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Oil Spill Sorbents: Testing Protocol and Certification Listing Program

by

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INTRODUCTION

A universally accepted standard method for testing oil spill sorbents is not currently employed by the majority of sorbent manufacturers. End-users are limited to manufacturers' and distributors' claims which may be perceived as being biased. Environment Canada has spearheaded a drive to develop an official Canadian standard for the testing and certification of sorbents using the Canadian General Standards Board (CGSB) as the certification body. It is anticipated that Environment Canada will provide a system to maintain an unprejudiced method for testing oil spill sorbents.

BACKGROUND

Environment Canada's Emergencies Engineering Division (EED) is mandated to evaluate existing technologies and act as a proving ground for technologies deemed new and innovative in areas of Oil and Chemical Spill Cleanup. The sorbent testing program had its beginnings in 1974 when Environment Canada released its first publication entitled "Selection Criteria and Laboratory Evaluation of Oil Spill Sorbents". Updates to this publication were release every four or five years. The time lag between publications and the limited number of sorbents tested were acceptable limitations to this program as interest in sorbents was relatively limited. Since that time; however, interest in sorbent performance evaluation has grown steadily. Recent events including the Exxon Valdez spill in Prince William Sound and the spills during the Gulf War spurred renewed interest in sorbents.

Manufacturers and Distributors were aggressively marketing their products to Government, Oil Spill Co-ops, and other Non-Government Organizations (NGOs). These end-users had limited third party data from which they could base a purchasing decision. First Responders, sceptical of the performance and safety aspects associated with some sorbents, requested that sorbents pass some sort of approval mechanism before being considered. It was this demand for an approval mechanism that catalyzed the development of the sorbent evaluation and certification program.

PROGRAM DEVELOPMENT

As requests for sorbent performance information grew, it became obvious that an ongoing evaluation system was warranted. Requests for "approving" or "certifying" sorbents could not be met simply because such a mechanism did not exist. At this point EED began talks with the Canadian General Standards Board (CGSB). This Federal Government Agency is one of only five National Standardizing bodies in Canada. A committee was formed through the CGSB consisting of equal representation from interested parties, producers, and end-users throughout North America. This led to the development of a new test procedure based upon work Environment Canada had performed in the past[1], but also incorporating methods from the American Society for Testing and Materials (ASTM)[2]. These protocols currently enjoy top status as sorbent test protocols in North America.

CGSB SORBENT CERTIFICATION AND LISTING PROGRAM

The CGSB Sorbent Certification and Listing Program currently consists of two documents. One is a standard for sorbent materials, while the other specifically defines testing procedures for sorbents used on crude oil and similar spills. The program is structured in this fashion to allow the introduction of additional testing protocols. One anticipated protocol will deal specifically with testing sorbents for use with aggressive chemicals.

Standard C**/CGSB-183.1 encompasses "Sorbent Materials" and relates to operational and performance criteria for the clean-up and control of oil and hazardous substances spills. It is within the "Sorbent Materials" document that testing protocol terms and calculations are explicitly defined. Sorbents are classified by physical type based on ASTM F726-81 (1986) as follows:

Type I:	sheet, pad, blanket, mat
Type II:	loose - unconsolidated, particulate material
Type IIIa:	pillows and socks - sorbent material contained by an outer fabric or netting.
Type IIIb:	booms - sorbent material contained by outer fabric or netting which has a lengthwise dimension exceeding other dimensions by a factor of at least five and whose sorption capacity would be significantly altered if cut to meet Type I size requirements.

Type IIIc:	sweeps
Type IV:	agglomerated unit - pom pom, yarn, or netting which offer low impedance to highly viscous fluids.

An Interim Standard is now in place, but is limited to testing Type I and Type II sorbents. It is anticipated that testing protocols for remaining Types will be incorporated into the official Standard during the fourth quarter of 1992.

Sorbents are also classified by category which determines the recommended type of application as follows:

L-W category:	sorbents which are recommended for sorbing spills on water or land.
L category:	sorbents which are recommended for sorbing spills exclusively on land.
W category:	sorbents which are recommended for sorbing spills exclusively on water.
I-S category:	sorbents which are recommended for sorbing spills in an industrial setting (aggressive chemicals).
ALTERNATE:	encompass all sorbents which technically fail tests, but possess at least one redeeming characteristic which warrants further consideration.

The Sorbent Materials Standard goes on to identify nine sorbent characteristics which should be considered. Specific labelling and Material Safety Data Sheets are a requirement, as are sturdy storage properties.

Testing Procedure

Standard C**/CGSB-183.2 covers laboratory conducted performance tests for all forms of sorbent materials, regardless of their mode of action, for the sorption of crude oil, its contained natural components, and mixtures thereof.

Performance Characteristics

Specific characteristics were initially identified as being highly desirable. They are as follows:

- Buoyancy: Data obtained would allow confirmation that a particular sorbent may be suited for use in a spill on water. Sorbents that sink may pose a threat to aquatic life by transporting hazardous liquids to the sediment causing infiltration into the entire food chain.
- Low Water Pick-up: Non-selective sorbents may pick up water in addition to oil if placed in an aquatic environment. This may not prove to be a major

hindrance if the sorbent remains floating; however, any water sorbed would displace the spilled oil, thus hindering performance.

- High Oil Pick-up: The rate of pick-up in addition to the sorbent's capacity would be tested. A sorbent's ability to be "self acting" could limit the application to specific spill scenarios.
- Reuse: Some sorbents allow the sorbed liquid to be extracted via mechanical or chemical means enabling reuse. This could limit the amount of solid waste generated during a spill cleanup operation. Safety aspects of attempting reuse should be carefully considered.
- Low Rate of Release: Liquids sorbed by most sorbents are released back into the environment to some degree. The extent of release will vary dramatically depending upon the sorbent used. The importance of this release depends upon the specific spill scenario, and storage equipment available at the spill site.

