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PETROLEUM COKE CATEGORY ANALYSIS AND HAZARD CHARACTERIZATION

Submitted to the US EPA

by

**The American Petroleum Institute
Petroleum HPV Testing Group**

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Petroleum Coke Robust Summaries located at <http://www.epa.gov/hpvis/index.html>

SUMMARY

The Petroleum Coke category consists of two substances; green coke and calcined coke. These two substances are grouped together in a category based on their similarity of manufacturing processes which results in similar physical chemical characteristics and chemical composition. The principal difference is the amount of residual hydrocarbon (also termed volatile matter) in the two products. Petroleum coke (both green and calcined) is a black-colored solid produced by the high pressure thermal decomposition of heavy (high boiling) petroleum process streams and residues. Green coke is the initial product from the cracking and carbonization of the feedstocks to produce a substance with a high carbon-to-hydrogen ratio. Green coke undergoes additional thermal processing to produce calcined coke. The additional processing removes volatile matter and increases the percentage of elemental carbon, which results in a lower potential for toxicity for calcined coke.

The hazard potential for the petroleum coke category has been characterized by evaluating existing data, testing green coke to fill data gaps, then 'reading across' the green coke results to the other category member, calcined coke. This is justified because, as stated above, green coke contains higher levels of volatile matter, and therefore, it is "worse case" by comparison to calcined coke. Physical-chemical properties, environmental fate, environmental effects and health effects are summarized below, and more fully discussed in the body of the category analysis. The primary routes for human exposure are dermal and inhalation. With the exception of *in vitro* studies, the mammalian health data provided in this report are from inhalation and dermal studies.

Physical-Chemical Properties:

Because petroleum coke (both green coke and calcined coke) is the substance remaining from treating heavy petroleum feedstocks with high temperature and pressure, many of the physical-chemical properties are not meaningful at ambient environmental conditions. At ambient temperature and pressure, petroleum coke exists as a solid, and because it consists predominantly of elemental carbon and a hardened residuum remaining from the feedstocks, the High Production Volume (HPV) Chemical Challenge Program physical-chemical endpoints either cannot be measured using recommended testing procedures or would not provide meaningful information.

Environmental Fate:

If released to the environment, both forms of petroleum coke would not be expected to undergo many of the HPV environmental fate pathways. Because petroleum coke is predominantly elemental carbon and a hardened residuum, it would not be subject to photolytic processes. These substances do not contain hydrolysable chemical bonds, nor are they susceptible to biodegradation by microorganisms. Depending on the particle size and density of the material, terrestrial releases will become incorporated into the soil or transported via wind or surface water flow. If released to the aquatic environment, petroleum coke will either incorporate into sediment or float on the surface, depending on the particle size and density in relation to water.

Ecotoxicity:

Aquatic and terrestrial ecotoxicity tests were performed to assess the hazard of green petroleum coke to representative aquatic organisms and terrestrial soil-dwelling invertebrates and vascular plants. Testing of selected terrestrial species was included because petroleum coke is sometimes used in a manner that can result in exposure to terrestrial organisms. Aquatic exposures were prepared as water accommodated fractions (WAFs) and attempts were made to analytically quantify specific organic and inorganic constituents of petroleum coke in the WAF solutions. None of those constituents of petroleum coke were present in the WAF solutions at

their analytical detection limits. Because a solubility level could not be established by analytical means, aquatic toxicity test endpoints were presented as nominal WAF loading rates. Loading rate refers to the total amount of petroleum coke added per unit volume of water to produce the WAF. Similarly, endpoints of terrestrial toxicity tests were reported as nominal concentrations of green petroleum coke in soil because constituents of petroleum coke could not be measured in soil at the established exposure level.

Aquatic Hazard: Results of acute aquatic toxicity testing of three species were:

Fish (fathead minnow, <i>Pimephales promelas</i>):	96-h LL_{50} > 1000 mg/L 96-h NOELR = 1000 mg/L
Invertebrate (<i>Daphnia magna</i>):	48-h EL_{50} > 1000 mg/L 48-h NOELR = 1000 mg/L
Alga (<i>Selenastrum capricornutum</i>):	96-h E_bL_{50} > 1000 mg/L 96-h E_rL_{50} > 1000 mg/L 96-h NOELR < 1000 mg/L

Green petroleum coke has a low potential to cause adverse effects on the aquatic environment.

Terrestrial Hazard: Results of terrestrial toxicity testing resulted in the following:

Earthworm (<i>Eisenia fetida</i>):	14-d LC_{50} >1000 mg/kg 14-d NOEC = 1000 mg/kg
Terrestrial plant (corn, <i>Zea mays</i>):	21-d LC_{50} >1000 mg/kg 21-d NOEC = 1000 mg/kg
Terrestrial plant (radish, <i>Raphanus sativus</i>):	21-d LC_{50} >1000 mg/kg 21-d NOEC = 1000 mg/kg
Terrestrial plant (soybean, <i>Glycine max</i>):	21-d LC_{50} >1000 mg/kg 21-d NOEC = 1000 mg/kg

Green petroleum coke has a low potential to cause adverse effect on the terrestrial environment.

Human Health Effects:

Humans can be exposed to petroleum coke primarily via the dermal and inhalation routes. The majority of the existing animal toxicity studies have been conducted on green coke which has a higher volatile matter content than calcined coke. Due to the physical-chemical characteristics of coke described above, and the lack of systemic toxicity observed in a mouse lifetime dermal study, inhalation was considered to be the route of exposure with the greatest potential to demonstrate hazard. The majority of the mammalian health data provided in this report describe inhalation studies.

Acute Toxicity: There are no single dose acute studies on petroleum coke. Repeated-dose inhalation studies on green coke demonstrated a low degree of toxicity with no treatment-related deaths. Based on the OECD 421 Reproductive/Developmental Toxicity Screening Test (see below), the acute inhalation LC_{50} for both green and calcined coke is estimated to be > 300 mg/m^3 . Petroleum coke has a low acute toxicity hazard potential.

Repeated-Dose Toxicity: No Screening Information Data Set (SIDS) guideline repeated-dose studies have been conducted on petroleum coke. Two-year carcinogenicity/chronic toxicity studies on green coke have been conducted in rats and monkeys. Inhalation of petroleum coke in these two studies caused inflammatory and non-oncogenic proliferative changes in the nose and lungs in rats, but not monkeys. These portal-of-entry effects were considered to be non-specific

responses of the respiratory tract to high concentrations of insoluble particles rather than compound specific-induced effects, and are supported by the lack of systemic toxicity observed in the two-year animal studies. Using results of two-year chronic toxicity/carcinogenicity studies in rats and monkeys, a conservative estimate of the portal-of-entry repeated-dose LOAEL was $< 10 \text{ mg/m}^3$, and the inhalation repeated-dose systemic NOAEL was estimated to be $>30 \text{ mg/m}^3$. Additionally, green coke was not carcinogenic in rats or monkeys at 30 mg/m^3 (the highest concentration tested). Petroleum coke repeated-dose hazard potential is low.

In Vitro Genetic Toxicity – Gene mutation: Green coke was not mutagenic in standard *in vitro* genetic toxicity tests in bacteria and mammalian cells. However, when tested in a modification of the *Salmonella* bacterial mutagenicity assay developed for petroleum substance testing, the dimethyl sulfoxide (DMSO) extracts of petroleum coke were mutagenic.

In Vivo Genetic Toxicity: Green coke has been evaluated in three inhalation studies for the ability to produce chromosome aberrations in a bone marrow cytogenetics assay. In the first study, no aberrations were observed in rats after 20 days of exposure to 10 or 40 mg/m^3 petroleum coke. In a second study, an increase in chromosomal abnormalities was seen after 5 days of treatment at the same exposure concentrations used in the first study. However, it was later determined that the slides from the second study had been misread, and that the results from the second study should be considered inconclusive. To resolve uncertainty, a third *in vivo* cytogenetics study was conducted on bone marrow from male and female rats in the chronic inhalation study. Chromosomal aberrations were not seen in this third study after 5 days, 12 months or 22 months of exposure to petroleum coke at 10 or 30 mg/m^3 . The weight of the evidence from these three studies indicates that green coke was not genotoxic in *in vivo* bone marrow chromosome cytogenetic assays. Petroleum coke has a low potential to cause genetic toxicity based on *in vivo* testing.

Reproductive and Developmental Toxicity: No reproductive or developmental effects were observed in an OECD 421 Reproductive/Developmental Toxicity Screening Test at green coke concentrations up to 300 mg/m^3 (the highest concentration tested). The parental systemic toxicity, reproductive toxicity, and developmental toxicity NOAELs were all $> 300 \text{ mg/m}^3$. The reproductive and developmental toxicity hazard potential for petroleum coke is low.

Carcinogenicity: Petroleum coke was not carcinogenic in three carcinogenicity studies. Rats and monkeys were exposed via inhalation five days/week for two years to 0, 10, or 30 mg/m^3 green coke. No excess cancers were observed. In a lifetime skin painting study, mice were exposed to 0 or $100 \mu\text{l}$ of 250 mg/mL green coke and no excess skin or visceral cancers were observed.

Conclusions: Based on the data summarized above and discussed in greater detail in the body of this document, both green coke and calcined coke (using read-across from green coke) have a low potential for inducing adverse effects to the environment and, with the exception of non-compound-specific, insoluble particle portal-of-entry effects, to human health.

1. DESCRIPTION OF PETROLEUM COKE

Petroleum coke is produced through the thermal decomposition of heavy petroleum process streams and residues. The three most common feedstocks used in coking operations are 1) reduced crude (vacuum residue), 2) thermal tar, and 3) decant oil (catalytically cracked clarified oil) (Onder and Bagdoyan, 1993). These feedstocks are heated to thermal cracking temperatures and pressures (485 to 505°C at 400 kPa) that create petroleum liquid and gas product streams. The material remaining from this process is a solid concentrated carbon material, petroleum coke (Ellis and Paul, 2000b; EC, 2003).

Petroleum cokes can be categorized as either green or calcined coke. The initial product of the coking process, green coke, is used as fuel, in gasification and metallurgical processes, or as feedstock to produce calcined coke. Calcined coke is produced when green coke is treated to higher temperatures (1200 to 1350°C). The primary use of calcined coke is in making carbon anodes for the aluminum industry. Other uses include making graphite electrodes for arc furnaces, titanium dioxide, polycarbonate plastics, steel, carbon refractory bricks for blast furnaces, packing media for anode baking furnaces, and material for cathodic protection of pipelines (Ellis and Paul, 2000a; EC, 2003).

1.1. Composition and Structure

Petroleum coke is composed primarily of elemental carbon organized as a porous polycrystalline carbon matrix. In green coke, the pores of the matrix are filled with a hardened residuum remaining from the coker feed (Al-Haj-Ibrahim and Morsi, 1992; Al-Haj-Ibrahim and Ali, 2005). This residuum is referred to as volatile matter¹ (sometimes referred to as residual hydrocarbon) because it distills off during the calcining process (Al-Haj-Ibrahim and Ali, 2005; ASTM International, 2004a). Volatile matter consists of the heavy hydrocarbons remaining from the feedstocks that have not undergone complete carbonization (EC, 2003). Green coke normally contains between 4% and 15% volatile matter, but can contain up to 21% (CONCAWE, 1993; Al-Haj-Ibrahim and Morsi, 1992; IUPAC, 1995). The temperature of the coking drum as well as cycle time and drum pressure all affect the amount of volatile matter in green and calcined coke (Ellis and Paul, 2000b). Because of the lower temperature used in its production, green coke contains higher levels of volatile matter than calcined coke.

