

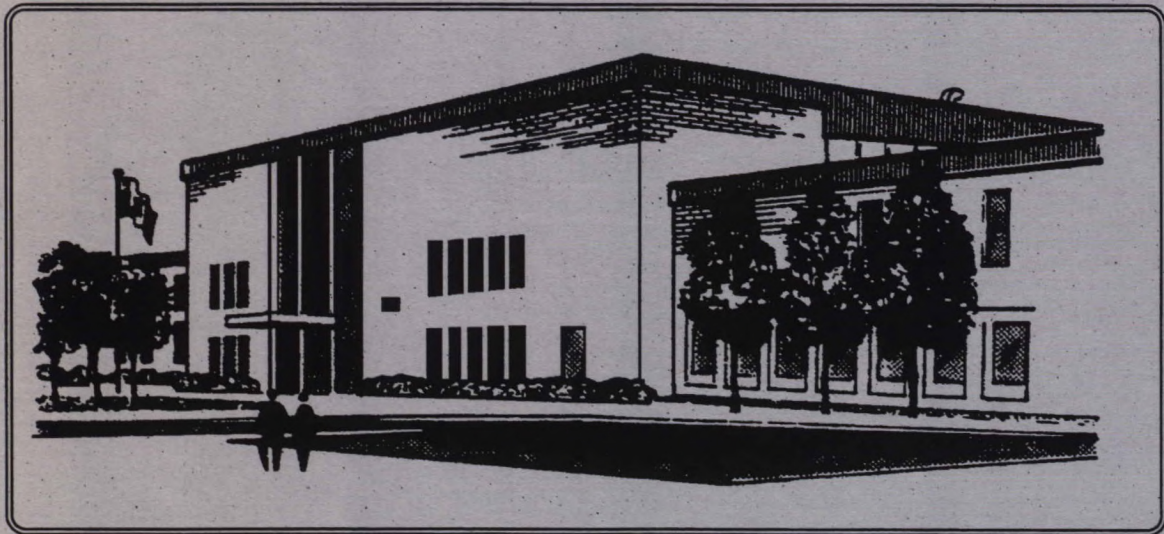
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ORIMULSION[®]
Shoreline Studies Program
Sediment Interaction Experiments



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ORIMULSION SHORELINE STUDIES PROGRAM
Sediment Interaction Experiments

by

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Emergencies Science Division
Environment Canada

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PREFACE

These preliminary investigations into Orimulsion behavior in sediments are part of the larger "Orimulsion Shoreline Studies Program". The objective of the Program is to develop scientific/technical information and direction on the behaviour and cleanup of Orimulsion on different types of shorelines and conditions. The goal is to deliver both operational guidance and scientific information of a quality required to provide spill planning and response teams with more informed technical support for decisions regarding shoreline treatment activities. The program consists of staged component studies which address issues related to Orimulsion on shorelines. Current outputs will feed into a comprehensive shoreline response guidance manual.

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SUMMARY

Orimulsion is a mixture of 70% bitumen and 30% water that is transported for use as a substitute for coal or fuel oil in power-generating plants. There is concern that an accidental spill of Orimulsion into the marine environment could pose special response problems. In particular, there are questions about how an Orimulsion spill would impact shoreline sediments and how oiled sediments could be treated. This project involved a series of experimental tests of Orimulsion-sediment interaction to answer these questions.

The approach used in the experiments was to expose sediments to Orimulsion (and its derivatives) under a range of environmental conditions. In particular, factors were tested that affect the penetration and retention of Orimulsion (and its derivatives) in sediments. A number of unique testing protocols and a descriptive terminology of Orimulsion derivatives were developed as part of the project.

Weathered bitumen is the viscous, sticky, often "ropey" mass that is a residual form of Orimulsion when moderate mixing energy is applied. This is the most likely derivative form of Orimulsion to reach the shore, although our observations suggest that it forms a relatively minor component of the total spill (<25%). *Weathered bitumen* does not penetrate sand or granules and shows minor penetration in pebbles before plugging (<4 cm). *Weathered bitumen* could possibly penetrate through cobble or boulder beaches until it reached a pebble or granule layer in the subsurface.

Dispersed bitumen is a non-sticky fluid of diluted Orimulsion (~20% bitumen content) that freely penetrates sediment coarser than granules but plugs in sand at about 4-5 cm. Penetration potential does not appear to be temperature-dependent. Retention values are greatest in sands (84,000 - 106,000 mg bitumen/kg sediment) although penetration is limited. Retention values in granules were ~50,000 mg/kg and in pebbles were 6,000 - 33,000 mg/kg, neither of which plugged. Retention values were higher in lower salinity water, probably due to loss of buoyancy in the bitumen particles. Higher initial loading produced proportionately higher retention in granules and pebbles. *Dispersed bitumen* appears to remain relatively stable under typical tidal flushing regimes. If sediments dry, a *weathered bitumen coating* quickly forms and is highly stable. If sediments remained moist (below 2 cm in sand and below 6-8 cm in granules and pebbles), however, *weathered bitumen coatings* did not form and the *dispersed bitumen* could be easily remobilized.

The *dispersed bitumen* can be remobilized by flushing, and the addition of a surfactant appears to substantially improve flushing effectiveness. *Weathered bitumen coating* can be remobilized by use of hot water (>30°C), but water at temperatures less than 20°C is ineffective at remobilizing the bitumen. A potential problem of flushing techniques is that remobilized bitumen is often neutrally or negatively buoyant, making it difficult to collect flushed particles.

Diluted bitumen is a non-sticky, brown-stained, transparent fluid with measured bitumen concentrations of 8% that forms when *dispersed bitumen* is further diluted by gentle mixing. Simple tests with clay-water mixtures showed that bitumen particles are scavenged by clay particles and sink. In a natural environment, the scavenged bitumen could be dispersed from high energy areas to lower energy areas, where it could ultimately settle. The more cohesive, more buoyant, higher concentration *dispersed bitumen* does not appear to be as sensitive to clay scavenging.

L'orimulsion est un mélange à 70 % de bitume et à 30 % d'eau, qui peut remplacer le charbon ou le mazout dans les centrales thermiques. On craint qu'un déversement accidentel d'orimulsion dans le milieu marin ne pose de problèmes particuliers à l'intervention. En effet, quelles en seraient les répercussions sur les sédiments du rivage ? Comment pourrait-on traiter les sédiments souillés ? À la faveur du projet, nous avons tenté de répondre à ces questions au moyen d'une série d'expériences sur l'interaction entre l'orimulsion et les sédiments.

L'expérience a consisté à exposer des sédiments à l'orimulsion (et à ses dérivés) dans une gamme de conditions du milieu. On a notamment expérimenté les facteurs de pénétration et de rétention de l'orimulsion (et de ses dérivés) dans les sédiments. Dans le cadre du projet, nous avons élaboré un certain nombre de protocoles expérimentaux inédits et une terminologie descriptive des dérivés de l'orimulsion.

Masse visqueuse, gluante, souvent filante, le *bitume vieilli* est le résidu du brassage modérément énergique de l'orimulsion. C'est son dérivé le plus susceptible d'atteindre le rivage, bien que, selon nos observations, il forme une fraction relativement mineure du volume total déversé (< 25 %). Il ne pénètre ni le sable ni les substrats granulaires et il pénètre peu les graviers avant d'en colmater les interstices (< 4 cm). Le *bitume vieilli* pourrait pénétrer le substrat des plages à galets ou à blocs pour s'arrêter au-dessus de l'horizon à graviers ou à granules.

Le *bitume dispersé* est un liquide non gluant d'orimulsion diluée (environ 20 % de bitume) qui pénètre librement les sédiments plus grossiers que les granules, mais qui, dans le sable, ne descend pas à plus de 4 à 5 cm. Le potentiel de pénétration ne semble pas dépendre de la température. Les indices de rétention sont maximaux dans les sables (84 000 à 106 000 mg de bitume par kilogramme de sédiment) bien que la pénétration soit limitée. Dans les granules et les graviers, l'indice de rétention a été de ~50 000 mg/kg et de 6 000 à 33 000 mg/kg, respectivement, sans colmatage. Les indices de rétention ont été supérieurs dans l'eau peu salée, probablement en raison de la baisse de la flottabilité des particules de bitume. Quand le volume initialement déversé a été plus important, la rétention dans les granules et les graviers a été proportionnellement plus élevée. Le *bitume dispersé* semble rester relativement stable sous les régimes ordinaires d'entraînement par la marée. Si les sédiments sont secs, il se forme rapidement un *revêtement de bitume vieilli*, très stable. Si les sédiments restent humides (à plus de 2 cm de profondeur dans le sable et à plus de 6 à 8 cm de profondeur dans les granules et les graviers), il ne se forme cependant pas de *revêtement de bitume vieilli*, et le *bitume dispersé* peut rapidement être remis en suspension.

Le *bitume dispersé* peut être délogé par balayage liquide, et l'adjonction d'un surfactif semble améliorer notablement l'efficacité de l'opération. Le *revêtement de bitume vieilli* peut être remis en suspension dans l'eau chaude (> 30 °C), mais, dans l'eau de température inférieure à 20 °C, la remise en suspension n'est pas efficace. Un problème susceptible est de survenir fréquemment au cours du balayage liquide : la flottabilité du bitume remis en suspension est souvent nulle ou négative, ce qui rend difficile la collecte des particules délogées.

Le *bitume dilué* est un liquide translucide, de teinte brune, non collant, renfermant une concentration mesurée de bitume de 8 %. Il se forme lorsque le *bitume dispersé* est davantage dilué par brassage peu énergique. Des essais simples avec des mélanges d'eau et d'argile ont montré le piégeage des particules de bitume par les particules argileuses. Captées par ces dernières, les particules de bitume coulent. Dans le milieu naturel, le bitume ainsi capté pourrait être dispersé dans les secteurs où le brassage est énergique, pour se retrouver dans les secteurs relativement calmes, où il pourrait finalement se déposer. Le *bitume dispersé* à plus forte concentration, dont la cohésion et la flottabilité sont supérieures, ne semble pas aussi vulnérable à l'effet épurateur de l'argile.

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1.1 Background

Orimulsion is an emulsion or suspension of bitumen particles in water and can be used as a coal or fuel oil substitute for use in power plants and other industrial applications. While there has been considerable study on Orimulsion behaviour at sea and on the impacts of spilled Orimulsion on coastal resources, there is limited information on Orimulsion-sediment interaction on shorelines. In particular, the penetration and retention characteristics are of interest to spill response planners as are the potential suite of protection and cleanup options that may be useful in treating a spill. This project addresses these knowledge gaps.

1.2 Project Objectives

The overall goal of this project was to provide initial information on Orimulsion-sediment interaction. That is, if Orimulsion is spilled, and reaches the shoreline, how will the Orimulsion or derivative forms of the Orimulsion interact with the beach sediments.

The specific objectives of the project were to:

1. conduct a series of experiments that could be used to estimate the potential retention and penetration of Orimulsion (or its derivatives) in commonly occurring beach sediments.
2. conduct a series of experiments to evaluate the potential of various cleanup options should the Orimulsion (or its derivatives) reach the shoreline.

A secondary objective of the project was to develop protocols for testing Orimulsion-sediment interaction as there appears to be little previous work and conventional techniques (see Harper *et al.*, 1995) were of uncertain use with Orimulsion.