Test Method

The following tests have been established to evaluate the performance of sorbents on oil and water. The procedures followed are condensed versions of the test methods outlined by the Canadian General Standards Board.

Degradation Pre-Test (Static): This test measures the sorbent's hydrophobic characteristics in addition to determining buoyancy of a sorbent. A test cell (crystallizing dish having a diameter of 190 mm) is filled with a layer of water approximately 80 mm deep. If Type II sorbent is being tested, a mesh basket having openings of approximately 1 mm is lowered into the crystallizing dish. The sorbent sample (Type I: 13 cm x 13 cm, Type II: 10 grams) is placed into the cell. The test cell is then covered and left for 15 minutes. After 15 minutes the sorbent is removed from the water and observations are noted. The sorbent is weighed to determine water pick-up. Samples that pass are then prepared for the Degradation Test (Static).

Degradation Pre-Test (Dynamic): This test is used to determine the buoyancy of sorbents in simulated wave conditions. If the sorbent passes this test for buoyancy, it is then very unlikely that the sorbent will sink in most applications. Sample pieces of the sorbent (Type I: 16 pieces of 3 cm x 3 cm, Type II: 3-5 grams) are placed in a 2 litre jar which is half filled with water. The container is then placed on its side and mounted on a shaker table set at a frequency of 10 cycles per minute for a duration of 15 minutes. The sorbent is then removed from the water and observations are noted. The sorbent is weighed to determine water pick-up.

Degradation Test (Static): This is a test for buoyancy, sorbent capacity, and oil retention. A sorbent sample from the static pre-test is placed on a 5 mm layer of crude oil floating on an 80 mm layer of water. The sample is left undisturbed for a period of at least 48 hours. The sorbent is then removed and hung from a balance (Type I: hung vertically using a clip, Type II: hung horizontally using a basket). Observations pertaining to the physical condition of the sorbent are recorded. The weight of the sorbent is measured as oil drips after 15 seconds, 30 seconds, 1 minute,

2 minutes, 5 minutes, and 30 minutes. A retention profile is obtained from this data, as is the sorbent's capacity. Mechanical compression is used to extract remaining liquid from the sorbent in order to determine water pick-up.

Degradation Test (Dynamic): This test follows the methodology of the Degradation Pre-Test (Dynamic) with the exception that 150 ml of crude oil is introduced into the 2 L jar. Observations of the sorbent's behaviour during agitation are recorded. After 15 minutes the sorbent is removed and weighed to determine oil pick-up. Mechanical compression is used to extract liquid from the sorbent to determine water pick-up for comparison with the static test.

L-W Category Test: This is a test for sorbent capacity and reuse. A fresh sorbent sample is placed on a 5 mm layer of crude oil floating on an 80 mm layer of water. The sample is left for a period of 15 minutes. The sorbent is then removed and left to drip for 30 seconds before being weighed (Type I: hung by clip, Type II: hung by basket). Observations pertaining to the physical conditions of the sorbent are recorded. Mechanical compression is used to extract remaining liquid from the sorbent for reuse testing and water content determination. The data is also compared with Degradation Test (Static) results.

L Category Test: This is a test for sorbent capacity, reuse and retention. A fresh sorbent sample is placed on a 7.5 mm layer of crude oil. The sample is left for a period of 15 minutes. The sorbent is then removed and hung from a balance (Type I: hung vertically using a clip, Type II: hung horizontally using a basket). Observations pertaining to the physical condition of the sorbent are recorded. The weight of the sorbent is measured as oil drips after 15 seconds, 30 seconds, 1 minute, 2 minutes, 5 minutes, and 30 minutes. A retention profile is obtained from this data, as is the sorbent's capacity. Mechanical compression is used to extract remaining liquid from the sorbent for reuse testing.

W Category: Data obtained from the L-W test and the Degradation Test (Dynamic) will determine if a sorbent should be designated for the W Category. A sorbent requiring agitation would not be recommended for use on land thus may fall into the W Category.

I-S Category Test: This testing procedure is currently under review.

Non Performance - Handling

This information is provided by the manufacturer for the benefit of the end-user, but is not a requirement for certification.

- Tensile Strength: This characteristic becomes extremely important when dealing with sorbent booms. This characteristic determines the ability of a boom to retain its' integrity under the strain of currents and wave action.
- Storage: Ideally, a sorbent would occupy a minimum of storage space, while

exhibiting a high sorption capacity. Storage space within facilities is often very limited.

- Disposal: Proper and safe disposal methods should be addressed before application of any sorbent to a spill. Regulations may limit options.
- Static Resistance: In very dry conditions (desert or arctic) static resistance becomes an important safety concern. Specific conditions would have to be met before a static spark could ignite a flammable liquid. Steps should be taken to ensure safe working practices are enforced and working environments should be carefully scrutinized for ALL possible sources of static charge.

FUTURE AREAS OF DEVELOPMENT

Test liquids used in the Interim Standard represent a cross-section of viscosities for oil were chosen based upon suitability and availability. It is the intention of the CGSB General Sorbent Committee to expand upon this list to encompass hazardous liquids which are frequently spilled during transportation and in industrial settings. It is also the intention of the committee to expand into the area of sorbent boom testing.

CONCLUSIONS

This program should benefit both manufacturers and users. Manufacturers will be given the opportunity to have their products tested by impartial third party laboratories and certified to that effect. Users will be able to select products from manufacturers and compare data objectively. The reader should note that this program is prototype in nature. EED hopes to expand this type of program to encompass booms, skimmers, and related spill response equipment. A centralized database of performance and non-performance data pertaining to oil and hazardous liquid spills is the long-term goal.