The specific chemical composition of any given batch of petroleum coke is determined by the composition of the feedstocks used in the coking process, which in turn are dependent upon the composition of the crude oil and refinery processing from which the feedstock is derived (Al-Haj-Ibrahim and Morsi, 1992; CONCAWE, 1993; Dalbey *et al.*, 1998; Ellis and Paul, 2000b). Cokes produced from feedstocks high in asphaltenes will contain higher concentrations of sulfur and metals than cokes produced from high aromatic feedstocks (Onder and Bagdoyan, 1993). This is because asphaltenes contain a disproportionate fraction of those heteroatoms (Onder and Bagdoyan, 1993; Siskin *et al.*, 2006). Most of the sulfur in coke exists as organic sulfur bound to the carbon matrix. However, the structure of organic sulfur compounds in petroleum coke is largely unknown, and no precise analytical methods are available to determine these structures (Al-Haj-Ibrahim and Morsi, 1992). Other forms of sulfur found in coke include sulfates and pyritic sulfur, but these rarely make up more than 0.02% of the total sulfur in coke (Al-Haj-Ibrahim and Morsi, 1992). Metals, mainly vanadium and nickel, occur as metal chelates or porphyrins in the asphaltene fraction (Ellis and Paul, 2000a,b). Some metals are intercalated in the coke structure and are not chemically bonded, so they become

¹Volatile matter is hydrocarbons that are driven out of petroleum coke at 950°C (1742°F) under strictly controlled conditions per ASTM method D 6374-99

part of the ash and particulates (Ellis and Paul, 2000b). Metal concentrations in coke normally increase upon calcining due to the weight loss from evolution of the volatile matter (Lee *et al.*, 1997; Ellis and Paul, 2000a). In practice, however, calcined cokes typically contain lower metal concentrations than many grades of green coke due to the selection of low-metal green cokes for calcining (Lee *et al.*, 1997).-

1.2. Coking Processes and Terminology

Petroleum coke is formed from two basic reactions, dealkylation and dehydrogenation (Onder and Bagdoyan, 1993).

Dealkylation – When high molecular weight compounds such as asphaltenes and resins are subject to elevated temperatures in the coker unit, the resulting carbon residue is a highly disordered and cross-linked structure. This is marked by a significant difference in the concentration of hydrogen atoms measured in the resin-asphaltene feed and the formed coke. The carbon to hydrogen ratio increases from a range of 8-10 in the feed to 20-24 in the coke. This amorphous character, combined with high concentrations of impurities, render the coke produced from resin-asphaltene compounds unsuitable for special applications.

Dehydrogenation – This mechanism depends on the dehydrogenation of heavy oils with subsequent condensation of free radicals to form high molecular weight compounds with high carbon-to-hydrogen ratios. The coke thus produced contains fewer cross-linkages and has a more crystalline appearance than the resin-asphaltene based coke. Coke formed from feedstocks such as thermal cracker tars, catalytic cracker slurry, and decant oil, which are high in aromatics and low in resin-asphaltenes, is a premium grade product suitable for calcining and graphitization.

Green coke can be produced by one of three processes: delayed, fluid or flexicoking. Delayed process coke is produced by a semi-continuous batch process and accounts for more than 92% of total coke production in the United States (Pace Consultants Inc., 2001). Fluid coke is produced by a continuous fluidized bed process. Fluid coke typically contains less volatile matter than delayed process green coke but more than calcined coke, and occurs as spherical grains less than 1 cm in diameter (CONCAWE, 1993). Flexicoke is produced by a variant of the fluidized bed process in which most of the coke (up to 97%) is converted to a low heating value (20 to 40 Btu/scf) fuel gas for use at the refinery where it was produced. Solid flexicoke has a smaller particle size than fluid coke and is dustier due to its lower volatile matter content (CONCAWE, 1993; Roundtree, 1998).

Depending on its physical form, green coke produced in delayed cokers may also be classified as shot, sponge or needle coke. Shot coke occurs as small, hard spheres and is derived from low API gravity and high asphaltene and resin petroleum precursors via the dealkylation reaction mechanism. Sponge coke is the most common form of green coke and it has a macroscopically amorphous appearance. Visibly, it has a dull black color and a porous consistency with walls and pores that vary in size. It is normally derived from virgin petroleum feedstocks, which contain large numbers of cross linkages. Gas bubble percolation inside the coke drum may also account for generation of some sponge coke. In reality, sponge coke is a mixture of shot and needle coke structures. Needle coke appears as silver-gray colored ocular structures (ribbon-like, crystalline needles) and is derived from feedstocks with high aromatic hydrocarbon content via the dehydrogenation reaction mechanism (Lee *et al.*, 1997; Ellis & Paul, 2000b).

Calcined coke is produced from green coke by a process of further heating at temperatures in excess of 1200°C (CONCAWE, 1993). Most uses other than for fuel or gasification require green coke to be calcined in order to improve its properties. The

process of calcining removes moisture, reduces the volatile matter to less than 0.4%, increases the density of the coke structure, increases physical strength, and increases the electrical conductivity of the material (Ellis and Paul, 2000a). When green coke is calcined, devolatilization of volatile matter occurs at 500 to 1000°C. Heating further to 1200 to 1400°C causes additional dehydrogenation, some desulfurization, and coke structural shrinkage (densification) (Ellis and Paul, 2000a). The result is a hard, dense substance with low hydrogen content, a low coefficient of thermal expansion, and good electrical conductivity. These properties along with low metals and ash contents make calcined petroleum coke highly desirable for use in the aluminum smelting industry (Ellis and Paul, 2000a). Calcined coke is characterized as either anode-grade coke or graphite needle-grade coke depending upon its physical and chemical characteristics, with needle-grade coke having a higher purity (i.e., lower ash, sulfur, and metals contents (Lee *et al.*, 1997) than anode-grade coke, which is used in electric furnaces in aluminum and steel smelting. The physical characteristics of petroleum coke are important in determining the suitability of a coke sample for a specific use. These characteristics are typically the real and bulk densities and, in the case of anode and needle grade coke, the resistivity and coefficient of thermal expansion. Fuel grade coke may also be characterized by its fuel value (Btu/lb).

Green coke and calcined coke are covered by two separate definitions of petroleum coke in the Chemical Abstract Service and EINECS Registry systems. They are: Petroleum coke and Coke (petroleum) calcined. The definitions of these substances are listed in Appendix 1.

1.3. Analytical Characterization

Physical and compositional characteristics considered important in petroleum coke include weight % ash, weight % sulfur, weight % volatile matter, nickel (mg/kg), and vanadium (mg/kg) (Lee *et al.*, 1997). Examples of selected physical and compositional characteristics between fuel grade green and aluminum grade calcined coke are shown in Table 1.

Properties ²	Fuel-Grade Green Coke	Anode-grade calcined Coke
Sulfur (wt%)	2.5 – 5.5	1.7 – 3.0
Ash (wt%)	0.1 – 0.3	0.1 – 0.3
Nickel (ppm)	N.D. ³	165 – 350
Vanadium (ppm)	200 – 400	120 – 350
Volatile matter (wt%)	9 – 12	<0.25
Bulk density (g/cm ³)	N.D.	0.80
Real density (g/cm ³)	N.D.	2.06

¹From Lee *et al.*, 1997

²The above values are given for illustration and may vary depending upon the feedstock or crude oil of origin

³Not determined

Analyses of green petroleum coke have measured various polyaromatic compounds (PACs) and metals in neat samples. Organic solvent extracts of green petroleum coke prepared for gas chromatographic analyses have revealed various parent and alkylated polyaromatic hydrocarbons (CONCAWE, 1993; Dalbey, *et al.*, 1998). Metals also have been measured in neat green coke samples by X-ray fluorescence or inductively coupled plasma spectroscopic methods (Ellis and Paul, 200a). Characterization data of green coke test samples used in HPV testing confirmed low concentrations of both PACs and metals in such preparations (Appendix B). In contrast, metals and selected PACs were

not found in detectable concentrations in aqueous WAF solutions used in aquatic toxicity tests conducted for the HPV testing program (Wildlife International Ltd., 2006a-c).

2. CATEGORY DEFINITION AND JUSTIFICATION

The petroleum coke category contains two substances (see Appendix 1 for full CAS definitions):

Coke (petroleum) [also known as green coke] CAS # 64741-79-3

Coke (petroleum), calcined CAS # 64743-05-1

These substances are grouped together in one category based on a similarity of their manufacturing processes, which results in similar physical chemical characteristics and chemical composition. Green coke undergoes additional thermal processing to produce calcined coke. The additional processing removes volatile matter and increases the percentage of elemental carbon, which results in calcined coke having a lower potential for toxicity. Therefore, the hazard potential for the petroleum coke category was characterized by testing green coke, then 'reading across' from the green coke results to calcined coke.

3. TEST MATERIALS

3.1. PREVIOUS STUDIES

Analytical data for green coke samples used in previous and new toxicity studies are presented in Appendix B.

3.2. NEW STUDIES

To select a sample of green coke for studies to fill data gaps² with the highest potential for health and environmental effects, delayed green coke analytical data from a database on U.S. coke dating since 1983 were evaluated (Pace Consultants, Inc., 2001). Samples of green coke produced from the delayed coking process were selected over cokes derived using the fluid or flexicoking processes because delayed green coke constitutes 92% or more of the U.S. coking production (Pace Consultants, Inc., 2001), and delayed green coke typically contains higher percentages of volatile matter (CONCAWE, 1993). Specifically, data from 1998 and 1999 were evaluated for sulfur (wt %), nickel (ppm), vanadium (ppm), and volatile matter (wt %). The 1999 dataset contained data on over 92% of the coke produced in the U.S. that year. No single candidate refinery produced green coke with the highest content in all four properties, so some compromise was required for test material producer selection. Table 2 summarizes the ranges of sulfur, nickel, vanadium and hydrocarbon content for coke produced by the five candidate refineries and lists the coke quality data properties from the candidate refinery selected to provide test material for studies to fill the HPV endpoint data gaps (Pace Consultants Inc., 2001).

Table 2¹

² OECD 203 Fish acute toxicity test; OECD 202 Invertebrate acute toxicity test; OECD 201 Algal growth inhibition test; OECD 208 Seedling emergence and growth of terrestrial plants; OECD 207 Earthworm acute toxicity test; OECD 421 Reproduction/developmental toxicity test

Comparison of Properties of Green Coke from Supplier Candidates and Selected Green Coke Supplier for HPV Test Material				
Property	Five Candidate Refinery Coke Quality Ranges		Coke Quality for Refinery that Provided HPV Testing Sample	
	Value	Percentile	Value	Percentile
Sulfur (Wt. %)	4.20 – 6.00	43 - 93	5.75	86
Nickel (ppm)	250 - 500	50 - 90	300	58
Vanadium (ppm)	1,000 – 1,500	65 - 84	1,200	75
Volatile Matter (Wt. %)	10.0 – 15.0	25 - 100	12.0	75

¹ Pace Consultants Inc., 2001

Detailed analysis of the selected green coke test sample is provided in Appendix B.