In the organization of this report, the general experimental design, terminology and testing variables are described in this section. The detailed experimental design for each experiment is included in the Results (Section 3) so that the rationale, experimental design, testing procedures and results are organized together.

2.1 Experimental Approach

Experimental Technique

In previous testing of oil-sediment interaction, we have used the following general approach to estimate oil retention and penetration in sediments.

- 1 sediment is loaded into a plexiglass column and the column is then filled with water,
- 2 a known volume of oil (*initial oil volume*) is layered onto the surface of the water and the water table lowered to simulate oil stranding on intertidal sediments,
- 3 the water table is lowered to 2-cm above the drain level in the column and the oil allowed to equilibrate in terms of penetration,
- 4 the water level is then raised (to simulate a rising tide) and the *floating oil volume* noted,
- 5 the "*retained oil volume*" in the sediments is computed as the residual between the *initial and floating oil volumes*; the penetration depth can be directly observed through the plexiglass.

This approach is dependent on the positive buoyancy characteristics of the oil and required modification for use with the Orimulsion because the bitumen particles are near-neutrally buoyant in seawater and negatively buoyant in brackish water. The Orimulsion (or its derivatives) does not form a distinct floating layer after raising the water level (Step 4) so the residual cannot be estimated.

While the general approach was retained, a sub-sampling procedure was used to estimate bitumen content of the water above the sediment so that the residual amount of bitumen retained within the sediment could be computed. The revised methodology is as follows:

- 1 sediment is loaded into a plexiglass column and the column is then filled with water,
- 2 a known weight of Orimulsion (*initial bitumen weight*) is layered onto the surface of the water (Fig. 1),
- 3 the water level is lowered and the Orimulsion (or its derivatives) allowed to "strand" on the sediments (Fig. 2),

- 4 the water table is lowered to 2-cm above the drain and the Orimulsion (or its derivatives) allowed to equilibrate within the sediments,
- 5 the water table is raised to above the sediments by filling from the bottom through the drain, and the water layer(s) above the sediment sampled with an automatic pipette,
- 6 the bitumen concentration in the water was computed by oven-drying the sample and correcting for salt content ("*suspended*" bitumen weight),

retained bitumen weight in the sediment is computed as *initial weight* minus the *suspended weight* (from concentration data)
- 7 the *suspended bitumen weight* in the water above the sediments was computed, and the *residual bitumen weight* retained within the sediments was estimated (*initial* minus *suspended* bitumen)
- 8 the concentration of bitumen in the sediments (milligrams of bitumen per kilogram of sediment) can be computed from the weight of bitumen retained, the volume of oiled sediment and the bulk density of the sediment.

While the technique is more complex than the previously used volumetric balance, it gave reproducible results. Our measurements of "bitumen content" of the Orimulsion averaged 70.2% by weight with 0.5% standard deviation (Table 1).

Table 1. Concentration of Bitumen in Orimulsion

| Test | Concentration (wt % "bitumen"/total wt) |
|----------------------------|--|
| 1 | 70.8 |
| 2 | 70.3 |
| 3 | 69.8 |
| 4 | 69.9 |
| Average: | 70.2 |
| Standard Deviation: | 0.50 |

Experimental Overview

Ten series of experiments, involving over 70 individual tests, were developed to address the objectives (Table 2). In general, each series was designed to isolate one or two experimental variables, such as sediment grain-size or temperature effects on retention/penetration.

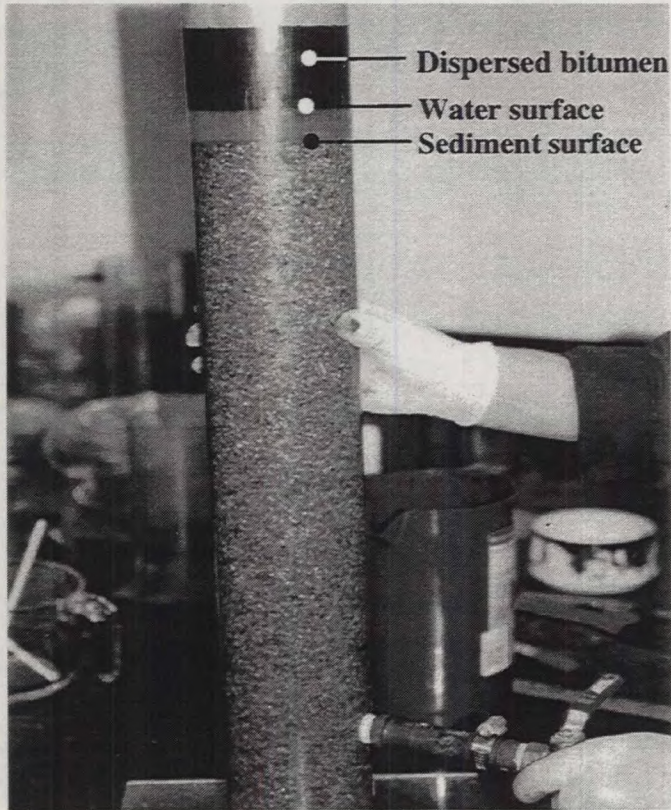


Figure 1. Initial experimental set-up. Layer of Orimulsion, which quickly dilutes to *dispersed bitumen*, is added to water surface.

Sediment surface

Figure 2. Penetration of *dispersed bitumen* into coarse sands as water table in the column is lowered.

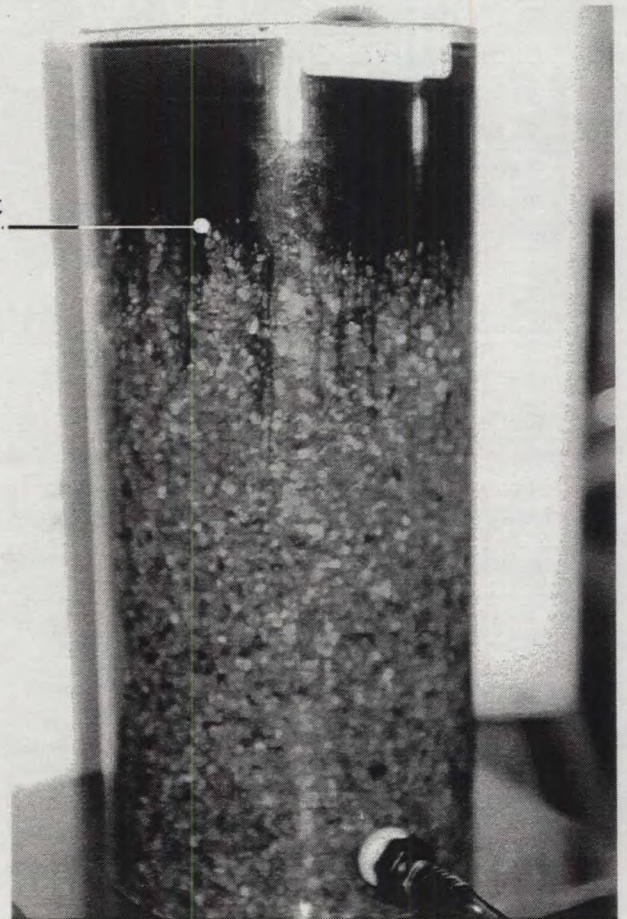


Table 2 Experimental Design

| General Objective | Series | Objective |
|---------------------------------|--------|---|
| Penetration and Retention Tests | 1 | evaluation of weathered bitumen/sediment interaction |
| | 2 | dispersed bitumen sediment interaction in saline water |
| | 3 | dispersed bitumen sediment interaction in brackish water |
| | 4 | effects of Orimulsion loading on retention/penetration |
| | 5 | effect of tidal flushing on Orimulsion-sediment interaction |
| | 6 | evaluation of <i>in situ</i> weathering of Orimulsion in sediment |
| Countermeasure Tests | 7 | evaluation of hydraulic flushing on Orimulsion in sediment |
| | 8 | effects of surfactant with flushing on Orimulsion in sediment |
| | 9 | remobilization of weathered bitumen coating from sediment |
| | 10 | effect of clay scavenging on Orimulsion |

2.2 Terminology

During the initial testing, it was recognized that as Orimulsion dispersed and weathered, a variety of "phases" of Orimulsion occurred. Each of these has slightly different properties that could influence experimental results. As such, a provisional terminology was developed that clearly identified each phase of the Orimulsion. Figure 3 provides a schematic representation of the different Orimulsion phases and Table 3 gives a summary description. It is important to note that "Orimulsion" only exists as Orimulsion when contained in its original concentration of 70% bitumen and 30% water; as soon as Orimulsion reaches a water surface, it begins to change into its derivative forms.

This terminology is considered provisional but necessary. The suggested terms were selected to be as descriptive of the Orimulsion phase as possible. There does not appear to be any standard or consistent Orimulsion terminology in use. The terminology is consistent with other phases of Orimulsion that have been described in the literature but no other sources have identified all these forms or their linkages.

The linkages indicated in Figure 3 are important in that they indicate the particular phases, the succession of phases required to reach certain "end phases", and the reversibility of some phases but not others.

