



Chapter 9 – Sulphur Cargoes

Sulphur is a relatively cheap commodity that is used in the manufacture of fertiliser. It is both a byproduct of the petrochemical industry and a naturally occurring mineral. After processing, it is often shipped in pelletised/solid form. This type of sulphur is the most common and is classified as IMSBC Code Group C. However, sulphur in crushed, lump and coarse grained form (UN 1350) is classed as IMSBC Code Group B and *International Maritime Dangerous Good Code (IMDG) Class 4.1*, as it carries a risk of fire. The Master should be aware of the form of sulphur being loaded.

Substantial quantities of sulphur are produced in the Alberta province of Canada, most of which is shipped from Vancouver. It is also shipped from ports that include San Francisco, Long Beach, Mariupol, Aqaba, Jubail and Basra. As such, sulphur cargoes are often generally described as ‘Canadian bright yellow formed sulphur’. Sulphur suppliers guarantee strict purity specifications to their customers and so are concerned with the risk of contamination. Sulphur cargo should therefore be kept separate from other cargoes that are strong oxidisers (including chlorate, fluorine, etc).

Dry sulphur does not react with bare steel, but wet sulphur (sulphur containing free water) is potentially highly corrosive. Cargoes of sulphur in bulk are normally stored in the open and so are exposed to inclement weather and consequent increased moisture content. Stock will also include a percentage of sulphur dust particles. To prevent contaminated air emissions, it is normal practice, particularly in Canada and the USA,

where loading wharves are situated in built-up areas and the dust is considered to be a pollutant, for the environmental authorities to insist upon the use of a water spray during handling to keep down the dust.

This practice, now widely adopted in other countries, may lead to difficulties during and after the period of sea transportation. However, despite the fact that very large quantities of sulphur are carried annually by sea, the vast majority are carried without significant damage to the carrying vessels.

9.1 Corrosion

When sulphur is loaded, any retained free water filters to the bottom of the holds during the voyage. From there, it is pumped out via the bilges. Some water remains on the tank tops and, together with the fines, this produces a sulphurous mud. A great deal of research has been undertaken to understand and mitigate corrosion to vessel structures during the handling and transportation of sulphur.

There are two processes whereby a corrosion reaction can occur: acidic corrosion and electrochemical corrosion.

9.1.1 Acidic Corrosion

This involves a reaction between an acid and elemental iron (steel). The acid involved is sulphuric acid (H_2SO_4). Corrosion does not become significant until the acidity of the solution decreases to pH 2 or below.

9.1.2 Electrochemical Corrosion

This involves a redox (reduction/oxidation) reaction between iron and sulphur. The specific requirements for this reaction to take place are that sulphur and iron must be in direct contact and that the sulphur must be wet.

For further information on the electrochemical process, see Reference 20. Typically, the characteristics of the reaction are as follows:

- The reaction has a maximum rate at around neutral pH (which is 7)
- the reaction displays auto-catalytic behaviour under anaerobic conditions (existing without the presence of oxygen) and the reaction product promotes further reaction to occur
- the reaction proceeds to a greater extent and at a higher rate under anaerobic rather than aerobic conditions
- the initial by-product of the corrosion process is ferrous sulphide (FeS), otherwise known as mackinawite. This is a black/brown substance that is spontaneously combustible when in contact with oxygen (this is a pyrophoric reaction)
- the reaction is temperature dependent as the rate approximately doubles for every 10°C rise in temperature.

Experience has shown that it is electrochemical rather than acidic corrosion that is responsible for the largest proportion of damage to a ship's hold structures on passage.

The *International Maritime Solid Bulk Cargoes Code* (IMSBC Code) (Reference 17) states in Section 9.3.1.10:

“Materials which present corrosive hazards of such intensity as to affect either human tissue or the ship’s structure shall only be loaded after adequate precautions and protective measures have been taken.”

The following measures should be adopted to minimise the risk of damage as a result of loading sulphur:

- Make good all damage to paint coatings on hopper tank plating, bulkheads, bulkhead stools, internal ship’s side plating, frames and internals to the height to which the cargo will be in contact. Loose rust and scale must be removed from the underside of hatch covers. Aluminium or epoxy resin based paints appear to be most effective
- while the current rules of Classification Societies do not require tank top plating to be coated, it is important and accepted that paint coatings provide protection to the plates during the carriage of sulphur, therefore, consider this precaution
- limewash as per the owner’s/shipper’s/charterer’s instructions and to the satisfaction of the pre-load surveyor
- cover the bilge strainer plates with hessian
- during the loaded voyage, maintain bilge levels below tank top level. Keep a careful bilge pumping record, which should also include estimates of the volumes of water ejected from the holds
- remove all residues of sulphur from the holds after completion of discharge and thoroughly wash down the holds with seawater and, finally, fresh water
- if corrosion has occurred, it must be removed by chipping or shot blasting before washing. The bare steel should be touched up with paint coatings.

The presence of chlorides, in the form of salts, such as sodium and potassium chlorides, can hasten the interaction between the moist sulphur and ship’s steel. Sodium chloride is a major constituent of both salt cake and dissolved materials found in seawater. Potassium chloride (potash) is regularly shipped from Vancouver. Any trace of these substances will lead to an accelerated corrosion effect, so hold cleanliness prior to loading is of the utmost importance.

To determine whether a vessel is likely to suffer from corrosion damage due to the carriage of wet sulphur, and to what degree, the following factors should be taken into account:

- Cargo-related factors and, in particular, residual cargo acidity
- length and duration of voyage
- temperatures encountered during the voyage
- effectiveness of lime washing and the condition of underlying paint coating
- proper bilge pumping to remove excess water.