4. PHYSICAL-CHEMICAL PROPERTIES

Petroleum coke is a product of extreme temperature and pressure treatments that convert heavy petroleum feedstocks into a solid substance composed predominately of carbon. Because of its structural and compositional characteristics, developing the physical-chemical and environmental fate endpoints of the HPV program would not be feasible using standard OECD testing methods.

4.1. Physical-Chemical Screening Information Data Set (SIDS)

The physical-chemical endpoints in the HPV chemicals program include the following:

- Melting Point
- Boiling Point
- Vapor Pressure
- Octanol/Water Partition Coefficient
- Water Solubility

Green petroleum coke exists as a solid substance composed of predominately carbon in a polycrystalline porous matrix. Approximately nine to 21% by weight of green petroleum coke is volatile matter that it is driven off during calcinations. This substance exists in green coke as a hardened residuum in the carbon matrix (Al-Haj-Ibrahim and Morsi, 1992; Al-Haj-Ibrahim and Ali, 2005). Due to the extreme temperature and pressure under which petroleum coke is produced, melting point, boiling point, and vapor pressure measurements would not reveal meaningful data at ambient environmental conditions.

For similar reasons, measurements of partition coefficient and water solubility are not possible for green petroleum coke. Partition coefficient and water solubility require analytical measurements of the test substance in n-octanol and/or water. While selected organic solvents have demonstrated an ability to extract some of the organic fraction from the neat green coke (Dalbey *et al.*, 1998; Clayton Environmental Consultants, 1983; Monarca *et al.*, 1982; Klonne *et al.*, 1987), attempts to measure selected hydrocarbon compounds and inorganic components of petroleum coke in water extracts failed at the detection limits of the analytical methods (e.g. 5 µg/L for the organic fraction, 0.4 µg/L to 200 µg/L for metals, and 5.1 mg/L for sulfur (Wildlife International, Ltd., 2007a-c). Because components in green petroleum coke were insufficiently soluble in water, neither water solubility nor partition coefficient measurements can be made.

Conclusions: The HPV physical-chemical endpoints for green or calcined petroleum coke either cannot be measured or would not provide meaningful data at ambient environmental conditions.

4.2. Assessment Summary for Physical-Chemical Endpoints

Green petroleum coke is a complex mixture of mostly elemental carbon with inorganic and organic constituents embedded in a solid poly-crystalline porous matrix. Under ambient environmental conditions, characteristics of melting point, boiling point, vapor pressure, partition coefficient, and water solubility cannot be measured in either green or calcined petroleum coke due to analytical limitations or the physical nature of petroleum coke.

5. ENVIRONMENTAL FATE

5.1. Environmental Fate Endpoints

5.1.1. Photodegradation

5.1.1.1. Direct

A prerequisite for direct photodegradation is the ability of one or more bonds within a chemical to absorb ultraviolet (UV)/visible light in the 290 nm to 750 nm wavelength range. Light wavelengths longer than 750 nm do not contain sufficient energy to break chemical bonds, while wavelengths below 290 nm are shielded from the earth by the stratospheric ozone layer (Harris, 1982a). Because petroleum coke consists of mostly elemental carbon, there are no chemical bonds upon which direct or indirect photochemical reactions may act. Photodegradation of residual constituents in petroleum coke (e.g., metals and high molecular weight hydrocarbons) would not be expected to take place. These substances are neither water-soluble nor volatile at ambient temperatures, thus would not engage in direct or indirect photochemical reactions. Therefore, direct photodegradation is not an important fate process for petroleum coke.

5.1.1.2. Indirect

Indirect photodegradation occurs in the atmosphere when organic chemicals react with photosensitized oxygen in the form of hydroxyl radicals. Atmospheric oxidation as a result of hydroxyl radical attack is not direct photochemical degradation but an indirect degradation process. Because petroleum coke consists mostly of elemental carbon and other residual constituents that are generally non-volatile at ambient temperatures, indirect photodegradation is not an important fate process for petroleum coke.

Conclusion: Direct and indirect photodegradation are not important fate processes for green or calcined petroleum coke.

5.1.2. Stability in Water

Hydrolysis of an organic molecule occurs when a molecule (R-X) reacts with water (H₂O) to form a new carbon-oxygen bond after the carbon-X bond is cleaved (Harris, 1982b). This reaction is referred to as nucleophilic substitution, where X is the leaving group being replaced by the incoming nucleophilic oxygen from the water molecule. The leaving group, X, must be a molecule other than carbon because carbon atoms lack sufficient electronegativity to serve as a good leaving group (i.e., carbon-carbon bonds are too stable to be cleaved by nucleophilic substitution). Chemicals that have a potential

to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters (Harris, 1982b).

Petroleum coke is composed of elemental carbon and other components that are not susceptible to nucleophilic substitution. Therefore, petroleum coke is not subject to hydrolysis, and this fate process will not be an important degradative pathway in the environment.

Conclusion: Hydrolysis is not an important degradative pathway for green or calcined petroleum coke.

5.1.3. Transport Between Environment Compartments Fugacity/Distribution

Elemental carbon and the residual components are neither sufficiently water soluble nor volatile in the environment to be evaluated by fugacity-based multimedia modeling. If released to the environment, petroleum coke is expected to be chemically and physically inert. Depending on the particle size and density of the material, terrestrial releases will become incorporated into the soil or transported via wind or surface water flow. If released to the aquatic environment, petroleum coke will either be incorporated into sediment or float on the surface, depending on the particle size and density in relation to water.

Conclusion: Green and calcined petroleum coke are expected to be chemically and physically inert in the environment, with transport related to particle size and density in relation to wind and water.

5.1.4. Biodegradation

Biodegradation occurs when microorganisms transform an organic molecule into carbon dioxide, water, and energy. The reduction or oxidation of chemical bonds in an organic molecule provides the energy and carbon to build new cell material. Petroleum coke is composed mainly of elemental carbon which does not contain the chemical bonds that microbes require for metabolism. Other constituents embedded in the carbon matrix include inorganic substances and high molecular weight hydrocarbon compounds remaining as residuum from the coking process. These constituents would not be expected to be available for microbial degradation. Therefore, biodegradation is not considered an important fate process for petroleum coke.

Conclusion: Biodegradation is not considered an important fate process for green or calcined petroleum coke.

5.2. Assessment Summary for Environmental Fate

Green and calcined petroleum coke are complex mixtures of mostly elemental carbon with inorganic and organic constituents embedded in the carbon matrix. In general, these constituents do not contain the chemical bonds that engage in photolytic or hydrolytic reactions. If released to the environment, petroleum coke would be expected to be non-reactive and either disperse or remain in the environmental compartment to which it was released.

Therefore, depending on factors such as particle size and density relationships of the petroleum coke and environmental media, releases to terrestrial or aquatic environments would result in incorporation of the material into soils/sediments or dispersal via wind/water action. Biodegradation would not be an important fate process because the

majority of the constituents in petroleum coke do not contain the chemical bonds needed for microbial metabolism.

6. ENVIRONMENTAL EFFECTS

6.1. AQUATIC TOXICITY

6.1.1. Aquatic Endpoints

The potential hazard of green petroleum coke to freshwater aquatic organisms was assessed by testing a fish (*Pimephales promelas*), an invertebrate (*Daphnia magna*), and an alga (*Selenastrum capricornutum*). All studies employed aqueous exposure solutions prepared as water accommodated fractions (WAFs) in accordance with OECD recommendations for testing complex mixtures having low water solubility (OECD, 2000a). Green coke used to prepare the WAF solutions was milled and sieved to approximately 2 mm grain size and was separated from the aqueous phase following a period of mixing. Under an aquatic spill scenario, adverse effects of petroleum coke on aquatic organisms potentially could arise due to physical effects of coke particulate matter on respiratory membranes of the organisms. The 2 mm grain size allowed the segregation of the solid particles following the preparation of the WAF solutions.

Prior to testing, the test sample of green petroleum coke was characterized for a series of specific inorganic constituents and predominantly un-alkylated polycyclic aromatic hydrocarbons (PAH). A subset of those analytes and compounds were used as markers in the WAF solutions during each aquatic toxicity test. Attempts to measure these constituents in fresh and aged WAF solutions used in the three aquatic toxicity tests showed their concentrations to be less than the minimum quantifiable limits for the methods used (detection limits were 5µg/L for PAHs, 0.4 µg/L to 200 µg/L for metals, and 5.1 mg/L for sulfur). The aquatic toxicity test endpoints are presented as nominal WAF loading rates. Acute effects on aquatic organisms are unlikely except at concentrations above the solubility limits of the measured constituents. However, the solubility limits could not be defined in these tests because of the extremely low solubility of those constituents from the coke matrix and the limits of the analytical methodology.

6.1.2. Acute Toxicity to Aquatic Vertebrates

The test with the fathead minnow (*P. promelas*) was conducted following OECD (OECD, 1992) and EPA guidelines (US EPA, 1996a) as a 96-hour static-renewal limit test using a negative control group and a single petroleum coke (green coke) WAF prepared at a loading rate of 1000 mg/L. Each experimental group consisted of 30 fish divided among three test chambers (10 fish/replicate). Test chambers were completely filled with no headspace and sealed to mitigate potential loss of any component during the testing period. Fresh WAF solutions were prepared daily and fish were transferred to the fresh solutions after approximately 24, 48 and 72 hours of the 96-hour exposure period (Wildlife International Ltd., 2006a).

No mortality occurred, and no clinical signs of toxicity were evident among the fish of the control and 1000 mg/L WAF exposure groups during the 96-hour exposure period. The endpoints of the test were defined as follows:

96-hour LL₅₀ > 1000 mg/L (WAF nominal loading rate)

96-hour no mortality level = 1000 mg/L (WAF nominal loading rate)

96-hour NOELR = 1000 mg/L (WAF nominal loading rate)

Conclusion: The results of this study indicate that WAFs of green petroleum coke are not acutely toxic to freshwater fish at the loading rate used in the test.

6.1.3. Acute Toxicity to Freshwater Invertebrates

The test with the freshwater invertebrate, *Daphnia magna*, was conducted following OECD (OECD, 1984a) and EPA (US EPA, 1996b) guidelines as a 48-hour static-renewal limit test using a negative control group and a single petroleum coke (green coke) WAF prepared at a loading rate of 1000 mg/L. Each experimental group consisted of 30 *D. magna* divided among three test chambers (10 animals/replicate). Test chambers were completely filled with no headspace and sealed to mitigate loss of any component during the testing period. Fresh WAF solutions were prepared after approximately 24 hours, and animals were transferred to the fresh solutions (Wildlife International Ltd., 2006b).

