

De-listing Protocol for Treated Spent Iron Sponge - September 2006

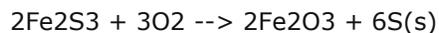
Foreword

Section 19(2) of the Hazardous Waste Regulation (formerly Section 19(2) of the Special Waste Regulation) allows hazardous wastes to be disposed to a landfill or used for other specified purposes provided the substance does not pose a hazard to human health or the environment as determined by protocols approved by the Director. In accordance with Section 19(1) of the Hazardous Waste Regulation (formerly Section 19(1) of the Special Waste Regulation), the attached protocol is approved for evaluation of treated spent iron sponge.

Iron sponge consists of wood shavings or wood chips impregnated with hydrated iron oxide. It is used for removal of H₂S in oil and gas processing operations. Exposure to H₂S and mercaptans produces iron sulphides and iron mercaptides. Infused with these contaminants, the iron sponge is referred to as spent iron sponge. In particular, the removal of H₂S results in iron sulphides as follows:



The spent iron sponge (iron sulphide) then becomes a class 4, reactive hazardous waste (either a pyrophoric solid or a self-heating substance). It may be re-oxidized or reverted, with exposure to air, to iron oxide and elemental sulphur, by the following reaction:



The reversion is spontaneous, and is controlled by keeping the sponge wet to prevent combustion, limiting the thickness of sponge to prevent heat build-up (the reaction is exothermic) and periodically raking the sponge to ensure exposure of all parts to air. The reversion appears to occur within a few days, and is assumed complete when all of the sponge has changed from a black colour to a colour varying from deep red to red-brown to grey-red. This is verified using the test procedure in the attached protocol, which would be carried out on small, homogeneous particles of spent iron sponge, to ensure that the substance is no longer either pyrophoric or self-heating.

Treated iron sponge which passes this test protocol may be managed in accordance with Section 19(2)(b)(i) of the Hazardous Waste Regulation (formerly Section 19(2)(b)(i) of the Special Waste Regulation).

L.T. Hubbard
Deputy Director of Waste Management

Application

This protocol is to be used when spent iron sponge has been reverted by exposure to air into iron oxide and elemental sulphur thus removing any hazards of spontaneous combustion. By using this approved protocol, a regional manager may authorize disposal of (treated) iron sponge to an authorized landfill. Disposal of the material must be subject to the provisions of the *Environmental Management Act*.

Protocol

The de-listing protocol for iron sponge:

- 1)** For each 5m³ batch of iron sponge that has been treated, a homogeneous, representative sample is required to adequately characterize the treated sponge. The Regional Waste Manager must be satisfied as to the sampling method.

- 2)** Each sample shall be tested according to the "Interim Compilation of Test Methods Under the Transportation of Dangerous Goods Regulations, VI.2 Division 4.2: Spontaneously Combustible Substances" (1), (attached). Only the test for the 10 cm cube sample is required (*i.e.* it is not necessary to determine the packing group for the purposes of de-listing an iron sponge special waste treatment residue).

- 3)** All samples must be determined to be non-pyrophoric and non-self-heating to pass the test and for the bulk treatment residue to be declared suitable for disposal to an authorized landfill in accordance with sections 19(2)(b)(i) of the Hazardous Waste Regulation.

(1) *Environment Canada. 1988. Interim Compilation of Test Methods Under the Transportation of Dangerous Goods Regulations, VI.2 Division 4.2: Spontaneously Combustible Substances. The CCREM Working Group on TDG Hazardous Wastes. pp. 141-145.*

Testing Procedure: Treated Iron Sponge

VI.2 Division 4.2: Spontaneously Combustible Substances If, in a reaction of a substance with air (oxygen), the heat generated is not conducted away fast enough, the substance may begin to self-heat which in turn may lead to spontaneous combustion. Therefore, in more specific terms, spontaneous combustion occurs when the rate of heat generation is greater than the rate of heat loss and the auto-ignition temperature is reached.

This division has been split into two groups of materials:

- pyrophoric substances; and
- self-heating substances.

Both groups have the same basic properties but differ in the degree of spontaneous combustion. Pyrophoric substances ignite, even in small quantities, within five minutes of coming into contact with air. Self-heating substances, on the other hand, ignite in air only when in large quantities and after long periods of time. They are generally liable to self-heating not spontaneous combustion.