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APPENDIX A

C**/CGSB-183.2

CANADIAN GENERAL STANDARDS BOARD
Draft Method for Testing Sorbents

1. **SCOPE**

1.1 This method covers laboratory-conducted performance tests for all forms of sorbent materials, regardless of their mode of action, for the sorption of crude oil, its contained natural components and mixtures thereof.

1.2 The testing and evaluation of a product against this standard may require the use of materials and/or equipment that could be hazardous. This document does not purport to address all the safety aspects associated with its use. Anyone using this standard has the responsibility to consult the appropriate health and safety practices in conjunction with any existing applicable regulatory requirements prior to its use.

2. **APPLICABLE PUBLICATIONS**

2.1 The following publications are applicable to this method

2.1.1 Canadian General Standards Board
25-GP-1M Method 44.1,

2.1.2 Environment Canada
A Catalogue of Crude Oil and Oil Product Properties, 1990 EETD.

2.2 Reference to the above publications and to other standards is to the latest issues unless otherwise specified by the authority applying this standard. The sources for the publications are shown in the Notes Section 13.

3. **PRINCIPLE**

3.1 The sorbent materials are tested using established tests for factors relating to performance and handling.

4. **SIGNIFICANCE AND USE**

This method is to be used as a basis for comparison of sorbents in a consistent manner and to present their characteristics and properties of value during their lifecycle. The sorbents shall be classified in the following types and categories.

4.1 Types

4.1.1 Type I: sheet, pad, blanket.

4.1.2 Type II: loose - unconsolidated, particulate material.

4.1.3 Type III: enclosed
Type III Series A: pillows and socks - sorbent material contained by an outer fabric or netting.
Type III Series B: booms - sorbent material contained by outer fabric or

netting which has a lengthwise dimension exceeding other dimensions by a factor of at least five and whose sorption capacity would be significantly altered if cut to meet Type I size requirements.
Type III Series C: sweeps

4.1.4 Type IV: agglomerated unit - pom pom, yarn, or netting which offer low impedance to highly viscous fluids.

4.2 **Categories**

4.2.1 The L-W category refers to sorbents which are recommended for sorbing spills on land or water.

4.2.2 The L category refers to sorbents which are recommended for sorbing spills exclusively on land.

4.2.3 The I-S category refers to sorbents which are recommended for sorbing spills in an industrial setting.

4.2.4 The W category refers to sorbents which are recommended for sorbing spills on water only.

4.2.5 The ALTERNATE category will encompass sorbents which do not meet the requirements of the above categories but possess at least one redeeming characteristic which warrants further consideration.

5. APPARATUS AND MATERIALS

5.1 Test Cells (open): The dimensions of the test cells shall be of a large enough size to enable sorbent sample to float freely within the test basket. The following is a recommended vessel for Type I and Type II sorbents: Pyrex 190 mm (diameter) X 100 mm (depth) crystallizing dish with a watch glass or glass plate cover to accommodate a sample size not less than 130 mm (L) by 130 (W) or 6 grams. Type IIIa, Type IIIb, and Type IV may require larger cells to accommodate the sorbent sample dimensions.

5.2 Test Cells (enclosed): Test cells for use with shaker table should be large enough to enable wave action to thoroughly mix water and test liquid with sorbent. A 4L glass jar with a screw type lid is recommended.

5.3 Basket for Type II test: The basket shall be of a sufficient size and strength to accommodate the sample size and weight when saturated. A stainless steel basket having 1.5 mm[1] openings is recommended. The basket must not be so tall as to interfere with the lid.

5.4 Basket type IIIa, IIIb, IV test: The basket shall be of sufficient size and strength to accommodate the sample size and weight when saturated. A stainless steel mesh having 5 mm openings is recommended.

[1] The mesh should retain the sorbent, yet allow free oil to drain away from the sorbent.

5.5 Cold room or ice-cooled bath or equivalent to maintain a temperature of 15°C.

5.6 Top Loading Balance: 0.01 g resolution. A range of up to 400 g is recommended for sorbents of Type I, Type II. A higher upper limit may be necessary for Type IIIa, Type IIIb and Type IV configurations.

5.7 20 cm diameter weighing pans (non-stick coated pan or lined pan recommended for ease in cleaning).

5.8 Wringer-type Press: Hand operated with a double roller design not dissimilar to wringer-type washing machines. Tension to rollers should approximate 200 Newtons (45 lb_f) (eg. 20 kg weight).

5.9 Plate Press: Hydraulic press or similar device able to apply 1000 Newtons (224 lb_f) of force (eg. 100 kg weight) on top plate measuring 15 cm x 15 cm.

5.10 Graduated Conical Centrifuge Tubes (100 ml capacity).

5.11 Shaker table capable of producing a frequency of 150 cycles/min and an amplitude of 3 cm (Eberbach Shaker Table or equivalent).

6. TEST LIQUIDS

6.1 The types of fluids to be tested should be representative of the wide variety of fluids that sorbents could be used to clean up. The testing will be restricted to the following liquids.