No immobility occurred, and no clinical signs of toxicity were evident among the invertebrates of the control and 1000 mg/L WAF exposure groups during the 48-hour exposure period. The endpoints of the test were defined as follows:

48-hour $EL_{50} > 1000$ mg/L (WAF nominal loading rate)

48-hour no immobility level = 1000 mg/L (WAF nominal loading rate)

48-hour NOELR = 1000 mg/L (WAF nominal loading rate)

Conclusion: The results indicate that WAFs of green petroleum coke are not toxic to freshwater aquatic invertebrates at the loading rate used in the test.

6.1.4. Acute Toxicity to Aquatic Plants

The test with the freshwater alga, *Selenastrum capricornutum*, was conducted following OECD (OECD, 1984b) and EPA (US EPA, 1996c) guidelines as a 96-hour limit test using a negative control group and a single petroleum coke (green coke) WAF prepared at a loading rate of 1000 mg/L. The WAFs were prepared in freshwater algal nutrient medium and added to sterile 300-mL BOD bottles. Each bottle was inoculated with algal cells to achieve an initial cell density of 5,000 cells/mL. BOD bottles were completely filled and sealed to mitigate loss of any component during the test period. Bottles were incubated under constant illumination, and cell densities were determined using a hemocytometer and microscope from samples taken at 24, 48, 72, and 96 hours. Cell count data were used to calculate the area under the growth curve (AUGC) and average specific growth rate (μ) (Wildlife International Ltd., 2006c).

Some slight inhibition of growth (AUGC) and growth rate (μ) were found in the 1000 mg/L WAF when compared to the control group at 72 hours (26% and 12%, respectively) and at 96 hours (28% and 7.1%, respectively). Differences were noted as statistically significant ($p = < 0.05$), although no such effect was observed in prior range finding testing of algae. The endpoints of the test were defined as follows:

72-hour $E_{bL_{50}} > 1000$ mg/L (WAF nominal loading rate)

72-hour $E_{rL_{50}} > 1000$ mg/L (WAF nominal loading rate)

72-hour NOELR < 1000 mg/L (WAF nominal loading rate)

96-hour $E_{bL_{50}} > 1000$ mg/L (WAF nominal loading rate)

96-hour $E_{rL_{50}} > 1000$ mg/L (WAF nominal loading rate)

96-hour NOELR < 1000 mg/L (WAF nominal loading rate)

Conclusion: The results indicate that WAFs of green petroleum coke may produce a slight growth inhibition in freshwater algae at the loading rate used in the test.

6.2. TERRESTRIAL TOXICITY

6.2.1. Terrestrial Endpoints

Petroleum coke is sometimes used in a manner that can result in exposure to selected terrestrial species. For example, it is used in soil as a grounding agent to protect sensitive installations from lightning strikes (NLSI, 2002), and it has been experimentally used as an absorbent for the removal of crude oil from soils (Narayannan and Arnold, 1997). Therefore the potential hazards to terrestrial organisms were evaluated.

The hazards of green petroleum coke to terrestrial organisms were assessed by testing an earthworm (*Eisenia fetida*), and three species of terrestrial plants (corn, *Zea mays*; radish, *Raphanus sativus*; and soybean, *Glycine max*). Testing methods followed OECD and/or EPA guidelines. All studies were conducted as limit tests using single maximum test concentrations of 1000 mg/kg (dry weight) of green petroleum coke incorporated into the soil. Petroleum coke used in terrestrial testing was milled to mean particle size of 3.3 μm . The small particle size permitted the incorporation of the substance in soil and maximized the potential for contact between the coke particles and the test species.

Prior to testing, the test sample of green petroleum coke was characterized for selected inorganic constituents and predominantly un-alkylated polycyclic aromatic hydrocarbons (PAH). It was anticipated that those analytes and compounds could be used as dose verification markers when analyzed in the soil during each test. Subsequent analytical method verification trials showed that the PAH markers were below analytical detection limits, while the inorganic metals were not greater than soil background levels. Therefore, all terrestrial effects tests were based on the nominal concentration of petroleum coke in soil.

6.2.2. Toxicity to Terrestrial Plants

Toxicity of green petroleum coke to terrestrial plants was evaluated in a 21-day limit test using petroleum coke at a concentration of 1000 mg/kg (dry weight) in soil. Un-treated soil was used in the negative control group. Test methodology followed OECD (OECD 2000b) and EPA (US EPA 1996 d, e) guidelines. Corn (*Zea mays*), radish (*Raphanus sativus*), and soybean (*Glycine max*) were exposed to the soil-incorporated petroleum coke and assessed for seedling emergence, survival, growth (measured as both seedling height and above-ground dry weight), and seedling condition. The control and exposure groups for each test species consisted of four replicate containers holding 1.87 kg (dry weight) of soil and 10 seeds (Wildlife International Ltd., 2006d).

Corn: No statistically significant differences ($p > 0.05$) were found for seedling emergence, seedling survival, seedling height, or shoot dry weight between the dosed and control groups. Condition scores revealed no treatment-related effects. The results for the test with corn were:

21-day $LC_{50} > 1000$ mg/kg (nominal concentration)

21-day NOEC = 1000 mg/kg (nominal concentration)

Radish: No statistically significant differences ($p > 0.05$) were found for seedling emergence, seedling survival, seedling height, or shoot dry weight between the dosed and control groups. Condition scores revealed no treatment-related effects. The results for the test with radish were:

21-day $LC_{50} > 1000$ mg/kg (nominal concentration)

21-day NOEC = 1000 mg/kg (nominal concentration)

Soybean: No statistically significant differences ($p > 0.05$) were found for seedling emergence, seedling survival, seedling height, or shoot dry weight between the dosed and control groups. Condition scores revealed no treatment-related effects. The results for the test with soybean were:

21-day $LC_{50} > 1000$ mg/kg (nominal concentration)

21-day NOEC = 1000 mg/kg (nominal concentration)

Conclusion: The results indicate that green petroleum coke is not toxic to terrestrial plants at the concentration tested.

6.2.3. Toxicity to Soil Dwelling Organisms

Toxicity of green petroleum coke to earthworms (*E. fetida*) was evaluated following OECD guidelines (OECD, 1984c) in a 14-day limit test using soil-incorporated petroleum coke at a concentration of 1000 mg/kg (dry weight). Un-treated soil was used in the negative control group. The test and control experimental groups consisted of four replicate containers each holding 750 g of soil and 10 earthworms. During the 14-day test, the earthworms were assessed for survival, burrowing behavior, general appearance, and mean body weight (Wildlife International Ltd., 2006e).

No mortality occurred in any replicate of the control or the 1000 mg/kg treatment groups, and in general, earthworms were normal in appearance. None of the earthworms of the control or treatment groups showed any aversion to the soil or in soil burrowing behavior. There were no statistical differences ($p > 0.05$) in earthworm body weight or change in body weight when measured at the end of the test. The results of the test were defined as follows:

14-day $LC_{50} > 1000$ mg/kg (nominal concentration)

14-day no mortality concentration = 1000 mg/kg (nominal concentration)

14-day NOEC = 1000 mg/kg (nominal concentration)

Conclusion: The results indicate that green petroleum coke is not toxic to earthworms at the concentration tested.

6.3. Assessment Summary for Environmental Effects

Petroleum coke (green coke) had no effects on aquatic vertebrates and invertebrates and only a slight effect on algae at a WAF loading rate of 1000 mg/L. Petroleum coke did not produce any adverse effects in earthworms and three species of terrestrial vascular plants at 1000 mg/kg soil. Green coke is considered to have a higher potential to induce

environmental effects than calcined coke due to green coke's higher concentration of volatile matter. In lieu of testing calcined coke, green coke testing results have been conservatively extrapolated to calcined coke (see Table 3). Overall, petroleum coke has an extremely low environmental hazard potential.

7. HUMAN HEALTH ENDPOINTS

Humans are primarily exposed to petroleum coke via the dermal and inhalation routes (CONCAWE, 1993). Due to the physical-chemical characteristics of coke described above (Section 1), and the lack of systemic toxicity observed in a mouse lifetime dermal study (Wingate and Hepler, 1982), inhalation was considered to be the route of exposure with the highest hazard potential. Consequently, the inhalation route of exposure was used in the one new study (OECD 421 Reproductive/Developmental Toxicity Screening Test) performed to fill HPV program data gaps for reproductive and developmental endpoints. Similarly, the majority of mammalian health data provided in this report are from inhalation studies.

The majority of the existing animal toxicity studies have been conducted on green coke which has a higher volatile matter content than calcined coke. There has been one repeated-dose study of limited scope in which calcined coke was tested for comparison to the green coke. Summary evaluations of the existing studies and the one newly completed study are presented below. Results are summarized in Table 3.

7.1. Human Health Effects

7.1.1. Acute Toxicity

There are no single-dose toxicity studies available on either green or calcined coke.

In the OECD 421 Reproductive/Developmental Toxicity Screening Test described in Section 7.1.2 below, male and female Sprague-Dawley rats were exposed for 6 h/day, 7 days/week to up to 300 mg/m³ green coke in the two-week range-finding study and up to 300 mg/m³ for a minimum of 35 days in the definitive study. No animals died prior to the scheduled termination of the studies. Consequently, the acute inhalation LC₅₀ for green coke in rats is estimated to be > 300 mg/m³ (HLS, 2006).

A repeated-dose inhalation study was conducted to compare lung responses to green and calcined coke (HLS, 1999). In this study, rats were exposed by nose-only inhalation for five days to 50 mg/m³ calcined coke or green coke. A silicon dioxide exposure group was also used as a benchmark to judge the potential for the coke samples to cause lung fibrosis. The average mass median aerodynamic particle sizes were 2.71 μm, 2.69 μm, and 1.74 μm for green coke, calcined coke and silicone dioxide, respectively. Lung response was evaluated by analysis of lung fluids at 7, 28 and 63 days after exposure. No animals died prior to the scheduled sacrifice date. Both green and calcined coke caused slight inflammatory responses in the lung, with the response to green coke being slightly higher. There was no indication of a fibrogenic response from exposure to either the green or calcined coke. The results from this study are consistent with results from the rat and monkey inhalation studies and the OECD 421 Reproductive/ Developmental Toxicity Screening Test described in more detail in section 7.1.2 below. Importantly, this study demonstrated that effects observed with calcined coke were less severe than those of green coke, thus supporting category read-across from green coke to calcined coke in this category analysis document.

Conclusions: There are no single dose studies on green or calcined petroleum coke. Repeated-dose and OECD 421 inhalation studies demonstrated a low degree of toxicity

with no treatment-related deaths. Based on the OECD 421 study, the acute inhalation toxicity of both green and calcined coke is estimated to be $> 300 \text{ mg/m}^3$.