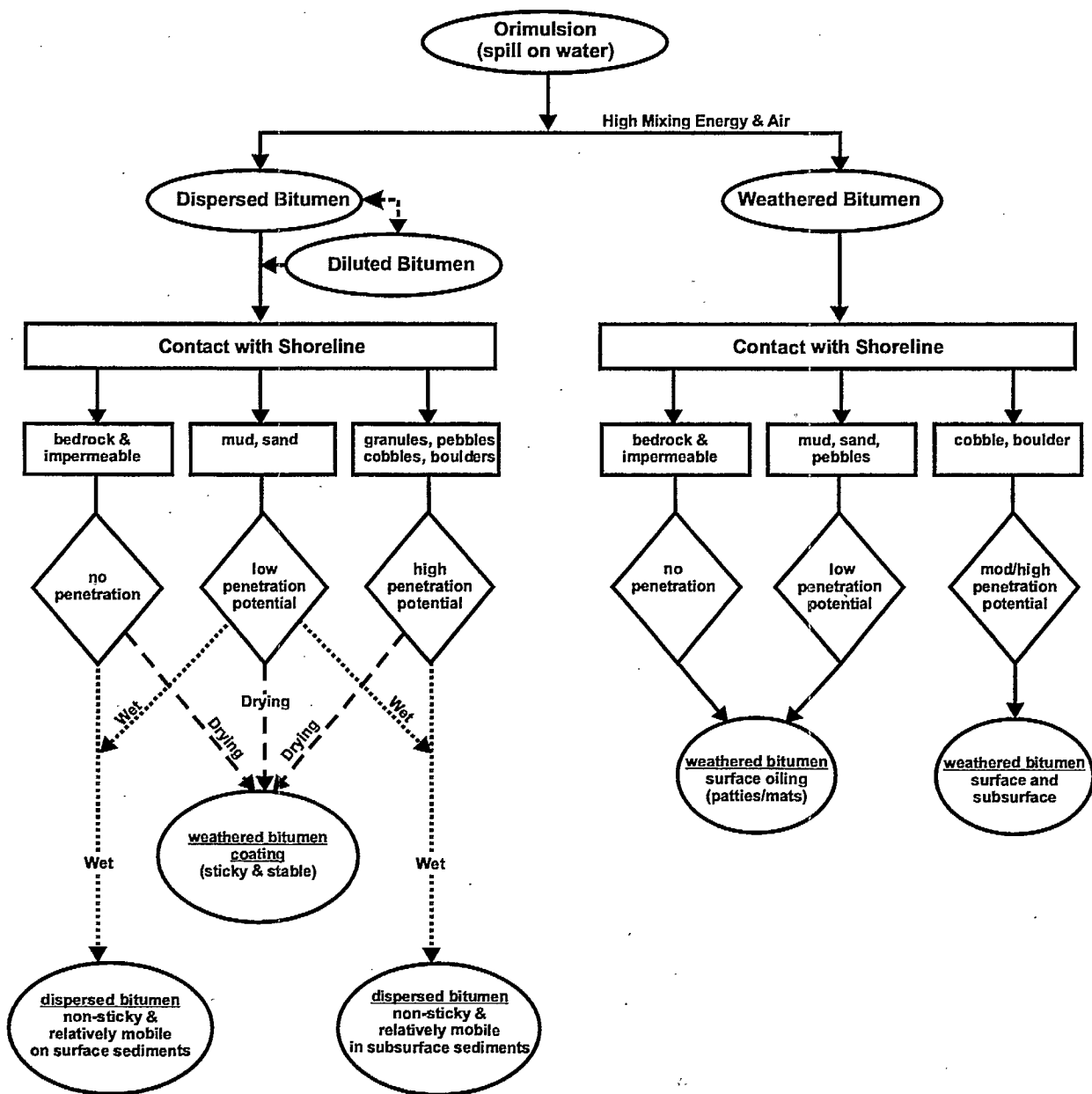


Figure 3. Schematic diagram of on-water phases of Orimulsion and types of Orimulsion phases after contact with the shore zone (see Table 3 for description of terms).

Table 3 Provisional Terminology of Orimulsion Phases

| Phase | Description |
|---|---|
| Orimulsion | Orimulsion is the fluid that has been provided for testing; it is specified to be 70% bitumen, 30% water and < 0.2% surfactant |
| Dispersed Bitumen | Appears as a dark chocolate colour, opaque and floats as a distinct layer at the top of a container; it is not sticky and pours easily. Partitioning of this layer was observed over time with gentle mixing resulting in a 'subphase'. This <i>Diluted Bitumen</i> layer is a light brown colour, semi-transparent and assumed to represent a dilute bitumen particles of near-neutral buoyancy; if left for a long period, particles gradually rise and coalesce into the dispersed bitumen layer but small amounts of mixing energy keep bitumen particles from coalescing near surface; this layer is believed to be sensitive to clay scavenging |
| Weathered Bitumen (on water) | black, highly opaque, very viscous, sticky, often a "tarry", "ropey" or "lumpy" consistency (Fig. 4); very buoyant; often incorporates air bubbles (possibly due to the artificial mixing technique) and forms a "skin" on the water surface; requires vigorous mixing and air to form. |
| Weathered Bitumen Coating (on sediments) | Hard, "tarry" coating on grains and within small pore spaces of the sediments; forms when dispersed bitumen is in contact with air. |

^a estimated by placing a small volume of Orimulsion on seawater in a flask, moderately shaking the flask and taking sub-samples with an automatic pipette after 10 minutes.

2.3 Testing Variables

Sediments

Three sediment types were selected for testing: medium pebble material, granule material, and medium sand. Sediment specifications are given in Table 4. Unimodal sediments were used as the sediment properties (e.g., bulk density-porosity) are easily controlled. Sediments were washed to remove any silt/clay coating. Since bulk densities were known, sediments could be packed to a uniform porosity of 40% in the columns.

Table 4 Test Sediment Specifications

| Sediment | Mean Size (mm) | Upper & Lower Screen Sizes (mm) | Mineral Density (g/cm ³) |
|-------------|----------------|---------------------------------|--------------------------------------|
| medium sand | 0.35 | 0.25 - 0.50 | 2.588 |
| granules | 3.5 | 2.36 - 4.75 | 2.785 |
| pebbles | 15.0 | 9.5 - 19.0 | 2.834 |

Water content of the sediments was not determined during the experiments. They were, however, left to drain and as such would generally represent a normal residual water content that one would expect above the capillary fringe.

Water Temperatures

Three water temperatures were used during the experiments to simulate a range of temperatures over which Orimulsion (or its derivatives) and sediment interaction could take place. The main testing temperature used was 15°C as this was the room temperature of the testing laboratory and provided a reasonable approximation of temperate summer water temperatures (BC, Great Lakes and Maritimes). The lower test temperature of 5°C was assumed to be representative of arctic summer conditions or temperate-coast winter conditions. The upper test temperature of 25°C was assumed to be representative of many tropical area waters.

Salinity

Initial ranging tests indicated that Orimulsion "floated" in salinities greater than 25 ppt and sank in salinities of less than 20 ppt. Artificial seawater of 32 ppt was used as representative of seawater conditions and artificial "brackish" water of 15 ppt was used to simulate brackish or estuarine water conditions. The seawater salinity was created by mixing Instant Ocean[®] into tap-water. The seawater reservoir was continuously aerated to assist with dissolution of the salts.

Test Cylinders

Sediments were packed to a uniform porosity (40%; computed by knowing the dry sediment density and the fill volume of the column) in plastic test cylinders (6.75 cm in diameter and 20 cm in height). The sediments were packed to 14 cm and water-levels were usually controlled to a depth of 10 cm below the sediment, allowing a 4 cm drain layer at the base of the column.

Artificial Weathering of Bitumen

The weathered bitumen was produced by placing equal volumes of Orimulsion and seawater in a container and recirculating the mixture through a high-speed, centrifugal pump. The highly viscous, "ropey" weathered bitumen could be produced in about 5-10 minutes of mixing.

Loading

Loadings of Orimulsion were noted for each experiment and were determined gravimetrically. They were generally in the range of 100g of Orimulsion (~70g of bitumen) per experiment unless noted otherwise (see Appendix A).

Each of the ten series is outlined in terms of the general experimental design, experiment numbers and appropriate results. Detailed experimental data is contained within the appendix.

3.1 Series 1 - Evaluation of Weathered Bitumen-Sediment Interaction

Weathered bitumen is the “ropey”, sticky, buoyant Orimulsion derivative that many associate as the main spill product; the *weathered bitumen* has been observed to form at sea during experimental sea trials with Orimulsion and has been formed by passing Orimulsion and seawater through high-speed pumps. Our laboratory observations suggest that the *weathered bitumen* forms only a small portion of the Orimulsion derivatives with most of the derivatives in the *dispersed bitumen* and *diluted bitumen* types (Fig. 1). Because of the high buoyancy and stable nature of the *weathered bitumen*, there is a high probability that this form of Orimulsion might reach the shoreline.

| | |
|--------------|--|
| Series: | 1 |
| Suite: | Weathered bitumen Penetration/Retention |
| Salinity: | 32 ppt |
| Temperature: | variable |
| Variables: | temperature and sediment size |
| Questions: | what is penetration potential of weathered bitumen/sediment types what is retention potential of weathered bitumen/sediment types |
| Method: | place a known mass of weathered bitumen on water surface lower water table observe maximum penetration depth raise water table remove residual floating weathered bitumen and weigh compute mass retained, conc. per m ³ of sediment |

Table 5 Series 1 Experiment Numbers

| Sediment | Temperature (°C) | | |
|-----------|------------------|----|----|
| | 5 | 15 | 25 |
| med. sand | 1 | 4 | 7 |
| granules | 2 | 5 | 8 |
| pebbles | 3 | 6 | 9 |

Weathered bitumen was created by mixing Orimulsion and seawater with a centrifugal pump; the weathered bitumen then placed on the test columns.

This series of experiments were designed to address the questions:

What is the penetration potential of weathered bitumen in different sediment types?

What is the retention potential of weathered bitumen in different sediment types?

Results

The “weathered bitumen” was too viscous to penetrate into all but the coarsest sediment (Table 6; Fig. 4). The only test where weathered bitumen penetrated was in the pebbles at 25°C.



Figure 4. *Tarry residue* on the surface of a coarse-sand test column.
Note the “ropey” nature and viscous consistency.

The implication is that weathered bitumen is unlikely to percolate into all but the coarsest beach sediments (cobble-boulder) during commonly occurring water-temperatures. However, the results do suggest that surface warming of the sediments by solar radiation could cause some percolation of the weathered bitumen into beach sediments. The weathered bitumen has the appearance of weathered bunker oil and in a stranding situation would be most likely to strand as "patties" or "mats" along the upper intertidal zone due to its cohesive nature and high buoyancy.

Table 6. Penetration and Retention of "Weathered Bitumen" in Sediments

| Sediment | Temperature | | | | | |
|----------|------------------|-------------------|------------------|-------------------|------------------|-------------------|
| | 5°C | | 15°C | | 25°C | |
| | Penetration (cm) | Retention (mg/kg) | Penetration (cm) | Retention (mg/kg) | Penetration (cm) | Retention (mg/kg) |
| sand | none | none | none | none | none | none |
| granules | none | none | none | none | none | none |
| pebbles | none | none | none | none | 4.5 | 113,777 |

3.2 Series 2 – Dispersed Bitumen-Sediment Interaction in Salt Water

Should an Orimulsion spill occur near the shore, it is possible that the Orimulsion derivative *dispersed bitumen* may reach the shore and come into contact with beach sediments. This series of experiments was designed to evaluate the potential impacts of *dispersed bitumen*-sediment interaction.

The questions addressed by the experiments are:

What is the penetration potential of dispersed bitumen if it reaches the shoreline?

What is the retention potential of dispersed bitumen if it reaches the shoreline?

| | |
|--------------|--|
| Series: | 2 |
| Suite: | Dispersed Bitumen Retention/Penetration (32 ppt) |
| Oil: | Dispersed bitumen |
| Salinity: | 32 ppt |
| Temperature: | variable |
| Variables: | temperature and sediment size |
| Questions: | what is penetration potential of dispersed bitumen/sediment types in saline water? what is retention potential of dispersed bitumen/sediment types in saline water? |
| Method: | place a known volume of Orimulsion on water surface of column take sample of Orimulsion with automatic pipette and determine conc. lower water table observe maximum penetration depth; observe concentration profile raise water table take "dispersed bitumen" and diluted bitumen conc. samples compute mass retained, conc. per m ³ of sediment |

Table 7 Series 2 Experiment Numbers

| Sediment | Temperature (°C) | | |
|-----------|------------------|----|----|
| | 5 | 15 | 25 |
| med. sand | 10 | 13 | 16 |
| granules | 11 | 14 | 17 |
| pebbles | 12 | 15 | 18 |

Results

The tests were conducted with 32 ppt seawater but can be compared to Series 3, which tested 15 ppt seawater, to evaluate the effect of salinity on Orimulsion retention and penetration.

Overall the results indicate that penetration/retention potential is not as sensitive to temperature as it is to sediment type (Table 8). Penetration depths did not vary significantly with temperature and retention values do not, in general, appear sensitive to temperature in any consistent pattern.

The results do indicate that penetration and retention potential are strongly dependent on sediment size. Orimulsion penetration “plugged” in all of the sand tests and retention values within the plugged sediment were 85,000 to 106,000 mg/kg. Neither the granules or pebble “plugged” during the experiments and retention values were in the range of 48,000 mg/kg in granules and 6,000 – 33,000 mg/kg for the pebbles.

