily analytical reports. Statistical quality control (SQC) is performed by X and R control charts to assure good precision and accuracy of data generated with acceptable repeatability and reproducibility. Besides SQC trending or plotting of data, other notable quality assurance checks include use of calibration standards for elemental and metals analyses, daily instrument calibration, and check lists without any known standards. For quality assurance (QA) program in addition to the QC/SQC system, round robin samples of petroleum cokes and coals are analyzed routinely, monthly or as required, for further evaluation of the quality control results.

RESULTS FROM QUALITY TREND ANALYSIS

Quality of green petroleum coke (Figures 1-4)

Figure 1 shows sulfur content of green petroleum cokes obtained from fourteen refineries (designated as coke type A to N) and analyzed during the period of December 19, 1996 to February 20, 1997. Daily, weekly and monthly data are included for trend evaluation. Delayed cokes are A to L, fluid coke is M and type N is delayed coke used for calciner feedstock. A, B and C are best fuel-grade cokes with lowest sulfur content in the range of 0.8-1.6 wt% (average 1.0-1.2 wt%), while L has highest sulfur content of 4.2-6.0 wt%. Sulfur content of fluid coke M is 2.8-3.2 wt%.

In Figure 2 cokes A, B and C have highest heating values (15,500-15,800 Btu/lb), again best suited for fuel feedstock. Heating value of fluid coke M is lowest, 14,300-14,700 Btu/lb.

Figure 3 illustrates ash content varies in the range of 0.2 to 0.5 wt% except for coke N with 0.1 wt% ash, which is used for calciner feedstock.
Vanadium content of cokes significantly varies from 300 to 1600 ppm (Figure 4), depending on origin of production refinery and their usages. Good fuel-grade cokes A to E have vanadium content in the range of 300 to 600 ppm. Calciner feedstock coke N has 300-340 ppm vanadium.

Quality specifications of calcined petroleum coke (Figures 5 and 6)

Three different calcined petroleum cokes selected from M/V ship samples are compared in Figures 5 and 6. Most of our analytical data for these samples are within the specification limits for export. Sulfur content, vibrated bulk density (VBD), real density (RD), vanadium, nickel and sodium metal contents are plotted with actually measured, specification high and low values.

QC/QA/SQC programs

Figure 7 presents a SQC trend X-chart for sulfur content of green petroleum cokes (type A, B, C, L, M and N). For simplicity of presentation, only three data series show average, upper control limit (UCL) and lower control limit (LCL). All data are statistically controlled with two standard deviation interval at 95% confidence level.

SQC trend X-chart for metal contents (V, Ni and Na) of calcined cokes are plotted in Figure 8. These data were generated during the period of July, 1996 to February, 1997. Although the trend shows slightly increases in metal contents (about 20-30 ppm) in the latter part of the period, most of data are within the specification limits for export.

In January, 1997 a QA round robin sample of petroleum coke was analyzed for metal contents using PE Optima 3000 (ICP-AES). Test method was ASTM D 5600 performed with two different dissolution acids, 20% HCl and 4% HNO3, respectively. Results of six analyses are summarized below.

	Concentration, ppm		
Metal	Average	Standard Deviation	ASTM RR Ranges
Si	61.2	25.6	19-94
	83.7 w/HCl	10.0 w/HCl	
	38.7 w/HNO3	4.5 w/HNO3	
Fe	46.5	1.8	17-94
V	402.8	4.4	24-59
Ni	168.2	3.5	17-23
Al	24.3	1.5	15-40
Ca	7.2	1.3	21-36
Na	34.5	6.1	10-31
Cr	0.5	-----	-----

With 20% HCl dissolution acid, silicon content of the coke is observed to be higher by 45 ppm than that with 4% HNO3 dissolution acid. Other metal contents are similar with both acids. Good standard deviation values were obtained, and all are within ASTM repeatability and reproducibility (RR) ranges.

SUMMARY

Quality of green (raw) and calcined petroleum cokes did not significantly change during the study period. Sulfur and metal contents (V, Ni and Na) of these cokes were statistically controlled, meeting the specification limits for export. In January, 1997 a slight increasing trend in metal contents (about 20-30 ppm) was observed. This increase may be speculated due to variety of reasons such as crude oil quality, coking and calcining process conditions, etc. QC/QA round robin results showed good repeatability and reproducibility in determination of metals present in petroleum coke by ICP-AES.