7.1.2. Repeated-Dose Toxicity

Two-year whole-body inhalation toxicity studies of sponge-form delayed process green coke were conducted in both Sprague-Dawley rats and Cynomolgus monkeys (IRDC, 1985; Klonne *et al.*, 1987). Both studies were conducted at concentrations of 10 and 30 mg/m^3 of green coke, which had been micronized into fine particles to aid in aerosol generation. The average mass median aerodynamic particle size of $3.1 \pm 1.9 \mu\text{m}$ was stable over the entire exposure period. The animals were exposed 6 h/day, 5 days/week, except holidays, for two years. Group sizes in the studies were four mature adult monkeys per sex per control and exposed groups, and 150 rats per sex per control and exposed groups. In life parameters evaluated for monkeys and rats included weekly clinical observation, blood and clinical chemistry analyses prior to exposure and at 1, 3, 6, 12, 18, and 24 months, and comprehensive eye examinations at the same intervals that blood chemistries were conducted. Ten rats/sex/group were pre-selected for cytogenetic evaluation (results presented below under Section 7.1.3.2 for *in vivo* genotoxicity) at five days, 12 months and 24 months of exposure; however due to high mortality in control and exposed groups, only five to eight rats per group were evaluated at 22 months, rather than 24 months. For rats, interim sacrifices were conducted at 5 days, 1, 3, 6, 12 and 18 months with terminal sacrifice at 24 months. Fasting body weights and the weights of heart, lung plus trachea, liver, gonads, adrenals, thyroid/parathyroids, kidneys, spleen and brain were recorded at each scheduled necropsy. Thirty-one designated tissues from ten rats/sex in the control and high exposure groups were examined microscopically after 3,6,12 and 18 months; all remaining animals from control and high exposure level groups were evaluated after 24 months of exposure. All animals sacrificed *in extremis* or found dead were also evaluated. Only lung plus trachea (at 12, 18 and 24 months) and nasal turbinates (at 24 months) were examined microscopically from rats in the 10 mg/m^3 exposure group. All monkeys were sacrificed after 24 months of exposure. The same 31 tissues were evaluated microscopically in control and high dose groups; weights for the same organs listed for rats were also obtained. Again, only lung plus trachea and nasal turbinates were microscopically evaluated for monkeys in the 10 mg/m^3 exposure group. There were no treatment-related effects on body weights or mortality in rats or monkeys.

The only treatment-related effects reported from these chronic studies were for the lungs in both rats and monkeys. There were dose-related increases in lung plus trachea weights and inflammatory changes in the lungs in rat and monkey petroleum coke exposed groups, accompanied by pigment accumulation (presumed to be test material) in the lung and associated lymph nodes. The lung histological changes in treated rats included pulmonary interstitial inflammatory responses with focal fibrosis, bronchiolization, sclerosis, squamous alveolar metaplasia and the presence of keratin cysts. The keratin cysts were considered to be an advanced stage of squamous alveolar metaplasia but were not considered to be an oncogenic response. The severity of the rat histological changes was related to the duration and concentration of exposure, and was considered to be non-reversible. These lung effects in the rat are considered a non-specific response of the lung to high concentrations of insoluble particles rather than compound specific induced effects, also referred to as rat lung particle overload, and are unlikely to be relevant to humans (Snipes, 1995; Mauderly and McCunney, 1996). By contrast, the primates exhibited lung and pulmonary lymph node pigment accumulation (presumed to be test material) at both exposure levels as a result of phagocytosis by pulmonary macrophages; however, inflammatory or metaplastic changes, as observed in the rats, were absent. Petroleum coke was not found to be carcinogenic by the inhalation route in either the rat or monkey study. In both rats and monkeys, the portal of entry LOAEL was $< 10 \text{ mg/m}^3$, and the systemic toxicity NOAEL was $> 30 \text{ mg/m}^3$.

Although not a guideline repeated-dose toxicity study, the OECD 421 Reproductive/Developmental Toxicity Screening Test (described in Section 7.1.4) provides additional evidence for the conclusion that petroleum coke has low repeated-dose toxicity. Male and female Sprague-Dawley rats (12/sex/group) were exposed via nose-only inhalation to 0, 30, 100 or 300 mg/m³ micronized green coke with an average mass median aerodynamic diameter of 2.29 µm. All rats were exposed for 6 h/day, 7 days/week for 2 weeks prior to mating. Males continued to be exposed for 28 days during the mating and post-mating periods. During the mating period, females were exposed until evidence of mating was observed or for 14 consecutive days. Once mated, female rats were treated daily during gestation (days 0-19) until euthanized on post-natal day 4. Viability, clinical observations, body weights, feed consumption, organ weights, macroscopic and microscopic findings were evaluated. The only exposure-related effects observed were portal-of-entry effects in the respiratory tract and associated lymphatic system effects (see Reproductive and Developmental section below). No systemic toxic effects were observed.

Additional support for the determination of low repeated-dose toxicity of petroleum coke is provided by a lifetime mouse dermal carcinogenicity study conducted on four samples of green coke and related substances (delayed process coke; fluid process coke; solid condensed emissions from delayed coke process; and process water from delayed process coke). Each of the petroleum coke samples was micronized and suspended in mineral oil, and applied to mouse skin three times per week for two years (Wingate and Hepler, 1982). Particle size was not provided in the assay or analytical reports. However, rough measurements based on scanning electron micrographs of the micronized particles indicate that particle size was uniform and approximately ≤ 5 µm in diameter. Groups of 25 male and 25 female C3H/HeJ mice were treated three times per week with 100 µl of 250 mg/mL test material dissolved in mineral oil. Body weights were taken once every two weeks, and clinical observation were made three times per week. Mice that died or were sacrificed in a moribund condition were necropsied and examined for occurrence of neoplasms in the viscera. Histological examination was limited to site of application and neoplasms found at necropsy. There were no treatment-related effects on survival or body weights. The number of visceral masses and other masses (other than treatment site) in the treated animals were comparable to controls. The only effect observed in the mice was a thickening of the skin in the area of treatment. None of the coke samples caused skin cancer in this study.

Conclusion: The repeated-dose inhalation and dermal toxicity studies indicate low systemic toxicity for green coke. In the inhalation studies there were portal-of-entry inflammatory changes in the lung attributed to non-specific particle burden, rather than a specific response to petroleum coke. Based on results of the two-year studies in rats and monkeys, the inhalation repeated-dose portal-of-entry LOAEL was < 10 mg/m³, and the systemic NOAEL was > 30 mg/m³.

7.1.3. Genetic Toxicity

7.1.3.1. *In Vitro*

Both delayed and fluid process green coke were evaluated for bacterial mutagenicity in the standard bacterial mutagenesis test using *Salmonella typhimurium* strains TA 1535, 1537, 1538, 98 and 100, with and without metabolic activation (S-9 from Aroclor 1254-induced Sprague-Dawley rats). The solvent used in these studies was dimethyl sulfoxide (DMSO). None of the coke samples produced a positive response in any of the tested strains at concentrations up to 10,000 µg/0.1 mL (Hazleton, 1981 a, b).

As part of a workplace study on PAH concentrations and mutagenicity of petroleum coke, petroleum pitch, and airborne particulate matter, Monarca *et al.* (1982) tested petroleum

coke in *Salmonella typhimurium* strains TA 98 and TA 100. Petroleum coke was ground in a mortar, then 50 grams were sequentially extracted with four solvents of increasing polarity (benzene, chloroform, methanol and acetone). Samples were taken at each extraction step, dried, weighed and dissolved in DMSO. The non-extractable residual material (99.71% of starting material) was also tested as a DMSO suspension. The five samples (four extraction steps & the non-extractable residue) were tested for mutagenic potential in TA 98 and TA 100 at 0.1 – 4 mg/plate with and without metabolic activation (liver S-9 from Aroclor 1254 induced male Sprague-Dawley rats). The criteria for a positive response were defined as the observations of a dose-related response and a three-fold or higher increase in revertants per plate as compared to controls. By these criteria, no mutagenic activity was observed in any of the coke solvent fractions or non-extractable residue.

Green coke (sponge-form delayed process; same sample as used in the rat and monkey two-year studies described in Section 7.1.2) was evaluated in a modified bacterial mutagenicity assay (Dalbey *et al.*, 1998; ASTM International, 2004b). It has been shown previously that the standard bacterial assay is insensitive to certain classes of materials, including petroleum substances (Blackburn *et al.*, 1984; 1986). In the modified assay, samples are typically dissolved in cyclohexane and subsequently extracted with dimethyl sulfoxide (DMSO) to produce aqueous compatible solutions which readily interact with tester bacteria. Additionally, hamster, rather than rat, liver homogenate (S-9) is used, and only one bacterial strain tested, *Salmonella typhimurium* TA 98. In this particular study, 200 mg green coke was extracted with 1 ml DMSO and the extract tested with metabolic activation. Green coke was positive in this assay with a mutagenicity index of 12.5.

Jongeneelen *et al.* (1989) tested four petroleum coke samples in a bacterial mutagenicity assay. Samples were sonicated in DMSO for 30 minutes, and the resultant suspension tested in *Salmonella typhimurium* strains TA 98 and TA 100 in the absence and presence of Aroclor 1254-induced S-9 metabolizing system. All four petroleum coke samples demonstrated a concentration-related doubling of the number of revertants as compared to controls in both tester strains in the presence of S-9 (species of origin not specified), and were therefore considered to be mutagenic by the study authors.

Delayed and fluid process coke samples were also evaluated in a mammalian cell mutagenicity test using the L5178Y mouse lymphoma cells (Hazleton, 1981 a, b). The tests were conducted on DMSO extracts of coke with and without metabolizing enzymes in the assay system (S-9 from polychlorinated biphenyl-induced Sprague-Dawley rats). Neither coke sample was mutagenic.

Conclusion: Green coke was not mutagenic in standard *in vitro* genetic toxicity tests in bacteria and mammalian cells. However, when tested in a modification of the standard bacterial assay developed for petroleum substance testing, DMSO extracts of petroleum coke were mutagenic in the *Salmonella* mutagenicity assay.

7.1.3.2. *In Vivo*

Fluid process green coke was evaluated for its ability to produce chromosome aberrations in a bone marrow cytogenetic assay (Hazleton, 1981b). Male Sprague-Dawley rats were exposed via inhalation to concentrations of 0, 10 and 40 mg/m³ petroleum coke with a particle size of less than 5 µm. Rats in the 10 mg/m³ group were exposed 6 h/day, 5 days/week for a total of 20 exposures. Rats in the 40 mg/m³ were exposed 6 h/day for 5 days only. Control rats were held for the full 28 days of the study before assessment. The day after the last exposure, colchicine was administered to inhibit mitosis and bone marrow was subsequently analyzed for chromosomal changes. There were no treatment-related chromosomal effects in any treatment group as compared to controls. Fluid process coke was not genotoxic in this study.

Delayed process green coke was evaluated for its ability to produce chromosome aberrations in a bone marrow cytogenetic assay (Hazleton, 1981a). Male Sprague-Dawley rats were exposed via inhalation to concentrations of 0, 10 and 40 mg/m³ petroleum coke with a particle size of less than 5 µm. Rats in the 10 mg/m³ exposure group were exposed 6 h/day, 5 days/week for a total of 20 exposures. Rats in the 40 mg/m³ were exposed 6 h/day for 5 days only. Control rats were held for the full 28 days of the study before assessment. The day after the last exposure, colchicine was administered to inhibit mitosis and bone marrow analyzed for chromosomal changes. There were no treatment-related chromosomal effects in the 10 mg/m³ exposure group. In the 40 mg/m³ exposure group, there were significant increases in the number of chromatid breaks, markers and total aberrations as compared to controls. The laboratory later determined that the slides had been inconsistently evaluated and misread in some cases. This study was therefore considered to be technically flawed and inconclusive.

