

KISH P & I LOSS PREVENTION CIRCULAR KPI-LP-59-2012 **(Pollution Prevention matters & Petroleum Coke Cargoes)**

➤ Introduction:

Petroleum coke ("petcoke") is a bulk by-product of oil refining. Among other end-uses, it is traded as a form of fuel (e.g. for cement manufacture) or an input to other industrial applications (e.g. smelting). It is commonly transported at sea in bulk carriers. As with most other bulk cargoes, after discharge there remain residues in the holds and on deck which must be cleaned before new cargoes can be loaded. The cleaning process typically entails dry sweeping, high pressure water washing, the application of a chemical cleaner and a final high pressure water wash. In theory, the dirty wash water is either disposed of at sea or discharged for treatment in land-based reception facilities. However, given increasingly stringent national and international legislation e.g. MARPOL, it is becoming ever more important to ensure that a proper disposal route is followed. It is also possible for vessels carrying petcoke to be involved in an incident which results in a loss of the cargo at sea. The purpose of this bulletin is to briefly describe the physical properties of petcoke, the environmental implications of its discharge or loss at sea, the properties and effects of petcoke cleaning agents and some of the national and international policies relating to its disposal.

The following information is as per The International Tanker Owners Pollution Federation Limited (ITOPF) assessments & guidelines.

➤ Petcoke Properties:

Petcoke is a black powder, granular or needle-like substance, consisting mainly of carbon (84-97%), produced during the thermal decomposition of heavy oils in refining. It exists in various forms, including green coke (also known as raw or delayed petcoke), calcineable, sponge, needle or regular petroleum coke.

Green petcoke is the product of delayed coking and contains significant hydrocarbon content. It has a distinctive hydrocarbon smell and, depending on the heating rate of the refining process, can contain from 4 to 15% volatile material, including Polycyclic Aromatic Hydrocarbons (PAH).



Property ¹	Fuel-Grade Green	Anode-Grade Calcined
Sulphur (wt%)	2.5-5.5	1.7-3.0
Ash (wt%)	0.1-0.3	0.1-0.3
Nickel (ppm)	Not determined	165-350
Vanadium (ppm)	200-400	120-350
Residual ^{2,3} hydrocarbon (wt%)	9-12	<0.25
Bulk density (g/cm ³)	Not determined	0.8
Real density (g/cm ³)	Not determined	2.06

(Petcoke Properties)

Calcined petroleum coke is derived from green coke by heating to high temperatures (> 1,200°C). This process removes virtually all of the hydrocarbon content (i.e. to < 0.1%). However in order to suppress dust, a small amount (< 0.3%) of oil might be added to the cargo. This may have implications in the case of loss or disposal at sea as the added oil may result in surface sheens. It is also common to use a fine water spray containing surfactants to suppress dust. The surfactant reduces the surface tension of the water, thus making it more effective at wetting the cargo and reducing the volume of water necessary. It is commonly applied in a dilute (between 100:1 and 3,000:1) form and normally classed as non-hazardous.

The exact properties of petcoke depend on the source of the crude oil feedstock and the heating process used. However, major components would be expected to be within the ranges illustrated in Table 1. Trace metals such as nickel and vanadium may be present at ppm levels. The specific gravity of petcoke ranges from 0.8-2.1 relative to water. Therefore, the product specification for each cargo must be consulted to determine if it will float or sink. As a rule of thumb, most petcoke products will sink in seawater. Petcoke is stable and insoluble in water and is therefore likely to form a slurry if discharged at sea.

➤ Petcoke Environmental Impact:

Petcoke Material Safety Data Sheets (MSDS), the classification of petroleum substances according to the EU dangerous goods directive and the GESAMP/EHS5 composite list of hazard profiles 2003/2004 all state that **petcoke is not considered a hazard to the marine environment**. It is also worth noting that, although petroleum coke is described as non-hazardous, there are potential human health effects relating to the small particulate matter within the powder or granules as inhaled (i.e. airborne) dust.

As previously mentioned, the hydrocarbon content of green or raw coke may form sheen on the water surface, although this is likely to be localised and non-persistent. The greatest concern following a bulk release of petroleum coke (e.g. in a ship casualty scenario) is the potential for smothering effects, particularly in low energy or shallow waters where spreading and dilution is reduced. A release near the shoreline may also cause a negative visual effect if significant black solids are washed onto the shore. Any increases in pH or sheen will be short lived, given sufficient water depth and water exchange. As far as the discharge of small quantities of petcoke within otherwise clean wash waters is concerned, it is not expected that there would be harmful effects to the marine environment as long as the hydrocarbon content of the cargo is sufficiently low. However, this comment should be read in the context of the governing legislation referred to below.

➤ Chemical agents used for cleaning:

As described above, the hold washing process typically also involves the use of chemical cleaning agents. A number of specialist cleaning products are available for this purpose. These may be general cleaning agents or marketed specifically for particular cargo residues. Some may contain hydrocarbon solvents, while others cleanse on the basis of their caustic properties. As such, they too

must be considered when studying the environmental implications of wash water disposal, particularly at sea. All cleaning products evaluated by the working group on the Evaluation of Safety and Pollution Hazards of chemicals (ESPH) and which were found by the Marine Environment Protection Committee to meet the requirements for potential discharge are listed in Annex 10 of the MEPC.2 circular.