6.1.1 Diesel Fuel Oil — Grade 2-D, Automotive diesel fuel oil
API GRAVITY: 39.4 (EETD 84) (15/15°C)
DENSITY: 0.827 g/ml @ 15°C (EETD 85) DYN. VISCOSITY: 2.7 cP @ 15°C (EETD 85)

6.1.2 Crude Oil — Alberta Sweet Mixed Blend
API GRAVITY: 37.0 (EETD 84) (15/15°C)
DENSITY: 0.839 g/ml @ 15°C (EETC 84) DYN. VISCOSITY: 9.2 cP @ 15°C (EETD 85)

6.1.3 Weathered Crude — Alberta Sweet Mixed Blend (7 day weathered-25% volumetric loss)
DENSITY: 0.883 g/ml @ 15°C (EETD 84) DYN. VISCOSITY: 48 cP @ 15°C (EETD 85)

6.1.4 Fuel Oil #6 — Bunker C Fuel Oil (Fuel Oil Number 6)
API GRAVITY 12.3 (EETD 88) (15/15°C)
DENSITY: 0.974 g/ml @ 15°C (EETD 84) DYN. VISCOSITY: 48,000 cP @ 15°C (EETD 88)

Care must be taken when dealing with volatile liquids to ensure excessive evaporation does not occur.

7. CONDITIONING

7.1 Sorbents shall be inspected upon receipt by the testing agency and damaged specimens shall be removed and placed as needed.

7.2 Condition all sorbent test specimens at 20 ± 3°C and 60 ± 5 % relative humidity for not less than 24 h prior to testing. Condition specimens in a fully exposed state with no coverings or wrapping that would hinder the ambient equilibration process.

8. NON-PERFORMANCE HANDLING

8.1 Storage
8.2 Disposal

9. PROCEDURE

9.1 Static Water Test: This procedure is designed to test for water pick-up under stagnant conditions. This test is performed at room temperature.

9.1.1 Type I Sorbent: The test cell is filled with a layer of water (80 mm). Approximately 130 mm x 130 mm square of a weighed sorbent sample is lowered into the test cell. The sorbent should float freely on the water. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes (± 20 sec) check the condition of the sorbent. If the sample sinks go directly to step 9.5, otherwise remove the sorbent vertically with a clip and let drain hanging over the cell for 30 seconds (± 3 sec). Place a tared weighing pan under the sorbent to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Retain the sorbent sample for use in the Static Long Term Sorption test. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run (g/g) deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.1.2 Type II Sorbent: The test cell is filled with a layer of water (80mm). A sorbent sample of approximately 200 ml is weighed then placed in a basket which is lowered into the test cell. The sorbent should float freely on the water. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes (± 20 sec) check the condition of the sorbent. If the sample sinks go directly to step 9.5, otherwise remove the sorbent with the basket and let drain over the cell for 30 seconds (± 3 sec). Place the basket over a tared weighing pan to catch any additional drips and immediately transfer the sorbent to the pan. Record the weight. Retain the sorbent sample for use in the Static Long Term Sorption test. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run (g/g) deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.1.3 Type IIIa Sorbent: *Not available at this time*
9.1.4 Type IIIb Sorbent: *Not available at this time*
9.1.5 Type IV Sorbent: *Not available at this time*

9.2 Long Term Static Sorption test: This procedure is designed to test for oil pick-up and determine hydrophobic properties of a sorbent sample. This test is performed at 15°C.

9.2.1 Type I Sorbent: Lower the wetted sample from the Static Water Test with a clip on a 5 mm layer of crude oil on excess water bath (80 mm or more) at 15°C. After a minimum of 24 hours check the condition of the sorbent. If the sample sinks go directly to step 9.5, otherwise remove the sorbent vertically with the clip and immediately hang from the balance. Place a tared

weighing pan under the hanging basket to catch any drips. Record the weight of the saturated sorbent at 30 seconds, 45 seconds, 1 minute, 2 minutes, 5 minutes, 15 minutes and 30 minutes. At the 30 minute mark transfer the sorbent to the pan. Transfer the sample and any residual liquid that remains in the pan to the wringer press and squeeze the sorbent through the press five times. Collect liquid in a graduated conical centrifuge tube for water content determination. If the meniscus is distinctly visible in the conical tube then water content may be read directly. Reweigh the pressed sorbent and record the value. If the meniscus is not distinctly visible, the emulsion may be broken by adding a small quantity of toluene to the centrifuge tube (approximately 10-20 ml). Observations should include but not be limited to: buoyancy, disintegration, and appearance. The sorbent must remain structurally sound at saturation while being held along a side (avoid hanging by corner) of the sample and must not sink. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run (g/g) deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.2.2 Type II Sorbent: Lower the basket containing the wetted sample from the Static Water Test on a 5 mm layer of crude oil on excess water bath (80 mm or more) at 15°C. After a minimum of 24 hours check the condition of the sorbent. If the sample sinks go directly to step 9.5, otherwise remove the sorbent with the basket and immediately hang the basket from the balance. Place a tared weighing pan under the hanging basket to catch any drips. Record the weight of the basket with the saturated sorbent at 30 seconds, 45 seconds, 1 minute, 2 minutes, 5 minutes, 15 minutes and 30 minutes. At the 30 minute mark transfer the sorbent to the pan. Determine and record the sample weight. Weigh the empty basket for future calculations. Transfer the sample and any residual liquid that remains in the pan to the plate press and squeeze the sorbent with 1000 Newtons of force (224 lb_f). This action may be cycled up to five times to extract remaining oil. Collect liquid in a graduated conical centrifuge tube for water content determination. If the meniscus is distinctly visible in the conical tube then water content may be read directly. Reweigh the pressed sorbent and record the value. If the meniscus is not distinctly visible, the emulsion may be broken by adding a small quantity of toluene to the centrifuge tube (approximately 10-20 ml). Observations should include but not be limited to: buoyancy, disintegration, and appearance. The sorbent must not sink. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run (g/g) deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.2.3 Type IIIa Sorbent: *Not available at this time*
9.2.4 Type IIIb Sorbent: *Not available at this time*
9.2.5 Type IV Sorbent: *Not available at this time*

9.3 Dynamic Test: This procedure is designed to test for water pick-up and to determine oleophilic properties of a sorbent sample under dynamic conditions. This test is performed at room temperature.