To resolve uncertainty, a third *in vivo* cytogenetics study was conducted on bone marrow from male and female rats in the chronic inhalation study described in Section 7.1.2. (IRDC, 1985; Klonne *et al.*, 1987). Analysis was conducted on male and female Sprague-Dawley rats after exposure for five days, 12 months and 22 months to concentrations of 0, 10 and 30 mg/m³ delayed process green coke dust. There were no significant differences from controls in chromosomal aberrations in any exposed animals at any of the three time points. Delayed process petroleum coke was not genotoxic under these test conditions.

Conclusion: The weight of the evidence from these three studies indicates that green coke was not genotoxic in *in vivo* bone marrow chromosome cytogenetic assays.

7.1.4. Reproductive and Developmental Toxicity

An OECD 421 Reproductive/Developmental Toxicity Screening Test (OECD, 1995) was conducted on delayed process green coke (HLS, 2006). A two-week range finding study was conducted to select exposure levels for the definitive study. Male and female Sprague-Dawley rats (12/sex/group) were exposed via nose-only inhalation to 0, 30, 100 or 300 mg/m³ micronized green coke with an average mass median aerodynamic diameter of 2.29 µm. All rats were exposed for 6 h/day, 7 days/week for 2 weeks prior to mating. Males continued to be exposed for 28 days during the mating and post-mating period. During the mating period, females were exposed until evidence of mating was observed or for 14 consecutive days. Once mated, female rats were treated daily during gestation (days 0-19) until euthanized on post-natal day 4. Viability, clinical observations, body weights, feed consumption, survival, organ weights, macroscopic and microscopic findings were evaluated in parental rats. Standard reproductive (mating indices, pregnancy rates, male fertility indices, gestation length, number of implantation sites and corpora lutea, pre- and post-implantation loss, pups per litter, live born and stillborn pups, and incidence of dams with no viable pups) and developmental (pup physical examination, viability, weight, sex ratio, litter survival indices, and mean pup survival indices) endpoints were evaluated.

The only exposure-related parental effects observed were portal-of-entry effects in the respiratory tract and associated lymphatic system effects. Lungs from all test substance-treated rats were slightly to severely discolored black. Lung weights were increased in a dose-related manner up to 37% in males and 58% in females. Inhalation of petroleum coke was associated with the presence of pigment deposits (presumed to be test material) in the lungs, mediastinal lymph nodes and nasal olfactory epithelium of most male and female rats, and in the lumens of the nasal turbinates and pharynx of male rats. Test substance-related changes characterized by proliferative and/or inflammatory responses were observed in the lungs in all test substance-exposed rats. In the mediastinal lymph nodes draining the lungs, hyperplasia of the paracortical T lymphocyte

population accompanied the deposition of pigment. In the larynx, minimal squamous metaplasia of the respiratory epithelium was also observed. These effects were considered non-specific responses to high concentrations of insoluble particles rather than compound-specific induced effects (Snipes, 1995). A parental portal-of-entry NOAEL could not be determined since effects were observed at the lowest exposure. The parental portal-of-entry LOAEL was $< 30 \text{ mg/m}^3$, the lowest concentration tested.

No parental systemic or reproductive toxicity was observed in either sex. There were no treatment-related effects on the offspring. The parental systemic, reproductive, and developmental NOAELs were $> 300 \text{ mg/m}^3$.

Conclusion: Based on the OECD 421 Reproductive/Developmental Toxicity Screening Test, petroleum coke demonstrated low reproductive and developmental toxicity. Parental systemic toxicity, reproductive toxicity, and developmental toxicity NOAELs were $> 300 \text{ mg/m}^3$, which was the highest concentration tested.

7.2. Health Effects Other

7.2.1. Carcinogenicity

Petroleum coke was not carcinogenic in three carcinogenicity studies, which have already been described in Section 7.1.2 *Repeated-dose Toxicity*. Rats and monkeys were exposed via inhalation five days/week for two years to 0, 10, or 30 mg/m^3 petroleum green coke and no excess cancers were observed. In a lifetime skin painting study, mice were exposed three times per week to 0 or $100 \mu\text{l}$ of 250 mg/mL petroleum green coke and no excess skin or visceral cancers were observed. Petroleum coke was not carcinogenic via the inhalation and dermal routes of administration at the highest concentrations tested.

7.3. Assessment Summary for Health Effects

Overall, petroleum coke has a low health hazard potential. Green coke is not acutely toxic with an acute inhalation toxicity NOAEL estimated to be $> 300 \text{ mg/m}^3$. Findings observed in inhalation repeated-dose and chronic studies were confined to respiratory system (portal-of-entry) inflammatory changes that were attributed to non-specific effects of insoluble particles rather than petroleum coke-specific effects. The repeated-dose portal-of-entry LOAEL and systemic NOAEL were $< 10 \text{ mg/m}^3$ and $> 30 \text{ mg/m}^3$, respectively. Green coke was not mutagenic *in vitro* in standard bacterial or mammalian cell assays. Green coke was mutagenic in modified *in vitro* bacterial assays developed to optimize detection of mutagenicity for certain classes of water-insoluble compounds that are negative in the standard bacterial assay. Green coke was not genotoxic in *in vivo* bone marrow chromosome cytogenetic assays. Green coke did not induce reproductive or developmental toxicity at exposures up to 300 mg/m^3 . The reproductive and developmental toxicity NOAELs were $> 300 \text{ mg/m}^3$. Green coke was not carcinogenic in two inhalation studies (rat and monkey; high exposure = 30 mg/m^3) and one mouse dermal study (one exposure level only = $100 \mu\text{l}$ of a 250 mg/mL coke solution).

Green coke is considered to have a higher potential to induce health effects than calcined coke due to green coke having higher levels of volatile matter as compared to calcined coke. Green coke testing results have been conservatively extrapolated to calcined coke in lieu of testing calcined coke. Results from green coke health testing and extrapolation to calcined coke are summarized in Table 3 on the next page.

8. MATRIX OF PETROLEUM COKE CATEGORY DATA

Table 3		
PETROLEUM COKE CATEGORY DATA MATRIX		
Endpoint	Petroleum Coke (Green) CAS # 64741-79-3	Petroleum Coke (Calcined) CAS # 64743-05-1
Physical-Chemical Properties		
Melting Point	N/A ^a	N/A
Boiling Point	N/A	N/A
Vapor Pressure	N/A	N/A
Partition Coefficient	N/A	N/A
Water Solubility	N/A	N/A
Environmental Fate		
Photodegradation	N/A	N/A
Stability in Water	N/A	N/A
Environ. Transport	N/A	N/A
Biodegradation	N/A	N/A
Environmental Effects		
Acute Fish ^b	LL ₅₀ > 1000 mg/L NOELR = 1000 mg/L	LL ₅₀ > 1000 mg/L NOELR = 1000 mg/L
Acute Daphnia	EL ₅₀ > 1000 mg/L NOELR = 1000 mg/L	EL ₅₀ > 1000 mg/L NOELR = 1000 mg/L
Algae	EL ₅₀ > 1000 mg/L NOELR < 1000 mg/L	EL ₅₀ > 1000 mg/L NOELR < 1000 mg/L
Terrestrial	LC ₅₀ > 1000 mg/kg NOEC = 1000 mg/kg	LC ₅₀ > 1000 mg/kg NOEC = 1000 mg/kg
Health Effects^c		
Acute ^d	LC ₅₀ > 300 mg/m ³	LC ₅₀ > 300 mg/m ³
Repeated-Dose Systemic Portal-of-entry	NOAEL > 30 mg/m ³ LOAEL < 10 mg/m ³	NOAEL > 30 mg/m ³ LOAEL < 10 mg/m ³
Genotoxicity, in vitro, bacterial Standard assay Modified assay (optimize organic extractable compounds)	negative positive	negative positive
Genotoxicity, in vitro, non-bacterial	negative	negative
Genotoxicity, in vivo	negative	negative
Reproductive toxicity	NOAEL > 300 mg/m ³	NOAEL > 300 mg/m ³
Developmental toxicity	NOAEL > 300 mg/m ³	NOAEL > 300 mg/m ³
Carcinogenicity Inhalation Dermal	negative negative	negative negative

^a N/A indicates that evaluation of endpoint is Not Applicable due to physical-chemical state. Technical discussions are presented in text to address these endpoints as appropriate.

^b Gray shading indicates category read-across from green coke empirical data to calcined coke.

^c Inhalation was the route of exposure unless otherwise indicated.

^d Yellow shading indicates values estimated from longer term studies

9. CATEGORY ANALYSIS CONCLUSIONS

It is appropriate for green coke and calcined coke to be grouped together in one category. This grouping is justified based on their manufacturing processes, which result in similar physical chemical characteristics and chemical composition. The hazard potential for the petroleum coke category was characterized by summarizing existing data, and testing delayed process green coke to fill in the data gaps identified in existing data. Green coke is considered to have a higher potential to induce environmental and/or human effects than calcined coke due to its higher volatile matter. Therefore, the green coke hazard study results have been conservatively extrapolated to calcined coke in lieu of testing calcined coke.

Petroleum coke is a complex mixture of mostly elemental carbon with inorganic and organic constituents embedded in the carbon matrix. In general, these constituents do not contain the chemical bonds that engage in photolytic or hydrolytic reactions. If released to the environment, petroleum coke would be expected to be non-reactive and either disperse or remain in the environmental compartment to which it was released. Therefore, depending on factors such as particle size and density relationships between the petroleum coke and environmental media, releases to terrestrial or aquatic environments would result in incorporation of the material in soils/sediments or dispersal via wind/water action. Biodegradation would not be an important fate process because the majority of the constituents in petroleum coke do not contain the chemical bonds needed for microbial metabolism.

Petroleum coke has an extremely low environmental hazard potential. Petroleum green coke demonstrated no effect on aquatic vertebrates and invertebrates, and only a slight effect on algae at 1000 mg/L (WAF). Petroleum green coke did not produce any adverse effects when tested against terrestrial soil-dwelling invertebrates and vascular plants at 1000 mg/kg soil.

Petroleum coke has a low health hazard potential. Green coke is not acutely toxic. The acute inhalation toxicity NOAEL was estimated to be $> 300 \text{ mg/m}^3$. Findings observed in repeated-dose and chronic inhalational toxicity studies were confined to portal-of-entry effects that are attributed to non-specific effects of insoluble particles rather than petroleum coke-specific effects. The repeated-dose portal-of-entry LOAEL and systemic NOAEL were estimated to be $< 10 \text{ mg/m}^3$ and $> 30 \text{ mg/m}^3$, respectively. Green coke was not mutagenic *in vitro* in standard bacterial or mammalian cell assays. Green coke was mutagenic in modified *in vitro* bacterial assays developed to optimize detection of mutagenicity for certain classes of compounds that are negative in the standard bacterial assay. Green coke was not genotoxic in *in vivo* bone marrow chromosome cytogenetic assays. Green coke did not induce reproductive or developmental toxicity at exposures up to 300 mg/m^3 . The parental systemic, reproductive, and developmental toxicity NOAELs were all $> 300 \text{ mg/m}^3$. Green coke was not carcinogenic in two inhalation (rat and monkey; highest exposure concentration was 30 mg/m^3) studies and one mouse dermal study (one exposure level only equal to $100 \mu\text{l}$ of a 250 mg/mL coke solution).

