Standard Operating Procedure

Title:	Pyrophoric Iron Sulphide SOP		
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1 Introduction and Purpose

The purpose of this Standard Operating Procedure (SOP) is to control and prevent the risk of pyrophoric combustion when disassembling installation components in which ferrosulphide (FeS) could have formed.

2 Scope

Pyrophoric iron sulphide can be formed on the internal surfaces of carbon steel equipment containing H_2S. Iron oxide present on the internal surfaces will react with the H_2S and form pyrophoric iron sulphide which, on exposure to oxygen can auto-ignite.

Caution: Pyrophoric Iron sulphide can be present where any loose scale, black sludge or coating is found. If found, wet down immediately.

3 Definition

Pyrophoric iron sulphide (FeS) is a black powdery/scaly compound formed by a chemical reaction between a sulphur compound such as Hydrogen Sulphide (H_2S) and iron oxide (Fe_3O_4 or Fe_2O_3) over a long period of time in an atmosphere virtually free of oxygen. These conditions are frequently found in vessels, pipes, valves and drilling tubulars. Even in an H_2S containing atmosphere the presence of a small amount of air (oxygen) prevents ordinary iron sulphide from becoming the pyrophoric form. However, it can form at very low H_2S concentrations (<0.1ppm) as long as the partial pressure of H_2S exceeds the partial pressure of oxygen in the environment.

When formed as a corrosion product it is usually very finely divided and oxidises rapidly on exposure to the oxygen in air. It may ignite spontaneously in an exothermic reaction. the speed and severity of the reaction is dependent on the amount of Iron Sulphide, particulate granule size and if the product is wet or dry. If the mixture is flammable one early indication of activity is a white fume of SO_2 being given off.

Particulate size can range from sub-micron to micron sizes, and this allows the product to migrate through the system. The product can also form an agglomerate when mixed with other contaminants to form a slurry or tar like product.

Pyrophoric iron sulphides formed at high temperatures are more reactive than those formed at low temperatures.

Whilst steps can be taken to reduce the formation of pyrophoric iron sulphide it must never be assumed that there can be an absolute prevention of the reaction. Therefore, any equipment constructed of carbon steel which is in contact with hydrocarbons containing H_2S should be treated as if it contained pyrophoric iron sulphide.

It is difficult to predict the presence of pyrophoric deposits. Therefore, reference must be made to any records of tanks/vessels/ pipelines and those tanks/vessels/ pipelines in similar service to ensure information is captured for future personnel.

4 Procedure

4.1 Handling Pyrophoric Iron Sulphide or Pyrophoric Dust

Great care should be taken when opening up equipment to the atmosphere. Oxygen will react with the pyrophoric debris in an environment which is not yet hydrocarbon-free and thereby cause an explosion and fire. Even when hydrocarbons are removed the pyrophoric debris can start burning spontaneously.

With pyrophoric matter, combustible material and ignition source are combined and will react in the presence of oxygen. Removal of hydrocarbons by, e.g., nitrogen purging of gas systems will remove the danger of explosion, but not necessarily the danger of fire.

The fire may not be noticeable to the naked eye, depending on the volume of dust. The dust may just disappear, or a sharp acidic smell may be noticed.

Dampening down with water will retard the reaction and allow safe removal of the debris. This may be the only practical method in large installations, e.g., storage tanks.

Once the material dries out there is a possibility of the exothermic reaction returning when the product comes into contact with oxygen.

The following equipment should be available and considered in the JHA;

- Powder fire extinguishers
- Continuous gas monitoring
- Supply of water for dampening of dust, flooding vessels or saturating filters
- Infrared Temperature Thermometer
- Sealable container or IBC for containing dust dispersed through water.
- Nitrogen Purging (vessels)
- Metal buckets/ trays

Note: Consideration must be given to known passing valves to ensure a suitable isolation is achievable

Personal Protective Equipment.

- Disposable Overalls, Fire retardant overalls underneath
- Full face mask, combination acid/gas particulate cartridge
- Gloves
- Safety boots
- Safety Glasses, when not wearing full face mask

Sulphur Dioxide Reaction

If the reaction is exothermic, the product of the reaction may be sulphur. When the sulphur is heated through the exothermic process sulphur dioxide may be released. The gas is colourless with a sharp, suffocating, acidic odour. Work must always be completed outside the hazardous area, in the field with good ventilation. Personal should stay upwind of the reaction.

4.2 Scale Removal and Disposal

The pyrophoric iron sulphide material must be thoroughly wetted with water to render it harmless and prevent oxidation. Continuous gas monitoring shall be carried out through the removal procedure. A means of extinguishing shall be available to deal with any fire.

It is important that any pyrophoric debris remains wet, preferably submerged in water, throughout the period of storage and transportation from the work site to a designated safe area for its disposal. If the product dries out it may become flammable.

The presence of pyrophoric deposits in a tank/vessel is suspected the lower part of the tank/vessel, which normally remains covered with liquid whilst in operation, should be emptied very slowly during decommissioning. During the entire gas-freeing period, water-flooding or water- spraying of the tank/vessel bottom sediments is recommended.

All pyrophoric iron sulphide removed shall be disposed of carefully, in fire safe containers e.g., metal buckets. No product shall be put into any general waste container. This also applies to scale where the presence of a proportion of pyrophoric iron sulphide is suspected, but not confirmed.

The container used for transporting the pyrophoric debris should be clearly identified and must never be transported together with flammable materials. It is also good practice to pack equipment that may contain pyrophoric debris, such as filter elements, in plastic bags to keep oxygen away. Equipment with large qualities of dust must be purged with nitrogen to create an inert atmosphere within the container.

All transport of pyrophoric iron sulphide material shall comply with Dangerous Goods Transport Rules. Iron Sulphide (FeS) is a class 4.2 product, packing group I.

Waste Disposal

The simplest way to manage the disposal of a small amount of debris containing pyrophoric iron is to place the pyrophoric debris in a dedicated safe location and oxidising the dust. This is achieved by sprinkling on a fire safe tray or leaving in its metal bucket exposing it to the atmosphere.

For larger amounts Iron Sulphide can be disposed of by flushing through water until the pyrophoric material has been dispersed within the water. This should then be sealed in a container and handed to a waste contractor for treatment and disposal. The waste contractor must be made aware of the pyrophoric properties of the waste.

Revision and Approval Details

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