9.2 Cleanliness

Prior to loading sulphur, it is recommended that the receiving holds are in a 'grain clean' condition, which requires:

- Removal of all residues of previous cargoes and hard and loose scale from the holds. Air wands should be used to dislodge residues of cargo from otherwise inaccessible areas
- thorough washing out of the holds with seawater
- thorough washing out of the holds with fresh water.

The IMSBC Code (Reference 17) states in Section 9.3.1.12:

"After discharge of cargoes, a close inspection shall be made for any residue, which shall be removed before the ship is presented for other cargoes."

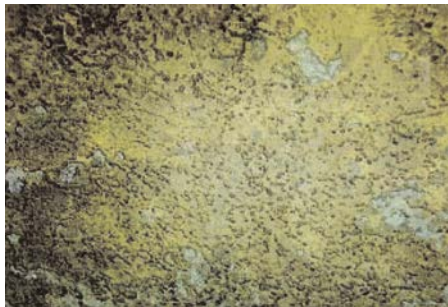


Figure 9.1: Pitting damage caused to tank top after 85 days' sulphur/steel contact.

9.3 Lime Washing

Applying lime wash to cargo hold structures does not totally eliminate corrosive reaction, but only acts to slow or mitigate it. Ideally, the lime wash is, or should be, applied over existing sound paint coatings. The lime wash acts in two respects: as an additional physical barrier and as an alkaline neutralising barrier between the wet sulphur and the bare steel/painted surface. The neutralising action of the lime wash will eventually result in it being 'consumed' by the sulphur. Once this happens, and in the absence of an intact paint coating, the sulphur is once again in direct contact with the ship's structure and the electrochemical corrosion process will resume. Experience with Canadian sulphur has shown that the application of a single layer of lime wash can provide good protection to the steel for about 30 to 40 days, and in some cases even longer.

It is recommended that a mixture of approximately 60 kg of lime to 200 litres of fresh water should be used. The lime wash should also be allowed to dry before loading commences, otherwise the protective 'glaze' may not form properly.

9.4 Gas Emissions

Hydrogen sulphide (H₂S)

During the passage and after discharge, bulk sulphur can emit small quantities of H₂S gas. As a consequence, all areas where sulphur is stowed or used, or which require the presence of personnel, must be thoroughly ventilated and tested before entry.

Sulphur dioxide (SO₂)

SO₂ may be generated during repairs involving heating/welding in spaces previously exposed to sulphur. Appropriate safety measures must be taken.

9.5 Flammability

The *International Maritime Dangerous Goods Code* (IMDG Code) (Reference 19) Class 4.1 defines flammable solids as:

“Solids which, under conditions encountered in transport, are readily combustible or may cause or contribute to fire through friction; self-reactive substances (solids and liquids) and polymerizing substances which are liable to undergo a strongly exothermic reaction; solid desensitized explosives which may explode if not diluted sufficiently.”

In 1989, following the results of a report from Alberta Sulphur Research, the Canadian Coast Guard declared that:

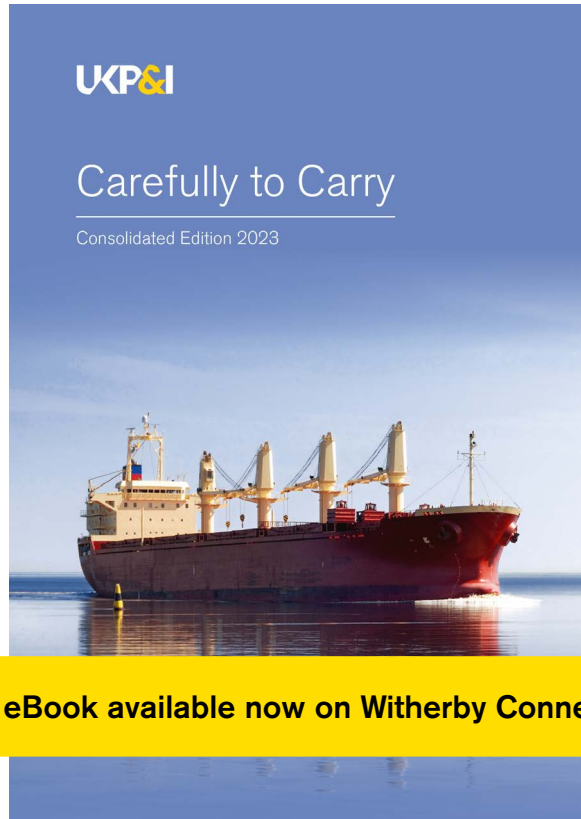
“Based upon the results of the tests, as submitted, it is agreed that formed sulphur does not meet the criteria for classification in Class 4.1.”

Masters should be aware that fire might occur when dry sulphur is being loaded, as a result of static electricity building up on the loading pipes. These fires may be extinguished by dowsing with sulphur or by the use of a fresh water spray. Ferrous sulphide is pyrophoric (ie it may spontaneously combust on contact with air) and can cause fire near the tank top during discharge. Such fires may be controlled with the careful application of a fine jet of fresh water.

However, sulphur that appears in crushed, lump and coarse grained form (UN 1350) carries an ignition risk under Class 4.1 of the IMDG Code. While not combustible, it is readily fusible by heat so should be loaded in a damp or wet condition to reduce the risk of fire/explosion.



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