9.3.1 Sample pieces of the sorbent (Type I: 4 pieces of 6 cm x 6 cm, Type II: 200 ml) are placed in a 4 litre jar which is half filled with water and sealed. The container is then placed on it's side and mounted on a shaker table set at a frequency of 150 cycles per minute and an amplitude of 3 cm for a duration of 15 minutes. If the sample sinks go directly to step 9.5, otherwise remove the sorbent by straining the contents of the jar through a mesh basket to catch the sorbent. The jar is half filled with fresh water and 10 ml of crude oil is added. The sorbent sample is returned to the jar which is then sealed. The container is placed on it's side and mounted on a shaker table set at a frequency of 150 cycles per minute and an amplitude of 3 cm for a duration of 15 minutes. The jar is allowed to settle for a period of 2 minutes, at which time observations are recorded. Observations include but are not limited to: quantity of sorbent submerged, physical appearance of sorbent, and persistence of oil sheen.

9.4 L-W test: This procedure will determine the amount of test liquid that a sorbent will pick up in 15 minutes. Fresh samples are used for this test which is performed at 15°C.

9.4.1 Type I Sorbent: The sorbent to be tested should be cut with a sharp edge to minimum dimensions of 130 mm x 130 mm square. The sorbent is then weighed and the value is recorded. The test cell is filled with an initial layer of water (80 mm or more) and a quantity of test liquid to produce the required thickness for the test. The required thickness for diesel fuel is 2.5 mm, while 5 mm is required for crude oil, bunker C, and weathered crude oil. The sorbent is lowered into the cell. The sorbent should float freely on the test liquid. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes $\pm$ 20 seconds (sorbent should be flipped at 8 minute mark) remove the sorbent with a clip and let drain hanging over the cell for 30 seconds ($\pm$ 3 sec). Place a tared weighing pan under the sorbent sample to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Transfer sample and any residual liquid that remains in the pan to the wringer press and squeeze the sorbent through the press five times. Reweigh the pressed sorbent and record the sample weight. Collect liquid in a graduated conical centrifuge tube for water content determination. If the meniscus is not distinctly visible, the emulsion may be broken by adding a small quantity of toluene to the centrifuge tube (approximately 10-20 ml). Each sorbent sample shall be tested through five complete sorption cycles or until it's sorbency is reduced to 50% of its initial value or until disintegration. Sorbents will be classified as High Reuse (5 cycles), Medium Reuse (3 or 4 cycles), Low Reuse (1 or 2 cycles), or No Reuse. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run deviates by more

than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.4.2 Type II Sorbent: The sample size of the sorbent to be tested should be approximately 200 ml. The sorbent is weighed and the value is recorded. The test cell is filled with an initial layer of water (80 mm or more) and a quantity of test liquid to produce the required thickness for the test. The required thickness for diesel fuel is 2.5 mm, while 5 mm is required for crude oil, bunker C, and weathered crude oil. The sorbent is placed in a basket which is then lowered into the cell. The sorbent should float freely on the test liquid. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes ± 20 seconds remove the sorbent with the basket and let drain over the cell for 30 seconds (± 3 sec). Place a tared weighing pan under the sorbent sample to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Weigh the empty basket for future calculations. Transfer the sample and any residual liquid that remains in the pan to the plate press and squeeze the sorbent with 1000 Newtons of force. This action may be cycled up to five times to extract remaining oil. Collect liquid in a graduated conical centrifuge tube for water content determination. Reweigh the pressed sorbent and record the sample weight. If the meniscus is not distinctly visible, the emulsion may be broken by adding a small quantity of toluene to the centrifuge tube (approximately 10-20 ml). All tests are triplicated with the median of the three runs being used for calculations. If the value of any run deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.4.3 Type IIIa Sorbents: *Not available at this time*
9.4.4 Type IIIb Sorbents: *Not available at this time*
9.4.5 Type IV Sorbents: *Not available at this time*

9.5 L Test: This procedure will test the amount of pure test liquid that a sorbent can pick up in 15 minutes. Fresh samples are used for this test which is performed at 15°C.

9.5.1 Type I Sorbent: The sorbent to be tested should be cut with a sharp edge to minimum dimensions of 130 mm x 130 mm square. The sorbent is then weighed and the value is recorded. The test cell is filled with an initial layer of test liquid. The required thickness for all test liquids is 7.5 mm. The sorbent is lowered into the cell. The sorbent should float freely on the test liquid. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes ± 20 seconds (sorbent should be flipped at 8 minute mark) remove the sorbent vertically with a clip and let drain hanging over the cell for 30 seconds ± 3 seconds. Place a tared weighing pan under the sorbent sample to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Transfer sample and any

