

Orimulsion containment and recovery*

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INTRODUCTION

Orimulsion is a fuel consisting of natural bitumen dispersed in fresh water (26–30%) which is stabilised (as a bitumen-in-water emulsion) by the addition of a small quantity of surfactant. The process of creating Orimulsion turns semisolid bitumen with a viscosity of 10 000 mPas into a mixture with a viscosity of 450 mPas. The composition of Orimulsion makes it, at first consideration, seem an unlikely fuel. The combination of modern emission control, independence from the fluctuations in world crude oil prices and proven reserves of 1.27 trillion barrels (Middle East crude reserves are estimated at only 267 billion barrels) make this a significant energy source for the future. The typical composition of Orimulsion is given in Table 1.

Orimulsion is clearly destined for increased consumption around the world and, with this, will inevitably come an increased risk of spillage and a requirement for appropriate spill control technologies. However, unlike conventional crude or fuel oils, we have no past spills or documented experiences to exploit. The development of containment and recovery systems must therefore rely on limited examinations of the product, and its fate and behaviour.

BEHAVIOUR

The earliest studies of Orimulsion behaviour, conducted in laboratories in the 1980s, indicated that the product would disperse naturally when spilled. However, in early 1989, the European marketing division of Bitumenes Orinoco approached the National Environmental Technology Centre (NETCEN) of AEA Technology, and Oil Spill Response Limited (OSRL), to examine their new product before the first import to the UK. This was the result of Bitumenes Orinoco's adopted proactive policy on prevention and preparedness; there was no legal requirement for such an action.

As a result NETCEN undertook to discharge Orimulsion in its annual sea trials programme to confirm the reported self-dispersing property expected from this emulsion. The discharge of a 200 L drum of Orimulsion at sea resulted in only a small patch of silver/grey sheen on the sea surface. However, approximately 1 h later, bitumen tar balls were located on the surface. The test was repeated with a second 200 L drum of Orimulsion producing the same results. Subsequent analysis confirmed that the bitumen was from the Orimulsion. Although the quantities of bitumen recovered were small, this first test indicated the problems of translating laboratory tests and results to the field. This was to be shown again and again with Orimulsion where laboratory studies would indicate results at odds with field experience.

These field trials indicated the need for further studies and so the examination of Orimulsion spill behaviour began in greater detail. Studies conducted in the UK, USA, Canada, France and Venezuela examined a range of scenarios, locations and treatment options to validate and develop an understanding of the fate and remediation options available for Orimulsion. From the resulting reports, the following conclusions on the fate, detection, containment, recovery and beach clean-up have been established.

THE FATE OF ORIMULSION

The following summarises our current understanding of the fate of Orimulsion, although work continues to refine these theories. The current maximum discharge at sea during tests has been only two tonnes and confirmation of theories will not be possible until larger discharges can be made. It is important to stress,

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however, that future larger discharges are envisaged only to assist in quantifying the percentage that will require recovery; the basic fate, and factors affecting it, are not expected to change.

The factors identified as affecting Orimulsion's fate are:

Salinity: The salinity of the water can affect Orimulsion in two ways.

- Increased salinity reduces the effectiveness of the surfactants by dehydrating the ethylene oxide sheath. It also acts by compressing the electrostatic double layer around the bitumen droplets. This allows the bitumen droplets to approach each other more closely and so increases the possibility for coalescence.
- The salinity affects the density of the water and as a result, in more saline water, Orimulsion will remain closer to the water surface (due to a greater density difference). This in turn reduces the rate of dispersion into the main body of water by restricting the vertical component of diffusion.

Both of these contribute to an increased potential for material to resurface in sea water whereas in fresh water it will tend to disperse more rapidly.

Dilution: Orimulsion contains excess surfactant in the aqueous phase, which is in equilibrium with the surfactant at the bitumen/water interface. The addition of Orimulsion to a body of water increases the average distance between droplets and reduces the likelihood of collisions. However, at the same time, the equilibrium is disturbed resulting in less excess surfactant concentration in the aqueous phase, reduced emulsion stability, and a greater chance of coalescence when droplets do approach one another. When Orimulsion is spilt the dilution will be controlled by the current, topography and sea state, which will affect the rate and extent of the dilution and leaching of the surfactant.