Based on the data presented in this report, both green coke and calcined coke (using read-across from green coke) have a low potential to cause adverse effects to the environment, and, with the exception of non-compound-specific, insoluble particle portal-of-entry effects, to human health.

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11. LIST OF ABBREVIATIONS AND ACRONYMS

API – American Petroleum Institute
BOD – biological oxygen demand
Btu/lb – British thermal unit per pound
Btu/scf – British thermal unit per standard cubic feet
AUGC – area under the growth curve
CASRN/CAS #/CAS No. - Chemical Abstract Service Registry Number
°C – degrees Celsius
CONCAWE – Conservation of Clean Air and Water in Europe
d - day
DMSO – Dimethyl sulfoxide
EINECS – European Inventory of Existing Commercial Chemical Substances
EL₅₀ – effective loading rate lethal to 50% of the test population
E_bL₅₀ – effective loading rate that causes 50% reduction in algal cell biomass
E_rL₅₀ – effective loading rate that causes 50% reduction in algal growth rate
EPA/US EPA – United States Environmental Protection Agency
g/cm³ – grams per cubic centimeter
h - hour
HLS – Huntingdon Life Sciences
HPV – High Production Volume
IRDC – International Research and Development Corporation
°K – degrees Kelvin
kPa - kilopascal
LC₅₀ – lethal concentration for 50% of the test population
LL₅₀ – lethal loading rate for 50% of the test population
Loading Rate – total amount of test substance added to dilution water to
prepare water accommodated fractions (WAFs) for ecotoxicity testing
LOAEL – lowest observable adverse effect level
mg/kg – milligrams per kilogram
mg/L – milligrams per liter
mg/m³ – milligrams per cubic meter
mL - milliliter
mm - millimeter
nm - nanometer
NOAEL – no observable adverse effect level
NOEC – no observable effect concentration
NOELR – no observable effect loading rate
OECD – Organization for Economic Cooperation and Development
OPPTS – US EPA Office of Prevention, Pesticides and Toxic Substances
PAC - Polycyclic aromatic compound
PAH – polycyclic aromatic hydrocarbon
PNA – polynuclear aromatic
ppm – part per million
SIDS – Screening Information Data Set
US EPA – United States Environmental Protection Agency
UV - ultraviolet
WAF – water accommodated fraction
wt% - weight percent
µg - microgram
µg/L – microgram/liter
> greater than
< less than
= equal to

12. GLOSSARY

NOTE: *The following terms are used in this document. To the extent possible definitions were taken from relevant authoritative sources such as EPA, OECD, ASTM and IUPAC.*

Bioavailability: The state of being capable of being absorbed and available to interact with the metabolic processes of an organism. Typically a function of chemical properties, physical state of the material to which an organism is exposed, and the ability of the individual organism to physiologically take up the chemical. Also, the term used for the fraction of the total chemical in the environment which is available for uptake by organisms. **(AIHA 2000)**

Calcined Coke: A petroleum coke or coal-derived pitch coke obtained by heat treatment of green coke to about 1600° K. It will normally have a hydrogen content of less than 0.1 wt.%. **(IUPAC 1995)**

Carbonization: The process by which solid residues with increasing content of the element carbon are formed from organic material usually by pyrolysis in an inert atmosphere. **(IUPAC 1995)**

Catalytic Cracking: The refining process of breaking down the larger, heavier, and more complex hydrocarbon molecules into simpler and lighter molecules. Catalytic cracking is accomplished by the use of a catalytic agent and is an effective process for increasing the yield of gasoline from crude oil. Catalytic cracking processes fresh feeds and recycled feeds. **(US DOE 2007)**

Category Member: The individual chemical or substance entities that constitute a chemical category.

Category: A chemical category, for the purposes of the HPV Challenge Program, is a group of chemicals whose physicochemical and toxicological properties are likely to be similar or follow a regular pattern as a result of structural similarity. These structural similarities may create a predictable pattern in any or all of the following parameters: physicochemical properties, environmental fate and environmental effects, and/or human health effects. **(US EPA 2007)**

Dose: The amount of a substance available for interactions with metabolic processes or biologically significant receptors after crossing the outer boundary of an organism. The **potential dose** is the amount ingested, inhaled, or applied to the skin. The **applied dose** is the amount presented to an absorption barrier and available for absorption (although not necessarily having yet crossed the outer boundary of the organism). The **absorbed dose** is the amount crossing a specific absorption barrier (e.g., the exchange boundaries of the skin, lung, and digestive tract) through uptake processes. **Internal dose** is a more general term denoting the amount absorbed without respect to specific absorption barriers or exchange boundaries. The amount of the chemical available for interaction by an particular organ or cell is termed the delivered or **biologically effective dose** for that organ or cell **(US EPA 2002)**.

Dose-Response Relationship: The relationship between a quantified exposure (dose) and the proportion of subjects demonstrating specific biological changes in incidence or in degree of change (response) **(US EPA 2002)**.

Ecological Effects – all endpoints (OECD definitions)

Fish, Acute Toxicity Test: In a four-day exposure, acute toxicity is defined by the LC₅₀, the concentration of test substance in water which kills 50% of the test population of fish.

Test methodology is described in OECD Guideline 203, in OECD Guidelines for the Testing of Chemicals.

***Daphnia* sp., Acute Immobilization Test:** In a one or two-day exposure, acute toxicity is defined by the EC₅₀, the concentration of test substance in water which causes immobilization to 50% of the test population of invertebrates. Test methodology is described in OECD Guideline 202, Part 1, in OECD Guidelines for the Testing of Chemicals.

Alga, Growth Inhibition Test: In a three-day exposure, growth inhibition is defined by the EC₅₀, the concentration of test substance in growth medium which results in a 50% reduction in either alga cell growth or growth rate relative to a control group. Test methodology is described in OECD Guideline 201, in OECD Guidelines for the Testing of Chemicals.

Elemental Carbon: Elemental refers to the adjective form of the word, *element*. Thus for example, in chemistry, it refers to matter composed of only one chemical element. Graphite and diamond are types of elemental carbon. (Wikipedia 2007a http://en.wikipedia.org/wiki/Main_Page)

Endpoint: In the context of the EPA High Production Volume Challenge Program, an endpoint is a physical-chemical, environmental fate, ecotoxicity, and human health attribute measurable by following an approved test methodology (e.g., OECD Guidelines for Testing of Chemicals). Melting point, biodegradation, fish acute toxicity, and genetic toxicity are examples of endpoints that are measured by an approved test method. (US EPA 1999)

Environmental Fate Effects – all endpoints (OECD definitions)

Photodegradation: The photochemical transformation of a molecule into lower molecular weight fragments, usually in an oxidation process. This process may be measured by Draft OECD Guideline, “*Phototransformation of Chemicals in Water – Direct and Indirect Photolysis*”. This process also may be estimated using a variety of computer models.

Stability in Water: This environmental fate endpoint is achieved by measuring the hydrolysis of the test substance. Hydrolysis is defined as a reaction of a chemical RX with water, with the net exchange of the group X with OH at the reaction center. Test methodology for hydrolysis is described in OECD Guideline 111, in OECD Guidelines for the Testing of Chemicals.

Transport Between Environmental Compartments: This endpoint describes the distribution of a chemical between environmental compartments using fugacity-based computer models. The results of the model algorithms provide an estimate of the amount of the chemical within a specific compartment. The environmental compartments included in many models are air, water, soil, sediment, suspended sediment, and aquatic biota.

Biodegradation: Breakdown of a substance catalyzed by enzymes *in vitro* or *in vivo*. As an endpoint in EPA’s HPV program, biodegradation is measured by one of six methodologies described in OECD Guidelines 301A-F, in OECD Guidelines for the Testing of Chemicals.

Exposure: Contact made between a chemical, physical, or biological agent and the outer boundary of an organism. Exposure is quantified as the amount of an agent available at the exchange boundaries of the organism (e.g., skin, lungs, gut). (US EPA 2002).

Feedstock: A refinery product that is used as the raw material for another process; the term is also generally applied to raw materials used in other industrial processes. **(Speight, 2007).**

Female Mating Index: Number of females with confirmed mating (sperm and/or vaginal plug)/number of females placed with males. **(HLS 2006).**

Green coke (raw coke): This is the primary solid carbonization product from high boiling hydrocarbon fractions obtained at temperatures below 900° K. It contains a fraction of matter that can be released as volatiles during subsequent heat treatment at temperatures up to approximately 1600° K. This mass fraction, the so-called volatile matter, is in the case of green coke between 4 and 15%, but it depends also on the heating rate. **(IUPAC 1995).**

Hazard Assessment: The process of determining whether exposure to an agent can cause an increase in the incidence of a particular adverse health effect (e.g., cancer, birth defect) and whether the adverse health effect is likely to occur in humans **(US EPA 2002).**

Hazard Characterization: A description of the potential adverse health effects attributable to a specific environmental agent, the mechanisms by which agents exert their toxic effects, and the associated dose, route, duration, and timing of exposure **(US EPA 2002).**

Hazard: A potential source of harm **(US EPA 2002).**

Health Effects – all endpoints (OECD definitions, unless otherwise specified)

Acute Toxicity: The adverse effects occurring within a short time-frame of administration of a single dose of a substance, multiple doses given within 24 hours, or uninterrupted exposure over a period of 24 hours or less. Exposure may be via oral, dermal or inhalation routes as described in OECD Guidelines 401, 402, 403, and 420 in OECD Guidelines for the Testing of Chemicals.

Developmental Toxicity: Adverse effects on the developing organism that may result from exposure prior to conception (either parent), during prenatal development, or postnatally until the time of sexual maturation. The major manifestations of developmental toxicity include death of the developing organism, structural abnormality, altered growth, and functional deficiency. **(US NLM 2007)**

Genetic Toxicity *in vivo* (Chromosomal Aberrations): The assessment of the potential of a chemical to exert adverse effects through interaction with the genetic material of cells in the whole animal. Genotoxicity may be studied in the whole animal using methods described in OECD Guideline 475, in OECD Guidelines for the Testing of Chemicals.

Genetic Toxicity *in vitro* (Gene Mutations): The assessment of the potential of a chemical to exert adverse effects through interaction with the genetic material of cells in cultured mammalian cells. Genotoxicity may be studied in cultured cells using methods described in OECD Guideline 476, in OECD Guidelines for the Testing of Chemicals.

Repeated Dose Toxicity: The adverse effects occurring due to repeated doses that may not produce immediate toxic effects, but due to accumulation of the chemical in tissues or other mechanisms, produces delayed effects. Repeated dose toxicity may be studied following methods described in OECD Guidelines 407, 410, or 412 in OECD Guidelines for the Testing of Chemicals.