The implications of the experiments are that (a) water temperature appears to have a minor effect on the dispersed bitumen penetration and retention but that (b) sediment grain size will strongly affect penetration and retention. The greatest retention is in medium to coarse sands, although these sediments are also likely to plug, limiting cleanup to a thin surface layer. In coarser sediments, concentrations of retained bitumen is lower but penetration depths may be greater so that the total volume of bitumen retained may be significant.

Table 8. Sediment and Temperature Effects on Orimulsion Penetration and Retention at 32 ppt Salinity

| Sediment | 5°C | | | 15°C | | | 25°C | | |
|----------|------------|---------------|---------------|------------|---------------|---------------|------------|---------------|---------------|
| | Depth (cm) | Retention (%) | Conc. (mg/kg) | Depth (cm) | Retention (%) | Conc. (mg/kg) | Depth (cm) | Retention (%) | Conc. (mg/kg) |
| sand | 6 | 58 | 84,807 | 5 | 60 | 105,722 | 6 | 55 | 86,843 |
| granules | 10 | 56 | 49,093 | 10 | 59 | 48,473 | 10 | 56 | 46,950 |
| pebbles | 10 | 8 | 6,197 | 10 | 39 | 33,142 | 10 | 21 | 17,618 |

3.3 Series 3 – Dispersed Bitumen-Sediment Interaction in Brackish Water

This experimental series replicated those of Series 2, except brackish water of 15 ppt was used. The series would simulate a spill of Orimulsion that occurred close to the shore in brackish or estuarine water.

| | |
|------------|--|
| Series: | 3 |
| Suite: | Dispersed Bitumen Retention/Penetration (15 ppt) |
| Oil: | Dispersed bitumen |
| Salinity: | 15 ppt |
| Variables: | temperature and sediment size |
| Questions: | what is the penetration potential of dispersed bitumen/sediment types in brackish water what is the retention potential of dispersed bitumen/sediment types in brackish water |
| Methods: | same as Series 2 |

Table 9 Series 3 Experiment Numbers

| Sediment | Temperature (°C) | | |
|-----------|------------------|----|----|
| | 5 | 15 | 25 |
| med. sand | 19 | 22 | 25 |
| granules | 20 | 23 | 26 |
| pebbles | 21 | 24 | 27 |

The questions addressed by the experiments are:

What is the penetration potential of dispersed bitumen if it reaches the shoreline?

What is the retention potential of dispersed bitumen if it reaches the shoreline?

Results

The behavior of Orimulsion in brackish water is substantially different than seawater – the Orimulsion sinks. The negatively buoyant behavior of the Orimulsion makes it difficult to interpret results (Table 10); the Orimulsion does not “flush out” of the sediments on a rising tide so it is assumed that Orimulsion would remain within the sediments after penetration under brackish water conditions.

All of the Orimulsion added to the granule and pebble test columns settled through the sediment, fully penetrated to the base of the column and remained in the column during the subsequent rising tide. As such it was assumed that all of the original bitumen was retained within the sediments. The sand partially plugged during the tests so it was possible to make estimates of the bitumen retained within the sediments.

Table 10. Sediment and Temperature Effects on Orimulsion Penetration and Retention at 15 ppt Salinity

| Sediment | 5°C | | | 15°C | | | 25°C | | |
|----------|------------|---------------|---------------|------------|---------------|---------------|------------|---------------|---------------|
| | Depth (cm) | Retention (%) | Conc. (mg/kg) | Depth (cm) | Retention (%) | Conc. (mg/kg) | Depth (cm) | Retention (%) | Conc. (mg/kg) |
| sand | 5 | 93 | 187,579 | 10 | 94 | 87,346 | 10 | 96 | 92,373 |
| granules | 14 | 100* | 60,571** | 11 | 100* | 58,857** | 13 | 100* | 61,714** |
| pebbles | 14 | 100* | 60,571** | 12 | 100* | 58,857** | 14 | 100* | 61,714** |

* assumed that all remained within sediments

** total initial weight of bitumen per entire sediment weight in column

There are several important implications of the results. First, it is unlikely that a dispersed Orimulsion would reach the intertidal zone if the ambient water were brackish (<20 ppt) because the Orimulsion would sink through the water to the seabed or be limited by a denser, saline layer. However, should a dispersed Orimulsion mixture reach the shoreline and the pore water within the beach was largely fresh or brackish (such as occur in many coarse beaches in temperate climates), the dispersed Orimulsion might penetrate freely through the sediments.

The results highlight the questions regarding the unknown behavior of Orimulsion in brackish water.

3.4 Series 4 - Effects of Orimulsion Loading on Retention and Penetration

This series of experiments was designed to evaluate the effect of Orimulsion loading in sediments. Different volumes (& masses) of Orimulsion were loaded onto columns and bitumen retention measured. Specifically these experiments addressed the question:

Does increased loading (i.e., more Orimulsion) cause increased retention within the sediments?

| | |
|--------------|--|
| Series: | 4 |
| Suite: | Loading |
| Oil: | Dispersed bitumen |
| Salinity: | 32 ppt |
| Temperature: | 15°C |
| Variables: | initial loading |
| Questions: | what is penetration potential of dispersed bitumen/sediment types for different loadings what is retention potential of dispersed bitumen/sediment types for different loadings |
| Method: | same as Series 2 |

Table 11 Series 4 Experiment Numbers

| Sediment | Temperature 15°C | |
|-----------|------------------|-------|
| | Light | Heavy |
| med. sand | 28 | 31 |
| granules | 29 | 32 |
| pebbles | 30 | 33 |

Results

The data (Table 12) indicate two general features: (1) fine sediments “plugged”, even under the relatively “light” loading levels so that even with substantially increased loading, there was little difference in oil retention within the sand and (2) higher loading levels result in higher retention levels, providing that sediments are sufficiently coarse to prevent “plugging” of pore space; a two-fold increase in loading resulted in approximately a two-fold increase in “bitumen” retention within the sediments.

Table 12. Effect of Loading Levels on Oil Retention

| Sediment | “Bitumen” Conc. in Sediment (mg/kg) | |
|-------------|-------------------------------------|----------------------|
| | Light Loading (95g) | Heavy Loading (189g) |
| medium sand | 144,944* | 198,538* |
| granules | 63,923 | 114,362 |
| pebbles | 42,898 | 98,685 |

* Orimulsion plugged sediments at a depth of 4.3 cm

3.5 Series 5 – Effects of Tidal Flushing on Orimulsion - Sediment Interaction

If Orimulsion becomes stranded in intertidal sediments, it is of interest to know how stable the retained residue is. The experiments involved initial oiling of the sediments with Orimulsion (approximately 100g loading) and subsequent measurement of retention of bitumen within the sediments after 5 and 10 tidal cycles. These experiments were designed to test the question:

Will tidal cycling be effective in dispersing Orimulsion from sediments?

Results

The results (Table 14) suggest that subsequent tidal flushing did not significantly reduce initial bitumen concentrations within the sediments. Comparison of the sand and granules testing indicates less than a 15% difference

in retained bitumen concentrations between 5-cycles and 10-cycles of flushing. The data from the pebbles tests actually show higher retention in the 10-cycle test but this result does not appear to be “real” and is within the error margin of testing.

Comparison of the tidal flushing data (Table 14) to the non-flushed data (Table 8) may suggest that substantial dilution occurred due to tidal flushing (e.g., a reduction of 45,000 mg/kg to 2,500 mg/kg for granules). However, the experimental techniques used in the two different series differ slightly - the tidal flushing series (Series 8) was not a closed system as drained water from each falling tide cycle was retained in a separate container and sampled after the tests. An unknown portion of the difference between Series 5 data and Series 8 data may be due to differences in experimental technique. As such, the overall significance is speculative; the data *may* indicate that tidal flushing may be very important initially but have a decreasing effect over time.

| | |
|--------------|---|
| Series: | 5 |
| Suite: | Tidal Cycling |
| Oil: | Dispersed bitumen |
| Salinity: | 32 ppt |
| Temperature: | 15°C |
| Variables: | Number of Tidal cycles |
| Questions: | what is penetration potential of dispersed bitumen/sediment types for different cycles what is retention potential of dispersed bitumen/sediment types for different cycles |
| Method: | place a known volume of Orimulsion on water surface of column take sample of Orimulsion with automatic pipette and determine conc. lower water table; collect “runoff” in container observe maximum penetration depth; observe concentration profile raise water table repeat raising and lowering steps 5 or 10 times as required take “dispersed bitumen” and dilbit conc. samples take runoff conc. sample compute mass retained, conc. per m ³ of sediment |

Table 13 Series 5 Experiment Numbers

| Sediment | Temperature 15°C | |
|-----------|------------------|-----------|
| | 5 cycles | 10 cycles |
| med. sand | 34 | 37 |
| granules | 35 | 38 |
| pebbles | 36 | 39 |

Table 14. Effect of Tidal Flushing on Sediment Bitumen Retention

| Sediment | % of Initial "Bitumen" Retained | | "Bitumen" Conc. in Sediments (mg/kg) | |
|-------------|---------------------------------|-----------------|--------------------------------------|-----------------|
| | 5 Tidal Cycles | 10 Tidal Cycles | 5 Tidal Cycles | 10 Tidal Cycles |
| medium sand | 83% | 58% | 36,369 | 27,954 |
| granules | 10% | 6% | 4,619 | 2,371 |
| pebbles | 0% | 0% | 0 | 0 |

3.6 Series 6 – Evaluation of *In Situ* Weathering of Orimulsion in Sediments

These tests were designed to estimate the time required for "weathered bitumen coating" to form within "oiled" sediments. That is, if a dispersed Orimulsion mixture is stranded on and penetrates into sediments, what length of time is required for the *weathered bitumen coating* to "set-up" on the sediments. The experiments involved: (a) initial stranding of the dispersed bitumen on sediments by the falling-tide technique, (b) subsequent draining of the sediments and (c) testing for "weathered bitumen coating" formation with depth after 2 days, 8 days and 20 days. The formation of "weathered bitumen coatings" was tested by placing oiled sediments in 15°C, 32 ppt salt water, gently shaking and observing if the oil easily separated from the sediment within two minutes (the *Weathered Bitumen Coating Test*). If the bitumen floated free of the sediments within the two minute period, the bitumen was considered mobile. If the bitumen remained adhered to the sediment after 2 minutes, the bitumen was considered non-mobile.

| | |
|--------------|---|
| Series: | 6 |
| Suite: | <i>In Situ</i> Weathering |
| Oil: | Dispersed bitumen |
| Salinity: | 32 ppt |
| Temperature: | ~15°C (room temp) |
| Variables: | time |
| Questions: | how long does it take weathered bitumen to form? (hours, days, weeks) will weathered bitumen form in wet sediments? will weathered bitumen form underwater? |
| Method: | put Orimulsion on water surface partially drain Orimulsion through column so there are "dry", wet and saturated zones. allow to stand in lab over specified time sample columns in 2 cm layers, using the Weathered Bitumen Coating Test for each sample note depth of Weathered Bitumen Coating for each time interval |

Table 15 Series 6 Experiment Numbers

| Sediment | Days | | |
|-----------|------|----|----|
| | 2 | 8 | 20 |
| med. sand | 40 | 43 | 46 |
| granules | 41 | 44 | 47 |
| pebbles | 42 | 45 | 48 |

Results

The results (Table 16) indicate that *weathered bitumen coating* forms at greater depths within pebbles and granules than within sand, presumably due to dryer nature of the coarser sediments.