Future studies of interest include: expansion of data base beyond the current study period, coal quality analysis for power plant fuels and metallurgical cokes, sampling and sample preparation, problem solving in QC/QA, and quality impacts on end-use products (aluminum anode, graphite electrode, TiO2, recarburization, etc.).

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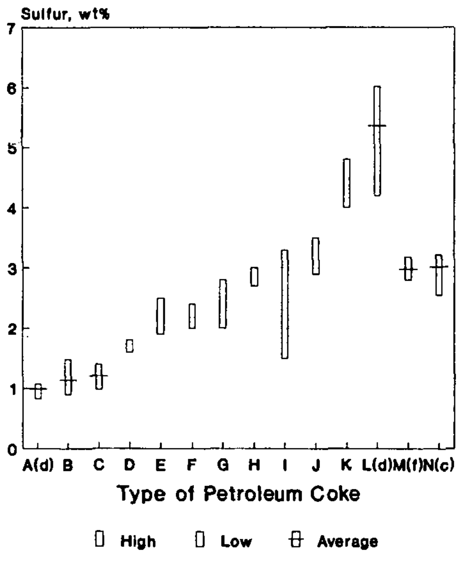
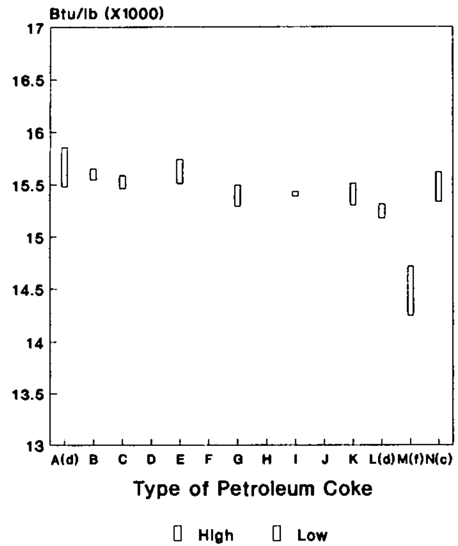
Figure 1. SULFUR CONTENT OF GREEN COKE



