UK P&I CLUB

Carefully to Carry

Direct reduced iron (DRI)

A brief article on DRI appeared in Carefully to Carry No.12 which was issued in December 1986. This present article deals briefly with the more recent and projected state of the market for the product, manufacturing technology and potential hazards still presented by the product when transported by sea.

The world market for steel is currently increasing and is expected further to increase very substantially over the next 20 to 25 years. The volume of steel produced by the now old-fashioned blast furnace process is already very low and will decline even more relative to the volume of steel produced by the electric arc process for which DRI is the raw material. The world production of DRI is currently almost 39 million tonnes per year and over the last decade has enjoyed an average growth rate of nearly 10% per year.

Close up of DRI pellets

There are two types of DRI. One is the so-called cold-moulded type and the other is the hot-moulded type. Both types are covered by separate schedules in the the IMO Code of Safe Practice for Solid Bulk Cargoes (the IMO BC Code). Hot-moulded DRI is produced by compressing into briquettes, at high temperature, freshly produced cold-moulded DRI pellets. The additional processing involved in producing hot-moulded DRI briquettes renders this type of DRI more expensive than cold-moulded DRI although as detailed here hot-moulded DRI is considerably less hazardous than the cold-moulded product.

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

"The carrier shall properly and carefully load, handle, stow, carry, keep, care for and discharge the goods carried."

Hague Rules, Articles iii, Rule 2

Carefully to Carry Advisory Committee

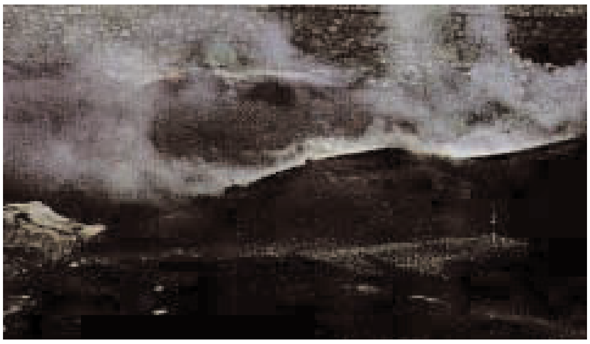
This report was produced by the Carefully to Carry Committee – the UK P&I Club's advisory committee on cargo matters. The aim of the Carefully to Carry Committee is to reduce claims through contemporaneous advice to the Club's Members through the most efficient means available.

The committee was established in 1961 and has produced many articles on cargoes that cause claims and other cargo related issues such as hold washing, cargo securing, and ventilation.

The quality of advice given has established Carefully to Carry as a key source of guidance for shipowners and ships' officers. In addition, the articles have frequently been the source of expertise in negotiations over the settlement of claims and have also been relied on in court hearings.

In 2002 all articles were revised and published in book form as well as on disk. All articles are also available to Members on the Club website. Visit the Carefully to Carry section in the Loss Prevention area of the Club website www.ukpandi.com for more information, or contact the Loss Prevention Department.

Hence although this product is hazardous, there is no reason to believe that the product is not generally acceptable for ocean transportation provided the various requirements set out in the schedule, at Appendix B, pages 69-72, of the IMO BC Code, 1998 Edition, are met.



DRI can heat to extreme temperatures when exposed to sea water

The remainder of this article will deal with the more hazardous cold-moulded product which is manufactured in the form of pellets (spheres) about one centimetre in diameter. These are produced from iron ore (i.e. 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. These pellets are then passed down through a furnace in which there is a counter-current flow of so-called reducing gas whereby the pellets are heated to a temperature below the melting point of iron. Concomitantly the reaction between the iron ore pellets and hot gas removes the chemically bound oxygen component from the iron oxide ore, thus leaving metallic iron pellets (i.e. 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 propensity to re-oxidise (i.e. rust) back to iron oxide at normal temperatures given the availability of sufficient oxygen. This process is however extremely slow in dry conditions. The rate of oxidation is substantially increased by the presence of water. If the water contains dissolved salts such as sodium chloride (e.g. sea water) the rate of reaction is very substantially further increased.

The oxidation process is exothermic; in other words 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. Hence heat build-up occurs quite rapidly.

Another property which 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 it is reported can be as low as 150oC.