Mixing energy/turbulence: Mixing energy and turbulence can be beneficial to the dispersion and dilution of Orimulsion and so reduce the probability of droplets coalescing even if the surfactant is destabilised. This theory has been tested experimentally where rough weather, and the use of an outboard motor to create turbulence, have both separately assisted Orimulsion dispersion.

Scale: As with any spillage the quantity discharged and the rate of release can affect the fate. The dilution process may dominate the process of excess surfactant loss and droplet collision following a small release of Orimulsion and efficient dispersion may result. The dilution process may be less rapid with a large instantaneous release and droplet collision and coalescence may be more likely to occur.

OBSERVATIONS FROM EXPERIMENTS AND SEA TRIALS

Considering the trials undertaken with Orimulsion since 1990, and the reports and information available to date, it is possible to conclude that the following stages occur in the fate of Orimulsion.

- 1 When Orimulsion initially enters the water, it is diluted by diffusion and turbulent mixing processes and spreads through the water column. The rate of vertical mixing of the Orimulsion is controlled by the density difference between the Orimulsion and the water into which it is spilled and the turbulence of the water into which it is spilled. Lateral mixing is only restricted by the level of turbulence.
- 2 A small amount of bitumen (estimated at 1% by volume of the bitumen content of the spill) will rise very rapidly to the surface where it forms a layer of sheen.

The remaining dispersed Orimulsion will remain in suspension indefinitely in turbulent or flowing water unless droplets coalesce to sizes greater than around 70 microns when they may rise to the surface. This conclusion is based on observations of the behaviour of conventional crude oil when treated with dispersants.

- 3A In freshwater spills the surfactant will assist in dispersion of the Orimulsion by inhibiting coalescence and thereby maintaining the droplet size below that at which buoyancy forces result in resurfacing of the bitumen.
- 3B In saline water the surfactant effectiveness is reduced. The droplets which collide are more likely to

Table 1 Orimulsion properties

Properties	Typical values
Water content, %	29.5
Median droplet size, μm	11
Density at 60 °F g/cm^3	1.0103
Apparent viscosity (300 °C/5 °F, 100/s), mPas	450
Pour point	37/3
Gross calorific value, Btu/lb	13 027
Metals content (p.p.m. in fuel)	
Nickel	80
Vanadium	310
Sodium	30
Magnesium	370
Elemental analysis (% wt)	
Carbon	60.10
Hydrogen	10.10
Oxygen	26.40
Nitrogen	0.35
Sulfur	2.85
Ash	0.20

coalesce and rise to the surface as bitumen. If turbulence is great, or if the spill is in flowing water, droplets may be rapidly diluted so that collision of droplets does not occur to any significant extent. Alternatively, if contained or forced together (see containment and recovery sections), droplets may concentrate, collide and resurface.

- 4** If bitumen does resurface it will initially tend to form a thin film of less than 0.1 mm, particularly in quiescent water. At this stage the bitumen will re-disperse if sufficient energy is available and dispersant treatment may be effective. If the bitumen is to be recovered from the sea surface, it will be necessary to thicken the film (it has not been possible to date to identify to what extent the bitumen will be formed into windrows and what thickness the bitumen will be in these layers).

If the surface Orimulsion reaches a thickness of around 0.5 mm then the recovery of the bitumen is possible using standard weir skimmers. However, the transfer pump will need to be a positive displacement type and the introduction of water is recommended to reduce pumping loads.

In summary, the fate of an Orimulsion spill is dependent on the circumstances and the countermeasures taken. For example:

For a small spill of Orimulsion, where there is no containment, the vast majority ($\approx 90\%$) can be expected to disperse. It has been shown that a 100 L spill in the centre of an open dock (250 m by 150 m by 6 m deep) resulted in only 3 L of bitumen on the surface. This equates to 3% of the total spilled or approximately 4.3% of the total bitumen.