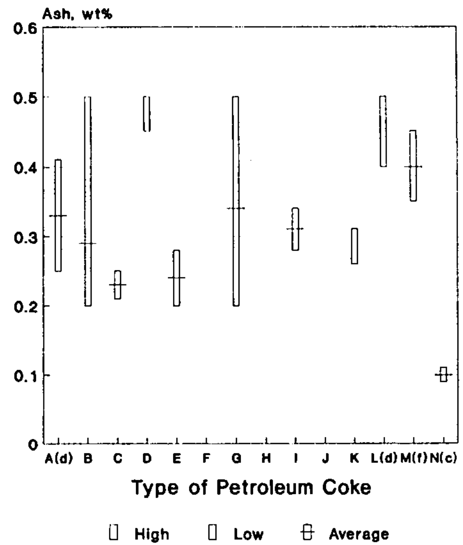
Period: 12/19/96-02/20/97

Figure 2. CALORIFIC VALUE OF GREEN COKE



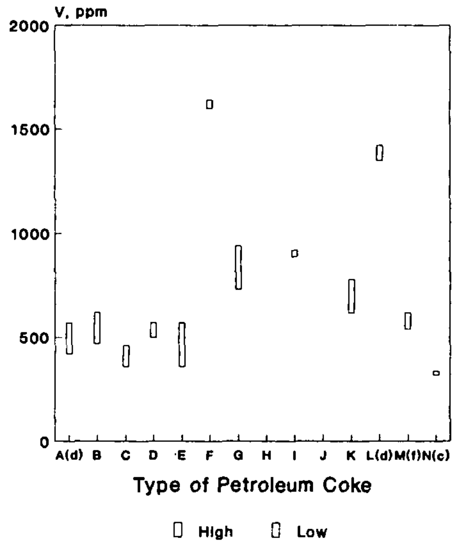
Period: 12/19/96-02/20/97

Figure 3. ASH CONTENT OF GREEN COKE



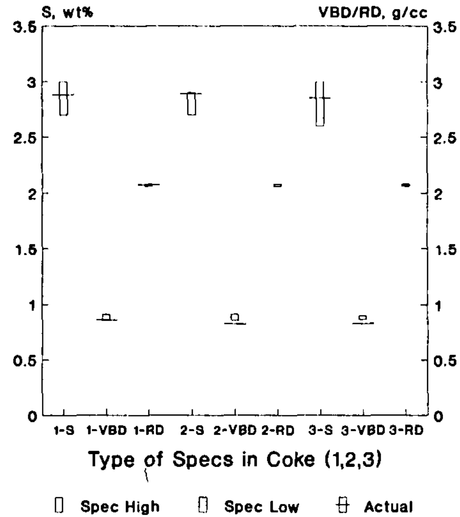
Period: 12/19/96-02/20/97

Figure 4. VANADIUM CONTENT OF GREEN COKE



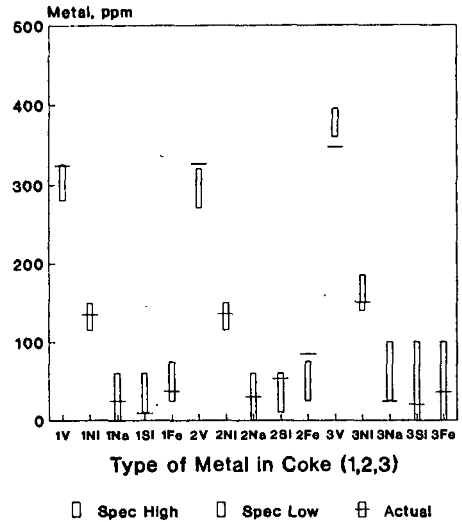
Period: 12/19/96-02/20/97

Figure 5. QUALITY SPECS OF CALCINED COKE
Aluminum Anode-Grade



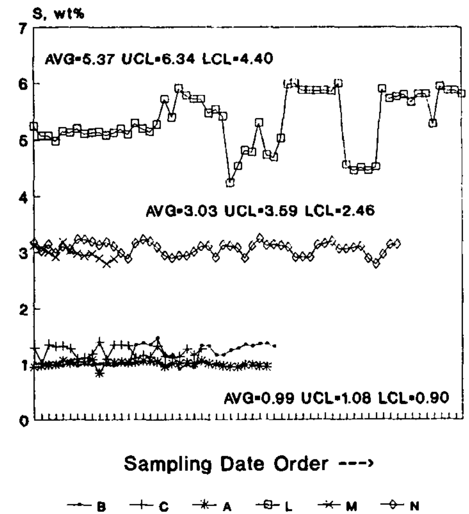
Period: 12/19/96-02/20/97

Figure 6. METAL CONTENT OF CALCINED COKE
Aluminum Anode-Grade



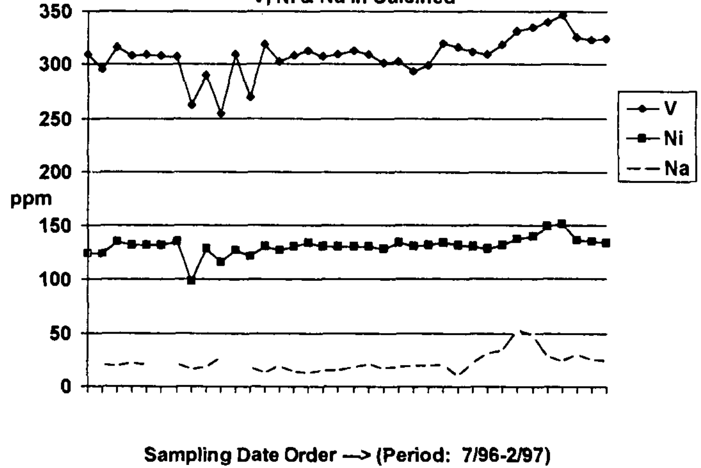
Period: 12/19/96-02/20/97

Figure 7. QC TREND CHART
Sulfur Content of Coke



Period: 12/19/96-02/20/97

Figure 8. QC TREND CHART
V, Ni & Na in Calcined



V: AVG=308.9 UCL=347.1 LCL=270.7
Ni: AVG=130.9 UCL=147.9 LCL=113.9
Na: AVG= 22.5 UCL= 40.7 LCL= 4.3