Weathered bitumen coating formed at greater depths over time (up to 8 days), although most of the formation appears to have occurred within the first two days. The maximum formation depth of the *weathered bitumen coating* was observed at 8 cm in the pebbles.

The implications of this result are two-fold: (1) the tenacious *weathered bitumen coating* will form at greater depths in coarse sediments, presumably due to lower sediment moisture contents and (2) the weathering process occurs quickly with little change after the first few days. The results suggest that keeping sediments wet may limit the depth and rate of *weathered bitumen coating* formation.

Table 16. In Situ Formation of Weathered Bitumen Coating within Sediments

| Sediment | Depth of Weathered Bitumen Coating Formation over Time | | |
|----------|--|--------|---------|
| | 2 days | 8 days | 20 days |
| sand | 2.0 cm | 4.5 cm | 3.8 cm |
| granules | 6.2 cm | 6.5 cm | 6.8 cm |
| pebbles | 6.5 cm | 8.0 cm | 7.5 cm |

3.7 Series 7 – Evaluation of Hydraulic Flushing on Orimulsion in Sediment

This set of experiments was designed to evaluate the effectiveness of flushing for removal of stranded bitumen. The specific questions addressed by the experiments are:

Is flushing effective in remobilizing Orimulsion derivatives from sediments?

What are the efficiencies associated with the flushing?

Orimulsion was stranded on sediments using the “falling tide” method, allowed to stand for a period of 4 hours and then flushed using different volumes of water. Differences in flushing efficiency were made

observationally by comparing oil retention using standard SCAT terminology (Owens & Sergy, 1994); oil retention was estimated in terms of “estimated % saturation” where completely oil-filled pores would be 100% saturated. Temperature and pressure effects of the flushing were not evaluated.

| | |
|--------------|---|
| Series: | 7 |
| Suite: | Hydraulic Flushing |
| Oil: | Dispersed bitumen |
| Salinity: | 32 ppt |
| Temperature: | 15°C |
| Variables: | number of rinses |
| Questions: | is manual flushing effective in re-mobilizing dispersed bitumen from sediments? what is the efficiency of manual flushing |
| Method: | drain Orimulsion through small diameter column allow to stand 4 hours flush through column compare columns side-by-side and note residue in sediment |

Table 17 Series 7 Experiment Numbers

| Sediment | Volume of Flush (L) | | |
|-----------|---------------------|----|----|
| | 1 | 2 | 3 |
| med. sand | 49 | 52 | 55 |
| granules | 50 | 53 | 56 |
| pebbles | 51 | 54 | 57 |

Results

The “% saturation” was estimated to the nearest 10% for each 0.5 cm layer of sediment and recorded. The averaged value for the entire column is provided in Table 18 as a general index of flushing efficiency.

The data suggest that the overall effect of flushing is to significantly reduce bitumen concentration in the sediment and that this effect is greatest for pebble-sized material. Estimated bitumen concentrations in all sediments were reduced by nearly 50% in all cases and by approximately 80% in the pebbles. The volume or duration of flushing appear to be important as only small changes occurred after two flushes but significant reductions were observed after three flushes.

The implication is that flushing may provide a viable means of reducing subsurface bitumen concentrations after Orimulsion comes into contact with a beach. However, in these column tests, the bitumen was flushed out of the column whereas on natural beaches, the flushing could carry the dispersed bitumen further into the sediments. Considerable care would be required in the determination of the eventual settling place of the bitumen.

Table 18. Average Visual Estimate of Oil Retention*

| Sediment | Volume of Flush | | |
|----------|-----------------|-----|-----|
| | 1 L | 2 L | 3 L |
| sand | 35 | 32 | 20 |
| granules | 38 | 33 | 18 |
| pebble | 35 | 26 | 7 |

* an estimate was made of each 0.5 cm thickness of “% saturation” with oil [bitumen] and an average computed for the 14 cm deep column.

3.8 Series 8 – Effects of Surfactant Flushing on Orimulsion in Sediment

These experiments were designed to test the effects of surfactants on flushing; they can be compared to the Flushing Tests (Series 7). The experimental procedure was the same as Series 7 but with the addition of 2 mL of surfactant (commercial dish soap) per litre of flush. Orimulsion was stranded on sediments using the “falling tide” technique, allowed to stand for four hours and then flushed with three different volumes of surfactant-water solutions.

| | |
|--------------|---|
| Series: | 8 |
| Suite: | Surfactant Effects |
| Oil: | Dispersed bitumen |
| Salinity: | 32 ppt |
| Temperature: | 15°C |
| Variables: | number rinses (with surfactant; compare to above) |
| Questions: | does the use of a surfactant increase the efficiency of flushing? |
| Method: | same as series 7 |

Table 19 Series 8 Experiment Numbers

| Sediment | Volume of Flush (L) | | |
|----------|---------------------|----|----|
| | 1 | 2 | 3 |
| granules | 58 | 59 | 60 |

Results

The results (Table 20) suggest that the use of a surfactant substantially increases the effectiveness of flushing; a significant amount of the original stranded bitumen was removed after three flushes. Comparison to the non-surfactant flushing (Table 18) shows that considerably greater efficiency can be achieved by using surfactant.

The implication is that the use of a surfactant in beach cleaning activities would improve the efficiency of flushing. However, as with other flushing activities, consideration of the eventual fate of the flushed material will be important.

Table 20. Average Visual Estimate of Oil Retention with Surfactant Flush*

| Sediment | Volume of Flush | | |
|----------|-----------------|-----|-----|
| | 1 L | 2 L | 3 L |
| granules | 33 | 15 | 4 |

* an estimate was made of each 0.5 cm thickness of "% saturation" with oil [bitumen] and an average computed for the 14 cm deep column.

3.9 Series 9 - Remobilization of Weathered Bitumen Coating from Sediment

A sticky *weathered bitumen coating* was observed to form within and on the surface of sediment grains after exposure to dispersed bitumen *and* air. This residue formed very cohesive "blocks" of sediment that resembled blocks of road asphalt. This series of tests was designed to determine if hot water could be used to remobilize the *weathered bitumen coating* and what temperature of water was required for remobilization.

| | |
|------------|---|
| Series: | 9 |
| Suite: | Weathered Bitumen Coating Remobilization |
| Oil: | Dispersed Bitumen |
| Salinity: | 32 ppt |
| Variables: | temperature |
| Questions: | at what temperature can weathered bitumen coatings be remobilized |
| Method: | place pebble with weathered bitumen coating in cup of seawater at appropriate temp. observe oil mobility |

Table 21 Series 9 Experiment Numbers

| Sediment | Temperature (°C) | | | | | | |
|----------|------------------|----|----|----|----|----|----|
| | 10 | 15 | 20 | 25 | 30 | 40 | 50 |
| pebbles | 61 | 62 | 63 | 64 | 65 | 66 | 67 |

The question that was addressed by the tests was:

At what temperature can weathered bitumen coatings be re-mobilized?

Tests were conducted by (a) placing a heavily-coated pebble (coated with dispersed bitumen then dried for several days to form a weathered bitumen coating) in a small container of seawater with a known temperature, and (b) noting the temperature at which the remobilization process occurred, using the *weathered bitumen coating test* described in Series 6.

Results

The results (Table 22) indicate that water temperatures of above 20°C are required to remobilize *weathered bitumen coating* and even at this temperature the remobilization process is not rapid (*weathered bitumen coating* required 4 minutes at this temperature to coalesce into veins, 10 minutes to coalesce into droplets). As such, it is assumed that *at least 10 minutes* of sustained 20°C temperatures would be required to remobilize the *weathered bitumen coating*.

Table 22. Temperature Effects on Weathered Bitumen Coating Remobilization

| Temp. (°C) | Sediment | Weathered Bitumen Coating Remobilized ? | Notes |
|------------|----------|---|--|
| 50 | pebbles | Y | rapid remobilization |
| 40 | pebbles | Y | rapid remobilization |
| 30 | pebbles | Y | Rapid to moderate remobilization |
| 25 | pebbles | Y | Moderate rate of remobilization |
| 20 | pebbles | Y | about 10 min required for remobilization |
| 15 | pebbles | N | no remobilization after 24 hr |
| 10 | pebbles | N | no remobilization after 24 hr |

3.10 Series 10 – Effect of Clay Scavenging on Orimulsion

This series of experiments was designed to evaluate the effect of clay particle interaction with clay particle interaction with various concentrations of Orimulsion. Two concentrations of Orimulsion were mixed with two clay concentrations and the interaction observed over time.

The experiments addressed the question:

Does clay scavenging create observable or measurable differences in *dispersed bitumen* or *dilute bitumen* concentrations?

| | | |
|--|--|-----------|
| Series: | 10 | |
| Suite: | Clay Scavenging | |
| Oil: | dispersed bitumen; dilute bitumen | |
| Salinity: | 32 ppt | |
| Variables: | clay content | |
| Questions: | does clay scavenging create observable or measurable differences in dispersed bitumen or diluted bitumen concentrations? | |
| Methodology: | <p>mix a slurry of Orimulsion and seawater so that dispersed bitumen and diluted bitumen layers form</p> <p>separate dispersed bitumen and diluted bitumen into separate containers</p> <p>introduce clay (est. 20 mg/L conc.) into containers</p> <p>observe residual suspensions after 1 hr and 5 hr</p> | |
| Table 23 Series 10 Experiment Numbers | | |
| | Clay Conc. (mg/L) | |
| Phase | <1 | 20 |
| dispersed bitumen | 68 | 69 |
| dilute bitumen | 70 | 71 |

Results

The results (Table 24) provide only a very general indication of Orimulsion and clay-particle interaction. No changes were noted in the higher concentration of the bitumen but some changes were noted in the "diluted bitumen". With the "diluted" bitumen suspension, sedimentation occurred almost immediately with the higher concentration of clay particles and after 5 hours in the lower concentration of clay particles. After 10 hours a noticeable layer of oil-clay particulates had formed in the higher clay-seawater concentration.

Table 24. Observations of Orimulsion Interaction in the Presence of Clay Particles

| Orimulsion Phase | Time | Clay Concentration | |
|--|-------|--|--|
| | | ~ 1 mg/L Conc. | 50 mg/L Conc. |
| Dispersed bitumen (est. 35% bitumen conc.) | 1 hr | no change | no change |
| | 5 hr | no change | no change |
| | 10 hr | no change | separation of layer but no sedimentation |
| Dilute Bitumen (est. <5% bitumen conc.) | 1 hr | no change | "dusting" of black particles on bottom |
| | 5 hr | "dusting" of particles on bottom of container | fuzzy layer of particles on bottom of container |
| | 10 hr | "dusting" of particles on bottom of container (but less than 50 mg/L after 1 hour) | continuous layer of particles on bottom; darker than previously noted; <1 mm thick |

No quantitative observations have been made but the qualitative observations suggest that clay-bitumen interaction does occur and likely will be an important dispersal mechanism for bitumen suspended in the water column.