If the Orimulsion is contained and significant dilution is prevented, then the percentage of the emulsion which destabilises will be increased. For example, a 50 litre spill of Orimulsion was contained in a relatively small area (20 m^2) of the dock for 69 h and approximately 80% of the bitumen was collected from the water surface. Although it is not suggested that this level of destabilisation would occur in a real spill, it does indicate that if the emulsion is prevented from diluting then there could be an increase in the amount of bitumen that resurfaces compared to the $\sim 10\%$ experienced in open water tests to date.

CONTROL AND RECOVERY

The identification of control and recovery techniques for Orimulsion was essential to allow the preparation of contingency plans prior to its import to the UK, Canada, Japan and Denmark for the

various test burns conducted at local power stations in those countries. The control of any spill requires not only a physical means of containing or deflecting the material but also relies on knowing where the material is, its condition and where it will move to in order to direct the deployment of resources. These are examined in the following sections:

Orimulsion spill control

- Detection
- Modelling
- Sub surface plume measurement
- Containment and deflection

The control of the spill must enable material to be brought to locations where it can be recovered. In the case of Orimulsion, recovery techniques need to be capable of dealing with material with a wide range of properties from dispersed, relatively low viscosity bitumen/water mixtures to high viscosity, adhesive and viscoelastic slicks of predominantly bitumen. Again the solutions to these are examined in the following sections:

Orimulsion recovery

- Bitumen recovery
- Combined containment and recovery
- Dispersed orimulsion
- Beach cleaning

ORIMULSION SPILL CONTROL

Detection

The first problem in controlling any spill, including that of Orimulsion, is to identify where the spill has occurred and to estimate the quantity involved. This is often accomplished by the use of aircraft which utilise well developed techniques of visual observation and airborne remote sensing. However, these detection methods rely in the main on the existence of one or more surface phenomena to indicate the location of the slick. Such phenomena include capillary wave suppression, thermal signature or colour contrast with the surrounding water. In the case of Orimulsion these can be difficult to detect.

In 1990 a discharge of 2 tonnes of Orimulsion was undertaken in the North Sea. On station during this discharge was one of the UK Marine Pollution Control Unit remote sensing aircraft equipped with Side Looking Airborne Radar (SLAR) and Infra Red/Ultra Violet (IR/UV) sensors. Although the quantities involved were small and therefore detection was more difficult, the observations made were assisted by a knowledge of the discharge time and attendance of several surface vessels which clearly indicated the location of the spill. Visual observation of the Orimulsion was possible but no image could be seen from the SLAR and only a faint image on the IR/UV line scanner. This is consistent with the bulk of the material being dispersed into the water column and so resulting in little capillary wave dampening or surface slick from which a thermal signature could be detected. The visual observation was in fact limited to observation of the subsurface cloud of Orimulsion.

As described earlier, spilled Orimulsion will initially form a cloud of dispersed bitumen. The surface above this cloud will probably be covered by a very light sheen containing an estimated 1% of the quantity of bitumen in the spill. By comparison with a conventional crude oil spill (for example 100 tonnes) which would initially form a surface slick containing 100% of the oil, a similar spill of Orimulsion may only result in a surface slick containing 0.7 tonne of bitumen. Clearly, the target for remote sensing is considerably reduced and even when detected may not indicate the true location of the bulk of the spilt material. The surface sheen will have been moved by currents and wind in the same way as a conventional oil. However, the wind will have had much less effect on the subsurface plume. Even experienced observers may mistake the plume for cloud shadows, underwater vegetation or suspended sediments because they give similar images.

In the later stages of the spill, it can be expected that detection will become easier assuming that there will be coalescence of the bitumen which then returns to the surface. In a crude oil spill, the collection of surface oil and formation of emulsion occurs in windrows. In the case of Orimulsion, the resurfacing material could initially be spread across a large area in the form of separate 'globs' and their subsequent behaviour is not known. With current knowledge we cannot say whether further surface coalescence will occur nor whether the patches of bitumen will form into windrows which can become the focus of recovery operations.