One product that is not on the MEPC recommended list but which is nonetheless marketed and used for petcoke and other hydrocarbon based cargoes is the non-hydrocarbon based cleaning agent "Aqua clean HD". It is water based and functions as a cleaner due to its alkali properties. Aqua clean HD itself is classed as a "dangerous good" (UN number 1719) of the type "caustic alkali liquid N.O.S. (not otherwise specified)". *The undiluted product is classed as harmful to aquatic organisms and may cause long term adverse effect in the aquatic environment, although the recommended dilution rate of 1:200 for actual use significantly reduces potential toxicity.* Thus, because of their potential dilution in use and propensity to dissolve in the sea, the key to understanding the potential for environmental impact of any such cleaning agents is the concentration profile over time following the loss or discharge at sea. In other words, the quantity involved the spill rate and the potential for water exchange.

➤ **International & National rules concerning the cargo-related discharge:**

The following brief note on the rules in the UK and US, as well as those promulgated by the IMO, may be useful for understanding the issues at hand.

Cargo residues and cleaning agents from tank washing are defined as "garbage" within the International Convention for the Prevention of Pollution from Ships (MARPOL). The differentiation between ships within and outside "special areas" is important because the discharge of petcoke cargo wash water is prohibited not only in close proximity to the shore but also within 6 IMO named "special areas". *These include the Mediterranean, the Gulf of Mexico, the wider Caribbean, the Baltic Sea, the North Sea and the Antarctic where the disposal of garbage at sea is heavily restricted.* The reasoning behind the universal 12 nautical mile limit is the reduced potential for dilution and mixing in shallow coastal areas; the reasoning behind the prohibition in special areas is that they are deemed to be highly vulnerable to pollution and have a reduced capacity to recover.

Further, any hydrocarbon "sheen" produced by discharged tank wash water would constitute a violation under MARPOL Annex 1 (concerning oil pollution). Discharge from bilge tanks in areas where permitted must pass through an oily water separator and monitoring system, plus the oil content of the discharge must not exceed 15ppm.

Legislation in the United States, such as the Clean Water Act (CWA), the Act to Prevent Pollution from Ships (APPS) and several Coast Guard regulations, implement the standards imposed by MARPOL and prohibit discharge of oily residues or MARPOL defined garbage within 12 nautical miles from shore.

In its guidance on the at-sea disposal of cargo tank washings and hatch washings, the UK Maritime and Coastguard Agency (MCA) states that:

".... after unloading some bulk cargoes many ships will wash their holds or decks to remove this excess or spilt material as it could contaminate the next cargo. In such cases this material can be disposed of at sea so long as it is inert, has been minimised by removing as much cargo residue as possible and any disposal complies with the 2008 Regulations and any other relevant legislation.

If the material is a marine pollutant, a hazardous or noxious material, or a material that could cause secondary pollution on contact with the sea (such as petcoke, which if disposed of at sea, can cause a sheen on the surface, which will put the ship in contravention of Annex 1 of MARPOL 73/78), then any washings should be disposed of on shore through appropriate reception facilities."

Type of Discharge	Ships Outside Special Areas	Ships Within Special Areas
Non recoverable cargo residues ⁷ contained in wash water	Discharge permitted e12nm from the nearest land and as far as practicable	Discharge only permitted e12nm from the nearest land ⁸ and as far as practicable if departure and destination are both within the special area and no adequate reception facilities are available at those ports ⁹ or in an emergency situation
Cleaning agents and additives ⁷ contained in cargo hold wash water	Discharge permitted	Discharge only permitted e12nm from the nearest land and as far as practicable if departure and destination are both within the special area and no adequate reception facilities are available at those ports or in an emergency situation
Mixed garbage	When garbage is mixed with or contaminated by other substances prohibited from discharge or having different discharge requirements, the more stringent requirements shall apply	
Oily mixtures from non tankers >400GT	Discharge is only permitted if the oil content of any bilge water discharged is below 15 parts per million (ppm); the Ship must be more than 12 nautical miles from nearest land and it must have in operation an approved oil discharge monitoring and control system, oily water separating equipment or oil filtering equipment	Discharge is only permitted if the oil content of any bilge water discharged is below 15 parts per million (ppm); the Ship must be more than 12 nautical miles from nearest land; and it must have in operation an approved oil discharge monitoring and control system, oily water separating equipment or oil filtering equipment with an alarm and automatic stopping device

➤ **Summary:**

Although petcoke is not officially classed as harmful to the marine environment (through the seven criteria in paragraph 3.2 of the 2012 guidelines for the implementation of MARPOL Annex V) and it could in theory be discharged while a vessel is en route and at least 12 nautical miles from the nearest land, petcoke cargo residue and wash water can contain a number of harmful components such as residual hydrocarbons, cleaning agents or dust suppressants. The presence of such components in sufficient quantity could therefore result in a particular cargo residue being considered as harmful to the marine environment.

The most likely impact is that an oily sheen may be visible on the water surface for a short time in the immediate vicinity of the discharge, with a localised and short term increase in the pH of the seawater. If the discharge is undertaken in sufficient depth of seawater with currents allowing a good water exchange, it is likely that any residues will quickly dissipate.

It is worth noting that the legislation regarding the discharge of any hold wash water from vessels is complicated, whether nationally or internationally. The minimum requirements worldwide tend to be in line with the MARPOL recommendations but may be more stringent in certain locations. As a result, operators are finding it ever more prudent to transfer tank wash water to shore side facilities for processing rather than discharge at sea in order to avoid potential environmental issues and possible litigation or fines. This can also be the case for petcoke wash water.