For practical reasons the procedure has been split into two tests, Test for Pyrophoric Substances and Test for Self-heating Substances. Both methods are described below in detail.

1. Test for Pyrophoric Substances

Pyrophoric substances include solids, liquids, mixtures and solutions. The test has been divided into one procedure for solids and another for liquids.

For Solids

The substances to be tested should be in powder form. A sample of 1 to 2 cm³ of the substance is required for each run of the test. This sample is poured from a height of 1 m onto a non-combustible surface and it is noted whether the substance ignites on the way down or within 5 minutes after settling. The test is carried out six times unless a positive result is obtained earlier.

For Liquids

Part 1

Materials

- porcelain cup 10 cm in diameter;
- diatomaceous earth (or silica gel).

Procedure

The porcelain cup is filled to a height of 5 mm with the diatomaceous earth (or silica gel), at room temperature and 5 mL of the liquid to be tested is poured into the cup. It is observed whether the liquid ignites within 5 minutes or not.

This test is repeated six times, unless a positive result is obtained earlier, in which case, no further testing is required. If a negative result is observed in all six runs then Part 2 of the test must be carried out.

Part 2

Materials

- syringe;
- indented dry No. 3 Whatman filter paper.

Note: This test must be carried out at $25 \pm 2^\circ \text{C}$ and a relative humidity of $50 \pm 5\%$ in a "constant temperature room".

Procedure

A 0.5 mL sample of the liquid is transferred to the filter paper using the syringe. It is observed whether there is any charring of the paper or ignition within 5 minutes after the liquid is introduced.

This test is repeated 3 times (using clean filter paper each time) unless a positive result is obtained earlier.

Results

For Solids

If the substance ignites in one of the test runs, it is considered pyrophoric and is classed as Division 4.2 Packing Group 1.

For Liquids

If the liquid ignites in Part 1 of the test for liquids, it is considered pyrophoric and is classed as Division 4.2 Packing Group 1.

If the liquid ignites or chars the filter paper in Part 2 of the experiment, it is pyrophoric and is classed as Division 4.2 with Packing Group 1.

2. Test for Self-heating Substances

Materials

- hot air circulating oven - inner volume over 9 litres and capable of controlling the internal temperature at $140 \pm 2^\circ \text{C}$;
- 2 cubic sample containers - made of stainless steel net, 270 mesh/square inch (mesh opening of 53 micrometers) with the top surfaces open (2 sizes: 2.5 cm per side and 10 cm per side);
- 2 cubic container covers - 28 mesh (mesh opening of 595 micrometers) stainless steel net, slightly larger than sample containers, i.e. so that the container fits in the cover;
- cover housing - 15 x 15 x 25 cm stainless steel cage of 28 mesh (mesh opening of 595 micrometers) net to cover the container cover;
- 2 Chromel - Alumel thermocouples - 0.3 mm diameter.

Procedure

Preparation:

The sample (powder or granular) should be in the form it will be transported in. The 10 cm sample container is filled to the brim with the sample and is tapped several times so that the powder settles. If the sample settles below the brim, more sample is added until the container is full. If it is heaped above the top, it is levelled off at the brim. One thermocouple is placed in the centre of the sample. The other thermocouple is placed between the oven wall and the container. The temperatures are measured and monitored continuously. For a diagram of this set-up refer to [Figure 3](#) below.

Experimental:

The temperature of the oven is raised to 140° C and is kept there for 24 hours. The temperature of the sample is monitored and recorded and it is observed whether spontaneous ignition occurs or if the temperature of the sample exceeds 200° C in the time period.

If spontaneous ignition does not occur and the temperature of the sample does not exceed 200° C, then no further testing is required. However, if a positive result is obtained, then the procedure is repeated with the 2.5 cm sample container to determine Packing Group.

Results

(a) Substance does belong in Division 4.2:

The 10 cm cube sample exhibits spontaneous combustion or its temperature exceeds 200° C in the 24 hour period.

(b) Determination of Packing Group:

Packing Group II

- A positive result is obtained with the 2.5 cm cube sample

Packing Group III

- A positive result is obtained with the 10 cm cube sample but a negative result with the 2.5 cm cube sample.

Figure 3: Suggested Set-up for Self-heating Substances