residual oil that remains in the pan to the wringer press and squeeze the sorbent through the press five times. Reweigh the pressed sorbent to determine and record the sample weight. Each sorbent sample should be tested through five cycles or until its sorbency is reduced to 50% of its initial value or until disintegration. Sorbents will be classified as High Reuse (5 cycles), Medium Reuse (3 or 4 cycles), low reuse (1 or 2 cycles), or No Reuse. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.5.2 Type II Sorbent: The sample size of the sorbent to be tested should be approximately 200 ml. The sorbent is weighed and the value is recorded. The test cell is filled with an initial layer of test liquid. The required thickness for all test liquids is 7.5 mm. The sorbent is placed in a basket which is then lowered into the cell. The sorbent should float freely on the test liquid. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes ± 20 seconds remove the sorbent with the basket and let drain over the cell for 30 seconds (± 3 sec). Place a tared weighing pan under the sorbent sample to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Weigh the empty basket for future calculations. Transfer the sample and any residual liquid that remains in the pan to the plate press and squeeze the sorbent with 1000 Newtons of force. This action may be cycled up to five times to extract remaining oil. Reweigh the pressed sorbent to determine and record the sample weight. Each sorbent sample should be tested through five cycles or until its sorbency is reduced to 50% of its initial value or until disintegration. Sorbents will be classified as High Reuse (5 cycles), Medium Reuse (3 or 4 cycles), low reuse (1 or 2 cycles), or No Reuse. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.5.3 Type IIIa Sorbents: *Not available at this time*
9.5.4 Type IIIb Sorbents: *Not available at this time*
9.5.5 Type IV Sorbents: *Not available at this time*
9.6 I-S Test: *not available at this time*

10. **CALCULATIONS** - Using data from section 9 calculate the following:

10.1 Static Water Test: Use values obtained in 9.1 and state value of water uptake as grams water per gram of sorbent.

10.2 Long Term Static Sorption Test: Use values obtained in 9.2 and state value of test fluid sorbed as grams of test liquid per gram of sorbent and state value of water uptake as grams water per gram of sorbent. Calculate and display

water percentage of total uptake. Calculate and draw profile of retention (curve) from values obtained at 30 sec, 45 sec, 1 min, 2 min, 5 min, 15 min, 30 min.

10.3 Dynamic Test: No calculations required - observations are recorded.

10.4 L-W Test: Use values obtained in 9.4 and state value of test fluid sorbed as grams of test liquid per gram of sorbent. (Volume of test liquid per gram of sorbent should also be calculated and recorded). Use values obtained in 9.3 and state value of water sorbed as grams of water per gram of sorbent. Calculate and display water percentage of total uptake. Determine reuse potential for each test liquid.

10.5 L Test: Use values obtained in 9.5 and state value of test fluid sorbed as grams of test liquid per gram of sorbent. (Volume of test liquid per gram of sorbent should also be calculated and recorded). Determine reuse potential for each test liquid.

10.6 I-S Test: *Not available at this time*

10.6 Reaction Time: A quantitative comparison will be made between long term sorption in 9.2 and the crude oil uptake in section 9.4. Any sorbent that has not reached 92% saturation by the 15 minute mark will be designated as a slow sorbent. (Assuming sorbents reach saturation within 24 hours).

10.7 Storage Density: The storage density is calculated (kg sorbent/m^3) based on manufacturer's packaging.

11. ADDITIONAL TESTS

11.1 An additional specialized test method may be employed by the authority having jurisdiction if these test methods are shown to severely hamper a sorbents performance.

12. REPORT

Data acquisition format - currently under review

13 NOTES

13.1 Related Publications

ASTM	F726-81 Sorbent Performance of Adsorbents F716-82 Sorbent Performance of Absorbents
Environment Canada	Selection Criteria and Laboratory Evaluation of Oil Spill Sorbents, an Update, Update II, Update III, Update IV.

13.2 The publications referred to in par. 2.1.1 may be obtained from the Canadian General Standards Board, Sales Unit, Ottawa, Canada, K1A 1G6. Telephone (819) 956-0425 or 956-0426.

13.3 The ASTM publications referred to in par 13.1 may be obtained from ASTM, 1916 Race Street, Philadelphia, PA 19103, U.S.A. or from the Standards Council of Canada, Standards Sales Branch, 350 Sparks Street, Suite 1200, Ottawa, Ontario K1P 6N7.

REFERENCES

1. S.L. Ross Environmental Reseach Limited for Environment Canada, Selection Criteria and Laboratory Evaluation of Oil Spill Sorbents, Update IV, EPS 3/SP/3, Environment Canada, 1991

2. Standard Method of Testing Sorbent Performance of Adsorbents, American Society for Testing and Materials, ASTM F 726-81 (1986)

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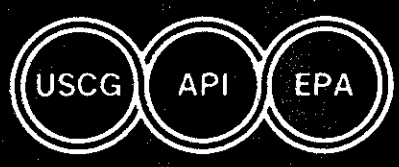

OIL POLLUTION CONTROL A COOPERATIVE EFFORT

OIL SPILL SORBENTS: TESTING PROTOCOL AND CERTIFICATION LISTING PROGRAM

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ABSTRACT: *Environment Canada's Emergencies Engineering Division is spearheading a program in conjunction with the Canadian General Standards Board that would see the development of a certification and listing program in addition to a national standard for the testing of sorbent materials. Funding for this program is provided by Environment Canada (EC), Canadian Coast Guard (CCG), Marine Spill Response Corporation (MSRC), U.S. Coast Guard (USCG), and U.S. Minerals Management Service (MMS).*

The test methods are based upon those defined by the American Society for Testing and Materials and previous test methods developed by Environment Canada for our series of reports entitled Selection Criteria and Laboratory Evaluation of Oil Spill Sorbents. This series, which was started in 1975, encompasses a number of commercially available oil spill sorbents tested with different petroleum products and hydrocarbon solvents.

The testing program will categorize the sorbents according to their operating characteristics. The main categories are oil spills on water, oil spills on land, and industrial use. The characteristics we will be evaluating with the new test protocols include initial and maximum sorption capacities, water pickup, buoyancy, reuse potential, retention profile, disintegration (material integrity), and ease of application and retrieval.

In the near future we plan to incorporate changes to the test that would involve increasing our list of test liquids to encompass spills in an industrial setting, in addition to testing sorbent booms and addressing the disposal problem.