Clearly further work will be required with larger quantities of Orimulsion to confirm if Orimulsion can be detected with aircraft sensors; until then, visual observation by well-briefed observers is the best means of airborne detection.

Modelling

Another tool in controlling a spill and the response to it is predictive modelling. In the aftermath of any spill, knowledge of the likely slick movement, properties and landfall can all enable more effective responses to be planned. There are a number of sophisticated oil spill models. Some of these models are capable of modelling the subsurface plume created by an Orimulsion spill and its subsequent movement. In combination with their abilities to predict movement of surface slicks, the models should be capable of simulating the properties and behaviour of Orimulsion. However, the movement of material from a subsurface plume to the surface has not yet been measured in the field, although progress is being made in the laboratory and also in planning how to make measurements at sea of droplet size and rates of coalescence.

The modelling of Orimulsion spills is therefore currently limited and requires the careful interpretation and application of results. The conduct of large scale sea trials will allow an improved understanding in the future and allow incorporation of properties into the modelling predictions.

Sub-surface plume measurement

In studies of oil and chemical pollution, the Turner fluorometer is a primary method of measuring subsurface concentrations of oil. These instruments enable oil concentrations to be measured in real time and can be rapidly deployed from a small boat. The rapid deployment of these instruments following spills from the *Braer* and *Sea Empress* has allowed real time information on the concentrations of oil in the water, the effectiveness of dispersants and the effects of clean-up operations to be determined.

These instruments have been optimised in an Orimulsion-specific calibration test to extend their use to Orimulsion. Subsequent trials with the instruments with Orimulsion spilled in a realistic situation and in laboratory calibration tests have demonstrated that the Turner 10 fluorometers can be used to detect Orimulsion at various depths and at very low concentrations (a few p.p.m.).

The instruments are potentially suitable for a number of roles:

- For research to enable the concentration of Orimulsion to be measured during sea trials. This in turn will assist in modelling of Orimulsion spills and the prediction of their movement, fate and likely concentrations.
- To provide response organisations with a means of detecting and measuring subsurface dispersed Orimulsion in the event of a spill, and with a postspill monitoring capability.
- As a detector for the protection of sensitive areas and resources, e.g. power stations where the instrument can be used to detect Orimulsion or other oils in the cooling water inlet before problems occur.
- As a spill detector at terminals to give warning day and night of small or large Orimulsion spills.
- As a waste outlet monitor to ensure Orimulsion is not discharged above discharge consent levels and for the detection of accidental spillage in the site drainage systems.

Containment and deflection

In response to conventional oil spills, the containment (for subsequent recovery) or deflection away from sensitive areas is a standard response. The spillage of Orimulsion will demand a similar response.

However, in this case, the material will only be on the surface in the later stages (where conventional booming techniques and equipment would be applicable) of the spill and only if material has coalesced and resurfaced. The containment of conventional oil is problematic and there is little information on the failure velocities of existing boom designs and even less information on the retention of subsurface material. In considering and selecting booms for use with Orimulsion, a large element of the choice has had to be based on observation of performance in test tanks and harbour test locations.

In the early stages of an Orimulsion spill, the plume of dispersed bitumen may need to be contained to prevent reaching sensitive areas or to assist in coalescing the material for subsequent recovery. Initial work on containment was geared to examination of the existing technologies or to the simple modification of these. To contain material dispersed in the water column an increase in boom draft (skirt depth) was clearly required. Work on the fate of Orimulsion has shown that the depth of the cloud depends on the density difference between the Orimulsion and the water. In sea water Orimulsion remains close to the surface (1.5–3 m), while in freshwater it may penetrate to a greater depth. Of course, the type of spill (slow leak or instantaneous release) and the kinetic energy imparted (hose burst, hull bottom damage, deck spill) will also affect depth of initial distribution before buoyancy effects take over.

