Chapter 10 – Direct Reduced Iron (DRI)

DRI is the raw material for the electric arc process of steel production, which is the primary method of steel production in the world (having superseded the blast furnace process in most countries). DRI is made by passing reducing gases over iron ore, usually in the form of pumps or pellets.

There are three types of DRI:

- Direct Reduced Iron (A) – briquettes, hot-moulded
- Direct Reduced Iron (B) – briquettes, lumps, pellets, cold-moulded
- Direct Reduced Iron (C) – byproduct fines.

Each is covered by a separate schedule in the *International Maritime Solid Bulk Cargoes Code* (IMSBC Code) (Reference 17). DRI is effectively categorised as an IMSBC Code Group B cargo (possesses a chemical hazard which could give rise to a dangerous situation on board ship). The primary hazard in its carriage comes from the risk of reaction with oxygen in the atmosphere. As such, the IMSBC Code requires that DRI B and DRI C cargoes are carried in an inert atmosphere with less than 5% oxygen content. It is important that the Master is aware of what type of DRI is being carried, to comply with the relevant requirements of the IMSBC Code. In some instances, a shipper may seek to obtain an exemption from the Code (under Section 1.5), however in these instances, the Master should seek confirmation from the company and the ship's P&I Club.

Hot-moulded DRI is produced by compressing freshly produced cold-moulded DRI pellets into briquettes at high temperature. The additional processing involved in producing hot-moulded DRI briquettes means this type of DRI is more expensive than cold-moulded DRI, although hot-moulded DRI is a considerably less hazardous product in terms of self-heating. By-product fines are also known to overheat during transit.

10.1 Hot-Moulded DRI

All DRI products are internally porous, but hot-moulded DRI has a considerably lower ratio of surface area to mass than cold-moulded DRI. Consequently, hot-moulded DRI is substantially less reactive with water and so less hazardous than cold-moulded. There have been only isolated serious heating incidents with hot-moulded DRI during transportation.

Therefore, although the product can be hazardous, it is generally acceptable for ocean transportation provided the various requirements set out in Appendix 1 of the IMSBC Code are met. The *Hazard* section in the schedule for Direct Reduced Iron (A) – Briquettes, hot-moulded, states:

"Temporary increase in temperature of about 30°C due to self-heating may be expected after material handling in bulk. The material may slowly evolve hydrogen after contact with water (notably saline water). Hydrogen is a flammable gas that can form an explosive mixture when mixed with air in concentration above 4% by volume. It is liable to cause oxygen depletion in cargo spaces. This cargo is non-combustible or has a low fire-risk."

Figure 10.1: Direct reduction plant which reduces iron ore to produce direct reduced iron.

10.2 Cold-Moulded DRI

Cold-moulded DRI is manufactured in the form of pellets (spheres) about 1 cm in diameter. These are produced from iron ore (principally iron oxide) which is crushed, partially freed from foreign material other than iron oxide and then compressed at normal ambient temperatures into iron oxide pellets. The pellets are passed down through a furnace, in which there is a counter-current flow of 'reducing gas', where they are usually heated to a temperature of between 800 and 1,050°C. This is below the melting point of iron at 1,538°C. The reaction between the iron ore pellets and hot gas removes the chemically-bound oxygen component from the iron oxide ore, leaving metallic iron pellets (cold-moulded DRI) with a sponge-like structure.

Once the pellets, consisting of approximately 90% metallic iron, have been produced and cooled, the product has a tendency to reoxidise (rust) back to iron oxide at normal temperatures if there is sufficient oxygen. This process is, however, extremely slow in dry conditions. The rate of oxidation is substantially increased by the presence of water and, if the water contains dissolved salts such as sodium chloride (as found in seawater), the rate of reaction is further increased very substantially.

The oxidation process is exothermic (heat is generated). All rusting processes are surface reactions and the reason why substantial heating can occur when wet DRI pellets react with atmospheric oxygen is that, because of their sponge-like structure, they have an extremely large surface area. It is important to appreciate that DRI is a poor heat conductor, so heat build-up occurs quite rapidly.

Another property that makes cold-moulded DRI very hazardous is that, although oxidation rates are insignificant in dry air at normal temperatures, the product will react with atmospheric oxygen at a rapid rate if heated to a temperature called the 'autoxidation temperature', which can be as low as 150°C. Therefore, if there is a focus of heating initiated in a cargo due to wetting, and this produces a rise in temperature of the cargo to above the autoxidation temperature, heating can spread to adjacent DRI cargo that would otherwise remain stable.

A final hazard associated with DRI pellets is that, if they become wetted and substantially increase in temperature, water may react with very hot iron to produce hydrogen, which is a potentially explosive gas. To retard or inhibit oxidation, the DRI pellets may receive during manufacture a special treatment called 'passivation'. This is dealt with in both the schedule for cold-moulded DRI in the IMSBC Code (Reference 17) and in a circular to Members on DRI that was issued by the International Group of P&I Clubs (Reference 21). The relevant section in the schedule for Direct Reduced Iron (B) – Lumps, pellets, cold-moulded briquettes, in Appendix 1 of the IMSBC Code reads:

"The ship shall be provided with the means to ensure that the requirement of this Code to maintain the oxygen concentration below 5% can be achieved throughout the voyage. The ship's fixed CO_2 fire-fighting system shall not be used for this purpose. Consideration shall be given to providing the vessel with the means to top up the cargo spaces with additional supplies of inert gas, taking into account the duration of the voyage.