4.1 *Weathered Bitumen* Oiling Scenario

The most likely scenario for shoreline oiling is stranding of *weathered bitumen*. This Orimulsion derivative is highly buoyant, sticky and appears to form into relatively cohesive "patties" or "mats". Our experiments suggest that it may represent a relatively small proportion of an overall Orimulsion spill volume (<25%).

Experimental results show that the *weathered bitumen* is unlikely to penetrate into sand or granules but will penetrate a short depth into pebbles (<5 cm). On cobble or boulder shorelines, the *weathered bitumen* would be expected to percolate through the boulder-cobble surface sediments until it reaches a layer of finer material which would limit penetration. The penetration potential does not appear to be temperature sensitive.

The *weathered bitumen* stranding scenario suggests that the oiling would be primarily a surface phenomenon on most sediment shorelines such as mud, sand and sand & gravel beaches. On coarse sediment beaches of well-sorted cobble or boulder, penetration into the subsurface may occur; oiling of this type is likely to be discontinuous due to the assumed stranded-oil forms of patties and mats.

We speculate that once the *weathered bitumen* had penetrated into the boulder-cobble sediment to some impermeable layer, it would be relatively stable and not easily remobilized. Our tests suggest that sustained temperatures of >25°C would be required to remobilize the *weathered bitumen coating*. Even if the *weathered bitumen coating* were remobilized, it may be difficult to recover as it is extremely sticky and only slightly positively buoyant; it may not float to the surface.

4.2 *Dispersed Bitumen* Oiling Scenario

Dispersed bitumen could reach the shore if (a) the spill is relatively close to the shore and (b) water salinities are >25 ppt. Our tests and previous tests have shown that *dispersed bitumen* will sink in salinities of <20 ppt so would be unlikely to float in suspension to the shore under these conditions. The dispersion rates for the *dispersed bitumen* are unknown but our studies indicate that a rapid initial dilution of Orimulsion (70% bitumen content) occurs even with low mixing energy to the *dispersed bitumen* phase (measured 20% bitumen content). Dilution will continue, depending on mixing energy such that a neutrally buoyant *diluted bitumen* fluid (measured bitumen content of <10%) forms beneath the slightly more buoyant *dispersed bitumen*. For this reason, it is assumed that a spill would have to occur relatively close to shore for *dispersed bitumen* to reach a beach.

Our laboratory tests showed that if *dispersed bitumen* reaches the shore, it will "plug" near the surface of sands (<5 cm penetration) under most conditions but will freely penetrate into coarser sediments. Our tests with relatively high loading levels of *dispersed bitumen* indicated that retention values of up to 84,000 to 106,000 mg bitumen/kg of sediment in sand (but limited penetration), 48,000 mg/kg in granules, and 6,000 to 33,000 mg/kg in pebbles can occur. The retention is closely related to the loading levels so lower loading levels, as might be expected in a spill, would produce lower retention concentrations.

Once the *dispersed bitumen* is in the subsurface sediments, there appear to be two principle weathering processes. First, where the sediments dry, the *dispersed bitumen* quickly forms a *weathered bitumen coating* on the grain surfaces and to a lesser extent at the grain-to-grain contacts. The *weathered bitumen coating* is very stable but can be remobilized with $>25^{\circ}\text{C}$ water. Our tests indicated that *weathered bitumen coatings* did not form below 4 cm in sand, 7 cm in granules and 8 cm in pebbles, even after 20 days.

The second process that appears to affect subsurface *dispersed bitumen* is gradual dilution to the *diluted bitumen* phase. Where sediments remain wet, the *dispersed bitumen* appears to remain non-sticky. While tidal flushing, a very slow water exchange process, did not substantially dilute the bitumen over our limited time-frame, flushing, especially with surfactant, was effective in removing the *dispersed bitumen* from the sediments. It is assumed that over time continual dilution of *dispersed bitumen* would occur under the influence of tidal flushing and wave-pumping of pore waters. As the *dispersed bitumen* was diluted to form *dilute bitumen*, this material could be clay scavenged.

The results of our testing suggest the following stranding and natural weathering scenario for a spill of *dispersed bitumen* reaching the shoreline. With a relatively heavy loading levels (i.e., close to the spill source), *dispersed bitumen* with concentration of approximately 20% bitumen would penetrate into granules and coarser sediments but would have limited penetration in sands (<5 cm). The *dispersed bitumen* would remain non-sticky and mobile in the mid- and lower-intertidal zones; it is assumed that dilution would continue with tide and wave mixing energy and bitumen particles would be dispersed away from the shoreline and gradually settling in deeper, quiescent areas offshore. In the upper intertidal zone, drying the *dispersed bitumen* would form *weathered bitumen coatings* in the surface sediments; this formation of tenacious *weathered bitumen coating* would be less than 10 cm thick in sand, sand & gravel, granules and pebbles but likely much deeper in cobble/boulder material (probably to the first layer of granules). *Dispersed bitumen* in the deeper subsurface would remain non-sticky and fluid, gradually dispersing over time.

Should the *dispersed bitumen* penetrate beaches with a high freshwater table, the penetration limit is uncertain as *dispersed bitumen* is negatively buoyant; however, on beaches with outcropping freshwater tables, the groundwater is usually an effluent and may serve to flush the *dispersed bitumen* from the sediments.

4.3 Comparison to Fuel Oil Experimental Data

The Orimulsion experimental data from this study can be compared to previous experimental studies involving similar methodology and controls. The SOCSEX II studies (Harper and Kory 1995; Harper *et al.*, 1995) used similar experimental columns, sediments and temperature controls but involved the use of crude oils and fuel oils. Comparable data is summarized below.

Data from three fuel oils were selected for comparison to the Orimulsion data. Oil retention data for unweathered Bunker C oil (at 15°C), weathered Bunker C oil (6% weathering by weight at 15°C) and slightly weathered IFO-180 fuel oil (2.5% weathering at 15°C) in sands, granules and medium pebbles are compared (Fig. 5). The SOCSEX II oil retention data were reported in litres of oil per cubic metre of sediment and were converted to milligrams of oil per kilogram of sediment. As such, a number of assumptions about the oil densities and bulk sediment densities were required but these parameters were carefully documented in the SOCSEX II methodologies.

Figure 5. Comparative data of oil retention for three fuel oils and Orimulsion for different sediments.

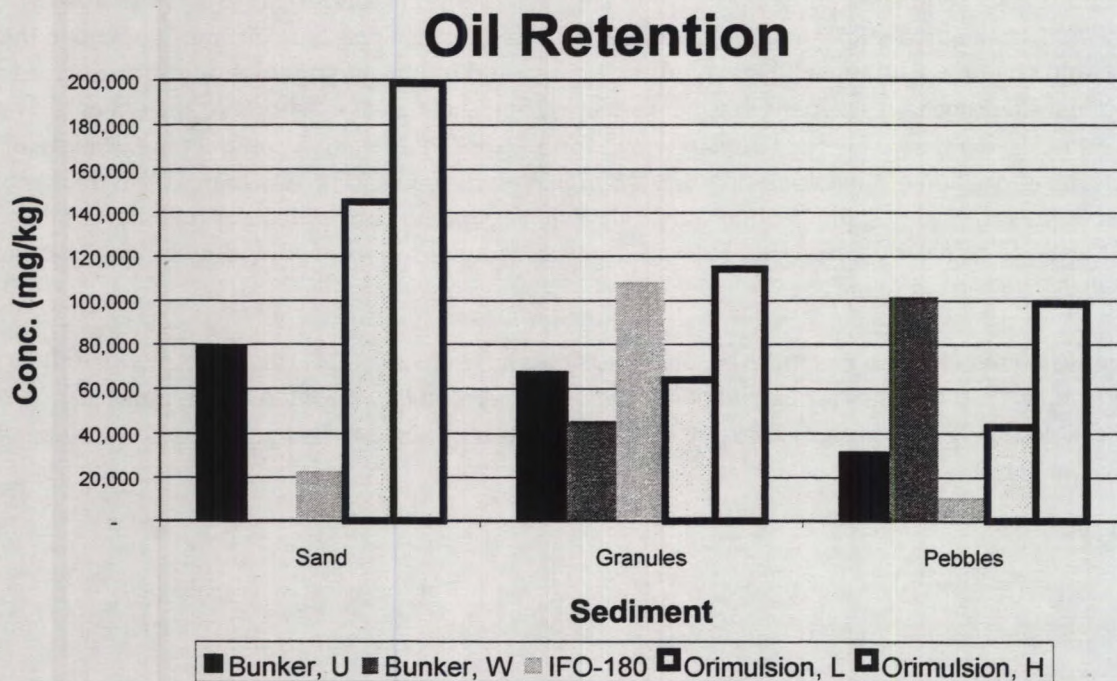


Figure 5. Oil retention in subsurface sediments for various oil types and sediment types. All tests were conducted at 15°C. [**Bunker, U** = unweathered Bunker C; **Bunker, W** = 6% weathered Bunker C; **IFO-180** = slightly weathered Fuel Oil No. 5; **Orimulsion, L** = light loading of Orimulsion (Table 12); **Orimulsion, H** = heavy loading of Orimulsion (Table 12)].

All of the oils are classified as "penetration-limited" for sands, as the oils plugged either at or very near the surface of the sediment. Both of the Bunker C oils plugged in the granules while the IFO and dispersed bitumen form of Orimulsion penetrated the full depth of the test columns (>10cm); the retention of dispersed bitumen is in the same order as the IFO-180 - about 60,000 to 100,000 mg/kg. For medium pebble experiments, the retention of dispersed bitumen is in the same range as the Bunker C retention.

These data provide the basis for preliminary comparison of Orimulsion-sediment interaction in comparison to fuel oil-sediment interaction. In sands, the penetration of the dispersed bitumen form of Orimulsion is likely to be greater than heavier fuel oils but in coarser sediments, penetration depths and retention values appear similar to both Bunker C and intermediate fuel oils (i.e., IFO-180).

For the *weathered bitumen* form of Orimulsion, penetration was limited in all sediments smaller than pebbles and only occurred in pebbles at relatively warm temperatures (25°C). Penetration of the *weathered bitumen* form was found to be less than any of the previous tests with fuel oils.

4.4 Limitations of Experimental Data

The experiments described in this report were designed to complement previous observations and to provide "initial ranging" indices of Orimulsion-sediment interaction. Laboratory tests of this type have inherent limitations. A few of the more significant limitations are listed below.

1. In terms of simulating stranding of a spill, a significant unknown is the "at sea" dispersion processes. In particular, we do not know what portion of an Orimulsion spill will form *weathered bitumen* (or how mixing energy controls the rate of formation) or how fast the *dispersed bitumen* phase dilutes so that we have realistic loading levels (e.g., our loading levels involved the use of *dispersed bitumen* with bitumen concentrations of 20% but in a natural spill this level of concentration might occur in only a small area).
2. Due to the limited height of our test columns used in the ranging tests, we were unable to evaluate the total depth of penetration of *dispersed bitumen* in granules and pebbles.
3. Because of the reconnaissance nature of the testing, no detailed geochemical analyses were conducted of bitumen concentrations in sediments so we have no means of cross-checking our bitumen-in-sediment estimates.
4. The ultimate fate of *dispersed or diluted bitumen* in sediments is still unknown. That is, once the bitumen is in the sediments, we know it is relatively mobile and non-sticky as long as it is kept wet, and we **assume** that it will gradually "disperse" from the sediments. However, because bitumen is near neutrally buoyant, it is probable that this process is much slower than that which occurs with conventional oils. In addition, the bitumen appears to be clay scavenged and ultimately sinks, but it is uncertain how or at what rate this process might occur within pore waters.
5. We evaluated Orimulsion derivatives in brackish water and found them to easily penetrate coarse sediments such as granules and pebbles. In view of the potential for a brackish water spill and settling of the *dispersed bitumen* to the seabed, it would be of interest to examine the interaction of the dispersed bitumen with finer sediments under totally subaqueous conditions.

