# Chapter 7 – Bitumen (Natural and Rock) and Petroleum Coke

The terms bitumen and asphalt are interchangeable and both refer to black or dark-coloured solids or very thick liquids that have been distilled from crude oil. The distillation process may occur within a refinery, resulting in processed bitumen/asphalt. It may also happen naturally, either when crude oil is exposed to heating and/or biological activity within the deposit, or when it undergoes weathering at or near the earth's surface. Either way, the distillation process separates the heavy molecular weight hydrocarbons, such as bitumen, from the lighter ones, such as methane and petroleum products.

Bitumen is extensively used in roadway construction as a 'glue' or binder in the production of asphalt concrete. To produce asphalt concrete, the sticky bitumen is heated and mixed with aggregates, such as rock chips, and it is then laid and rolled to form the road surface. Asphalt/bitumen may also be referred to as 'tar' or 'pitch'. These liquid bitumens, or 'natural' bitumens, are carried in tankers.

## 7.1 Bitumen Rock

As it is necessary to heat bitumen to enable mixing with aggregates during road construction, some companies have decided to exploit alternatives to refined bitumen. One alternative is to use natural asphalt/bitumen deposits where the 'glue' is already mixed into the rocks.

As an example, at Buton Island in South-East Sulawesi, Indonesia, natural bitumen/asphalt is found at the surface in association with limestone. These deposits are locally referred to as Aspal Buton or asbuton rock asphalt and can be utilised directly (or mixed with traditional road-making materials but with much less processing). This avoids the need for excessive heating of the bitumen to enable it to mix with aggregates during road construction. While the Indonesian deposits have been known since 1920, and it is estimated there are 300 million tonnes available, it is only recently that they have been extensively exploited and offered for shipment.

The asbuton deposits consist of about 20 to 30% bitumen/asphalt integrated into about 70 to 80% limestone and can be divided into several types, based on their physical characteristics. The two main deposits currently being exploited are:

- Kabungka (since 1980) – these are hard deposits (the softening point is about 100°C) with relatively low asphalt content. They break easily when crushed but do not release the asphalt without extensive heating
- Lawele (since 2003) – these are soft deposits (the softening point is about 60°C) with relatively high asphalt content. They require slightly lower temperatures and readily deform during processing, such that the asphalt coats the grains of limestone. This makes the grains better able to stick to other aggregates during the production of asphalt concrete. This variety is the main variety being exported to date.

**Figure 7.1: Bitumen rock.**

When asbuton rock asphalt is dried and crushed to form a granular material, it is referred to as Buton Rock Asphalt (BRA), and it is this name that may be included on cargo documents when the product is presented for ocean carriage in bulk. Shippers may also refer to the product using the name of the source and then add BRA, for example 'Lawele BRA'. Alternatively, they may simply describe it by the general name 'natural bitumen/asphalt'.

**Figure 7.2: Buton Rock Asphalt (BRA) cargo is often loaded from barges.**

### 7.1.1 Application of the IMSBC Code (Reference 17)

Shippers tend to describe their cargo with respect to its intended use, so bitumen rock may be described as 'natural bitumen'. This may cause shipowners, charterers of bulk carriers and P&I Clubs to query the nature of the cargo because natural bitumen is a product carried in a tanker. Even more confusing, it appears that this product is more than 50% 'rock', which means it would be a solid cargo. This is a concern for Masters, owners and P&I Clubs.

Natural bitumen/asphalt or bitumen/asphalt rock is not listed in Appendix 1 (the individual schedules section) of the *International Maritime Solid Bulk Cargoes Code* (IMSBC Code), but the advice is to treat this cargo like any other bulk cargo that is not listed in Appendix 1.

The IMSBC Code makes provision for the carriage of new and unlisted cargoes in Section 1.3. This section describes the processes shippers should undertake to gain certification from the load port competent authority (CA). IMO Circular MSC.1/Circ.1453/Rev.1 sets out guidelines for dealing with cargoes not listed in

the Code in a manner that complies with the requirements of the IMSBC Code. This circular may be found in the Supplement to the IMSBC Code (Reference 17).

Section 1.3 of the IMSBC Code states that, for any bulk cargo not listed in Appendix 1, the shipper must provide the IMO CA of the load port with details of the cargo characteristics and properties prior to loading. Based on this information, the CA of the load port will assess the acceptability of the proposed cargo for safe shipment.

