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# HAZARDS ASSOCIATED WITH CARRIAGE OF MINERAL CARGOES, INCLUDING SODIUM METABISULFITE


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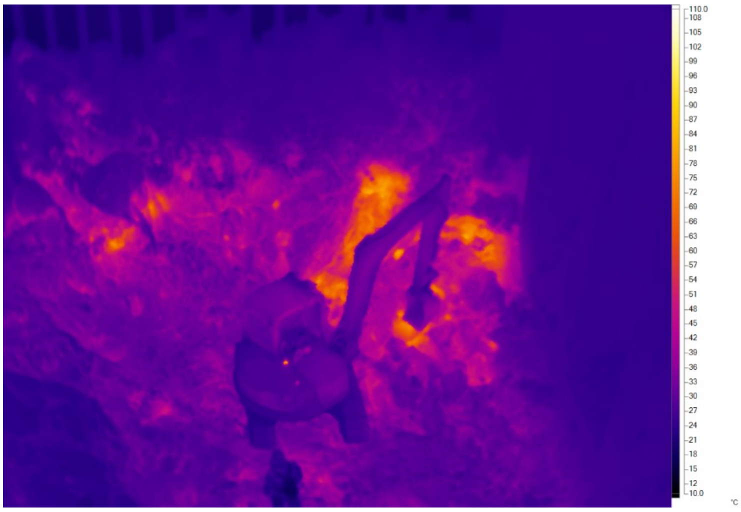
A number of serious incidents have occurred in recent months involving mineral compounds (i.e. inorganic chemicals) in bags carried as general cargo. Besides a potentially serious risk of harm to individuals, the incidents have led to damage to vessels and loss of cargo, together with the problems that arise from them, such as the complication of dealing with port authorities, delays and associated claims, as well as contamination of the vessel and other cargoes and finally, the difficulty of arranging disposal of the hazardous residues.

Toxic corrosive gases being released from a cargo hold containing a reacting cargo (image taken from South African Maritime Safety Authority (SAMSA) website).

The cargoes involved in the incidents typically comprise inorganic chemical compounds commonly used in industry and agriculture for purposes such as water treatment and as fertilizers[1], although organic chemical cargoes have also been involved in incidents. The chemicals have typically been carried in Flexible Intermediate Bulk Containers (FIBCs), which invariably comprise woven polypropylene bags, typically with polythene liners. Such bags are not robust and can be readily damaged during transfer operations, becoming punctured, scuffed or torn during handling, or damaged by overloading heavy items of cargo, such as machinery packing cases or steel stock, for example. FIBCs that do not have a stack rating should not be stacked more than one tier high but incidents involving multiple tiers of unrated FIBCs have come to light, raising the prospect of stows or bags collapsing, leading to further release of their contents.

[1]The cargoes have included: calcium nitrate granular, zinc sulfate monohydrate, ferrous sulfate monohydrate, sodium metabisulfite, sodium carboxymethyl cellulose, mono ammonium phosphate, mono calcium phosphate, magnesium sulfate anhydrous, and magnesium nitrate hexahydrate.

The incidents have principally occurred during discharge, with a number following periods of rain. Rainwater can penetrate any damaged bags at the surface of the stow or similarly react with any exposed, spilled cargo present. The cargoes also tend to be hygroscopic, meaning that they can absorb moisture from the atmosphere which could also lead to reactions in or between cargoes. Once reacting, a number of toxic, corrosive and asphyxiating gases and compounds can be released, together with the generation of heat in the affected zones of cargo. The decomposition products themselves may also react further.



*Thermal image showing cargo at elevated temperatures within a cargo hold (image taken from SAMSA website).*

The gases released in incidents have included sulfur dioxide and nitrogen dioxide. Typically, the odours of the gases produced are readily detected by individuals below toxic levels. However, this should not lead to complacency as personnel can be overcome or caught unawares by pockets of gas in poorly ventilated areas or in the event of release of significant volumes of gas from an opening in a hold. These gases attack the eyes and respiratory system, causing irritation to the eyes, nose and throat at low levels, but higher levels can lead to nausea, vomiting, stomach pain, corrosive damage to the airways, eyes and lungs, and even to obstruction and death[2]. Significantly, the damage caused by inhaling the gases can develop over a period after exposure so that harmful effects on, or symptoms displayed by, individuals may not be immediately recognized as a result of exposure. Furthermore, dust created by the cargoes can become trapped in clothing, which when subsequently affected by sweat can becoming irritating and lead to redness and blisters. The gases released can also dissolve in sweat, becoming acidic and be retained against the skin.

[2]US Department of Health & Human Resources, information papers on sulfur dioxide and nitrogen oxides.