The increase in draft of booms is not technically limited. However, practically the limitation is on the vessels towing capability or on the strength of the moorings that must hold the boom. NETCEN (Warren Spring Laboratory) was involved in the development and testing of the original Jackson Trawls' Net Boom a semi-permeable barrier developed in the 1980s. This boom uses dan poles on alternate sides at one metre intervals to maintain a length of knotless nylon in an upright position. The boom in this configuration was developed for containment of Beatrice Crude (a high wax crude oil) and the permeability was required to allow long lengths of boom to be employed. The design allowed the position of the floats on the dan poles to be easily altered to produce a deep draft semipermeable boom (at the expense of freeboard).

Working in conjunction with the manufacturer, this boom was tested at Liverpool docks in 1991 where it was demonstrated to be able to retain a dispersed Orimulsion cloud in conditions of limited water movement. Subsequently a new boom was developed from this original model which incorporated an even greater depth of skirt and a simplified float system. This was subsequently tested in calm waters, in both a U-configuration for its ability to contain Orimulsion and in a deflection mode. Subsequent work has allowed a number of alternative designs to be developed giving buyers a choice of competing suppliers.

Jackson Net II Boom—Jackson Trawls

Ayles Fernie Orimulsion Boom—Ayles Fernie

Ori Boom—Cape Canaveral Marine Services

The development of these booms was a result of experimentation conducted in the UK and USA by the manufacturers and BITOR marketing companies. The aim of the development was to provide alternatives to the Jackson Net Boom which would offer a range of types to suit local conditions, commonality with existing stockpiles and to introduce competition as well as bring broader expertise to addressing the design of the containment equipment.

No boom design will be 100% effective in containing Orimulsion even in calm water—bitumen could pass under any of the booms listed above. However, the presence of the boom will increase the possibility of coalescence and increase the amount of material recovered.

ORIMULSION RECOVERY

Bitumen recovery

The bitumen which can be produced from an Orimulsion spill has properties which make recovery with the full range of skimmers impossible. This is not a unique situation and in part explains the variety of skimmer designs and recovery systems available throughout the world. The high viscosity of the bitumen (> 10 000 mPas) and its cohesive and adhesive properties make the high viscosity skimmers (designed for Heavy Fuel Oil and crude oil emulsion recovery) the obvious starting point. A selection could have been

made based on experience but this would not have identified specific limitations. Although information is available on the viscosities which could be handled by these skimmer systems, there is no information on the effects of the viscoelastic and adhesive properties and their effect on recovery. Therefore a number of practical tests and trials had to be undertaken to prove the bitumen could be recovered and to establish the best equipment for use following an Orimulsion spill.

In the recovery of high viscosity oils and emulsions, the screw pump is a common choice for skimmers. It was therefore a natural first choice for recovery of the bitumen which can result from a Orimulsion spill. A series of test were conducted using the Desmi 250 series skimmer at Oil Spill Response Limited's base at Southampton, at Nelson Dock Liverpool and at CEDRE in France. This pump was selected as representative of the range of screw pumps available.

The tests demonstrated the skimmers ability to pump the bitumen and its suitability for employment in an Orimulsion spill. The only restriction found was when the bitumen layer was thickened (simulating a contained area of a spill or a dock wall) as the bitumen formed a layer which would not flow over the wear of the skimmer. Lowering the weir allowed the bitumen to move over the weir but also allowed large amounts of water into the skimmer. In later tests at CEDRE the thick accumulations of bitumen had to be assisted into the pump

It is not only the flow properties of the natural bitumen which has an impact on subsequent approaches to recovery. It is also the thickness of the bitumen and whether it is in the form of patches, skin or tar balls/lumps and the age (degree of weathering) of the bitumen that are important. In the early stages of a spill, the bitumen which is produced is very viscous and cohesive (adhesive and viscoelastic) and the elastic property leads to self-feeding once pumping is initiated. However, because of these same properties, it is also desirable when handling the material using 'grab' techniques to keep surfaces water wetted to facilitate easier bitumen removal. However, after a few days at sea, the bitumen becomes oxidised/weathered and loses much of its cohesive property.

One recommended method for recovery of the thicker layers is the WP 1 30 (also known as the Roto 30) or its larger version the Roto 70. This skimmer uses a snail's shell rotating cage to feed an inbuilt screw pump. Alternatively, the Water Witch vessel can recover high viscosity product easily as, in effect, it is a floating excavator.

