UK P&I CLUB

Carefully to Carry

Sulphur cargoes

Sulphur is a relatively cheap commodity, which is used in the manufacture of fertilizer. It is not only a byproduct of the petrochemical industry, but also found in its natural form. After processing, it is often shipped in prilled form.

Substantial quantities of sulphur are produced in the Alberta province of Canada, most of which is shipped from Vancouver. It is shipped from other ports, including San Francisco, Long Beach, Aqaba and Jubail. Sulphur shipped from Vancouver is generally described as 'Canadian bright yellow formed sulphur'. The sulphur suppliers warrant strict purity specifications to their customers and so are concerned at the risk of contamination.

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 afforded exposed storage and are thus subject to inclement weather and consequent moisture content. The stock will also include a percentage of sulphur dust particles. In order to prevent contaminated air emissions, it is the practice, especially 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 loading ports, may lead to difficulties during and after the period of ocean transportation. 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.

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, produces a sulphurous mud. A great deal of research has been undertaken to understand and mitigate corrosion to vessels' structures during the handling and transportation of sulphur.

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

Acidic corrosion
This involves a reaction between an acid and elemental iron (steel). The acid involved is sulphuric acid (H2SO4). Corrosion does not become significant until the acidity of the solution increases to or below pH2.

Electrochemical corrosion
It has been established that the electrochemical reaction involves a redox (reduction/oxidation) reaction between iron and sulphur. The specific requirements for this reaction to take place are that sulphur and iron are in direct contact and that the sulphur must be wet.

"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.

Much of what we know about the electrochemical process is based upon research carried out in the 1980-90s at the University of Calgary by Professor JB Hyne and Dr Dowling. This work has established the characteristics of the reaction as follows:

- The reaction has a maximum rate at around neutral pH.
- The reaction displays auto-catalytic behaviour under anaerobic conditions (existing without the presence of oxygen) - 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 Makinawite – a black/brown substance, spontaneously combustible upon contact with oxygen.
- The reaction displays typical temperature dependence – 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 occurring to a ship's hold structures on passage.

The IMO Code of Practice for Solid Bulk Cargoes (IMO BC Code) 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 should only be loaded after adequate precautions and protecting measures have been taken."

The following prudent measures, to preclude risk of damage as a result of loading sulphur, should be adopted:

- Make good all damages 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 intimate contact, and loose rust and scale removed from the underside of hatchcovers. Aluminium or epoxy resin based paints appear to be most effective.
- Whereas the current rules of Classification Societies do not require tank top plating to be coated, it is important and accepted that paint coatings serve to provide protection to the plates during the carriage of sulphur.
- Lime wash as per 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 upon completion of discharge and thoroughly wash down the holds with sea water and finally fresh water.
- Should corrosion have occurred, it must be removed by chipping or shot blasting before washing. The bare steel 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 for example, a major constituent of both salt cake and dissolved materials found in sea water, while 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 summarise, in order to determine if 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 condition of underlying paint coating
- Proper bilge pumping to remove excess water.

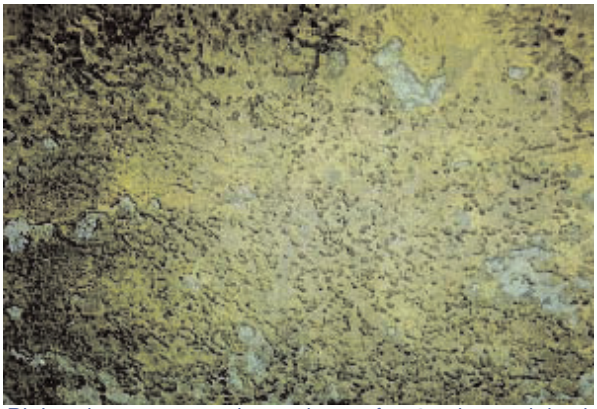
Cleanliness

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

- Removal of all residues of previous cargoes, hard and loose scale from the holds. Access to the upper regions of the holds should be gained by safe equipment. Air wands should be used to dislodge residues of cargo from otherwise inaccessible areas.
- Thoroughly wash out the holds with sea water.
- Thoroughly wash out the holds with fresh water.

The IMO BC Code also states in Section 9.3.1.12:

"After discharge of materials, a close inspection should be made for any residue, which should be removed before the ship is presented for other cargo; such an inspection is particularly important when materials having corrosive properties have been transported."



Pitting damage caused to tank top after 85 days sulphur/ steel contact

Lime washing

It should be noted that applying lime wash to cargo hold structures does not totally eliminate, but acts to slow or mitigate the corrosive reaction. Hence ideally, the lime wash is, or should be, applied over existing sound paint coatings. The lime wash acts then in two respects – as an additional physical barrier and also as an alkaline neutralising barrier between the wet sulphur and bare steel / painted surface. The lime wash's neutralising action 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 can 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 30-40 days, and in some cases even longer.

It is recommended that a mixture of approximately 60kg 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.

Gas emissions

Hydrogen sulphide

There are circumstances during the passage and after discharge whereby bulk sulphur can emit small quantities of hydrogen sulphide gas. All areas in which sulphur is stowed or used or which require the presence of personnel should therefore be thoroughly ventilated.

Sulphur dioxide

Masters should also be aware of the possibility that sulphur dioxide may be generated during repairs involving heating/ welding in spaces previously exposed to sulphur. Appropriate safety measures should be taken.

Flammability

A research report on the properties of formed sulphur was produced in 1989 by Alberta Sulphur Research Ltd., focussing on whether formed sulphur was a flammable solid within the meaning of the IMDG Code (IMO International Maritime Dangerous Goods Code) Class 4.1: Flammable Solids definition. The result of tests included in the report led to the following declaration from the Canadian Coast-guard on 7 August 1989 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."*

However, 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 can be extinguished by dowsing with sulphur or by the use of a fresh water spray. Ferrous sulphide is pyrophoric (may spontaneously combust on contact with air) and can cause fires near the tank tops during discharge. Such fires maybe be controlled with the judicious use of a fine jet of fresh water.

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