A universally accepted, standard method for testing oil spill sorbents is not currently employed by the majority of sorbent vendors. Because of differences in the testing methodologies that currently exist, end users are limited to manufacturers' and distributors' claims which may be perceived as being biased. Environment Canada is leading a drive to develop an official Canadian standard for the testing and certification of sorbents using the Canadian General Standards Board (CGSB) as the certification body. It is envisioned that Environment Canada will provide a system to maintain an unprejudiced method for the testing and certification of oil spill sorbents.

Environment Canada's Emergencies Engineering Division (EED) is mandated to evaluate existing technologies and act as a proving ground for technologies deemed new and innovative in areas of oil and chemical spill cleanup. The sorbent testing program had its beginnings in 1975 when Environment Canada released its first publication entitled "Selection Criteria and Laboratory Evaluation of Oil Spill Sorbents." Updates of this publication were released every four or five years. The time lag between publications and the limited number of sorbents tested were acceptable limitations to the program as interest in sorbents was relatively limited. Since that time, however, interest in sorbent performance evaluation has grown steadily. Recent events, including the *Exxon Valdez* spill in Prince William Sound and the spills during the Gulf War, spurred renewed interest in sorbents. Manufacturers and distributors were aggressively marketing their products to government, oil spill co-ops, and other nongovernment organizations. These end users had limited third party data from which they could base a purchasing decision. First responders, sceptical of the performance and safety aspects associated with some sorbents, requested that sorbents pass some sort of approval mechanism before being considered. It was this demand that catalyzed the development of the sorbent evaluation and certification program.

Program development

As requests for sorbent performance information grew, it became obvious that an ongoing evaluation system was warranted. Direct comparisons between sorbents tested for different updates of the selection criteria reports were discouraged as the testing procedure evolved over time, and the oil properties, which affect performance, did not remain constants. Requests for "approving" or "certifying" sorbents could not be met, simply because such a mechanism did not exist. At this point EED began talks with the Canadian General Standards Board (CGSB). This federal government agency is one of only five national standardizing bodies in Canada. A committee was formed through the CGSB consisting of equal representation from interested parties, producers, and end users throughout North America. This led to the development of a new test procedure based upon work that Environment Canada had performed in the past,[2] but also incorporating methods from the American Society for Testing and Materials (ASTM).[1] These protocols currently enjoy top status as sorbent test protocols in North America.

CGSB sorbent certification and listing program

The CGSB sorbent certification and listing program currently consists of two documents. One is a standard for sorbent materials, while the other specifically defines testing procedures for sorbents used on crude oil and similar spills. The program is structured in this fashion to allow the introduction of additional testing protocols. One anticipated protocol will deal specifically with testing sorbents for use with chemicals used in industrial settings.

Standard C**/CGSB-183.1 encompasses "Sorbent Materials" and relates to operational and performance criteria for the cleanup and control of oil and hazardous substances spills. Within this document, testing protocol terms and calculations are explicitly defined. Sorbents are classified by physical type based on ASTM F726-81[1] as follows:

Type I: sheet, pad, blanket, mat
Type II: loose—unconsolidated, particulate material
Type IIIa: pillows and socks—sorbent material contained by an outer fabric or netting
Type IIIb: booms—sorbent material contained by outer fabric or netting that has a lengthwise dimension exceeding other dimensions by a factor of at least five and whose sorption capacity would be significantly altered if cut to meet Type I size requirements
Type IIIc: sweeps—sorbent material that has a lengthwise dimension exceeding other dimensions by a factor of at least five
Type IV: agglomerated unit—pom-pom, yarn, or netting that offers low impedance to the migration of highly viscous fluids onto its body of material

An interim standard is now in place; but it is limited to testing Types I, II, and IIIa sorbents. It is anticipated that testing protocols for the remaining types will be incorporated into the official standard during the fourth quarter of 1992.

Sorbents are also classified by category, which determines the recommended type of application, as follows:

L-W: sorbents recommended for sorbing spills on water or land
L: sorbents recommended for sorbing spills exclusively on land
W: sorbents recommended for sorbing spills exclusively on water
I-S: sorbents recommended for sorbing spills in an industrial setting (aggressive chemicals)
Alternate: all sorbents that have technically failed tests, but which possess at least one redeeming characteristic which warrants further consideration

The sorbent materials standard goes on to identify nine sorbent characteristics that should be considered. Specific labeling and material safety data sheets are a requirement, as are durable storage properties.

Testing procedures

Standard C**/CGSB-183.2 covers laboratory conducted performance tests for all forms of materials, regardless of their mode of action, for the sorption of crude oil, its contained natural components, and mixtures thereof.

Performance characteristics

Specific characteristics initially identified as being highly desirable follow.

- Buoyancy: Data obtained would allow confirmation that a particular sorbent may be suited for use in a spill on water. Sorbents that sink may pose a threat to aquatic life by transporting hazardous liquids to the sediment causing infiltration into the entire food chain.
- Low water pickup: Nonselective sorbents may pick up water in addition to oil if placed in an aquatic environment. This may not prove to be a major hindrance if the sorbent remains floating; however, any water sorbed would displace the spilled oil, thus hindering performance.
- High oil pickup: The rate of pickup in addition to the sorbent's capacity would be tested. A sorbent's ability to be "self-acting" could limit the application to specific spill scenarios.
- Re-use: Some sorbents allow the sorbed liquid to be extracted via mechanical or chemical means enabling re-use. This could limit the amount of solid waste generated during a spill cleanup operation. The safety aspects of attempting re-use should be carefully considered.
- Low rate of release: Liquids picked up by most sorbents are released back into the environment to some degree. The extent of release will vary dramatically depending upon the sorbent used. The importance of this release depends upon the specific spill scenario and storage equipment available at the spill site.