The Tar Hawk (inclined belt) skimmer, developed in the USA, has also been successfully tested in trials with Orimulsion in the USA and Venezuela.

A number of other items have been tested and found unsuitable, although manufacturers are currently working to modify the designs of some for Orimulsion applications. The difficulties encountered are not particular to Orimulsion but would apply to other high viscosity materials, viz. problems of pump feeding and removal of high viscosity materials from the pick up system (oil mops and brush arrangements).

Combined containment and recovery

Containment and recovery systems can be used in combination for an Orimulsion spill. Some conventional oil spill systems operate in this way, e.g. incorporation of a skimmer into the containment boom. In the case of Orimulsion, a combined system was envisaged for smaller vessels and therefore pollution equipment manufacturers were approached (Ro-Clean Desmi and Jackson Trawls) to develop ideas. This resulted in two systems employing fish trawling principles.

The first of these is the Ro Clean Desmi, Scan Trawl which was successfully tested. The scan trawl net was able to pick up weathered lumps of bitumen and accumulate them in the disposable cod-end.

It was also proposed to consider a mesh reduced in size from 5 mm² to 3.5 mm². The manufacturer will consider the effects of this on drag and towing forces as part of their development. The trawl net is not, however, a new idea; in fact it has been available and utilised for oil spill clean-up for a number of years.

Dispersed orimulsion

The different strategies adopted around the world mean that, in some circumstances, it will be desirable to recover the subsurface plume of bitumen. During work on recovery of surface bitumen it was observed

that subsurface bitumen could be forced to coalesce by the use of a high volume screw pump or air flotation.

It is thought that the high volume pump resulted in increased coalescence of bitumen by increasing the droplet collision rate. The resultant larger droplets rose more rapidly to the surface. The air flotation effect was achieved by inserting a boom inflation pump into the water. A proportion of the rising air bubbles passing through the Orimulsion plume attached themselves to the bitumen droplets, thus increasing their overall buoyancy, and droplets which would otherwise have remained suspended, rose to the surface where they formed into a bitumen skin.

This idea was subsequently developed by INTERVEP into a practical system of forced air coalescence. The system uses a pump which transfers water and the bitumen droplets (125 L/s) into a three stage separation system to produce a visually clear effluent. A prototype of this unit has already been successfully employed in sea trials off Venezuela.

Beach cleaning

In planning for any spill, we must assume that some of the product *may* reach the shore. A series of trials were therefore undertaken at CEDRE's artificial beach facility. The results of these tests are shown below.

Mechanical screening of sandy beaches is efficient when applied to weathered bitumen stranded on soft sand beaches. The Rolba 150 D beach cleaning machine was tested and successfully demonstrated in this role.

Manual collection can also be efficient for the removal of large bitumen patches and tar balls.

Cautious use of pressure washing with solvents can remove bitumen from hard surfaces such as rocks, structures and equipment. The manual removal of excess bitumen is strongly recommended prior to solvent application.

Pebble cleaning can be achieved by removing the sediments from the beach and washing them in a cement mixer or dedicated beach material washing plant with the assistance of solvents to release the material. The types of solvents recommended are those with low aromatics content.

SUMMARY

Since its introduction into world markets, Orimulsion has been the subject of considerable press and public attention. The picture presented by the media has not always been a balanced view. Attention has focused on the differences between Orimulsion and conventional oils and the potential for a spillage and the damage that could result. The considerable advances made towards reducing the risks by the use of double-hulled tankers, double-loading hoses and investment in spill research have not been reported with such vigour.

The work conducted on Orimulsion to date has built on our existing knowledge base related to crude oil spill technology and this has enabled us to reach a position of reasonable understanding within just a few years. We have identified control and recovery technologies and proven that these are successful in operations with Orimulsion. As with conventional oils, there are gaps in our knowledge and capabilities but further work is already underway to ensure that we will be prepared when an Orimulsion spill does occur.

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