5.1 Conclusions

1. *Weathered bitumen* is the Orimulsion derivative that is most likely to reach shorelines. It is highly viscous and sticky with similar characteristics to weathered heavy fuel oils. It is unlikely to penetrate into sediments finer than pebbles but may penetrate into well-sorted cobble or boulder sized sediments.
2. *Dispersed bitumen* is an Orimulsion derivative that could reach the shoreline in a fluid form. Our laboratory observations suggest that dispersed bitumen will penetrate freely into granules and pebbles but will "plug" near the surface of sands (or sand and gravel).
3. As long as *dispersed bitumen* remains wet within the sediments, it appears to remain fluid and non-sticky; however, if the *dispersed bitumen* dries, it forms a tenacious *weathered bitumen coating* on the surface of grains and at the grain-to-grain contacts. Once a *weathered bitumen coating* forms, it is difficult to remobilize. Our tests suggest that *weathered bitumen coatings* form relatively quickly to depths of 4 cm in sands, 6-7 cm in granules and 7-8 cm in pebbles. It is assumed that *weathered bitumen coatings* would form to greater depths in cobbles and boulders where greater air circulation occurs within pores.
4. *Dispersed bitumen* can be flushed from sediments although normal tidal flushing does not appear sufficiently energetic to flush out the *dispersed bitumen*. Surfactants increase the effectiveness of flushing.
5. A concern with the flushing and with the dilution of *dispersed bitumen* from sediments in general is the ultimate fate of the bitumen particles. The particles are near neutrally buoyant and do not coalesce at the water surface when remobilized. This is a significant unknown in terms of the ultimate fate of bitumen in the coastal environment.

5.2 Recommendations

1. Shoreline oiling scenarios from an Orimulsion spill are highly speculative at present. In particular, there does not appear to be reliable information on the formation of Orimulsion derivatives. Our own laboratory observations suggest that *weathered bitumen* may constitute only a minor amount of the spill volume, with larger portions going into the *dispersed* and *diluted bitumen* phases. Knowledge of the relative volumes of derivatives is critical as is the "dilution rate" of Orimulsion to *dispersed* or *dilute bitumen*.
2. Loading levels of *dispersed bitumen* on the shore are highly speculative (i.e., they are tied to the dilution rates mentioned in Recommendation 1). The loading levels that we used are probably very high and although they provide upper limits on retention, they may not be realistic. In addition, lower loading levels might result in penetration into finer sediments (e.g., bitumen concentrations <5%).

3. There is a significant unknown in terms of the ultimate fate of the bitumen particles. We know that *dispersed bitumen* will remain relatively non-sticky and mobile if kept wet and we assume that as long as it is mobile, that it will eventually be dispersed from beach sediments into the water column and dispersed. However, the mechanism, rate and ultimate fate of the dispersal process is unknown. It is likely that the dispersion rate may be slower than that of conventional oils such as crude oil because the bitumen particles are more neutrally buoyant.
4. The role of clay scavenging may be important. Our laboratory observations showed that high clay concentrations in *dilute bitumen* were effective in removing bitumen (i.e., a sinking agent). The overall rate at which this process occurs is unknown as is the ultimate fate of the bitumen-clay flocculates.
5. Orimulsion derivatives may sink in fresh water. We did not examine sub-aqueous Orimulsion derivatives or their interaction with sediments. These processes will be of significant interest in the evaluation of spills in estuarine waters.
6. Comparative data of Orimulsion retention to heavy fuel oil retention indicates comparable values. The experiments were conducted at different times, however, and it is uncertain if minor variations in experimental techniques would effect retention. In addition, it is our impression that the *dispersed bitumen* remains more mobile within the sediments than heavy fuel oils and this may result in faster natural dispersion rates *after* initial oiling has occurred. Specific experiments could be used to refine Orimulsion dispersion rates, at least on a comparative basis to other common fuel and crude oils.
7. The penetration and retention of *weathered bitumen* into cobble/boulder sediment was not tested. Given that the preliminary scoping data shows that penetration is likely and that the stranding of *weathered bitumen* on coarse-sediment shorelines is a likely oiling scenario, quantitative testing may be warranted.

Harper, J.R., G.A. Sergy and T. Sagayama 1995. Subsurface oil in coarse sediments experiments (SOCSEX II). Proceedings of the 18th Annual Arctic Marine Oilspill Project (AMOP) Technical Seminar, Edmonton, AB, p.867-886.

Harper, J.R. and M. Kory 1995. Stranded Oil in Coarse Sediments Experiments (SOCSEX II). Contract Report by Coastal & Ocean Resources Inc., Sidney, BC for Environment Canada, Edmonton, AB 60p. + appendices.

Owens, E.H. and G.A. Sergy 1994. Field guide to the documentation and description of oiled shorelines. Emergency Science Division, Environment Canada, Edmonton, AB

APPENDIX A

Experimental Data Sheets

SERIES 1: Tarry Residue Penetration/Retention: 25 C 32 ppt Seawater

| Exp # | Sed Weight (g) | TR added (g) | Max Pen (cm) | Comments |
|--------------|-----------------------|---------------------|---------------------|--|
| 7 Med Sand | 1550 | 60.3 | 2 mm | TR mass suspended on sed surface, min penetration |
| 8 Granules | 1750 | 59.8 | 1 | TR mass just penetrated sed surface, min penetration |
| 9 Pebbles | 1750 | 63.7 | 4.5 | TR penetration, adhered to sed upon filling. |

SERIES 2 : Dispersed Bitumen Retention/Penetration : 5 C : 32 ppt seawater

| Exp # | Temp (C) | Sed Wgt g | Ori Added g | Bit added (g) | Penetr. cm | Bit Recov. g | Bit Ret g | % Ret | kg Bit/ | | Comments |
|-------------|----------|-----------|-------------|---------------|------------|--------------|-----------|-------|---------|---------------|-------------------|
| | | | | | | | | | m3 Sed | mg Bit/kg sed | |
| 10 Med Sand | 5 | 1550 | 99.1 | 69.6 | 6 | 12.0 | 57.6 | 58.1 | 135.4 | 84,807 | Disbit suspension |
| 11 Granules | 5 | 1750 | 108.9 | 76.4 | 10 | 15.1 | 61.4 | 56.3 | 86.6 | 49,083 | Disbit suspension |
| 12 Pebbles | 5 | 1750 | 101.8 | 71.5 | 10 | 63.7 | 7.7 | 7.6 | 10.9 | 6,197 | Disbit suspension |
| 13 Med Sand | 15 | 1550 | 100.4 | 70.5 | 5 | 10.7 | 59.8 | 59.6 | 168.75 | 105,722 | Disbit suspension |
| 14 Granules | 15 | 1750 | 102.4 | 71.9 | 10 | 11.3 | 60.6 | 59.2 | 85.48 | 48,473 | Disbit suspension |
| 15 Pebbles | 15 | 1750 | 106.1 | 74.5 | 10 | 33.1 | 41.4 | 39.0 | 58.45 | 33,142 | Disbit suspension |
| 16 Med Sand | 25 | 1550 | 107.5 | 75.5 | 6 | 16.5 | 59.0 | 54.8 | 138.62 | 86,843 | Disbit suspension |
| 17 Granules | 25 | 1750 | 105.1 | 73.8 | 10 | 15.1 | 58.7 | 55.8 | 82.80 | 46,950 | Disbit suspension |
| 18 Pebbles | 25 | 1750 | 103.6 | 72.7 | 10 | 50.7 | 22.0 | 21.3 | 31.07 | 17,618 | Disbit suspension |

SERIES 3 : Dispersed Bitumen Retention/Penetration : 5 C : 15 ppt seawater

| Exp # | Sed Wgt (g) | Ori Added (g) | Bit Added (g) | Penetration (cm) | Bit Recov. (g) | Bit Ret (g) | % Ret | kg Bit/ m3 Sed | mg Bit/ kg sed | Comments |
|-------------|----------------|------------------|------------------|---------------------|-------------------|-------------|-------|-------------------|-------------------|---|
| 19 Med Sand | 1550 | 107.6 | 75.5 | 4.7 | 7.85 | 67.7 | 90 | 203.2 | 127,279 | Disbit suspension throughout column |
| 20 Granules | 1750 | 107.1 | 75.2 | 14 | | 75.2 | 100 | 75.8 | 42,051 | 9.043 g in runoff; Ori sank upon addition |
| 21 Pebbles | 1750 | 105.2 | 73.9 | 14 | | 73.9 | 100 | 74.5 | 41,324 | 15.7089 g in runoff |
| 22 Med Sand | 1550 | 105.1 | 73.8 | 10 | 7.85 | 65.9 | 89 | 93.0 | 58,270 | Disbit suspension throughout column |
| 23 Granules | 1750 | 100.9 | 70.8 | 11.5 | | 70.8 | 100 | 86.9 | 48,197 | 4.8936 g in runoff; Ori sank upon addition |
| 24 Pebbles | 1750 | 107.6 | 75.5 | 12.5 | | 75.5 | 100 | 85.2 | 47,285 | 3.0737 g in runoff; Ori sank upon addition |
| 25 Med Sand | 1550 | 108.3 | 76.0 | 10 | 7.85 | 68.2 | 90 | 96.2 | 60,255 | Thick creamy dibit layer observed adhering to surface |
| 26 Granules | 1750 | 113.9 | 80.0 | 13 | | 80.0 | 100 | 86.8 | 48,176 | 4.3291 g in runoff; Ori sank upon addition |
| 27 Pebbles | 1750 | 103 | 72.3 | 14 | | 72.3 | 100 | 72.9 | 40,429 | 9.1305 g in runoff; Ori sank upon addition |

Series 4 : Loading : 15 C : 32 ppt Seawater

| EXP# | Sed | Wgt Sed (g) | Ori Added (g) | Blit Added (g) | Penetration (cm) | Blit In Sub g/8mL | Sampled (mL) | Retained Bit (g) | % Retained | Ori kg/m3 Sed | Ori mg/kg Sed |
|------|----------|-------------|---------------|----------------|------------------|-------------------|--------------|------------------|------------|---------------|---------------|
| 28 | Med Sand | 1550 | 149.0 | 104.6 | 5.8 | 0.2745 | 276.43 | 95.1 | 90.9 | 231.4 | 144,944 |
| 29 | Granules | 1750 | 134.6 | 94.5 | 10 | 0.4221 | 276.43 | 79.9 | 84.6 | 112.7 | 63,923 |
| 30 | Pebbles | 1750 | 131.1 | 92.0 | 10 | 1.0838 | 283.52 | 53.6 | 58.3 | 75.7 | 42,898 |
| 31 | Med Sand | 1550 | 269.6 | 189.2 | 5 | 1.7716 | 347.31 | 112.3 | 59.4 | 316.9 | 198,538 |
| 32 | Granules | 1750 | 268.2 | 188.3 | 10 | 1.0440 | 347.31 | 143.0 | 75.9 | 201.7 | 114,362 |
| 33 | Pebbles | 1750 | 274.5 | 192.7 | 10 | 1.6652 | 333.14 | 123.4 | 64.0 | 174.0 | 98,685 |