- If no specific hazards are identified, the load port CA can authorise shipment, and the competent authorities of the flag State and the port of unloading should be informed of this authorisation
- if hazards have been identified by the load port CA, the flag State CA and the port of unloading CA should confer to agree the appropriate carriage conditions.

In either case, the load port CA should provide the Master with a certificate that states the cargo characteristics and required conditions for carriage and handling. Cargoes that are not listed in the IMSBC Code and non-IMSBC Code cargoes without a CA certificate should not be accepted.

To complete the procedures for dealing with unlisted cargoes, the IMO requires the CA of the load port to submit an application to the Organization, within one year from the issue of the certificate, to incorporate the new solid bulk cargo into Appendix 1 of the IMSBC Code. This mandatory requirement is detailed in Section 1.3.2 of the IMSBC Code, with the format covered in Section 1.3.3.

One of the major problems is that not every state that ships this type of product actually has a CA. Shipowners are advised not to carry insufficiently certified bulk cargoes.

## 7.2 Petroleum Coke Bulk Cargo: Tank Washing, Cleaning Products and Discharge Implications

Petroleum coke ('petcoke') is a bulk byproduct of oil refining. Most petcoke (approximately 75%) is sold as a fuel for power generation and cement production, with the higher quality petcoke sold for use in the calcining industry. As with most other bulk cargoes, after discharge, the residues that remain in the holds and on deck 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.

Historically, the dirty wash water was either disposed of at sea or discharged for treatment in land-based reception facilities. However, given increasingly stringent legislative requirements, it is becoming ever more important to ensure that a proper disposal route is followed (see Section 7.2.4). It is also possible for ships carrying petcoke to be involved in an incident that results in loss of the cargo at sea.

Petcoke is not officially classed as harmful to the marine environment and it could, in theory, be discharged while a vessel is en route and at least 12 nautical miles from the nearest land. However, petcoke cargo residue and wash water can contain a number of harmful components such as residual hydrocarbons, heavy metals, cleaning agents or

dust suppressants. The presence of such components in sufficient quantity could result in a particular cargo residue being considered harmful to the marine environment by a national authority.

Generally, the impacts of a discharge of petcoke residue and cleaning products within hold wash water will depend on the volume and location of the discharge. However, the most noticeable effect is likely to be an oily sheen that 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 and that no environmental effects will be observed.

The legislation regarding the discharge of any hold wash water from ships is complicated, both nationally and internationally. The minimum requirements worldwide tend to be in accordance with the MARPOL recommendations (as outlined in Table 7.2), but may be more stringent in certain locations. As a result, it is prudent for operators 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 is also true for petcoke wash water.

### 7.2.1 Physical Properties

Petcoke, also known as green delayed coke, consists mainly of carbon (84–97%) and is produced during the thermal decomposition of oil in refining. It exists in various forms, including needle coke, sponge coke and shot coke, which have different microstructures and differ in sulphur content and impurity levels. Crude oil quality is key to determining which of these types is produced – cokes produced from feedstocks high in asphaltenes contain higher concentrations of sulphur and metals.

Green petcoke is the product of delayed coking and has significant hydrocarbon content. It has a distinctive hydrocarbon smell and, depending on the heating rate of the refining process, can contain from 4 to 21% of volatile material, which consists mainly of residual hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs).

| Property | Fuel-grade coke (green petcoke) | Anode-grade coke (processed calcined petcoke) |
|---|---|---|
| Sulphur (wt%) | 2.5–6.0 | 1.7–3.0 |
| Ash (wt%) | 0.1–0.3 | 0.1–0.3 |
| Nickel (ppm) | 250–500 | 165–350 |
| Vanadium (ppm) | 1,000–1,500 | 120–350 |
| Residual hydrocarbon (wt%) | 9–21 | <0.25 |
| Bulk density (g/cm$^3$) | Not determined | 0.8 |
| Real density (g/cm$^3$) | Not determined | 2.06 |

**Table 7.1: Representative range values for properties of petcoke.**

Calcined petroleum coke (which can be further processed to become anode-grade petcoke) is derived from green (or fuel-grade) petcoke by heating to high temperatures (>1,200°C). This process removes virtually all of the hydrocarbon content (ie to <0.1%). It is common to use a fine water spray containing surfactants to suppress dust. The surfactant reduces the surface tension of the water, making it more effective at wetting the cargo and reducing the volume of water necessary for the task. The surfactant is commonly applied in a dilute (between 1:100 and 1:3,000) 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 7.1. 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. Generally, 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.