In a number of cases, substantial volumes of toxic gas have been produced, which have required vessels to leave port promptly in order to remove the risk of contamination of the port environment and any threat to local inhabitants and other port users. Wetting of the cargo can lead to significant heating as well as to corrosive conditions, and fires have broken out in the packaging. Fire can then spread if other combustible materials are present.

*Fire burning in packaging amongst bags of mineral compound cargo.*

Liquid residues draining from or remaining in the cargo, or condensed on surfaces in the cargo hold, can be highly acidic and they are corrosive to skin, as well as to exposed steel and other metals. Gas production and heat generation can be exacerbated when two or more of the powder cargoes have become mixed and then wet, or by water dissolving one cargo that flows into another incompatible cargo below.

One chemical common in these incidents is sodium metabisulfite. Sodium metabisulfite is a white, or yellowy-white, powder or crystalline solid with a slight sulfurous odour. It has the chemical formula $Na_2S_2O_5$ and is a type of chemical known as a reducing agent. It is also known by other names[3] such as sodium disulfite, disodium disulfite, pyrosulfurous acid or sodium pyrosulfite.

[3]The English spelling of 'sulfur' is sulphur and correspondingly its compounds can be written sulphite, pyrosulphite and so on.

*Moisture affected and decomposed sodium metabisulfite, having produced other yellow sulfur compounds.*

Sodium metabisulfite, having a theoretical 67% by weight sulfur dioxide content, is prepared by saturating a hot solution of sodium bisulfite with sulfur dioxide and then cooling until the crystal salt forms. Wetting the solid essentially reverses this process, releasing sulfur dioxide and under the acidic conditions formed, causes further decomposition to release the full sulfur dioxide content. While sulfur dioxide is soluble in water it can also be released as a gas. It is a toxic, choking, pungent gas that has a smell characterized as that of burnt matches.

Being a reducing agent, sodium metabisulfite will react readily with oxidizing agents, which include chemicals such as nitrate-containing fertilizers, with which substances it has been carried. The reactions lead to the release of further toxic and corrosive gases, such as nitrogen dioxide mentioned above, which can also produce strong acids upon mixing with water.

At present, sodium metabisulfite is not listed individually as a dangerous cargo in the International Maritime Dangerous Goods (IMDG) Code or the International Maritime Sold Bulk Cargo (IMSBC) Code and material safety data sheets for the chemical do not tend to assign it to hazard classes under most national or international transportation codes. This absence of sodium metabisulfite from the codes could well be because its carriage has not previously led to significant incidents such as those that have occurred recently. This in turn might be a result of recent changes in the mode of transport of sodium metabisulfite and the other inorganic chemicals mentioned above. A newsletter[4] from IUMI has recently highlighted such changes and the effects for carriage of items and materials as general

[4]IUMI Eye Newsletter March 2022

cargo. It should be noted that because a substance is not listed in one of the safety codes, it does not mean the substance is safe to carry. The codes provide guidance on the carriage of substances not listed in them and typically, a shipper should obtain a letter from a competent authority stating that the substance in its packaging is safe for carriage and a vessel provided with relevant information concerning conditions for carriage.

*Operations to remove reacted cargo from a cargo hold (image taken from SAMSA website).*

On a practical level, when carrying sodium metabisulfite, all measures should be taken to avoid wetting it, or any other chemicals loaded with it, at any stage. Hatches on holds containing the substance should not, for example, be left open unnecessarily and the hatch covers should be fully sealed against the ingress of water during the voyage. Cargo handling operations should cease and the hatches closed if rain is imminent. Ideally, sodium metabisulfite should be stowed away from oxidizing agents, or other incompatible chemical cargoes with which it might unintentionally mix. The bags for all such cargo should be protected from damage by other items in order to avoid spillage and possible cross-contamination. A further relevant hazard is that because sodium metabisulfite can absorb atmospheric moisture and might release sulfur dioxide during a voyage, proper safety precautions and checking, such as taking gas readings and hold ventilation, should be undertaken if and when entry to the hold is contemplated.

*Operations to remove elevated temperature cargo from a cargo hold (image taken from SAMSA website).*

As indicated above, a chemical cargo should be accompanied with information stating that it is safe to be carried, in its packaging and with relevant safety information on it, such as its full and proper description, its grade and a material safety data sheet (MSDS) or other information relevant for emergencies. Thus, vessels loading sodium metabisulfite, or a chemical suspected to be sodium metabisulfite, should expect to be provided the relevant information, whether there are any specific carriage or loading conditions and whether it is compatible with other chemicals with which it is being loaded. A vessel might therefore request such information it if it is not supplied, preferably prior to commencing loading. Those responsible for the stowage of the cargo would be expected to ensure that it is protected from damage by other cargoes.

Burgoynes has experience of investigating incidents involving bagged mineral cargoes, including sodium metabisulfite and our expert chemists are available to provide technical advice on live incidents.

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