Series 5 : Tidal Cycling : 5 Cycles:15 C : 32 ppt Seawater

MED SAND 34: 1550g Sed, 96.3g Ori (67.6g bit)

| Tidal Cycle # | 1 | 2 | 3 | 4 | 5 | H2O final (g) | Retained (g) | % Ret | kg Bit/ m3 Sed | mg Bit/ kg Sed | Comments |
|------------------|---|--------|--------|------|--------|---------------|--------------|-------|----------------|----------------|-------------------------------|
| Penetration cm | 5 | 10 | 14 | 14 | 14 | | | 83.39 | 56.81 | 36,369 | T R in runoff @ 3rd cycle |
| Runoff Ori g/8mL | 0 | 0.0491 | 0.0889 | 0 | 0.0717 | | | | | | Full penetration on 2nd cycle |
| Vol. Sampled mL | 0 | 195 | 280 | 0 | 560 | 184 | | | | | Slow draining; plugging? |
| Ori Total g | 0 | 1.20 | 3.11 | 0.00 | 5.02 | 1.90 | 56.37 | | | | Clear final runoff |

GRANULES 35: 1750g Sed, 110.1g Ori (77.29g bit)

| | | | | | | | | | | | |
|------------------|-----------|---------|-----------|--------|----------|--------|--------|-------|------|-------|---------------------------------|
| Penetration cm | 14 | 14 | 14 | 14 | 14 | | | 10.46 | 8.15 | 4,619 | TR in runoff @ 2nd cycle |
| Runoff Ori g/8mL | 0.0135 | 0.5688 | 0.4791 | 0.1458 | 0.0346 | 0.0035 | | | | | Drains easily; full penetration |
| Vol. Sampled mL | 75 | 528 | 315 | 312 | 285 | 127 | | | | | High TR in runoff beaker |
| Ori Total g | 0.1265625 | 37.5408 | 18.864563 | 5.6862 | 1.232625 | 5.7556 | 8.0837 | | | | |

PEBBLES 36: 1750g Sed, 103.4g Ori (72.59g bit)

| | | | | | | | | | | | |
|------------------|----|---------|--------|--------|-----|-----|--------|-------|-------|--------|---------------------------------|
| Penetration cm | 14 | 14 | 14 | 14 | 14 | | | -5.73 | -4.19 | -2,377 | TR in runoff @2nd cycle |
| Runoff Ori g/8mL | 0 | 0.7633 | 0.4696 | 0.0582 | 0 | 0 | | | | | High T.R. content |
| Vol. Sampled mL | 0 | 432 | 430 | 411 | 365 | 106 | | | | | Drains easily; full penetration |
| Ori Total g | 0 | 41.2182 | 25.241 | 2.990 | 0 | 7.3 | -4.159 | | | | High TR in runoff beaker |

Series 5 : Tidal Cycling : 10 Cycles:15 C : 32 ppt Seawater

MED SAND 37: 1550g Sed, 105.1 g Ori (74.48 g Bit)

| Tidal Cycle # | 3 | 5 | 7 | 9 | 10 | H2O final (g) | Retained (g) | % Ret | kg Bit/ m3 Sed | mg Bit/ kg Sed | Comments |
|------------------|--------|--------|--------|--------|------|---------------|--------------|-------|----------------|----------------|--|
| Penetration cm | 14 | 14 | 14 | 14 | 14 | | | 58.0 | 43.51 | 27,854 | Tar Res in runoff @ 3 flushes |
| Runoff Ori g/8mL | 0.1765 | 0.1849 | 0.0123 | 0.0358 | 0 | | | | | | Full penetration on 2nd flush |
| Vol. Sampled mL | 425 | 530 | 670 | 570 | 210 | 127 | | | | | Slow draining; plugging? |
| Ori Total g | 9.38 | 12.25 | 1.03 | 2.55 | 0.00 | 6.10 | 43.17 | | | | Clear final runoff High TR in runoff final beaker |

GRANULES 38: 1750g Sed, 107.0g Ori (75.11 g Bit)

| | | | | | | | | | | | |
|------------------|--------|--------|--------|--------|--------|--------|------|-----|------|-------|---------------------------------|
| Penetration cm | 14 | 14 | 14 | 14 | 14 | | | 5.5 | 4.18 | 2,371 | TR in runoff @ 2nd cycle |
| Runoff Ori g/8mL | 0.6970 | 0.0000 | 0.0000 | 0.0000 | 0.0018 | 0.0035 | | | | | Drains easily; full penetration |
| Vol. Sampled mL | 750 | 555 | 512 | 590 | 288 | 120 | | | | | Clear final runoff |
| Ori Total g | 65.34 | 0.00 | 0.00 | 0.00 | 0.06 | 5.55 | 4.15 | | | | High TR in runoff final beaker |

PEBBLES 39: 1750g Sed, 105.6g Ori (74.13 g Bit)

| | | | | | | | | | | | |
|------------------|--------|--------|--------|--------|--------|--------|-------|------|-------|--------|--|
| Penetration cm | 14 | 14 | 14 | 14 | 14 | | | -3.1 | -2.28 | -1,292 | TR in runoff @2nd cycle |
| Runoff Ori g/8mL | 0.5539 | 0.0287 | 0.0000 | 0.0003 | 0.0000 | 0.0000 | | | | | High T.R. content |
| Vol. Sampled mL | 950 | 750 | 740 | 675 | 370 | 106 | | | | | Drains easily; full penetration |
| Ori Total g | 65.78 | 2.69 | 0.00 | 0.03 | 0.00 | 7.90 | -2.26 | | | | Clear final runoff High TR in runoff final beaker |

Series 6: In Situ Weathering: 15 C 32 ppt seawater

| Exp # | Days | Ori added (g) | Bit Coating Depth (cm) | Comments |
|-------------|------|---------------|------------------------|--------------------------------------|
| 40 Med Sand | 2 | 69.8 | 2 | |
| 41 Granules | 2 | 73.2 | 6.25 | |
| 42 Pebbles | 2 | 74.7 | 6.5 | |
| 43 Med Sand | 8 | 77.4 | 4.5 | |
| 44 Granules | 8 | 75.8 | 6.5 | Disbit 1.3 cm above liquid Ori layer |
| 45 Pebbles | 8 | 72.4 | 8 | Disbit at liquid Ori interface |
| 46 Med Sand | 19 | 76.0 | 3.75 | ? more "air tight" than exp 43 |
| 47 Granules | 19 | 81.2 | 6.75 | Disbit 1.25 cm above liquid layer |
| 48 Pebbles | 19 | 78.1 | 7.5 | Disbit at liquid Ori interface |

Series 7: Flushing: 1.0L,15 C, 32 ppt Seawater

| Med Sand | Class. | Granules | Class. | Pebbles | Class. |
|-------------|---------|-------------|---------|-------------|---------|
| EXP 49 | | EXP 50 | | EXP 51 | |
| 1.5 | MOR 30% | 1.5 | OP 80% | 1.5 | OP 80% |
| 5 | LOR 20% | 11.5 | MOR 30% | 12.5 | MOR 30% |
| 0.5 | OP 80% | 1 | HOR 60% | 6 | Column |
| 6.5 | MOR 40% | 6 | Column | 0 | |
| 0.5 | OP 80% | 0 | | 0 | |
| 6 | Column | 0 | | 0 | |
| EXP 52 | | EXP 53 | | EXP 54 | |
| 7 | MOR 25% | 1.5 | OP 80% | 1.5 | OP 80% |
| 2 | HOR 60% | 5.5 | LOR 25% | 12.5 | LOR 20% |
| 4.7 | MOR 40% | 6 | MOR 30% | 6 | Column |
| 0.3 | OP 80% | 1 | HOR 60% | | |
| 6 | Column | 6 | Column | | |
| EXP 55 | | EXP 56 | | EXP 57 | |
| 9 LOR 15% | | 5 LOR 10% | | 14 LOR <10% | |
| 0.5 HOR 60% | | 8.5 MOR 20% | | 6 Column | |
| 4 MOR 20% | | 0.5 HOR 60% | | | |
| 0.5 OP 80% | | 6 Column | | | |
| 6 Column | | | | | |

Series8: Surfactant Effects: 15 C: 32m ppt Seawater: Granules

GRAPH

| EXP 58 | | EXP 59 | | EXP 60 | |
|--------|---------|--------|---------|--------|---------|
| 1.5 | OP 80% | 1 | HOR 50% | 13.5 | LOR <5% |
| 11.5 | MOR 25% | 12.5 | LOR 10% | 0.5 | HOR 50% |
| 1 | HOR 60% | 0.5 | HOR 60% | 6 | Column |
| 6 | Column | 6 | Column | 0 | |

Series 9 : Tarry Residue Remobilization : 32 ppt Seawater

| Exp # | Temp C | Comments |
|--------------|---------------|---|
| 61 | 10 | No change in composition after 60 minutes. Tarry residue film remained intact on pebble surface. 24 Hrs later @ 15 C T.R. remobilized Oil film observed on surface. |
| 62 | 15 | No observable remobilization after 90 minutes. T.R. film unchanged. 24 Hrs later @ 15 C T.R. remobilized leaving tiny droplets covering a relatively clean pebble. |
| 63 | 20 | Tiny bubbles form (<1mm) @ 2 min. After 4 min TR starts coalescing into thick veins of TR ; bare pebble showing. After 10 min TR organized into clumps covering @ 30% of pebbles, connected by thin veins of TR. After 24 Hrs @ 15 C pebble clear and covered with tiny TR droplets; film observed on water surface. |
| 64 | 25 | Tiny (<1mm) bubbles observed after 2 min. Veins appearing , joining clumps covering @ 30% of pebble, after 5 min. After 24 Hrs @ 15 C pebble clear and covered with tiny TR droplets; film observed on water surface. |
| 65 | 30 | TR coalesced after 1 min forming thick veins, tiny bubbles. After 10 min 50 % of pebble clean with thin veins connecting thick pathces. Few larger droplets forming (1-2mm). 30 min <10% of pebble coated. After 24 Hrs @ 15 C pebble clear and covered with tiny TR droplets; film observed on water surface. |
| 66 | 40 | TR coalesces immediately, after 2 min pebble 30% clear with TR veins and small bubbles. At 4 min 50% of pebble clear. At 10 min 70% of pebble clear. At 30 min small TR droplets forming and rising to surface. 60 min > 90% of pebble clear; small droplets interconnected with fine veins. After 24 Hrs @ 15 C pebble clear and covered with tiny TR droplets; film observed on water surface. |
| 67 | 50 | TR coalesces immediately. Within 2 min 90% of TR had formed into tiny droplets with bubbles at the tips. At 4min droplets were rising to the surface. By 20 min most of pebble was clear; 30 min pebble clear but fringed in tiny droplets. Unchanged over 24 Hrs. |

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