Hence, if there is a focus of heating initiated in a cargo due to wetting and this produces a rise in temperature of that cargo to above the autoxidation temperature, heating can spread to adjacent DRI cargo which 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 a matter which is dealt with in both the schedule for cold-moulded DRI in the 1998 Edition of the IMO BC Code and in a circular to Members on DRI which was issued by the International Group of P&I Clubs in July 1982. The relevant section in the schedule in the IMO BC Code which contains reference to 'passivation' reads:

A "Shippers should provide the necessary specific instructions for carriage, either:

1) maintenance throughout the voyage of cargo spaces under an inert atmosphere containing less than 5% oxygen. The hydrogen content of the atmosphere should be maintained at less than 1% by volume; or

2) that the DRI has been manufactured or treated with an oxidation and corrosion-inhibiting process which has been proved, to the satisfaction of the competent authority, to provide effective protection against dangerous reaction with sea water or air under shipping conditions.

B The provision of paragraph (A) above may be waived or varied if agreed to by the competent authorities of the countries concerned, taking into account the sheltered nature, length, duration, or any other applicable conditions of any specific voyage."

With regard to the reference to 'inert atmosphere' in the previous quotation, it is important to stress that the inerting gas used must be nitrogen. If carbon-dioxide is used this can be reduced by hot iron to carbon monoxide which is hazardous both from the viewpoints of severe toxicity and flammability.

In the International Group of P&I Clubs' circular of 1982 there was particular comment on paragraphs A(2) and B from the schedule from the IMO BC Code as previously quoted. The relevant part of the circular reads:

"In relation to paragraph A(2), the major manufacturers in Germany have used a chemical 'passivation' process to inhibit oxidation/corrosion. However, there has recently been a serious fire onboard a ship carrying this product and there must be serious doubts about whether such a passivation process renders the cargo safe for carriage by sea.

The undersigned Assocations continue to believe that the only proven method of carrying this cargo safely is by maintaining the cargo hold in an inert atmosphere and believe the most effective method of providing an inert atmosphere is by injecting the inert gas at the bottom of the stow in order to force out the air within the stow. Therefore the detailed advice to shipowners and Managers on pages 2 and 3 of the circular of August 1981 stands.

On present information, it is not thought that the length or nature of the voyage contemplated (IMO paragraph B) can ever justify the waiver of the requirement of maintaining the cargo in an inert atmosphere."

In the 1980s there was a lull in trans-ocean shipments of cold-moulded DRI. However, in the 1990s, numerous ocean shipments were effected. The Committee is aware that many shipments have been made in bulk carriers with no attempts having been made at the outset and during the voyage to maintain the cargoes under an inert gas (nitrogen) atmosphere. Under recent trading conditions and with shipments made in ordinary bulk carriers, the practicality on long trans-ocean voyages and the economics of shippers or shipowners providing and maintaining such inert conditions must be regarded as questionable. It is however understood that shipments of cold-moulded DRI not claimed to be passivated have been carried on relatively short voyages under inert gas with no reports of untoward incidents, although it is presumed that the costs of providing the inert conditions are borne by the shippers.

The Committee has learned that certain shipments of cold-moulded DRI forwarded for ocean transport in certain regions are claimed to have undergone a certain degree of ‘passivation’ treatment. There are reasonable indications that this treatment does indeed provide satisfactory protection against serious heatgenerating oxidative reactions under circumstances where the product becomes wetted with up to a few percentage units of fresh water. However, clear evidence has emerged that the ‘passivation’ treatment provides no effective protection against the occurrence of serious heating problems when the product is wetted by sea water. 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 water would be sufficient to initiate very serious heating problems.

Characteristics of burning DRI

Aspects of burning DRI are:

- Hot spots propagate relatively slowly. It may take a day or more for propagation to occur through a stow. This allows opportunity for actions to be taken. Clearing DRI away from bulkheads, making a fire-break between heating DRI and adjacent cargo spaces is one of the few options onboard.
- Temperatures can also become sufficiently elevated so that if water is sprayed over it, the DRI can evolve hydrogen – 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, thus creates flame as the hydrogen burns.
- Neither the fuel, which is iron, nor the combustion products, iron oxides, are gaseous, therefore no flame appears. DRI when burning is similar in appearance to burning charcoal, glowing red hot but without flame. However, as mentioned earlier, there may be a reaction between very hot DRI and moisture – possibly even atmospheric moisture – producing hydrogen, 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 with burning DRI, an added safety measure would be to inert the tanks – dry ice or CO2 injected through sounding pipes/breathers is recommended. This does not conflict with earlier advice, as the CO2 will not be in contact with the burning DRI.

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