Test method

The following tests have been established to evaluate the performance of sorbents on oil and water. The procedures are condensed versions of the test methods outlined by the Canadian General Standards Board.

Degradation Pre-Test (static). This test measures the sorbent's hydrophobic characteristics in addition to determining its buoyancy. A test cell (crystallizing dish having a diameter of 190 mm) is filled with a layer of water approximately 80 mm deep. If Type II sorbent is being tested, a mesh basket having openings of approximately 1 mm is lowered into the crystallizing dish. The sorbent sample (Type I: 13 cm × 13 cm, Type II: 10 grams) is placed into the cell. The test cell is then covered and left for 15 minutes. After 15 minutes the sorbent is removed from the water and observations are noted. The sorbent is weighed to determine water pickup. Samples that pass are then prepared for the Degradation Test (static).

Degradation Test (static). This is a test for buoyancy, sorbent capacity, and oil retention. A sorbent sample from the static pre-test is placed on a 5 mm layer of crude oil floating on an 80 mm layer of water. The sample is left undisturbed for a period of at least 24 hours. The sorbent is then removed and hung from a balance (Type I: hung from one edge using a clip, Type II: hung using a basket). Observations pertaining to the physical condition of the sorbent are recorded. The weight of the sorbent is measured as oil drips after 30 and 45 seconds, and 1, 2, 5, 15, and 30 minutes. A retention profile is obtained from this data, as is the sorbent's capacity. Mechanical compression is used to extract remaining liquid from the sorbent to determine water pickup.

Degradation Pre-Test (dynamic). This test is used to determine the buoyancy of sorbents in simulated wave conditions. If the sorbent passes this test for buoyancy, it is then very unlikely that the sorbent will sink in most applications. Sample pieces of the sorbent (Type I: 4 pieces of 6 cm × 6 cm, Type II: 10 grams) are placed in a 4 liter jar that is half filled with water. The container is then placed on its side and mounted on a shaker table set at a frequency of 10 cycles per minute for a duration of 15 minutes. The sorbent is then removed from the water and observations are noted.

Degradation Test (dynamic). This test follows the methodology of the Degradation Pre-Test (dynamic) with the exception that 10 mL of crude oil is introduced into the 4 L jar. Observations of the sorbent's behavior during agitation are recorded. After 15 minutes, the sorbent is removed and observations pertaining to the condition of the sorbent and of the water are noted.

W Category Test. This is a test for sorbent capacity and re-use. A fresh sorbent sample is placed on a 5 mm layer of crude oil floating on an 80 mm layer of water. The sample is left for a period of 15 minutes. The sorbent is then removed and left to drip for 30 seconds before being weighed (Type I: hung by edge with clip, Type II: hung by basket). Observations pertaining to the physical conditions of the sorbent are recorded. Mechanical compression is used to extract remaining liquid from the sorbent for re-use testing and water content determination. The data are also compared with Degradation Test (static) results.

L Category Test. This is a test for sorbent capacity, reuse, and retention. A fresh sorbent sample is placed on a 7.5 mm layer of crude oil. The sample is left for a period of 15 minutes. The sorbent is then removed and hung from a balance (Type I: hung by an edge using a clip, Type II: hung using a basket). Observations pertaining to the physical condition of the sorbent are recorded. The weight of the sorbent is measured as oil drips after 30 and 45 seconds and 1, 2, 5, 15, and 30 minutes. A retention profile is obtained from this data, as is the sorbent's capacity. Mechanical compression is used to extract remaining liquid from the sorbent for re-use testing.

L-W Category. Data obtained from the L Test, W Test and the Degradation Test (dynamic) will determine if a sorbent should be designated for the L-W Category.

I-S Category Test. This testing procedure is currently under review.

Nonperformance—handling. This information is provided by the manufacturer for the benefit of the end user, but is not a requirement for certification.

- Tensile strength: This characteristic becomes extremely important when dealing with sorbent booms. It determines the ability of a boom to retain its integrity under the strain of currents and wave action.

- Storage: Ideally, a sorbent would occupy a minimum of storage space, while exhibiting a high sorption capacity. Storage space within facilities is often very limited.
- Disposal: Proper and safe disposal methods should be addressed before application of any sorbent to a spill. Regulations may limit options.
- Static resistance: In very dry conditions (desert or arctic), static resistance becomes an important safety concern. Specific conditions would have to be met before a static spark could ignite a flammable liquid. Steps should be taken to ensure that safe working practices are enforced and working environments should be carefully scrutinized for all possible sources of static charge.

Future areas of development

Test liquids used in the interim standard represent a cross-section of viscosities for oil and were chosen based upon suitability and availability. It is the intention of the CGSB General Sorbent Committee to expand upon this list to encompass hazardous liquids that are frequently spilled during transportation and in industrial settings. The committee is currently expanding into the area of sorbent boom testing.

Conclusions

This program should benefit both manufacturers and users. Manufacturers will be given the opportunity to have their products tested by impartial third-party laboratories and certified to that effect. Users will be able to select products from manufacturers and compare data objectively. The reader should note that this program is prototype in nature. EED hopes to expand this type of program to encompass booms, skimmers, and related spill response equipment. A centralized data base of performance and nonperformance data pertaining to oil and hazardous liquid spills is the long-term goal.

Acknowledgments

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2. S.L. Ross Environmental Research Limited, 1991. Selection Criteria and Laboratory Evaluation of Oil Spill Sorbents, Update IV. EPS 3/SP/3. Environment Canada, Ottawa, Ontario