Reproductive Toxicity: The occurrence of biologically adverse effects on the reproductive systems of females or males that may result from exposure to environmental agents. The toxicity may be expressed as alterations to the female or male

reproductive organs, the related endocrine system, or pregnancy outcomes. The manifestation of such toxicity may include, but not be limited to, adverse effects on onset of puberty, gamete production and transport, reproductive cycle normality, sexual behavior, fertility, gestation, parturition, lactation, developmental toxicity, premature reproductive senescence, or modifications in other functions that are dependent on the integrity of the reproductive systems. **(US EPA 1996f)**

Heavy Petroleum Process Streams: Petroleum streams boiling higher than approximately 650°F (345°C), including distillation residues and the absence of low-boiling components. **(Altgelt and Boduszynski 1994).**

Lowest-Observed-Adverse-Effect Level (LOAEL): The lowest exposure level at which there are statistically or biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group **(US EPA 2002).**

No-Observed-Adverse-Effect Level (NOAEL): The highest exposure level at which there are no biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group; some effects may be produced at this level, but they are not considered adverse or precursors to adverse effects **(US EPA 2002).**

Petroleum (crude oil): A naturally occurring mixture of gaseous, liquid, and solid hydrocarbon compounds usually found trapped deep underground beneath impermeable cap rock and above a lower dome of sedimentary rock such as shale; most petroleum reservoirs occur in sedimentary rocks of marine, deltaic, or estuarine origin **(Speight 2007).**

Petroleum Coke: A solid, carbonaceous residue produced by thermal decomposition of heavy petroleum fractions or cracked stocks, or both **(ASTM 2005).**

Polycyclic aromatic compound (PAC): PAC includes multi-ringed aromatic hydrocarbons in which one or more atoms of nitrogen, oxygen or sulfur (a heteroatom) replace one of the carbon atoms in a ring system. The PACs can be grouped according to the heteroatom they contain. **(API 2007)**

Polycyclic Aromatic Hydrocarbon (PAH): A fused aromatic-ring compound consisting only of carbon and hydrogen. Similar compounds include chrysene, pyrene, benzo[a]pyrene, perylene, etc. Naphthalene, the simplest PAH consists of two fused benzene rings. **(API 2007]**

Polynuclear Aromatic (PNA): This term is an obsolete term that is not recognized as valid by either the International Union on Pure and Applied Chemistry or the American Chemical Society. Historically, the term was used to describe the multi-ringed aromatic hydrocarbons now called PAHs. **(API 2007]**

Portal-of-Entry Effect: A local effect produced at the tissue or organ of first contact between the biological system and the toxicant **(US EPA 1994).**

Read Across: Read-across can be regarded as using data available for some members of a category to estimate values (qualitatively or quantitatively) for category members for which no such data exist. **(OECD 2007)**

Residues: Residues, also called residua or resids, are those fractions which are non-distillable under given conditions and remain at the bottom of a distillation tower. **(Altgelt and Boduszynski 1994).**

Systemic Effects or Systemic Toxicity: Toxic effects as a result of absorption and distribution of a toxicant to a site distant from its entry point **(US EPA 2002).**

Target Organ: The biological organ(s) most adversely affected by exposure to a chemical or physical agent **(US EPA 2002)**.

Thermal Cracking: A refining process in which heat and pressure are used to break down, rearrange, or combine hydrocarbon molecules. Thermal cracking includes gas oil visbreaking, fluid coking, delayed coking, and other thermal cracking processes (e.g., flexicoking). **(US DOE 2007)**

Thermal Decomposition: Thermal decomposition is a chemical reaction where a chemical substance breaks up into at least two chemical substances when heated. **[Wikipedia 2007b http://en.wikipedia.org/wiki/Main_Page]**

Volatile Matter: The mass loss on heating expressed as a percent loss of the moisture free sample used. Samples having a thermal history above 600° C are excluded. Volatile matter is determined by measuring the mass loss of the coke when heated under the exact conditions of the ASTM standard method D 6374 – 99). To ensure the sample is moisture free it is dried to a constant weight at 95 to 105° C prior to the procedure. The procedure involves heating the sample to 950 ± 20 ° C for five minute periods to constant mass (± 0.5 mg) **(ASTM 2004a)**.

APPENDIX A - Category Members

CAS No.	EINECS No.
64741-79-3 Coke (petroleum) A solid material resulting from high temperature treatment of petroleum fractions. It consists of carbonaceous material and contains some hydrocarbons having a high carbon-to-hydrogen ratio (API, 1985).	265-080-3
64743-05-1 Coke (petroleum), calcined A complex combination of carbonaceous material including extremely high molecular weight hydrocarbons obtained as a solid material from the calcining of petroleum coke at temperatures in excess of 1,000°C (1800°F). The hydrocarbons present in calcined coke have a very high carbon-to-hydrogen ratio (API, 1985).	265-210-9

APPENDIX B – Composition of Green Coke Samples Used in Toxicology Studies

Sample	Delayed Process Green Coke - 2003 Sample ¹				API Sample # 4-1-140 ²	Micronized Delayed Process Green Coke – 1981 sample ³	
	pellet (initial) ⁴	pellet (final) ⁵	micro-nized (initial)	micro-nized (final)	Delayed Process Coke	1981 Analysis	1984 Analysis
Average Mass Median Aerodynamic Particle Size, µm	2000*	2000*	2.3/3.3*		≤ 5**	3.1	3.1
Elemental Analysis, % wt							
Carbon					89.93	89.97	89.58
Hydrogen					3.71	5.04	3.89
Oxygen					1.3	1.62	2.14
Sulphur	7.4		5.8		3.36	3.27	3.42
Nitrogen					1.1	1.1	1.2
Other Analysis, % wt							
SiO ₂					0.04	<0.04	<0.02
Ash					0.21	0.19	0.28
Trace Metals, ppm							
Al (aluminum)	321	205.1	300.2	250.7			
As (arsenic)	<19.3	<2.3	<29.6	<2.3	<0.001	0.3	0.7
B (boron)	<19.3		<29.6				
Ba (barium)	<19.3	7.74	<29.6	6.9			
Be (beryllium)	<9.6		<14.8				

Sample	Delayed Process Green Coke - 2003 Sample ¹				API Sample # 4-1-140 ²	Micronized Delayed Process Green Coke – 1981 sample ³	
	pellet (initial) ⁴	pellet (final) ⁵	micro-nized (initial)	micro-nized (final)	Delayed Process Coke	1981 Analysis	1984 Analysis
Bi (bismuth)	<19.3		<29.6				
Ca (calcium)	178	81.7	121.6	158.7			
Cd (cadmium)	<9.6		<14.8				
Co (cobalt)	<9.6	1.9	<14.8	1.7			
Cr (chromium)	<9.6	3.9	<14.8	4.6			
Cu (copper)	<11.6	1.8	<17.8	2.3			
Fe (iron)	310	215.9	247	276.1			
Hg (mercury)					<1	<1	<0.01
K (potassium)	<28.9	10.9	<44.4	20.5			
Li (lithium)	<9.6	<1.2	<14.8	<1.16			
Mg (magnesium)	77.4	50.3	60.9	65.5			
Mn (manganese)	<19.3	5.3	<29.6	7.3			
Mo (molybdenum)	<19.3	16.7	<29.6	16.0			
Na (sodium)	133	87.8	114.6	99.0			
Ni (nickel)	367.1	319.6	351.7	304.6	95	78	85
P (phosphorus)	<19.3	19.8	30.3	25.0			
Pb (lead)	<19.3	4.88	<29.61	7.4			
Pd (palladium)		<6.9		<6.9			
Pt (platinum)		3.8		4.5			
S (sulfur)	73920		58060				
Sb (antimony)	<48.2		<74.0				
Se (selenium)	<19.3		<29.6		4.5	<0.2	<0.5
Si (silicon)	743.2	86.75		204			
Sn (tin)	<28.9	<2.3		<2.3			

Sample	Delayed Process Green Coke - 2003 Sample ¹				API Sample # 4-1-140 ²	Micronized Delayed Process Green Coke – 1981 sample ³	
	pellet (initial) ⁴	pellet (final) ⁵	micro-nized (initial)	micro-nized (final)	Delayed Process Coke	1981 Analysis	1984 Analysis
Ti (titanium)	12.9	11.7	<14.8	14.4			
V (vanadium)	1938	1559	1805	1580	145	140	130
Zn (zinc)	12.0	8.9	<14.8	11.2			
Benzene Extract, % wt					1.79	2.08	2.64
PAHs, ppm							
Naphthalene	3.6	3.6	11	11			
1-methyl naphthalene	2.7	3.1	10	12			
2-methyl naphthalene	11	12	26	26			
Acenaphthene	ND	0.18	ND	0.51			
Acenaphthylene	ND	0.12	ND	0.5			
Fluorene	0.34	0.37	1.5	1.5	11	ND	ND
Phenanthrene	0.69	0.64	7.8	8.2	ND	ND	ND
Anthracene	ND	0.29	3.3	3.6			
Pyrene	1.3	1.2	8.6	10	ND	165	158
Fluroanthene	ND	0.1	1.4	1.6			
Benzofluorenes					ND	ND	ND
Benzo(a)anthracene	0.58	0.59	7.1	8	544		
Benzp(a,b)anthrcene						280	287
Chrysene	0.88	1.1	9.4	10	126	210	255
Benzo(a)pyrene	1.8	1.7	11	13	440	175	190
Benzo(e)pyrene					110	85	134
Beno(b)fluoranthene	0.52	0.62	3.8	3.9	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND	1.5			

Sample	Delayed Process Green Coke - 2003 Sample ¹				API Sample # 4-1-140 ²	Micronized Delayed Process Green Coke – 1981 sample ³	
	pellet (initial) ⁴	pellet (final) ⁵	micro-nized (initial)	micro-nized (final)	Delayed Process Coke	1981 Analysis	1984 Analysis
Perylene					ND		
Methyl benzo(a)pyrene					ND	ND	
Benzo(g,h,i)perylene	1.1	1.4	8.7	12	439	120	167
Dibenzo(a,h)anthracene	0.49	0.51	4.1	4.3	ND	NQ	ND
Benzo(g,h,i)fluoranthene					ND	ND	ND
Indeno(1,2,3-cd)pyrene	0.34	0.45	3.5	3.3			
Dimethylbenz(a)anthracene							ND
Methylbenzo(g,h,i)perylene							377
Coronene					ND	ND	ND

Toxicology study(s) in which samples were used:

¹ OECD 203 Fish acute toxicity test; OECD 202 Invertebrate acute toxicity test; OECD 201 Algal growth inhibition test; OECD 208 Seedling emergence and growth of terrestrial plants; OECD 207 Earthworm acute toxicity test; OECD 421 Reproduction/developmental toxicity screening test

² Mouse dermal carcinogenicity study; *Salmonella* assay; mouse lymphoma cell assay

³ Rat chronic inhalation study; Monkey chronic inhalation study; *Salmonella* assay; Rat *in vivo* cytogenicity assay

⁴ initial refers to analyses conducted prior to initiation of the toxicology studies

⁵ final refers to analyses conducted following completion of the toxicology studies

ND = not detected

NQ = detected, but not quantifiable

Blank cells = analysis not performed

* values are average mean particle size

** size not measured; value estimated from scanning electron micrographs

References: Aveka, Inc., 2003; CONCAWE, 1993; Chevron Products Company, 2003, 2005; Lancaster Laboratories, Inc., 2003, 2005.