### 7.2.2 Environmental Effects of Petroleum Coke

Environmental toxicity studies have shown that, in general, petcoke has a low potential to cause adverse effects on both aquatic and terrestrial endpoints in plants and animals. Consequently, petcoke Material Safety Data Sheets (MSDS), the EU CLP Regulation (on classification, labelling and packaging of substances and mixtures), and the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection/Evaluation of Harmful Substances (GESAMP/EHS) list of hazard profiles, all indicate that petcoke is not considered a hazard to the marine environment. No updates have been added in relation to petcoke in the latest versions of the IMSBC (2022) and MARPOL Annex V, indicating that the substance is considered non-hazardous. However, recent evidence suggests that petcoke is not as inert as initially thought, with environmentally significant substances (nickel and vanadium) being detected in petcoke water leachates; these might impact the growth of algae when discharged overboard in low-dilution environments.

It is worth noting that, although petcoke is described as non-hazardous, there are potential human health effects relating to the small particulate matter within the powder or granules when inhaled as dust (ie airborne). In order to suppress dust, a small amount of oil may be added to the cargo, which may have implications if there is a spill or discharge at sea that results in surface sheens.

The hydrocarbon content of green or raw coke is likely to form an oily sheen on the water's surface, although in favourable conditions this is likely to be localised and non-persistent. The greatest concern following a bulk release of petcoke (eg, 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 governing legislation.

### 7.2.3 Cleaning Products

The high content of oil in green coke poses difficult cleaning problems during the hold washing process, which 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 that are evaluated by the working group on the Evaluation of Safety and Pollution Hazards of chemicals (ESPH) and found by the Marine Environment Protection Committee (MEPC) to meet the requirements for potential discharge, are listed in Annex 10 of MEPC.2/Circ.27. 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 a loss or discharge at sea. In other words, the quantity involved, the spill rate and the potential for water exchange.

### 7.2.4 National and International Guidance and Restrictions on Discharge

It is important to be aware that 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 this is permitted must pass through an oily mixture separator and monitoring system, and the oil content of the discharge must not exceed 15 ppm.

| Type of discharge | Ships outside special areas | Ships within special areas |
|---|---|---|
| Non recoverable cargo residues contained in wash water | Discharge permitted ≥12 NM from the nearest land and as far as practicable | Discharge only permitted ≥12 NM 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 |
| Cleaning agents and additives contained in cargo hold wash water | Discharge permitted | Discharge only permitted ≥12 NM 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 >400 GT | Discharge is only permitted if the oil content of any bilge water discharged is below 15 parts per million (ppm); the ship must be >12 NM 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 only permitted if the oil content of any bilge water discharged does not exceed 15 parts per million (ppm); the ship must be >12 NM 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 |

**Table 7.2: Summary of MARPOL discharge provisions for petcoke wash water (modified to include oily mixtures).**

**Note that cargo residues and cleaning agents from tank washing are defined as 'garbage' under MARPOL.*

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 in MGN 385, 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."*

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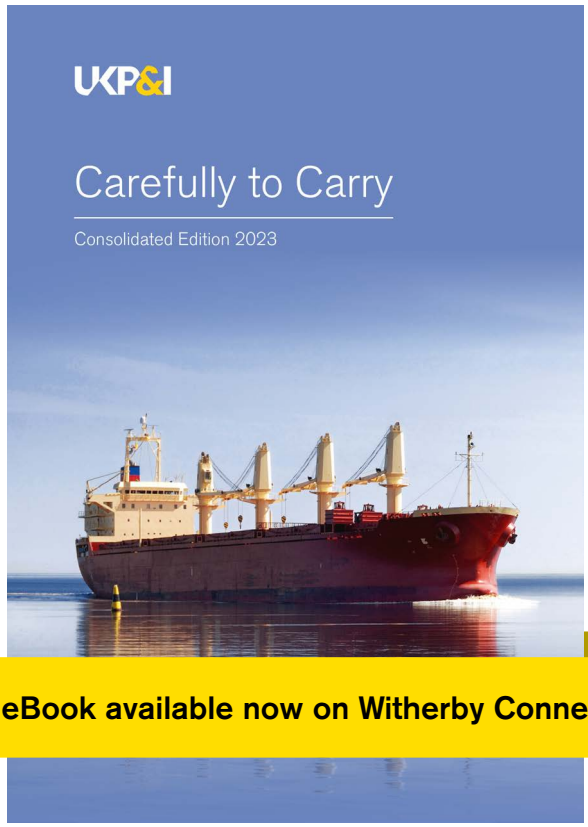


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