The ship shall be provided with the means for reliably measuring the temperatures at several points within the stow, and determining the concentrations of hydrogen and oxygen in the cargo space atmosphere on voyage whilst minimizing as far as practicable the loss of the inert atmosphere.

The ship shall not sail until the master and a competent person recognized by the competent authority of the port of loading are satisfied:

.1 that all loaded cargo spaces are correctly sealed and inerted;

.2 that the temperature of the cargo has stabilized at all measuring points and that the temperature does not exceed 65°C; and

.3 that, at the end of the inerting process, the concentration of hydrogen in the free space of the holds has stabilized and does not exceed 0.2% by volume." (Reference 17)

With regard to the reference to 'inert atmosphere', it is important to stress that the inerting gas used must be nitrogen. If CO_2 is used, it can be reduced by hot iron to carbon monoxide (CO), which is hazardous in terms of both severe toxicity and flammability.

In the 1980s, there was a lull in transocean shipments of cold-moulded DRI but trade stepped up again in the 1990s. During the 1990s, shipments in bulk carriers were undertaken with no attempts at the outset or during the voyage to maintain the cargoes under an inert gas (nitrogen) atmosphere. Under more recent trading conditions, and with shipments made in ordinary bulk carriers, the practicality and economics on long transocean voyages of shippers or shipowners providing and maintaining such inert conditions must be regarded as questionable. It is understood that shipments of cold-moulded DRI where the cargo was not claimed to be passivated have been carried on relatively short voyages under inert gas with no reports of untoward incidents, and it is presumed that the costs of providing the inert conditions are borne by the shippers.

Some shipments of cold-moulded DRI forwarded for ocean transport in certain regions have undergone a degree of passivation treatment and there are reasonable indications that this treatment does provide satisfactory protection against serious heat-generating oxidative reactions, in circumstances where the product becomes wetted with up to a few percentage units of fresh water.

However, clear evidence has emerged that passivation treatment provides no effective protection against the occurrence of serious heating problems when the product is wetted by seawater. It has been estimated that the containment of a bulk stow of this type of cold-moulded DRI with as little as 60 litres of seawater would be sufficient to initiate very serious heating problems.

10.3 Characteristics of Burning DRI

The characteristics are as follows:

- Hot spots propagate relatively slowly. It may take a day or more for propagation to occur through a stow, which allows the opportunity for action to be taken. Clearing DRI away from bulkheads and making a firebreak between heating DRI and adjacent cargo spaces are two of the few options available
- temperatures can become sufficiently elevated so that, if water is sprayed over DRI, it can evolve hydrogen through catalytic dissociation of the water by the hot metallic surface of the DRI. Sufficient concentration of hydrogen, coupled with a heat source, will result in the hydrogen igniting. A light spray of water, insufficient to quench combustion, can therefore result in burning hydrogen with flames

- neither the fuel, which is iron, nor the combustion products, iron oxides, are gaseous, so no flame appears. Burning DRI is similar in appearance to burning charcoal, glowing red hot but without flame. However, there may be a reaction between very hot DRI and moisture, possibly even atmospheric moisture, which produces hydrogen, as described above, which burns with a blue flame. This flame often appears as a blue haze, best visible in low light conditions
- when fuel oil double-bottom tanks are below a hold containing burning DRI, an added safety measure would be to inert the fuel tanks. Dry ice or CO_2 injected through sounding pipes/breathers is recommended. This does not conflict with earlier advice, as the CO_2 will not be in contact with the burning DRI.

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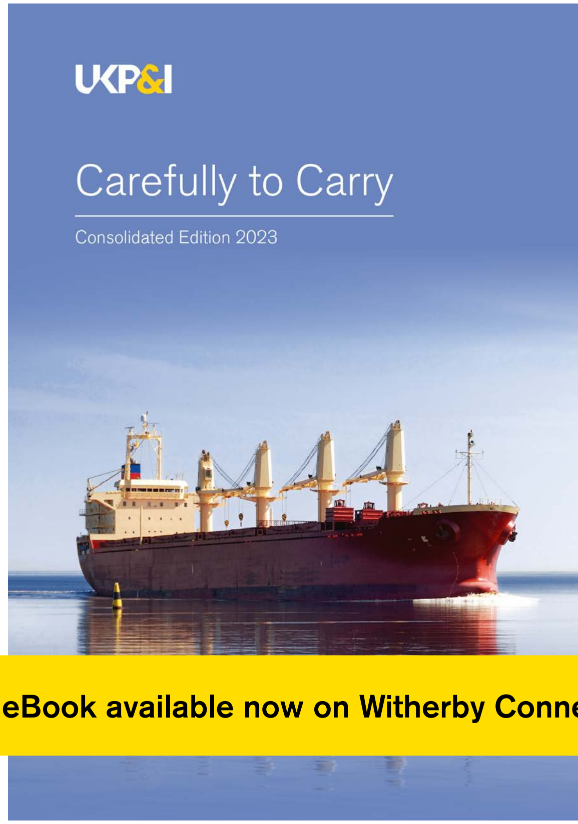

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